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Organotransition metal [3 + 2] cycloaddition reactions

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Contents

Abstract

The review, covering the literature of roughly the last three decades, describes the [3 + 2] cycloaddition reactions of metalla dipolarophiles M=X with organic 1,3-dipoles, and of metalla 1,3-dipoles, M–X=Y and X–M=Y, with organic dipolarophiles. The resulting 5-membered metalla heterocycles can undergo consecutive insertion and/or reductive elimination reactions to give synthetically interesting organic heterocycles. The reactivity of the organometal 1,3-dipoles is explained by extensive series of isolobal transformations to classic organic 1,3-dipoles. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Metalla dipolarophiles; Organic dipolarophiles; Isolobal transformations

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1. Introduction, definitions, scope

Cycloaddition reactions in organic chemistry are not only among the synthetically most useful reactions,

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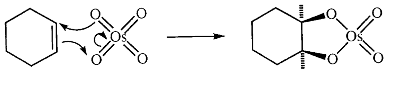
they are also among the theoretically and mechanistically best understood reactions. When a (transition) metal is involved in a cycloaddition reaction, this situation has not been reached yet. As has been pointed out and defined in an earlier review, [1] there are three different ways in which a metal can be involved in a cycloaddition reaction:

(i) In metal-assisted cycloaddition reactions, [1] we are dealing with an organic reaction in which carbo- or heterocycles are formed, and in which the metal is present in at least one of the reactants and possibly in the product, but not within the formed ring. It is present as a substituent which exerts a decisive influence on the activation barriers, and on the chemo-, regio-, and stereoselectivity of the reaction.

(ii) In metal-catalysed cycloaddition reactions, [2,3] the metal fragment does not form stable complexes with either of the reactants nor with the product. It is only present in reactive intermediates. Within the catalytic cycle it normally plays a role comparable to the metal-assisted case. However, it is just as well possible that the metal is directly involved in a cycloaddition step as in the following, third category.

(iii) In organometal cycloaddition reactions, an ML_n fragment forms an integral part of at least one of the reactants, and the resulting initial products are therefore, metallaheterocycles. Naturally, these initial metallaheterocycles need not necessarily be the final products, but can react further and undergo insertion and/or reductive elimination reactions. In this way, new organic ligands are formed. Organometal cycloaddition reactions are therefore equally interesting for organometallic and organic synthesis.

The present review collects work from the author's laboratories and others on [3 + 2] organometal cycloaddition reactions, i.e. reactions according to category (iii) which combine a 3- and a 2-atom reactant resulting (initially) in a five-membered metallacycle. The term organometal indicates that a metal-to-carbon bond of some kind is either present in one of the reactants or is formed in the cycloaddition reaction. This implies that reactions which might aptly be termed 'inorganic' are outside the scope of this review. They will nevertheless be mentioned in cases where they form a complementary example for an organometallic reaction. The following examples are meant to illustrate that type of inorganic cycloaddition reactions. A classical example is the preparation of 1,2-glycols through oxidation of olefins by osmium tetraoxide [4] or potassium permanganate. In both cases a 5-membered metallacycle, an osmate or manganate ester, respectively, are initially formed in a [3 + 2] cycloaddition step (Eq. (1)Eq. (2)). In a recent example of the osmylation reaction, [5–7] the X-ray crystal structure of the cycloadduct, $C_{60}(OsO_4)$(4-*t*-butylpyridine)$_2$, provided the first direct evidence for the proposed structure of fullerene C_{60}.



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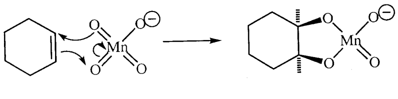
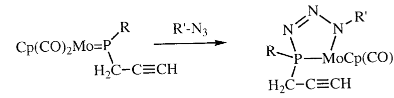


(2)

Other examples are the formation of 1-molybda-2-phosphatriazolines (Eq. (3)) [8], and of tetrazolato complexes of platinum(II), palladium(II) rhodium(I) or iridium(I) (Eq. (4)) [9,10], by cycloaddition of nitriles to σ^3, λ^4-phosphanediyl and azido complexes, respectively. In these two examples the metal is present in the 2-atom component, whereas is the last example, where diphenylacetylene cycloadds to a platinum bis-(dichlorosilylene) complex (Eq. (5)), [11] the metal is again part of the 3-atom component.



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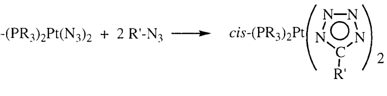

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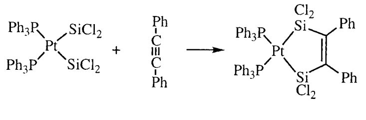


(5)

In the interesting cycloaddition reactions of metal dithiolenes to olefins, [12–16] giving 1-nickela-2,5-dithia-cyclopentanes, there is also no metal-to-carbon bond involved, and they have to be considered 'inorganic' in this context. The same is true for the cycloaddition of olefins to ON–Co(Cp)–NO [17–19].

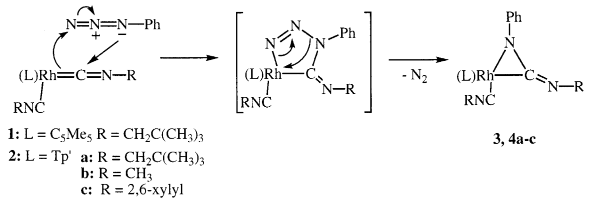
The review is intended to give an account of the progress during roughly the last 30 years, and to demonstrate that some theoretical understanding has been achieved by either using MO correlation diagrams or isolobal relations to organic 1,3-dipolar cycloaddition reactions. Comprehensiveness of the literature coverage is not a primary goal.

As in the inorganic examples above, the metal atom in organometal cycloaddition reactions can be part of either the 2- or the 3-atom component which are combining to form the five-membered cycloadduct. The review is subdivided accordingly, and already from the table of contents it is clearly visible that in the vast majority of cases the metal is part of the 3-atom component. Archetypal for organic [3 + 2] cycloaddition reactions are the 1,3-dipolar cycloaddition reactions as developed by Huisgen [20,21]. In these reactions, e.g. carbon–carbon multiple bonds as the 2-atom component, or dipolarophiles, react with 1,3-dipolar reagents as the 3-atom component. Therefore, in the first part of this review, i.e. in Section 2, a few reactions are collected, in which a metal–carbon, metal–heteroatom, or metal–metal multiple bond, the metalla–dipolarophile, reacts with a 1,3-dipole. In the second part, i.e. in Section 3, metalla-1,3-dipoles react with carbon–carbon or carbon–heteroatom multiple bonds.

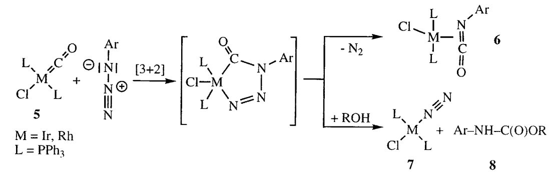
2. Reactions with the metal in the 2-atom component, metalla–dipolarophiles

2.1. M–C multiple bonds as dipolarophiles

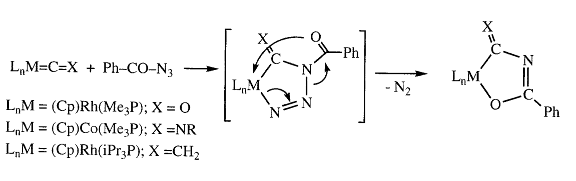
Metal-to-carbon multiple bonds are present in metal carbene, vinylidene, or carbyne complexes. However, it has long been recognised [22–24] that in low-valent metal carbonyl, $L_nM–C≡O$, and isocyanide complexes, $L_nM–C≡NR$, metal-to-ligand π-back bonding gives the M–C bonds substantial double-bond character which can be visualised in the resonance forms $L_nM=C=O$, and $L_nM=C=NR$. These metal carbon bonds are inherently reactive towards 1,3-dipolar reagents because of the nucleophilic character of the metal and the electrophilicity of the carbon atom. The following examples exemplify their reactivity towards various 1,3-dipolar reagents.



Scheme 1.

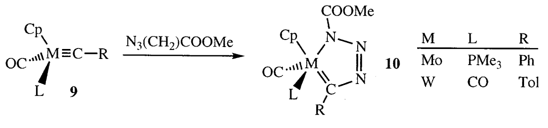


Scheme 2.



Scheme 3.

Aryl azides add across the rhodium carbon bond in isocyanide complexes $L_nRh=C=NR$ (**1**, **2a–c**) to form (unsymmetrical) η^2-carbodiimide complexes **3**, **4** according to the reaction sequence shown in Scheme 1[25]. From the regioselective formation of only one of the two possible co-ordination isomers, it has been concluded that the elimination of nitrogen from the intermediate five membered metallacycle and the formation of the carbodiimide–nitrogen bond in **3** and **4** proceed in a concerted fashion. The X-ray structure of the hydrotris(3,5-dimethylpyrazolyl)borate complex **4a** has been determined. Analogously, vinylidene complexes $CpRh(=C=CHR(P^iPr_3)$ cycloadd aryl azides $R'–N_3$ across the Rh=C bond to give, after elimination of nitrogen, ketenimine complexes $CpRh[\eta^2\text{-}N,C\text{–}R'N=C=HR)(P^iPr_3)$ [26]. Complementary is the related formation of ketenimine complexes from the reaction of metal isocyanides with diazoalkanes [27]. Collman [28,29] has reported on the reaction of carbonyl iridium and rhodium complexes with organic azides $Ar–N_3$ **5** (Ar = 2-furoyl, phenyl, 4-tolyl). Depending on the presence or absence of methanol or ethanol in the reaction medium, an isocyanate complex **6** or a dinitrogen complex **7** and free carbamate **8** are formed. As opposed to the suggested mechanism, the reaction most likely proceeds as shown in Scheme 2. Analogous reactions have later been reported by Werner [30,31]. Aroyl azides $R–CO–N_3$ are suggested by Werner to add to metal carbonyl [30], isocyanide [32], and vinylidene [33,34] complexes by either first eliminating N_2 and forming an acyl nitrene complex [30] which then rearranges to the isolated 5-membered metallacycle, or that the acyl nitrene cycloadds in [3 + 2] fashion to the M=C bond [32]. However, it is at least as likely that the intact azido group cycloadds to the M=C bond and then N_2 is eliminated (Scheme 3). Methyl azido formiate and acetate cycloadd regioselectively across metal–carbyne [35] and metal–carbene [36,37] M≡C and M=C bonds in **9** and **11** (Eq. (6)Eq. (7)). Of the resulting five-membered triaza–metalla complexes **10** and **12**, only the shown regio-isomers are found, and N_2 does not eliminate, neither thermally nor photochemically.



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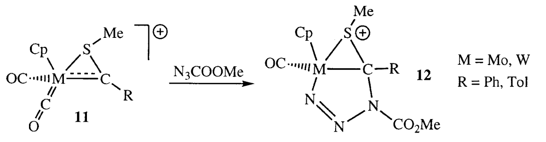

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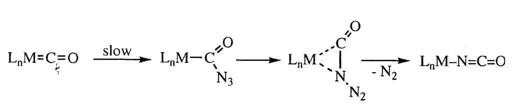
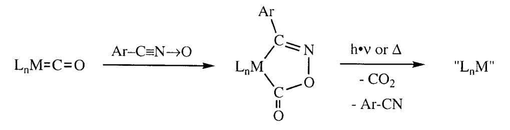


(8)

Very early already, the reaction of metal carbonyls with azide ion [38], and vice versa of azide complexes with carbon monoxide [39–41] to yield isocyanato complexes was reported by Beck. However, here the authors claim that the reaction does not proceed via a cycloaddition with concomitant or successive elimination of nitrogen, but that the incoming azide ion never forms a bond to the metal (Eq. (8)), and the reaction proceeds analogous to the Curtius degradation.

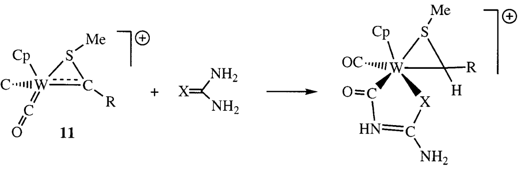
Thio- and seleno-urea can react as 1,3-dipoles and cycloadd to η^2-thiocarbene complexes **11** (Scheme 4) [42]. Here the dipole has the choice between the metal–carbene and the metal–carbonyl carbon bond and selectively adds across the latter. The authors state that when, e.g. comparable carbyne complexes $[Cp(CO)LM{\equiv}CR]$ [43] (M = Mo, W; R = Me, Ph, P-Tol, NEt_2; L = CO, PR_3) are reacted with azido esters, being stronger 1,3-dipoles, the addition does not take place at the a metal–carbonyl carbon bond, but at the metal–carbyne bond. The same is true for these complexes with aryl azides as 1,3-dipoles, giving 1-metalla-2,3,4-triazoles [44].

Aryl nitrile *N*-oxides ($R{-}C{\equiv}N^+{-}O^- \leftrightarrow R{-}C^+{=}N{-}O^-$), in situ prepared from aryl hydroxamic acid chlorides and a base, are classical 1,3-dipoles which cycloadd across the M=C=O (M = Ir, Rh, Re, Co) metal-to-carbon bond in low-valent metal carbonyl complexes (Eq. (9)) [31,45,46]. Depending on the metal and ligands L_n, the resulting 4-metallaisoxazolin-5-ones have very different stability. Thermally and photochemically they can eliminate carbon dioxide and the aryl nitrile to form highly reactive, coordinatively unsaturated species L_nM which in hydrocarbon solvents results in the activation of the solvent C–H bonds [46–48].

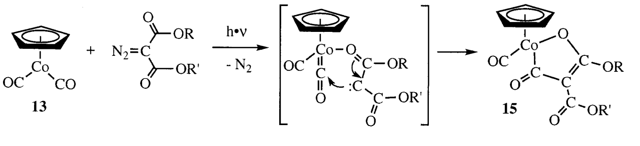


(9)

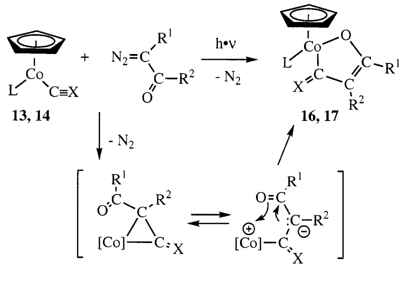
When photochemically nitrogen is eliminated from α-diazoesters [49,50] (Scheme 5) and ketones [51] (Scheme 6) in the presence of cobalt carbonyl or isocyanide complexes (Cp)LCo–C≡O (**13**) and (Cp)LCo–C≡N–R (**14**), five-membered cobalta heterocycles **15**–**17** are formed. For the formation of **15**–**17**, the authors suggest a stepwise mechanism with an initial [2 + 1] addition of the carbene to the Co=C=X bond as indicated between square brackets, however, without experimental evidence.



Scheme 4.



Scheme 5.



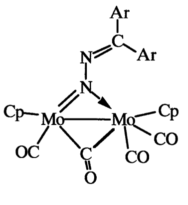
L = PMe_3, PPh_3, PMe_2Ph, $PMePh_2$
X = O, NMe, N-(S)-CH(Me)Ph
R^1 = Ph
R^2 = H, Ph, C(O)Ph

Scheme 6.

A very rare example of a multiple bond between a metal and a heteroatom as dipolarophile is the reaction of the Mo=P bond in (2,4,6-*t*-$Bu_3C_2H_2O$)($HC{\equiv}CCH_2$)P=Mo(Cp)$(CO)_2$ with the 1,3-dipole diazomethane in ether at − 30 °C [52]. The resulting five-ring, a molybda, phospha, diaza cyclopentene, is stable at that temperature, and only above − 10 °C nitrogen is eliminated to the phospha, molybda cyclopropane.

2.2. M–M multiple bonds as dipolarophiles

Cycloadditions to metal–metal multiple bonds appear to be limited to diazoalkanes. Diazoalkanes are classical 1,3-dipoles. Though, in many cases a dimetalla cyclopropane [53–56] or cyclopropene [53,57] is the final product, for the initial attack different coordination modes have been discussed [57–59] and also characterised [57,60,61]. The structures of compounds **18**, [57,60] **19**, [57] **20**, [61] have been elucidated by X-ray crystallography. For the conversion to the M–M-μ-alkylidene complexes and prior to N_2-elimination, in several of the publications a five membered dimetalla–



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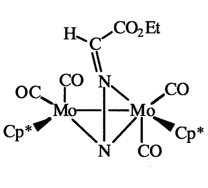

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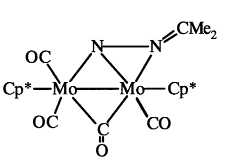

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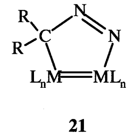

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pyrazoline **21** is invoked as intermediate or transition state, [55–58,61] analogous to the very often isolable intermediates in the cyclopropanation of olefins with diazoalkanes.

3. Reactions with the metal in the 3-atom component, metalla-1,3-dipoles

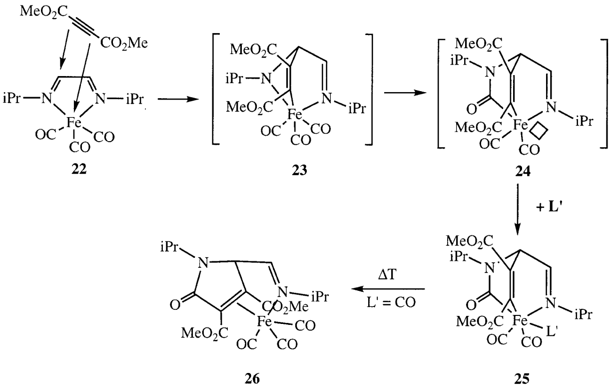
3.1. Cycloaddition reactions with metalla 1,3-dipoles $L_{4(5)}M{-}X{=}C$ (M = Fe(0), Ru(0), Mn(I); X = N, O, S)

Section 3.1 is adapted from Ref. [62] and reproduced with permission by the Royal Society of Chemistry. The reason to present this work from the authors own laboratories in some more detail before that of other authors is, that here the electronic properties of 1,3-dipolar fragments, and possible variations and synthetic applications have been clearly worked out so they can be referred to later in Section 3.2.1.

The chemistry that is collected in this section came forth from an attempt to eventually prepare the first iron(0) η^2-alkyne complex. In an investigation on (1,4-diaza-1,3-diene)$Fe(CO)_2(\eta^2$-olefin) complexes [63] it was found that the stability of the iron–olefin bond increased strongly with increasing π-acidity of the olefin. So the idea was, analogously to the preparation of the olefin complexes, to photochemically substitute a CO-ligand in (diazadiene)$Fe(CO)_3$ for the supposedly very good π-accepting dimethyl acetylenedicarboxylate (DMAD). As it turned out, there was no chance to irradiate the tricarbonyl complex in the presence of DMAD, because a very fast thermal reaction immediately consumed the reactants. This was readily recognised from the immediate disappearance of the intense colour of the (diazadiene)$Fe(CO)_3$ complex on the addition of DMAD. All (diazadiene)$Fe(CO)_3$ complexes have a very intense MLCT transition in the visible region which, depending on the diazadiene, makes them intensely red, violet (*N*-alkyl or aryl α-diazabutadienes, DAB), blue (2-pyridine-*N*-aryl carbaldimines, *R*-Pyca), or green (bipyridine, *o*-phenanthroline). The fascinating chemistry that came forth from this initial observation will be summarised below.

3.1.1. 1,3-Dipolar cycloaddition of activated alkyne to the Fe–N=C fragment

3.1.1.1. The reaction of (DAB)$Fe(CO)_3$ with dimethyl acetylenedicarboxylate (DMAD). The originally observed reaction which has been mentioned above is shown in Scheme 7. In the crude ^{1}H-MNR of the reaction mixture, two apparently isomeric products could be identified in a ratio of ca. 9:1. In an attempt to separate them by column chromatography, the isomer ratio was inverted to 1:9. From this it was obvious which was an intermediate (**25**) and which the final product (**26**). Compound **26** could be isolated and fully characterised, also by X-ray structural analysis [64]. So it was concluded that the isomerisation consisted of a reductive elimination to form the 1,5-dihydropyrrol-2-one and recoordination of its olefinic double bond.

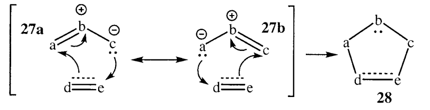


Scheme 7.

The thermally labile intermediate **25** could be isolated and characterised by X-ray analysis [65] when the reaction was performed in the presence of trimethyl phosphite as additional ligand L′ in place of carbon monoxide. By this, the metal becomes more electron-rich, and reductive elimination does not occur. With the structure of **25** being firmly established, the mechanism shown in Scheme 7 was conceived, and it was realised that the Fe–N=C fragment resembles a 1,3-dipole [66]. By ^{13}CO labelling studies [67] and from the X-ray structure of **25** with $L' = P(OMe)_3$ it was shown that the additional ligand L′ is always stereospecifically incorporated *trans* to the inserted carbonyl. The initial bicyclo[2.2.1] cycloadduct **23** could not be observed, even at very low temperatures—obviously because CO insertion is faster than the cycloaddition step. Later, when the 1,3-dipole was modified (Section 3.1.2), stable representatives of **23** could be obtained. The crystal and molecular structures of homologues of **23** could be determined in the iron system [66,68] for ruthenium [69] and manganese [70].

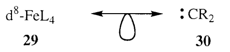
With the formation of **23**, two interdependent stereocentres are formed, the bridgehead iron and carbon atoms. The imine carbon atoms in **22** are prochiral, and the alkyne can approach either of them from either the *re*- or *si*-face. With chiral substituents at the nitrogen atoms, the approach of one face may be favoured over the other. This would lead to diastereoselectivity which has been investigated with different types of diazadiene ligands and a series of chiral N-substituents [71]. Depending on both, the type of diazadiene (C_2 and non C_2 symmetric), and the chiral N-substituents, diastereoselectivities ranging from 0 to > 99% have been observed.

3.1.1.2. The isolobal relation of the Fe–N=C fragment with an azomethine ylide. Huisgen defined a 1,3-dipole [20,21] as a species that may be described (Eq. (10)) by zwitterionic octet structures **27a**↔**27b**,[1] and may undergo cycloaddition reactions of the type 3 + 2 → 5 with suitable multiple bonds (dipolarophile d=e) to give a neutral five-ring **28**.



(10)

This general description of a 1,3-dipole can be easily recognised in the iron–imine system with the aid of the isolobal relation **29**–**30** (Eq. (11)) and, derived from it, **31**–**32** (Eq. (12)).



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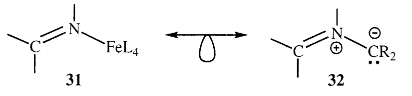
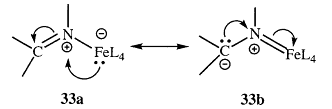


(12)

In the well-known isolobal analogy [72,73] **29**–**30** between a d^8 ML_4 fragment and a carbene, the four ligands L at the iron correspond to, e.g. the three CO ligands and one of the two imine units in **22**. If, by way of *n*-donation, an imine is added to **29** and **30**, respectively, structures **31** and **32** are obtained, of which **31** is equivalent to **22**, while **32** resembles one resonance structure of an azomethine ylide, a classical 1,3-dipole. When the relevant atom arrangement in **31** is substituted into the general formula **27a**↔**27b** of a 1,3-dipole, the resulting organometal 1,3-dipole **33a**↔**33b** in fact represents a valence-bond description of the DAB ligand properties. Earlier MO calculations on the model compound [(HN=CH–CH=NH)Fe(CO)$_3$] [74] had shown that indeed the frontier orbitals of **22** are C=N–Fe based, i.e. both the HOMO and LUMO have strongly mixed metal d, ligand π* character [75].



From this it seemed reasonable to formulate the initial reaction step in Scheme 7 in terms of a 1,3-dipolar cycloaddition reaction of the alkyne across the Fe–N=C fragment, resulting in the (in this case not observable) ferrabicyclo[2.2.1] intermediate **23** from which the isolated products **25** and **25** are readily explained.

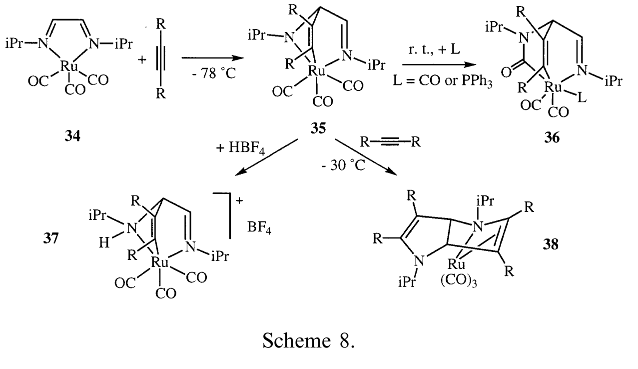
3.1.2. Adding variety to the 1,3-dipolar system

The concept of 1,3-dipolar cycloadditions was supported by CAS–SCF calculations by Dedieu and Liddel [76] on both the organic and inorganic species. Both are nucleophilic dipoles with relatively high lying HOMO and LUMO energies, the metalla-1,3-dipoles at slightly higher energy. Cycloaddition reactions of nucleophilic 1,3-dipoles are HOMO-controlled, i.e. the interaction of the dipole HOMO with the dipolarophile LUMO is predominant, and the reactivity of the dipole can be increased by either decreasing the HOMO–LUMO gap, and/or increasing the HOMO energy.

Variations to the system, to explore their influence on the reactivity, can be brought about by either changing the metal atom, the hetero atom, or the electronic properties of the additional ligands on the metal.

3.1.2.1. Changing the metal

Reactions of (DAB)Ru(CO)$_3$. With ruthenium instead of iron, [69,77] the 1,3-dipolar reactivity clearly increased. The same reaction pathway is followed, but the activation barriers further along the reaction coordinate are different from the iron system. The reaction of **34** with one equivalent of DMAD (Scheme 8) [69] proceeds instantly at − 78 °C and, as opposed to the iron system, the bicyclo[2.2.1] adduct **35** is stable at that temperature. After protonation of the amido nitrogen in **35** with HBF$_4$, which inhibited CO-insertion, **37** is stable at room temperature (r.t.), and its X-ray structure could be determined. On warming the solution of **35** to r.t. in the presence of CO or PPh$_3$, CO-insertion occurs as in the iron system to give **36**.



Scheme 8.

Double cycloaddition of DMAD

In the presence of excess DMAD, the increased 1,3-dipolar reactivity of **34**, or rather **35**, leads to a second cycloaddition to give the 1,4,3a,6a-tetrahydro pyrrolo[3,2-b]pyrrol (THPP) complex **38**. In **38**, the coordination of the THPP ligand to the metal is highly dynamic [69,78,79] and at $T > 30$ °C it readily dissociates from the metal. The Ru(CO)$_3$ fragments immediately form Ru$_3$(CO)$_{12}$ and, unfortunately, cannot be

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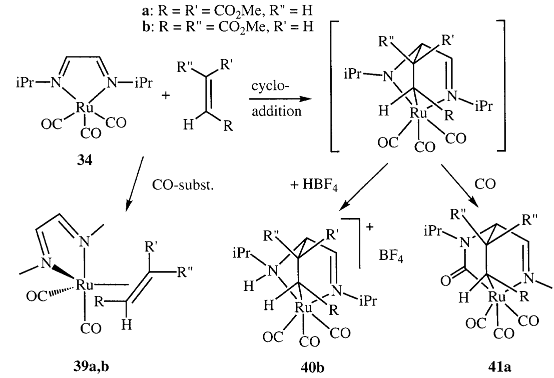
[1] The literal 1,3-dipole results from localising two of the four electrons at the onium centre b^+, which gives rise to the sextet structures $^+a–b–c^- \leftrightarrow {}^-a–b–c^+$. They demonstrate the ambivalence of 1,3-dipoles, which may at both termini have nucleophilic and electrophilic properties alike.

intercepted by excess diazadiene to regenerate **34** in order to make the formation of THPP catalytic.[2] In the iron system, the double cycloaddition to THPP could only be observed when the dipole was further activated by exchanging the CO ligands for isocyanides (Section 3.1.2.2).

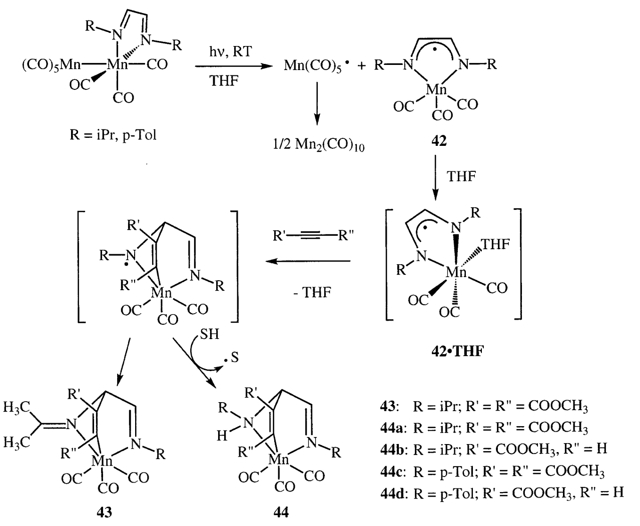
Olefins as dipolarophiles

The reactivity of **34** is also sufficient to cycloadd olefins such as dimethyl fumarate and maleate (Scheme 9) [77]. The conservation of the *cis*- and *trans*-configuration of the olefins in products **40b** and **41a** indicates that the reaction is stereospecific and most likely a concerted process. The CO ligands in **34** are thermally labile, for which reason **34** is only stable in solution under an atmosphere of CO [81]. It is therefore, not surprising that the substitution products **39a**,**b** are formed as side products.



Scheme 9.

[(DAB)Mn(CO)$_3$]$^\bullet$: a test-case for the isolobal relation. Stufkens et al. [82,83] had shown by means of ESR spectroscopy, that in [(DAB)Mn(CO)$_3$]$^\bullet$ radicals, obtained photochemically by homolytic cleavage of the metal–metal bond in binulear complexes [Mn$_2$(CO)$_8$-(DAB)], the unpaired electron does not reside at the metal atom, but is mainly localised in the π*-orbital of the DAB ligand. The radical [(DAB)Mn(CO)$_3$]$^\bullet$ (**42**) is therefore best described as a 16-electron d^6 Mn(I) species, i.e. [(DAB$^{\bullet -}$)Mn$^+$(CO)$_3$]. Comparing this with the homologous (DAB)Fe(CO)$_3$ (**22**) shows that now we have a d^6 ML$_4$ fragment instead of the d^8 ML$_4$ fragment in **22** which was an isolobal analogue of carbene. If the isolobal concept holds, the C=N–Mn(I)L$_4$ present in **42** should not behave as a 1,3-dipole. Indeed, when Mn$_2$(CO)$_8$(DAB) was irradiated in hexane (to generate **42**) in the presence of DMAD or methyl propynoate (MP) as dipolarophiles, no cycloaddition but extensive decomposition took place [70]. The only product that could be identified was Mn$_2$(CO)$_6$(DAB), which is also formed in the absence of any other reactants or ligands [82]. When instead the same experiments were performed in THF, a coordinating solvent, the bicyclo[2.2.1] cycloaddition products **44**, and in case of R = *i*-Pr, a mixture of **43a/44a** (Scheme 10) was obtained in 60–70% yields. The plausible explanation is, that a donor solvent molecule (THF) can coordinate weakly to the 16-electron species **42**, and hence act temporarily as an additional ligand in **42·THF**, as shown in square brackets. In that case, a d^6 ML$_5$-fragment is obtained, which is isolobally related to a d^8 ML$_4$-fragment, and consequently the relevant L$_5$Mn–N=C fragment is isolobal with the azomethine ylide and hence a 1,3-dipole. The bicyclo[2.2.1] cycloadducts **43**/**44** cannot undergo migratory CO-insertion, because the nitrogen has no lone pair to nucleophilically attack a carbonyl carbon. Unfortunately, the only crystalline material suitable for X-ray analysis turned out to be a mixed crystal of **43a** and **44a**, both present in the unit cell, which could not be distinguished individually. The geometry of the nitrogen bridge was therefore, disordered and averaged between sp^2 and sp^3.



Scheme 10.

It has to be stated, that complexes (DAB)M(CO)$_4$ (M = Cr, Mo, W), which just as **42·THF** contain a d^6 ML$_5$ fragment, do not react with dipolarophiles. This can be rationalised in the following way: (i) The extra electron in the LUMO, or rather SOMO, of the DAB ligand in **42·THF** increases the reactivity of the 1,3-dipole sufficiently; and (ii) the carbonyl ligands in (DAB)M(CO)$_4$ bind too strongly to the metal and cannot be lost as easily as THF from manganese in order to avoid an increase of the coordination number to seven during the cycloaddition.

3.1.2.2. *Changing the additional ligands: isocyanides for carbon monoxide.*

The choice to replace carbonyl lig-

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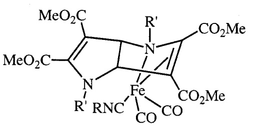
[2] A ruthenium-catalysed cycloaddition strategy for the synthesis of functionalized γ-butyrolactones (Section 3.1.2.3.1) from ketones, alkenes or alkynes, and carbon monoxide has recently been reported [80].

ands in **22** for isocyanides had two reasons: (i) while CO is a pronounced π-acceptor, isocyanides R–NC are better σ-donating/less π-accepting [84–89] and their electronic and steric properties can be varied by the choice of R. Increased donation to the metal should raise the HOMO-energy of the 1,3-dipole and increase its reactivity; (ii) just like CO, isocyanides are known to undergo insertion reactions, [84,85,90] and their introduction opened the possibility to obtain new, isocyanide inserted compounds, and further, in mixed complexes, it should be possible to study the intramolecular competition between CO and isocyanide insertion in the initial cycloadducts.

*Reactivity of (DAB)Fe(CO)$_2$(RNC) (**45**).* With Pd/C catalysis, one CO ligand in complexes **22** can be selectively substituted for an isocyanide R–NC to give **45** [91]. When **45** is reacted with DMAD at – 60 °C, three types of products, **46–48**, are obtained in 60–95% total yields after column separation [78].



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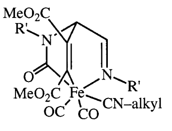

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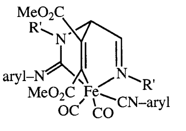
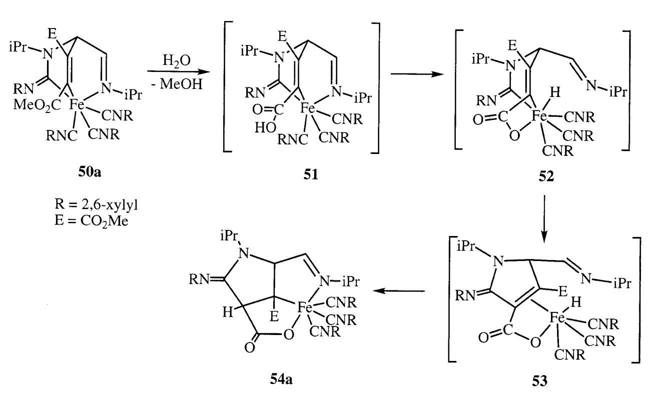


48

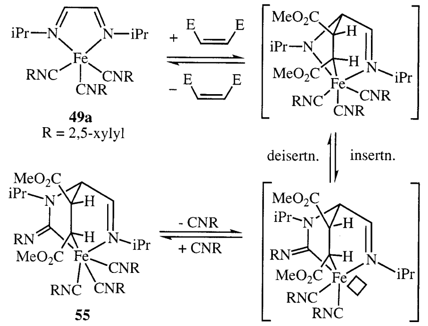
The product distribution depends on the isocyanide used. Only with aromatic (R = *o*-tolyl, 2,6-xylyl), and not with aliphatic isocyanides (R = *t*-Bu, *sec*-Bu, benzyl) isocyanide insertion products **48** are formed. Arylisocyanide insertion is obviously very fast since the competing formation of **47** from CO insertion is not observed; complexes **46** are only minor products with aryl isocyanides. With aliphatic isocyanides, the THPP complexes **46**, from double cycloaddition of DMAD (Section 3.1.2.1.1), are the major products (70 ≥ 95% of the product mixture) and indicate a strongly increased 1,3-dipolar reactivity, i.e. the intermolecular second cycloaddition outruns the intramolecular CO insertion. As opposed to the ruthenium compound **38**, the THPP ligand in **46** is much more strongly bound to the metal and can only be decomplexed oxidatively with Ce(IV), or under 80 bar of CO pressure, however, it also shows dynamic behaviour on the NMR time-scale [78].

*Reactions of (DAB)Fe(RNC)$_3$ (**49**) with DMAD, [92] olefins, [93,94] and hetero allenes [95–97].* Complexes **49**, (DAB)Fe(RNC)$_3$, had been known in the literature from spectroscopic evidence only, and were supposedly very labile [98]. However, it was possible to prepare **49a–c** (**a**: R = 2,6-xylyl, **b**: R = *t*-Bu, **c**: R = *c*-hex) in synthetically useful amounts [92]. In particular **49a** proved to be the optimally activated 1,3-dipole, which not only reacts with the greatest variety of dipolarophiles, but also exhibited some very surprising and interesting consecutive reactions.

The reaction of **49a–c** with DMAD [92] proceeds in principle completely analogous to the reaction of (DAB)Ru(CO)$_3$ (**34**), i.e. giving THPP complexes by double cycloaddition in the case of the aliphatic isocyanides (**b**, **c**), and isocyanide insertion with the aromatic 2,6-xylyl isocyanide **a**. Just as complexes **25** with L′ = trimethyl phosphite (Scheme 7) and **47**, the respective bicyclic complex **50a** (Scheme 11) does not reductively eliminate a pyrrolinone imine, probably again due to the increased σ-donor capacity of the isocyanide ligands that increase the electron density at the iron(II) centre. However, in the presence of water, **50a** finds an alternative pathway for which a plausible mechanism is depicted in Scheme 11.



Scheme 11.

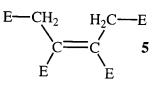


Scheme 12.

The first step would consist of a hydrolysis of one ester function to the acid, giving **51**. The hydroxyl group then oxidatively adds to the electron rich Fe(II) centre forming **52** with a formal iron(IV) centre. Simultaneously, the imine moiety is displaced from the metal. From the high oxidation state, a reductive elimination regenerates the iron(II) oxidation state by forming a 1,5-dihydro-2-iminopyrrole followed by recoordination of the double bond to give complex **53**. The stable tricyclic end product **54a**, the structure of which has been established by X-ray crystallography, is formed by formal insertion of the ring double bond into the metal–hydrogen bond and recoordination of the pending imine group. The implication that the new proton originates from water has been confirmed by performing the reaction in D$_2$O instead of H$_2$O. ^{2}H-NMR unequivocally proved the incorporation of deuterium at the former alkyne carbon atom.

The reaction of **49a**, i.e. containing the aromatic 2,6-xylyl isocyanide ligand, with dimethyl maleate in pentane (Scheme 12) [93,94] proceeds with stereospecific cycloaddition of the *cis*-olefin and consecutive isocyanide insertion to form the bicylo[2.2.2] complex **55**, which precipitates as a yellow powder in 95% isolated yield. The structure of **55** has been confirmed by X-ray crystallography. Very surprisingly, at slightly elevated temperature in benzene solution, the whole reaction sequence was cleanly reversed, which could be monitored by temperature dependent NMR spectroscopy. When a solution of pure **55** in C_6D_6 is kept at 333 K, the signals of **55** disappear and the signals of **49a**, dimethyl maleate, and 2,6-xylyl isocyanide grow in, and finally replace them until the solution is cooled down again. It is an indication of the microscopic reversibility of the reaction, that also the reverse reaction is stereospecific, with only dimethyl maleate and no fumarate being formed. This temperature-controlled molecular self-assembly and -disassembly is unique, considering all the steps involved, and the ease with which these steps occur. During the process, C–C, C–N, Fe–C σ-bonds, and an Fe–CNR donative bond are formed and broken. Another intriguing aspect of the reverse disassembly reaction is that the reaction represents the first unequivocally established case of an isocyanide deinsertion reaction.

The influence of the type of isocyanide ligand on the reactivity of **49** towards olefins is dramatic. Complexes **49b**,**c**, containing the aliphatic isocyanides **b** or **c**, give the usual cycloaddition products only with the very reactive dipolarophile DMAD, while with dimethyl maleate obviously a totally different reaction pathway becomes more favourable and products **56**, a dimer of dimethyl maleate, and the tricyclic complexes **57b**,**c** are obtained [94].



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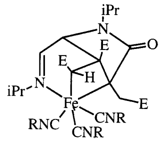
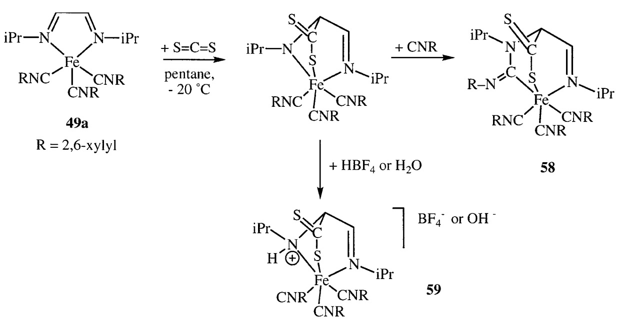


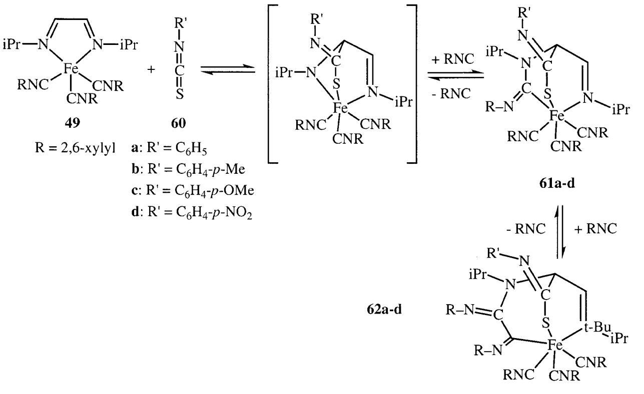
57b,c

This must be a consequence of the high electron density at the metal and the resulting weaker metal–isocyanide coordinative bond in **49b**,**c** (inferior π back-bonding as compared to the aromatic isocyanides). The observation that the reaction between **49b**,**c** and dimethyl maleate is strongly retarded in the presence of excess isocyanate suggests that substitution of one of the terminal aliphatic isocyanides for a better π-accepting olefin via a dissociative pathway apparently becomes much faster than a cycloaddition reaction.

Complexes **49** also cycloadd the C=S double bonds in heteroallenes CS_2, COS, [95] and aryl isothiocyanates [96,97]. The reaction of **49a** with CS_2 (Scheme 13) gave an 80% yield of the expected bicyclo[2.2.2] complex **58**, the structure of which has been established by X-ray crystallography [95]. When the reaction was performed in the presence of water or HBF_4, the amido nitrogen bridge in the initial bicyclo[2.2.1] adduct was protonated, which inhibited the insertion of isocyanide, and **59** was isolated in 80% yield. When S=C=O gas was bubbled through a pentane solution of **49a**, a product analogous to **59** was isolated because, apparently, the carbonyl sulfide gas was moist. Because no crystals suitable for X-ray analysis could be obtained, it could not be established with certainty whether the C=O or the C=S bond has been cycloadded.



Scheme 13.



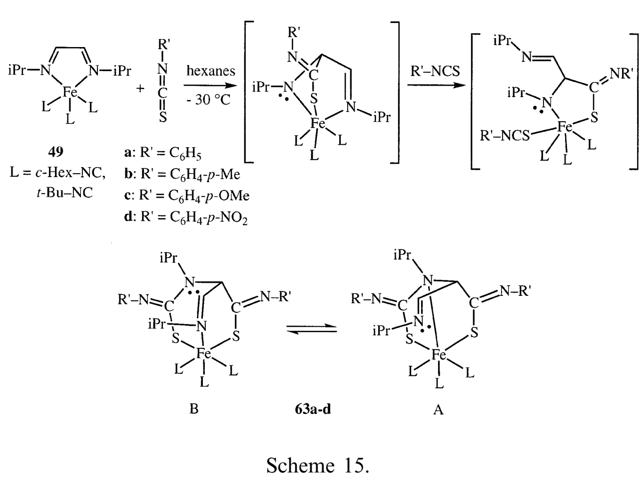
Scheme 14.

With aryl isothiocyanates **60a**–**d** (Scheme 14) complex **49a** reacted in the familiar way by cycloaddition of the C=S bond and isocyanide insertion to form the bicyclo[2.2.2] adducts **61** [96]. The structure of **61a** has been determined by X-ray crystallography. In the presence of a second equivalent of isocyanide, the bicyclo[3.2.2] products **62a**–**d**, resulting from a second isocyanide insertion, could be isolated. This reaction is cleanly thermally reversible, and by temperature dependent NMR spectroscopy, the thermodynamic parameters of an isocyanide insertion/deinsertion reaction could be determined for the first time. At high temperatures the reaction sequence is reversed all the way to **49**, however, at these temperatures the thermal stability of

49 is not sufficient to establish a stable equilibrium. The crystal structure of **62** could not be determined, because the equilibrium between **61** and **62** is obviously not frozen in even at very low temperatures. When a saturated solution of pure **62c** in ether–dichloromethane (5/1) was set away at − 80 °C, after several months crystals of **61c** and not **62c** were obtained. So, the dynamic equilibrium had completely shifted towards the side of **61c**, because, due to its lower solubility, this complex was withdrawn from the equilibrium by precipitation.

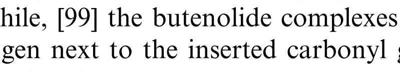
The labilisation of the coordinative bonds due to the strong σ-donation of the aliphatic isocyanide ligands in **49a**,**b**, which has already been mentioned above, obviously also plays a role again in the reaction of **49a**,**b** with aryl isothiocyanates (Scheme 15) [97]. The X-ray structure of one of the isolated products **63** (**63c** with L=*t*-Bu–NC) indicates a [3.2.0] bicyclic complex with a coordinated amido nitrogen and an uncoordinated imine nitrogen (A). Temperature dependent NMR spectroscopy, however, indicates a dynamic competition of these two nitrogen atoms for the coordination site. Just as in all previous cases, the terminally coordinated aliphatic isocyanides do not insert in the initial bicyclo[2.2.1] cycloadduct, but rather an external isothiocyanate is inserted, most likely after precoordination by displacement of the imino group.

3.1.2.3. Changing the heteroatoms. Just as the variations of the metal (Section 3.1.2.1) and of the additional ligands (Section 3.1.2.2), the variation of the heteroatom in the 1,3-dipole cannot be done arbitrarily. A suitable synthetic route to and the stability of the resulting starting compound are the limiting factors. So, just as the complexes (DAB)Ru(CO)$_3$ (**34**) and (DAB)Fe(RNC)$_3$ (**49**), several of the 1,3-dipoles in this section had to be prepared and reacted in situ. Their identity, however, was beyond doubt—either through spectroscopic characterisation and comparison with stable representatives of the same type, or at least from a complete characterisation of their reaction products.



Scheme 15.

Oxygen instead of nitrogen: α-imino ketones and α-imino esters. The earlier mentioned CAS–SCF calculations [76] had already shown that the isolobal analogy between the L$_4$Fe–N=C fragment **31** and the azomethine ylide **32** (Eq. (12)) could be extended to an L$_4$Fe–O=C fragment **64** and a carbonyl ylide **65** (Eq. (13)), and that the oxygen homologues would have slightly higher HOMO and LUMO levels, and a smaller HOMO–LUMO gap. From these properties, an increased 1,3-dipolar reactivity could be expected.

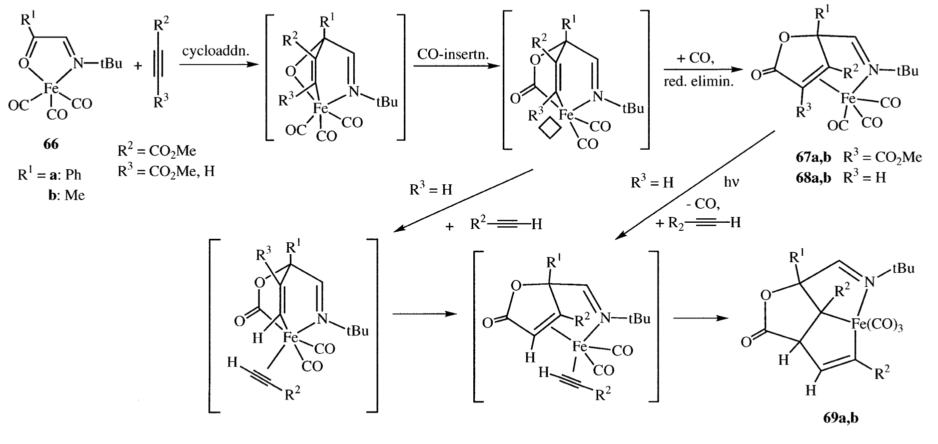


(13)

In order to compare the 1,3-dipolar reactivity of the L$_4$Fe–N=C and the L$_4$Fe–O=C fragments, i.e. to investigate the chemoselectivity of a dipolarophile towards them, a series of suitable complexes with an Fe–N=C and an Fe–O=C fragment within the same molecule, namely (α-imino ketone)Fe(CO)$_3$ (**66**) [99,100] and (α-imino ester)Fe(CO)$_3$ (**70**), [101–103] were prepared and reacted with activated alkynes (Schemes 16–18).

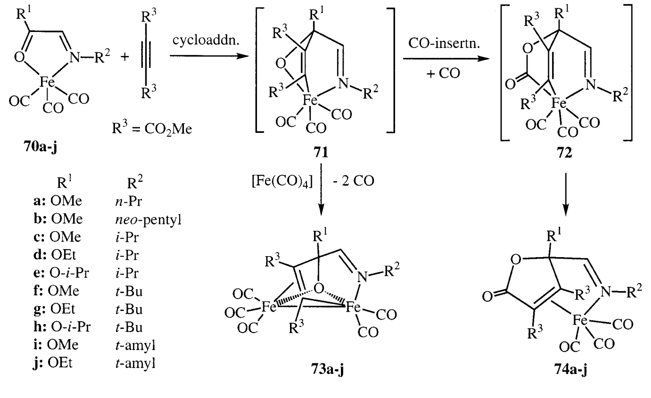
When complexes **66a**,**b** were reacted in pentane solution at − 78 °C under an atmosphere of CO with DMAD (Scheme 16), the butenolide complexes **67a**,**b** were formed in a clean reaction and could be isolated in 85 and 65% yields, [100] i.e. the reaction proceeded with complete chemoselectivity for the Fe–O=C fragment. When the same reaction was performed at − 50 and − 30 °C, respectively, with methyl propynoate (MP) as dipolarophile, [99] the butenolide complexes **68a**,**b** with the hydrogen next to the inserted carbonyl group were formed, again with complete chemo- and regioselectivity. As minor side-products, complexes that had incorporated two moles of the alkyne (**69a**,**b**) were observed. In the absence of CO, and with two equivalents of MP, exclusively the tricyclic complexes **69a**,**b** were formed in moderate yields. Complexes **69a**,**b** can also be prepared in almost quantitative yields by irradiation of the corresponding complexes **68a**,**b** in the presence of excess MP at r.t., which strongly supports the mechanism indicated in Scheme 16. X-ray structural analysis of **69b** has confirmed that of the possible regioisomers only the one shown in Scheme 16 is formed.

The different reaction temperatures in the cycloadditions of **66a**,**b** with DMAD and MP (*vide supra*) already indicated that not only the dipolarophile has a marked influence on the reactivity, but also the substituent R^1 (phenyl vs. methyl) in the 1,3-dipole. However, in either case the cycloaddition was completely selective for the Fe–O=C moiety. In order to probe in how far the reactivity of the Fe–O=C dipole could be further attenuated by the choice of R^1, an extended series of imino ester complexes **70** [102] was reacted with the two dipolarophiles DMAD and MP [103]. Instead of the aryl or alkyl groups R^1 in **66**, complexes

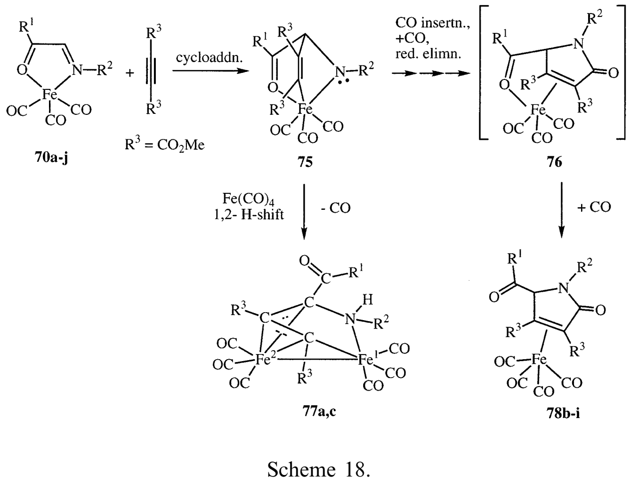


Scheme 16.

70 bear an electronegative oxygen atom. The less reactive dipolarophile MP again reacted exclusively with the more reactive Fe–O=C dipole. However, with the more reactive DMAD, the Fe–N=C dipole becomes competitive, and both the butenolide complexes **74** (Scheme 17) and pyrrolinone complexes **78** (Scheme 18) are formed. The weakly coordinating ester carbonyl group in **76** is displaced by an extra CO ligand in **78**. The initial bicyclo[2.2.1] cycloadducts **71** and **75** also undergo a side reaction with $[Fe(CO)_4]$ species, present from the in situ preparation of **70**, to give the binuclear products **73** and **77**. All product structures have been confirmed by X-ray crystallography.



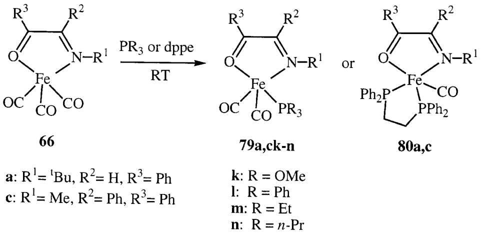
Scheme 17.



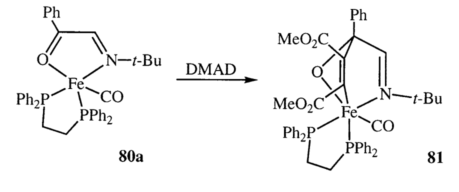
Scheme 18.

The steric bulk of both substituents R^1 and R^2 clearly influences the product distribution. Increasing the bulk of R^1, e.g. in the series **c** → **e**, or **f** → **h**, results in an increasing preference for the Fe–N=C fragment, while increasing the bulk of R^2 (**a**, **c**, **f**) favours the Fe–O=C fragment.

In the stable and isolable imino ketone complexes **66a** and **66c** (Scheme 19), at r.t., one or two carbonyl ligands could be exchanged for phosphorus ligands **k**–**n** [**k** = $P(OMe)_3$, **l** = PPh_3, **m** = PEt_3, **n** = $P(n\text{-}Pr)_3$] or dppe ($Ph_2P–CH_2–CH_2–PPh_2$) [68]. The resulting complexes **79**/**80** were prepared in the notion that the increased donor capacity of the phosphorus ligands, as compared to CO, would increase π-backdonation into the imino ketone LUMO and thus increase the reactivity of the 1,3-dipole. This was indeed the case, and complexes **79**/**80** were found reactive towards acetylenes (DMAD, MP, phenyl acetylene), olefins (dimethyl maleate) and aryl isothiocyanate (Scheme 19). Not all



Scheme 19.



(14)

cycloaddition products were isolable, though, and could only be spectroscopically characterised. The most remarkable result, however, was that for the first time in the iron system the initial bicyclo[2.2.1] adduct was directly observable. In the reaction of the dppe complex **80a** with DMAD (Eq. (14)), complex **81** was even the stable end product of which single crystals could be grown to determine its X-ray structure. CO insertion does not occur in this case, which is obviously due to the *trans* disposition of the oxygen bridge and the only carbonyl ligand, as evidenced by the crystal structure of **81**.

Sulphur instead of nitrogen: di-thiooxamide (DTA). The coordination chemistry of DTA ligands towards carbonyl iron has been studied to find out if it was possible to at least prepare in situ mononuclear chelate (σ-*S*,σ-*S*′-DTA)$Fe(CO)_3$ complexes (**82**) in order to investigate their 1,3-dipolar behaviour [104]. This proved successful with DTA ligands **a**–**d** (Scheme 20). However, only the reaction of **82a** with DMAD gave an isolable [3 + 2] cycloadduct **83a**. In **83a**, an $[Fe(CO)_4]$ fragment, present in solution from the in situ generation of **82a**, has coordinated to the sulfide bridge. This inhibits carbonyl insertion and stabilises the cycloadduct. Extensive decomposition is observed when the reaction with DMAD is done with pure **82a**, i.e. in the absence of $[Fe(CO)_4]$, and the only isolable product is a small amount of **83a**. When **82d** is reacted with an excess of DMAD, no [3 + 2] cycloaddition takes place, and only small amounts of **84d**, as the result of two [2 + 2] cycloaddition reactions, can be isolated.

The cycloaddition of the C=O bond of ketones across the M–N=C fragment in complexes (*t*-Bu–N=CH–CH=N–*t*-Bu)$_2$M (M = Zr, Hf) [105] leads to octahedral complexes with two *N*,*N*,*O*-terdentate ligands, HC(N$^-$–*t*-Bu)(CH=N–*t*-Bu)C(R,Ph)–O$^-$. Though a new C–C bond is formed, we are here in fact dealing with an 'inorganic' 1,3-dipolar cycloaddition reaction, as defined in Section 1, because no metal-to-carbon bond is involved. However, the example shows, that even in early transition metal complexes the M–N=C fragment exhibits 1,3-dipolar behaviour.

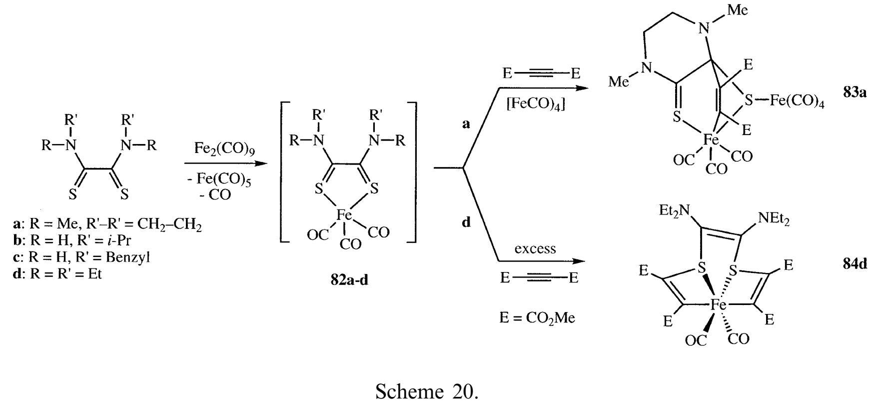
3.2. Cycloaddition reactions with other metalla 1,3-dipoles

3.2.1. M–X–Y dipoles, the metal in terminal position of the 3-atom component

Werner [106–109] has reported on the 1,3-dipolar properties of the cobalt acetimidoyl complex **85** (Scheme 21). Complex **85** is not observable (though the corresponding *tert*-butylimidoyl complex [110], and the homologous rhodium acetimidoyl complex [106] have been isolated) but reacts with acetone, acetaldehyde, benzaldehyde, phenyl isothiocyanate and various nitriles as dipolarophiles to give five membered metallacycles **86**–**88**. The addition of acetone is reversible, and complex **86** can be used as an isolable source of **85**.

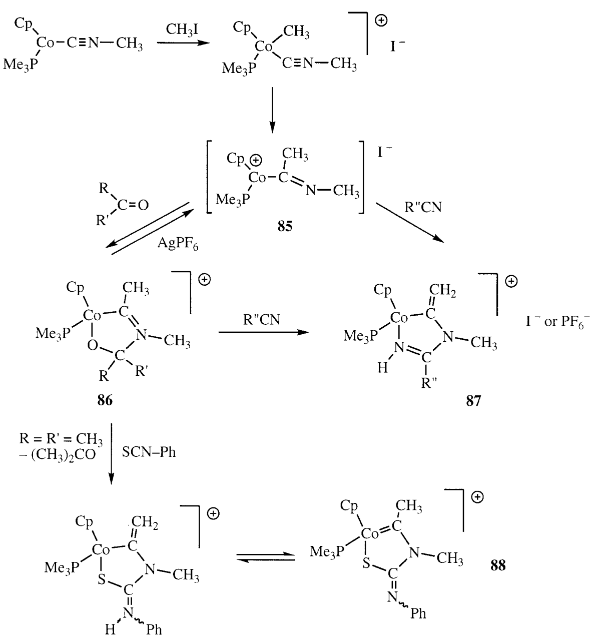
Cenini et al. [111,112] have reported that the platinum nitrosobenzene complex $[Pt(PPh_3)_2(PhNO)]$ (**89**) has a η^2-bonded nitroso ligand and inserts carbon dioxide, carbon disulphide, and unsaturated carbon compounds into the platinum–nitrogen bond (top of Scheme 22). This description is formally correct, but with the knowledge of the isolobal relations discussed in Section 3.1.1.2, it seems much more plausible to describe the reaction as a 1,3-dipolar cycloaddition of **89** occurring from a terminal, *O*-coordinated form $L_2Pt{-}O{=}N{-}Ph$ (**A**). $L_2Pt(0)$ is a $d^{10}ML_2$-fragment which, according to the isolobal relation between d^{n+2}-ML_2 and d^nML_4, [72] is isolobal with the d^8ML_4-fragment discussed in Section 3.1.1.2, and hence **A** is a 1,3-dipole which reacts with the typical dipolarophiles to give the metallacycles **90**–**93**.

The addition of various electron-poor olefins to metal–dioxygen complexes $(PPh_3)_2MO_2$ (M = Pt, Pd), to give metalla-2,3-dioxolanes, [113] has been described as a stepwise process involving a nucleophilic addition of $(PPh_3)_2M^+{-}O{-}O^-$ to the olefin, however, from the electronic situation it might just as well proceed in a concerted fashion involving a $(PPh_3)_2M \leftarrow O{=}O$ species, analogous to structure **A** in Scheme 22. The addition of various carbonyl compounds to $(PPh_3)_2PtO_2$ has also been reported, [114–118] but as there are no

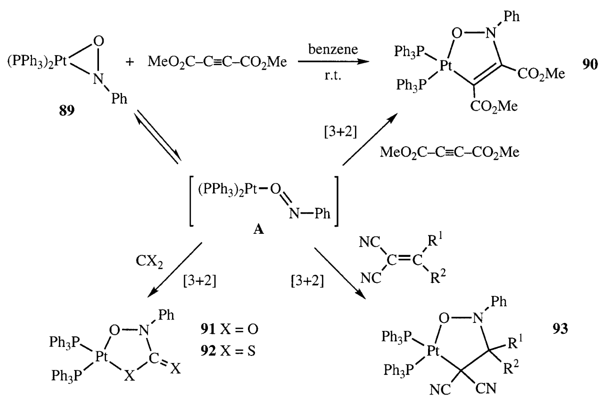


a: R = Me, R'-R' = CH_2–CH_2
b: R = H, R' = *i*-Pr
c: R = H, R' = Benzyl
d: R = R' = Et

Scheme 20.



Scheme 21.

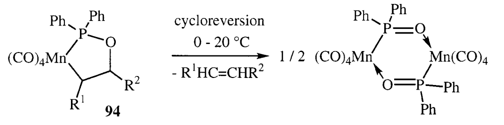


Scheme 22.

metal–carbon bonds involved, these are by definition 'inorganic' and outside the scope of this review.

The stoichiometric and catalytic reactions of $L_2Ni(0)$ complexes with isocyanates and aldehydes, [119,120] imines, [121] alkynes, [122,123] alkenes, [124–129] and allenes [130] to give five-membered nickelacycles, which have been described by Hoberg et al. can be understood by the same isolobal argumentation. The first reaction step would then generate the 1,3-dipolar species **A** by ligand displacement in the $L_nNi(0)$ precursor, mostly Ni(cyclododeca-1,5,9-triene) or Ni(cycloocta-1,5-diene)$_2$, $(COD)_2Ni$, by phosphines or TMEDA and phenyl isocyanate. A generic example of these reactions is shown in Scheme 23, and Schemes 24–28 show consecutive reactions of some of the obtained nickelacycles to give organic products.

In Section 3.1.2.1.2, the electronic situation of the cycloaddition of alkyne to the 1,3-dipolar MnL_5–N=C species has been discussed in terms of the isolobal analogy between a d^8ML_4 and a d^6ML_5 fragment, and it has been stated that the electronically and structurally equivalent complexes $(DAB)M(CO)_4$ (M = Cr, Mo, W) do not undergo this cycloaddition reaction obviously only because it is difficult to exceed the coordination number 6. Lindner [131–133] has reported that complexes **94** and **95** (Eqs. (15) and (16)), formally cycloadducts of olefins to d^6-ML_5–P=O fragments but obtained in a different way, undergo the shown thermal [3 + 2] cycloreversion reactions and thus give evidence of d^6-ML_5–P=O being a 1,3-dipole. The isolobal series CH_2–d^8ML_4–d^6ML_5, which has been exemplified in Section 3.1.2.1.2, can be extended to d^4ML_6. Cp_2Mo in complex **96** is such a fragment coordinated to CS_2, and the reaction with electron-deficient alkynes (Eq. (17)) has been reported in 1988 [134]. Already 15 years earlier, a related reaction of CS_2 complex **97** with dimethyl acetylenedicarboxylate (Eq. (18)) had been reported by Wakatsuki [135]. Here once again a d^8ML_4 fragment, namely $Cp(PPh_3)Rh$, is present. A related but intramolecular reaction is that of **98**, Tp*(MeCN)Ir(η^1-CH=CH–R)(η^1-CH_2–CH_2–R) (R = H, Me; Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) producing the aromatic iridapyrrole **100** (Eq. (19)) [136]. The gain of aromatisation energy is the driving force for the tautomerisation of the unobserved **99** to **100** by a 1,2 hydrogen shift.



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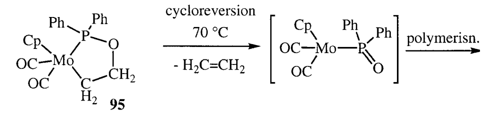

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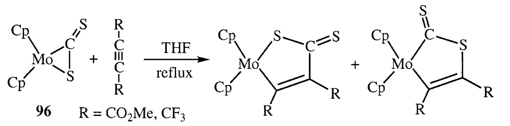

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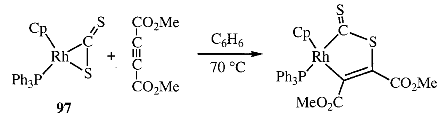

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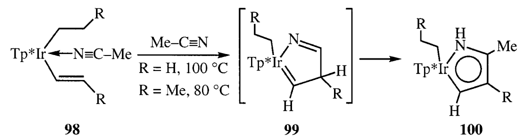

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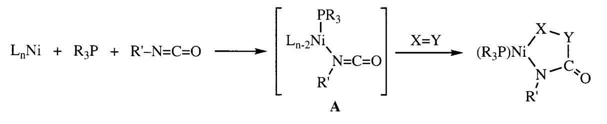
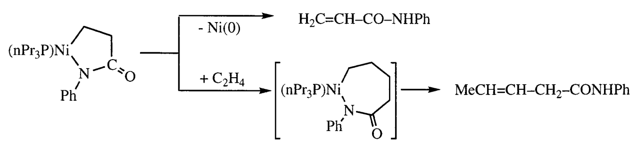
3.2.2. X–M–Y dipoles, the metal in central position of the 3-atom component

As has been stated many times, 1,3-dipolar cycloaddition reactions may proceed either by way of a cyclic

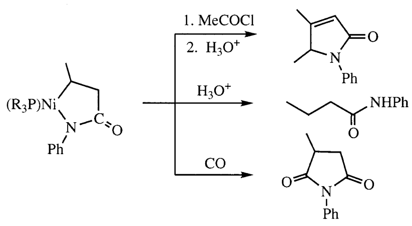


L_n = $(COD)_2$, 1,5-hexadiene, cyclododeca-1,5,9-triene
R = Et, nPr, cHex, Ph
R' = Me, nBu, tBu, cHex, Ph, pTol
X=Y = $H_2C{=}CH_2$, $Me\text{–}CH{=}CH_2$, $Ph\text{–}CH{=}CH_2$, $H_2C{=}CH\text{–}(CH_2)_{0,2,3}\text{–}CH{=}CH_2$, $R''\text{–}C(H){=}O$ (R'' = H, Ph), Ph–CH=N–Ph, $R'''\text{–}C{\equiv}C\text{–}R'''$ (R''' = Ph, CO_2Me)

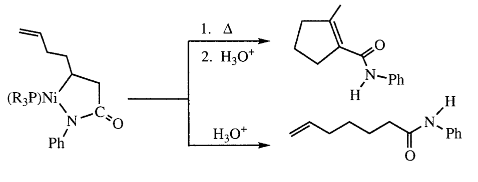
Scheme 23.



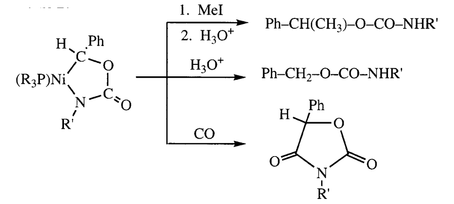
Scheme 24.



Scheme 25.

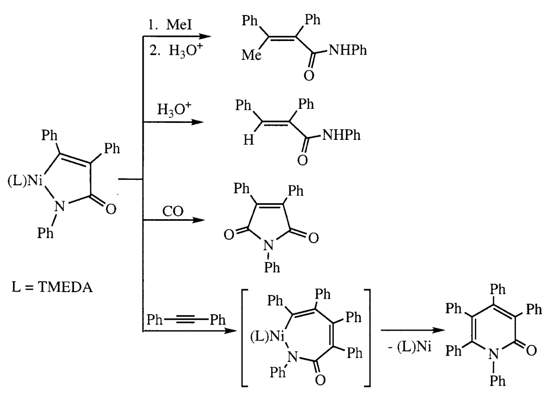


Scheme 26.

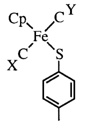


Scheme 27.

transition state in a concerted fashion, or by a stepwise process through a charge-separated, zwitterionic intermediate. In the organometal cycloaddition reactions discussed in this section, this mechanistic aspect has been addressed in one case by Enemark et al. [137,138] The 1,3-dipolar systems investigated by Enemark are represented by structures **101** [137] and **102** [138]. Complexes **101** were reacted with dimethyl acetylenedicarboxylate (DMAD) to give **103**. This reaction of **101** and of $(Cp)(CO)_3W\text{–}SR$ with DMAD and hexafluoro butyne-2 had earlier been reported by Davidson, [139–141] and a stepwise mechanism had been suggested [141]. The reaction of $(Cp)(CO)_3W\text{–}SR$ with $HC{\equiv}CCN$ has also been reported [142]. However, kinetic measurements, [137] i.e. the influence on the rate of solvent polarity and of Hammett parameters, and the observed chemoselectivity for CX or CY, strongly suggests that the reaction follows a concerted pathway. A MO correlation diagram for the reaction, which includes all π-type orbitals of the RS–Fe–CO fragment, which lie in the same plane as the reacting π-orbitals of the incoming alkyne, shows no symmetry-imposed barriers for a concerted 1,3-dipolar [3 + 2] cycloaddition reaction of the type $[_{\pi}4 + _{\pi}2]$. Sharp et al. [143–145] have studied comparable reactions of complexes $CpM(SMe)(CO)_3$ (M = Mo, W) and $CpM(SMe)(CO)_2$ (M = Fe, Ru) with CF_3-substituted alkynes where metalla five-rings analogous to **103** are formed. Schenk [146] has reported the reaction of $(Cp)(PPh_3)(CO)Ru\text{–}SR$ (R = Me, CH_2Ph) with DMAD, again to give metalla five-rings analogous to **103**.

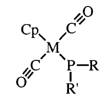


Scheme 28.



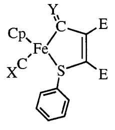
CX, CY = CO
CX = CS; CY = CO
CX = CO; CY = CNMe
CX = CS; CY = CNMe
Z = OMe, H, Cl, NO_2

101



M = Fe
R = R' = Ph

102



X = Y = CO
X = S; Y = O
X = O; Y = NMe
X = S; Y = NMe

103

Contrasting these results with the aryl thiolate complexes **101** are the observations with phosphido complexes **102** [138]. The reaction with DMAD and methyl propiolate[3] [138] gives the cycloadducts analogous to **103**, but the reaction with dimetyl fumarate and maleate (Scheme 29) is stereoselective, but not

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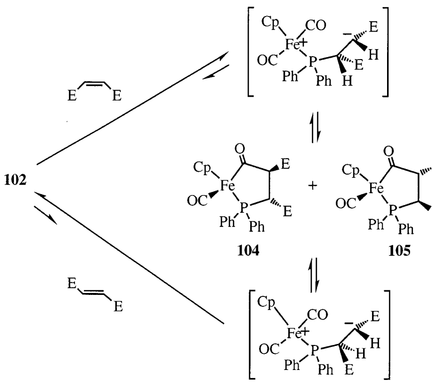
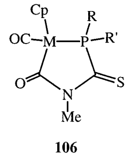
[3] Analogous reactions of $Cp(CO)_3M\text{–}PPh_2$ (M = Mo, W) with DMAD and methyl propiolate have been reported by Morris [147].



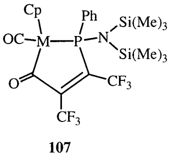
Scheme 29.

stereospecific, and indicates a stepwise mechanism that allows rotation about the C–C bond of the reacting alkene. The two observed diastereomeric metalla heterocycles **104** and **105** are obtained in the same ratio of 1.2:1, regardless of whether the *cis*- or the *trans*-olefin is used. When **102** is reacted with an excess of dimethyl maleate, this is catalytically isomerised to dimetyl fumarate. The authors conclude, that ‘the dissimilar mechanisms for these superficially comparable reactions may be a consequence of the subtle differences in the spatial nature and character of the phosphido and thiolate ligand lone pairs, the steric influence of the additional substituent of the phosphide ligand, and the differing dipolarophiles’.

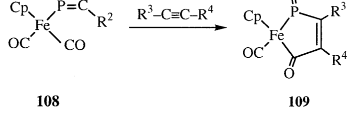
Complexes **102** (M = Fe, R = R′ = Ph, R = R′ = *t*-Bu, R = Ph, R′ = *t*-Bu; M = Ru, R = R′ = *i*-Pr) also react with methyl isocyanide to give **106** [148]. Reaction of complex **102** (M = Fe, R = Ph, R′ = N{SiMe$_3$}$_2$) with CF$_3$C≡CCF$_3$ gives ferracyclopentenone **107** [149]. Complexes of phosphaalkenes (**108**) (Eq. (20))[150–153] or diphosphenes (**110**) (Scheme 30) [153–157] react correspondingly with activated alkynes or hexafluoro acetone to give **109** or **111** and **112**, respectively.



106



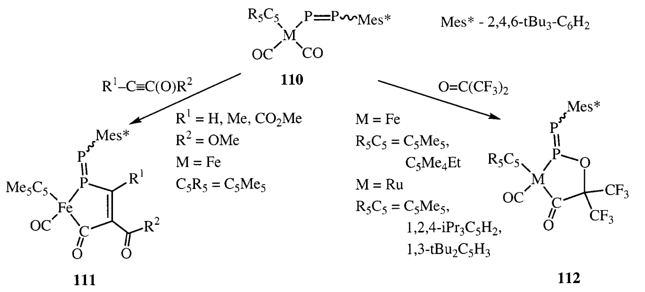
107



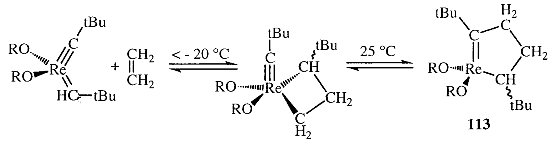
R^1, R^2	R^3, R^4
SiMe$_3$, SiMe$_3$	MeO$_2$C, MeO$_2$C
SiMe$_3$, Ph	MeO$_2$C, Me
NMe$_2$, NMe$_2$	Ph, C(O)tBu
	H, MeO$_2$C
	H, EtO$_2$C

(20)

Schrock [158] has described an interesting reaction where no heteroatom at all is involved, namely the reversible cycloaddition of ethylene to a C≡Re=C fragment to give rhenacyclopentene **113**. However, the reaction does not actually represent a [3 + 2] addition, but proceeds via an initial rhenacyclobutane by a [2 + 2] addition.

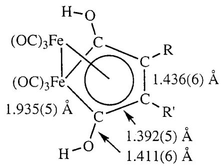


Scheme 30.

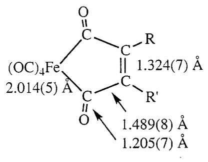


(21)

Sappa et al. [159,160] have reported the formation and crystal structures (for R = R′ = Et) of (among other products) compounds **114** and **115** from the reaction of pentacarbonyl iron in alkaline methanol at reflux with internal and terminal alkynes. The products are obviously the result of a [3 + 2] cycloaddition of the alkyne across the carbon atoms of the O=C=Fe=C=O fragment. Comparable and much cleaner is the formation of **116** from (bipy)Ni(CO)$_2$ and diphenyl acetylene or butyne-2 at r.t. in THF [161].

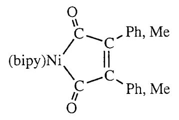


114



115

R	R′
H	Et
H	nPr
Me	Me
Et	Et



116

Concluding remarks

The concept and principle of 1,3-dipolar [3 + 2] cycloaddition reactions as conceived and developed by Huisgen can be readily extended to organometal 1,3-dipoles and, to a lesser extent, to organometal dipolarophiles. The number of examples reported in the literature, where multiple bonds between a metal and a (hetero)atom react with organic 1,3-dipoles, is much smaller than that of cases where a metalla 1,3-dipole reacts with a wide variety of dipolarophiles. In this review, it has been demonstrated by extended series of isolobal transformations that almost any fragment of a metal complex, that can be isolobally related to one of the 1,3-dipoles of Huisgen, indeed undergoes $[3+2]$ cycloaddition reactions with suitable dipolarophiles, provided that the maximum coordination number of the metal is not exceeded. The initially resulting 5-membered metalla heterocycles can, by consecutive insertion and/or reductive elimination reactions, be converted to a great variety of synthetically interesting organic heterocycles, which by other routes would be very difficult to prepare.

It is clear that the synthetic potential of organometal $[3+2]$ cycloaddition reactions is by far not exhausted and should further be investigated and exploited. Of particular interest would be catalytic versions of the type of reactions that have been discussed in this review. To my knowledge, there is only one example, where an organometal $[3+2]$ cycloaddition reaction has been explicitly discussed as a mechanistic pathway for the catalytic synthesis of organic heterocycles [80].

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