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Synthesis and reactivities of diazoalkane complexes

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CONTENTS

ABSTRACT

Diazoalkane complexes have been attracting wide interest because of their rich coordination chemistry. Diazoalkane ligands, derived from either free diazoalkanes or other precursors such as coordinated dinitrogen, azines, and hydrazones, display numerous coordination modes acting as π- and/or σ-bound terminal, bridging, or chelating ligands to form mono- or multimetallic complexes. The reactivities of coordinated diazoalkanes are largely affected by their coordination modes. The variety of reactivities observed for these coordinated diazoalkanes is quite different from those of free diazoalkanes. In this review are described the synthesis, structures, and reactivities of diazoalkane complexes.

1. INTRODUCTION

Diazoalkanes $R^1R^2CN_2$ are of significant importance in organic synthesis because of their high reactivity. Thermal or photochemical decomposition of diazoal-

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kanes provides one of the most general ways for generating carbene intermediates [1]. Furthermore, diazoalkanes serve as the typical so-called 1,3-dipoles and undergo, with retention of the C–N bond, cycloaddition reactions which constitute useful methods for the synthesis of heterocyclic compounds [2]. However, the great difficulty of synthesizing particular diazoalkanes with desired structures as well as the toxicity and instability of diazoalkanes with low molecularity often set limitations to the utilization of these potential reagents.

Reactions of diazoalkanes with metal compounds have been extensively investigated. The decomposition of diazoalkanes is well known to be catalysed by a wide range of transition metal ions and complexes. This has been utilized, for example, for the reactions of diazoalkanes with alkenes affording cyclopropanes [3], products of the same type as those formed on thermal and photochemical decomposition in the presence of alkenes. However, in the metal-catalysed systems, complexes containing a carbene unit are suggested to be the actual reactants instead of free carbene intermediates. Detailed studies of these reaction systems have contributed to the progress in metal–carbene chemistry [4,5]. In addition, a significant number of diazoalkane complexes have been isolated in stable forms from the reaction of certain transition metal complexes with diazoalkanes [4]. Interestingly, the coordination modes of the diazoalkanes displayed at mono- and multimetallic centres are quite diversified. The trapping and concurrent stabilization of highly reactive species are among the important functions featured in these organometallic compounds. Investigation of the reactivities of diazoalkanes coordinated to transition metal centres in various forms might lead not only to the elucidation of the details of metal-catalysed diazoalkane carbenoid reactions but also to the exploitation of the metal-assisted novel reactivities of these molecules.

Equally important is the relevance of the chemistry of diazoalkane complexes to the chemistry of N_2 fixation [6]. The development of reaction systems in which the N_2 molecule is converted into a nitrogen-containing organic compound under mild conditions is one of the most challenging topics in transition metal chemistry and diazoalkanes are intriguing objectives as nitrogenous products from these systems.

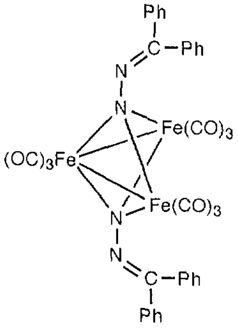
In this review, we first classify the diazoalkane complexes reported to date in terms of the coordination modes of the diazoalkane ligands, and then the preparation and reactivities of the diazoalkane complexes will be summarized. (Throughout this review, two N atoms and the C atom attached to the N atom are denoted as $N_\alpha=N_\beta=C_\alpha$ for clarity.) Studies of metal-mediated organic reactions of diazoalkanes are not dealt with here, since in most of these systems the intermediate metal–diazoalkane species are not defined. Significant emphasis will be put on the chemistry of the Mo and W diazoalkane complexes derived from dinitrogen complexes containing tertiary phosphines as the ancillary ligands. In these complexes diazoalkane ligands with diverse substituents are readily available from molecular nitrogen in the coordination sphere. However, many diazoalkane complexes originate from the free diazoalkanes. The reader can refer to earlier reviews [4,7,8] which relate to the topics of this article.

2. COORDINATION MODES OF DIAZOALKANE LIGANDS

Reactions of diazoalkanes with transition metal complexes affording complexes with diazoalkane ligands were initially reported for those of $[Fe(CO)_5]$ or $[Fe_3(CO)_{12}]$ with diaryldiazomethane; one product from these reactions was characterized as a trinuclear cluster $[Fe_3(NNCPh_2)_2(CO)_9]$ (**1**) containing the μ_3-η^1-diazoalkane ligand [9]. On the contrary, monomeric diazoalkane complexes were isolated by treatment of $[Ni(Bu^tNC)_2]$ or $[Ni(COD)_2]$ with diazofluorene and diphenyldiazomethane [10], in which the diazoalkanes are η^2 bonded to the Ni(0) centre through the N–N multiple bond (e.g. $[Ni(diazofluorene)(Bu^tNC)_2]$ (**2**)) [11]. Subsequent reactions of these diazofluorene complexes with substituted alkenes afforded the cyclopropanation products [11], demonstrating the close relevance of these diazoalkane complexes to the carbenoid reactions of diazoalkanes catalysed by metal complexes. Following this pioneering work, many diazoalkane complexes have been prepared and their structures unequivocally characterized by X-ray analyses as summarized below.

2.1 *Diazoalkane ligands coordinated to single metal centres*

Well-defined monomeric complexes reported to date contain either the η^2-bound diazoalkane ligands through the N–N multiple bonds or the η^1-diazoalkane ligands coordinated at the terminal nitrogen atom. Other coordination modes of diazoalkanes are also possible involving π binding through the C–N bond, the cycloadduct at the N_α and C_α atoms, and η^1 coordination at the C_α atom. However, unambiguous examples of these types are yet unknown, although complexes of the third type are frequently assumed to be initial intermediates prior to metal–carbene species in the transition-metal-catalysed carbenoid reactions using diazoalkanes [3].



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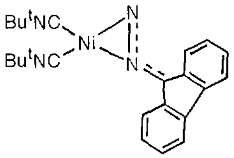

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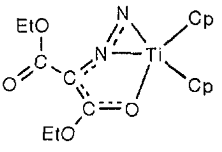
In $[Ni(diazofluorene)(Bu^tNC)_2]$ (**2**) [11], the diazofluorene ligand coordinates to the Ni atom at two N atoms. The coordination sphere around the Ni atom is essentially planar and the diazofluorene ligand is almost coplanar. The N–N distance at 1.245(4) Å corresponds to the N–N double bond and is much elongated from that of free diazofluorene (1.125(4) Å), while the C–N distance at 1.334(4) Å is intermediate between the C–N single and double bonds and comparable with that in free diazofluorene (1.323(4) Å). The N–N–C linkage is bent by 133.8(3)° in contrast to the linear C–N–N linkage in free diazofluorene. An analogous η^2-diazoalkane ligand was observed in $[Ru(NNC_5Cl_4)(CO)_2(PPh_3)_2]$ [12]. These complexes exhibit strong ν(NN) bands associated with the diazoalkane ligands in the region 1480–1520 cm^{-1}.

In addition to these low valent complexes of late transition metals, the titanocene derivative $[Cp_2Ti\{NNC(COOEt)_2\}]$ (**3**; $Cp = \eta^5\text{-}C_5H_5$) contains the side-on bound diazoalkane ligand [13]. In **3**, the Ti atom further interacts with one carbonyl O atom in the ethoxycarbonyl group. Vanadium complexes $[Cp_2V(NNCR_2)]$ (R = COOEt, Ph) may also contain diazoalkane ligands of this type [13].

The η^1-diazoalkane ligands coordinating at the N_α atom to the monometallic centre occur more frequently and, interestingly, accumulated data have revealed substantial structural diversity displayed at the M–N–N–C core.

The diazoalkane complexes most thoroughly studied to date are Mo and W complexes of the types *trans*-$[MX(NNCR^1R^2)(dppe)_2]^+$ (**4**; dppe = $Ph_2PCH_2CH_2PPh_2$) and *cis,mer*-$[MX_2(NNCR^1R^2)(PMe_2Ph)_3]$ (**5**; X = halide) readily synthesized from the dinitrogen complexes *trans*-$[M(N_2)_2(dppe)_2]$ and *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ respectively (vide infra). As illustrated by the X-ray analyses of *trans*-$[WF(NNCMeCH_2COMe)(dppe)_2][BF_4]$ (**4a**) [14], *trans*-$[WBr(NNCMe_2)(dppe)_2]Br$, and *trans*-$[WBr\{NNCH(CH_2)_3OH\}(dppe)_2][PF_6]$ [15], the diazoalkane ligands in these complexes are considered to be a formal four-electron donor represented as $[M \equiv N^+ - N = CR^1R^2]$. This formalism also satisfies the eighteen-electron count of the central metal. In **4a**, for example, the W–N–N linkage is essentially linear (174(2)°), while the N–N–C bond is bent with the angle



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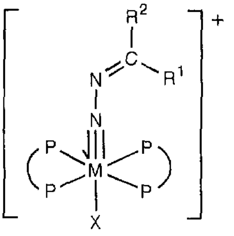

M = Mo, W
P P = $Ph_2PCH_2CH_2PPh_2$

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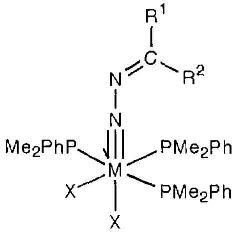

M = Mo, W
X = Cl, Br, I

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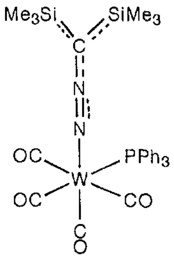
of 125(2)°, exemplifying the sp^2 character of the N_β atom. The observed N–N and N–C distances at 1.32(2) and 1.30(3) Å, both being intermediate between a single and a double bond, suggest some contribution of the resonance structure $[M^-{=}N^+{=}N{-}C^+R^1R^2]$ towards the predominating structure shown above. This feature is supported by the observation that the C_α atom is susceptible to attack by nucleophiles in certain dppe complexes [16]. The short W–N distance of 1.77(2) Å is consistent with W–N multiple bonding. More recent X-ray analyses for the dppe complexes *trans*-$[WBr(NNCCl_2)(dppe)_2][PF_6]$ [17], *trans*-$[WBr(NN\overline{CNMeCH_2CH_2N}Me)(dppe)_2][PF_6]$ [18], *trans*-$[WF\{NNCMeCH(CONHPh)_2\}(dppe)_2][BF_4]$, and [*trans*-$\{(dppe)_2WF\}_2(\mu\text{-}NNCHCHMeCHMeCHNN)]$ [19], as well as the PMe_2Ph complexes *cis,trans*-$[WCl_2(NNCMeR)(PMe_2Ph)_2(L)]$ ($R = Me$, $L = C_2H_4$; $R = Ph$, $L = p\text{-}MeC_6H_4CHO$) [20], *cis,trans*-$[WCl_2(NNCMePh)\{{=}C(Me)NHBu^t\}(PMe_2Ph)_2]$ [21], and *mer,trans*-$[WBr_3(NNCMePh)(PMe_2Ph)_2]$ [22] have demonstrated a similar structural feature of the diazoalkane ligands in these complexes. The IR spectra of these diazoalkane complexes exhibit characteristic ν(C=N) bands in the region between 1510 and 1590 cm^{-1}. A series of diazoalkane complexes $[M(NNCHR)(CO)(S_2CNR'_2)_2]$ and $[M(NNCHR)X_2(S_2CNR'_2)_2]$ ($M = Mo$, W; $R = Ph$, $p\text{-}MeC_6H_4$; $R' = Me$, Et; $R'_2 = (CH_2)_4$) has also been reported, whose spectroscopic data indicate the presence of the similar four-electron donating singly-bent diazoalkane ligands [23].

Diazoalkane ligands of this type have also been observed in complexes such as $[Cp_2Ti(NNCPh_2)(PMe_3)]$ [24], $[Cp_2NbH(NNCPh_2)]$ [25], $[Cp_2NbCl\{NNCPh(C_6H_4Br\text{-}o)\}]$ [26], and $[Mo(NNCPh_2)(OBu^t)_4]$ [27], as well as the dinuclear complex $[CpMo({=}CR_2)(NNCR_2)MoCp(CO)_3]$ ($R = p\text{-}MeC_6H_4$) [28]. However, for the former Ti and Nb complexes, the electron count of the Ti and Nb atoms implies that the two-electron donating structure, e.g. $[M{=}N^+{=}N{-}C^-R^1R^2]$, may be predominant.

In contrast to the relatively high valent Mo and W diazoalkane complexes with formal d^2 or d^1 metal centres described above, the low valent W complex with a d^6 configuration $[W\{NNC(SiMe_3)_2\}(CO)_4(PPh_3)]$ (**6**) has the two-electron donating diazoalkane ligand with an essentially linear W–N–N–C linkage (W–N–N and N–N–C angles, 176(1)° and 170(1)° respectively) [29]. Significant differences are also observed between bond lengths within this ligand and those within the high valent dppe and PMe_2Ph complexes. Thus, the W–N distance at 2.16(1) Å in **6** is much longer, signifying a W–N single bond. The N–N and N–C bond lengths at 1.17(2) Å and 1.34(1) Å are intermediate between a double and a triple bond and between a single and a double bond respectively. In particular, quite a short N–N bond presents a sharp contrast to those in the singly bent diazoalkane ligands described above. These bonding parameters suggest that the two N atoms in the diazoalkane ligand in **6** both possess approximate sp hybridization. The Cr analogue of **6** has been similarly prepared. Coordination of diazoalkane to the zero-valent Mo and W centres also occurs on treatment of *trans*-$[M(N_2)_2(dppe)_2]$ with



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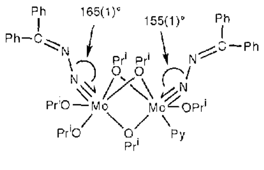
$N_2CHCOOEt$, yielding *trans*-$[M(NNCHCOOEt)_2(dppe)_2]$. However, the structure of the diazoalkane ligands in these complexes is uncertain [30].

There exist several complexes with the formal two-electron donating diazoalkane ligand but its structure corresponds to an intermediate between the linear and the singly bent forms. The well-defined complexes included in this class are $[IrCl(NNC_5Cl_4)(PPh_3)_2]$ [31] and $[CpMn\{NNC(COOMe)_2\}(CO)_2]$ [32]. The M–N–N linkages in these complexes are almost linear and the N–N distances correspond to a bond order between a double and a triple bond as observed in **6**. However, in contrast to **6**, the N–N–C linkages are bent with angles of 141(1)° in the former and 151(1)° in the latter. Furthermore, the Ir–N and Mn–N bonds at 1.82(1) and 1.80(1) Å are significantly shortened from the W–N distance in **6**. The M–N–N angles and the N–N distances as well as the high NN stretching frequencies (1850–1910 cm^{-1}) are indicative of the two-electron donating structure $[M{\leftarrow}N{\equiv}N^+{-}C^-R^1R^2]$ as predominating but some multibonding nature of the M–N moieties and the bent N–N–C linkages might suggest perturbation by the structure $[M{=}N^+{=}N{-}C^-R^1R^2]$ to some extent. Similar four- and five-coordinate Ir complexes with the NNC_5X_4 ligand (X = Cl, Br) have been subsequently reported [33]. The diazoalkane ligand with this type of structure seems also to be present in $[IrCl\{NNC(COPh)_2\}(PPh_3)_2]$ [34], $[IrMe(NNCPh_2)(PPr^i_3)_2]$, and $[RhCl(NNCPh_2)(PPr^i_3)_2]$ [35].

In the dinuclear complex $[Mo_2(NNCPh_2)_2(OPr^i)_6(py)]$ (**7**; py = pyridine), two diazoalkane ligands terminally bound to each inequivalent Mo centre exist [27]. An interesting feature demonstrated for these diazoalkane ligands is the large distor-



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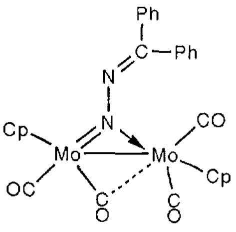
tion from 180° of one of the Mo–N–N angles. A contribution of the doubly bent structure [Mo=N–N=CPh$_2$] has been claimed to explain the observed Mo–N–N angle of 155(1)°.

2.2 Diazoalkane ligands coordinated to bi- and multimetallic centres

Since the initial characterization of the trinuclear diazoalkane complex **1**, a substantial number of diazoalkane complexes with bi- and multimetallic cores have been isolated. One well-defined coordination mode observed for the diazoalkane ligand at the dinuclear centre is the μ_2-η^1 binding using only the N$_\alpha$ atom. Complexes included in this type are [Cp$_2$Mo$_2$(NNCPh$_2$)(CO)$_6$] (**8**) [36], [W$_2${NNC(C$_6$H$_4$Me-*p*)$_2$}$_2$(OBu^t)$_6$] [27], and [V$_2$(NNCHSiMe$_3$)$_2$(OC$_6$H$_4$OMe-*o*)$_4$] [37]. For example, within the coordinated N$_2$CPh$_2$ of **8**, the N–N–C linkage is bent with an angle of 122(1)° and the N–N and N–C bond lengths of 1.35(1) and 1.28(1) Å are suggestive of bond orders of 1.2 and 2. The Mo–N distances are not equal at 1.914(8) and 2.083(8) Å. These data indicate that **8** is best described by the resonance of two structures containing a formal four-electron donating diazoalkane ligand **8a** and **8b**, with **8a** predominant. A coordination mode of this type is also proposed for the so-called A-frame complex [Rh$_2$(NNCR^{1}R^2)(CO)$_2$(dppm)$_2$] (R^1 = COOEt, R^2 = H, COOEt, dppm = Ph$_2$PCH$_2$PPh$_2$) [38].

Another well-established type of binding of a diazoalkane ligand to a dinuclear centre is the μ-η^1:η^2 coordination, in which the N$_\alpha$ atom bridges two metal centres and the N$_\beta$ atom further coordinates to one of the two metals. This mode was found in the fully characterized complexes [{Cp*Mo(CO)$_2$}$_2$(NNCMe$_2$)] (**9**; Cp* = η^5-C$_5$Me$_5$) [39], its NNCHCOOEt analogue [36], [(μ-η^5:η^5-C$_{10}$H$_8$)(CpZrCl)$_2$(NNCPh$_2$)] (**10**) [40], and [(CpTiCl)$_2$(NNCPh$_2$)$_2$] [41]. In [(Cp'$_2$Zr)$_2$-(NNCHPh)$_2$] (**11**); Cp' = η^5-C$_5$H$_4$Me), one diazoalkane ligand coordinates in this μ-η^2:η^1 manner, while the other binds in the μ-η^1 manner described above [42].

For the diazoalkane ligand in **9**, the three Mo–N distances are essentially similar (2.12(1)–2.13(1) Å) and the M$_1$–N$_\alpha$–N$_\beta$ and N$_\alpha$-N$_\beta$–C$_\alpha$ linkages are significantly bent (113(1)° and 133(1)°):



8a

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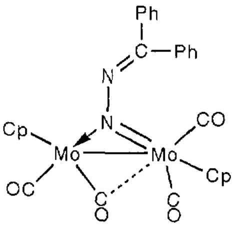

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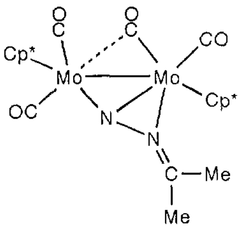

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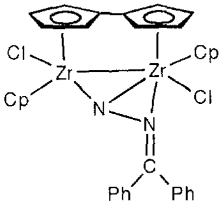

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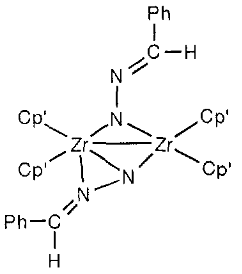

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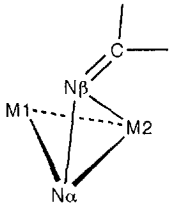
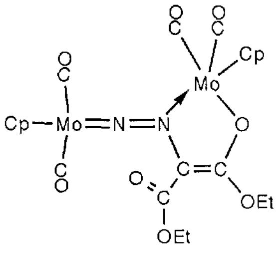


On the contrary, the Zr–N bond lengths in **10** differ considerably from each other. Thus, in contrast to the M_1–N_α distance at 2.073(2) Å, the M_2–N_α and M_2–N_β distances are lengthened to 2.209(3) Å and 2.255(3) Å respectively, indicating that the NN moiety in **10** is more weakly bound to the M_2 centre than in **9**. A much larger M_1–N_α–N_β angle of 152.1(2)° in **10** than those in **9** is consistent with this feature. Within the μ-η^2:η^1-NNCHPh ligand of **11**, the M_1–N_α–N_β angle further increases to become almost linear (174.1(6)°), although the Zr–N distances are comparable with those in **10**. The N–N distances in all these complexes are in the range 1.32–1.37 Å, corresponding to a bond order between 1 and 2.

The $NNC(COOEt)_2$ ligand in $[(CpMo)_2\{NNC(COOEt)_2\}(CO)_4]$ (**12**), produced from the reaction of $[Cp_2Mo_2(CO)_4]$ with the free diazoalkane, displays a unique bridging mode between two Mo atoms [36]. In **12**, the Mo–Mo triple bond in the starting Mo complex is completely disrupted. The N_α atom in the



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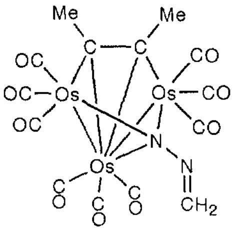
$NNC(COOEt)_2$ ligand binds to one Mo atom as a three-electron donor, which is suggested by the Mo–N distance at 1.86(1) Å estimated to be a double bond. On the contrary, the other Mo atom is bound to the N_β atom as well as one O atom in the COOEt group. Both the Mo–N and the Mo–O distances at 2.21(1) and 2.14(1) Å correspond to a single bond. The N–N and N–C distances at 1.24(1) Å and 1.42(1) Å are typical of a bond order of 2 and 1 respectively. These data indicate that the structure shown below is predominant.

Diazoalkanes can also bind to trinuclear centres. The μ_3-η^1 coordination mode has been characterized unequivocally for $[Fe_3(NNCPh_2)_2(CO)_9]$ (**1**) mentioned already [9] and $[Os_3(NNCH_2)(\mu_3\text{-}MeCCMe)(CO)_9]$ (**13**) [43]. In **1**, the six Fe–N distances lie in the range 1.91–1.98 Å and the N–N and N–C lengths are at 1.39 and 1.31 Å (mean values). The bonding parameters within the $NNCH_2$ ligand in **13** are comparable with those in **1**; the Os_1–N, Os_2–N, Os_3–N, N–N, and N–C distances are at 2.05(1) Å, 2.09(1) Å, 2.20(1) Å, 1.38(1) Å, and 1.30(2) Å respectively, and the N–N–C linkage is bent by 121.0(1)°. The Os complex $[Os_3(NNCH_2)(\mu_3\text{-}PhCCPh)(CO)_9]$ closely related to **13** [44] and $[(CpCo)_3(NNCPh_2)(\mu_3\text{-}CO)]$ [45] may presumably be classified into this type.

A diazoalkane ligand coordinated to a tetranuclear centre has been found in the Ru_5 cluster $[Ru_5(NNCPh_2)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu_2\text{-}PPh_2)(CO)_{12}]$ (**14**) [46]. Cluster **14** has a metal core of a square and a triangle mutually fused at one Ru–Ru edge and the N_α atom in the diazoalkane ligand binds to three Ru atoms composing the triangle, while the N_β atom is attached to one Ru atom out of this triangle. The N–N distance of 1.40(1) Å and the C–N bond length at 1.30(2) Å are consistent with the canonical form represented in the chart.

3. GENERATION OF DIAZOALKANE LIGANDS IN THE COORDINATION SPHERE

Most of the diazoalkane complexes described above have been prepared from the reactions of metal precursors with free diozoalkanes. In these reactions the parent complexes have either a coordinatively unsaturated metal centre or an easily replace-



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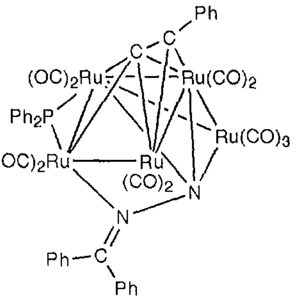

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able labile ligand, and in some cases a metal–metal bond that is susceptible to addition of diazoalkanes. Several alternative methods to synthesize diazoalkane complexes have also appeared, in which the diazoalkane moiety has its origin in nitrogenous compounds other than free diazoalkane. Development of reaction systems in which relatively stable nitrogen-containing compounds can readily be converted into reactive diazoalkanes is of significant importance and the metal-assisted transformation of coordinated dinitrogen into the diazoalkane ligands described below is particularly noteworthy. In this section, preparation of diazoalkane ligands from nitrogenous precursors in the coordination sphere will be summarized.

3.1 Diazoalkane ligands from coordinated dinitrogen

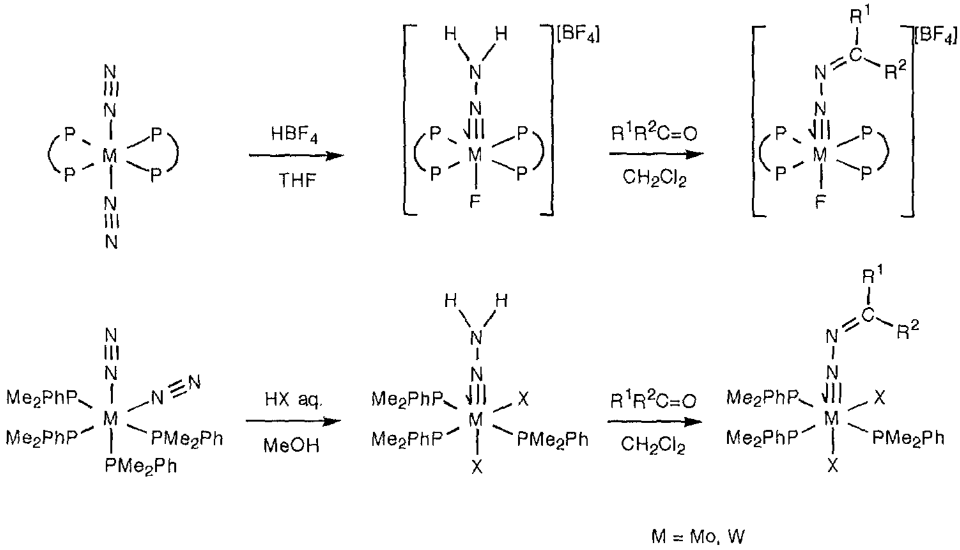
A variety of dinitrogen complexes involving almost all the d block transition metals have been reported already. However, complexes whose dinitrogen ligands are highly activated and amenable to transformations into nitrogenous compounds are still limited. The Mo and W dinitrogen complexes of the type $[M(N_2)_2(P)_4]$ ($P =$ tertiary phosphine) are therefore noteworthy in terms of the exceptionally versatile reactivities they display [6]. In particular, the facile reactions converting the dinitrogen ligands into various organodinitrogen ligands are of particular interest; these include the formation of a number of diazoalkane complexes from *trans*-$[M(N_2)_2(dppe)_2]$ and *cis*-$[M(N_2)_2(PMe_2Ph)_4]$.

A convenient method to synthesize diazoalkane complexes from these dinitrogen complexes involves the initial protonation of the dinitrogen ligand forming the hydrazido(2-) ligand ($MNNH_2$) and its subsequent condensation at the nucleophilic terminal N atom with various aldehydes and ketones to give the singly bent η^1-diazoalkane ligand (Scheme 1). As expected, the latter condensation reaction is much accelerated by the addition of a catalytic amount of aqueous acid. This synthetic route was first found for the complexes with dppe ligands, *trans*-$[MF(NNCR^1R^2)(dppe)_2][BF_4]$ (**4**) [14,47,48], and then extended to the PMe_2Ph complexes *cis,mer*-$[MX_2(NNCR^1R^2)(PMe_2Ph)_3]$ (**5**) [49,50]. Although similar diazoalkane complexes, *trans*-$[MBr(NNCR^1R^2)(dppe)_2]Br$, were obtained from the reactions of the dinitrogen complexes with $R^1R^2CBr_2$ under photo-irradiation [16,51], i.e.

$$\text{trans-}[M(N_2)_2(dppe)_2] \xrightarrow[\text{benzene}]{R^1R^2CBr_2\ /\ h\nu} \text{trans-}[MBr(NNCR^1R^2)(dppe)_2]Br \qquad (1)$$

$M = Mo, W$

this route was not applicable to the PMe_2Ph complexes. Furthermore, since there are many more organic carbonyl compounds than the *gem*-dibromides, the former condensation method provides a more versatile pathway towards formation of diazoalkane complexes than the latter. From the W(V) hydrazido(2-) complexes



Scheme 1

$[WX_3(NNH_2)(PMe_2Ph)_2]$ and ketones, the W(V) diazoalkane complexes *mer,trans*-$[WX_3(NNCR^1R^2)(PMe_2Ph)_2]$ can be prepared analogously [21]. On the contrary, although the yield was low, the dichlorodiazomethane complex *trans*-$[WBr(NNCCl_2)(dppe)_2]^+$ was isolated from the reaction of $[WBr(NNH_2)(dppe)_2]^+$ with $Ph_2I^+Cl^-$ in $CHCl_3$–aqueous K_2CO_3 [18].

3.2 Diazoalkane ligands from other precursors

Some diazoalkane complexes can be prepared by use of nitrogenous compounds such as azines and hydrazones. Benzaldehyde azine PhCH=NN=CHPh reacts with the carbene complexes $[Ta(CHBu^t)X_3(THF)]$ ($X = OC_6H_3Pr^i_2$-2,6, $SC_6H_2Pr^i_3$-2,4,6) to give $[Ta(NNCHPh)X_3(THF)]$ with the concurrent formation of $PhCH{=}CHBu^t$ (Eq. 2) [52]:

$$[Ta(CHBu^t)X_3(THF)] + PhCH{=}NN{=}CHPh \xrightarrow{\text{ether}} [Ta(NNCHPh)X_3(THF)] + PhCH{=}CHBu^t \qquad (2)$$

$$X = OC_6H_3Pr^i_2\text{-}2,6,\ SC_6H_2Pr^i_3\text{-}2,4,6$$

These Ta diazoalkane complexes correspond to intermediate stages for the formation of the μ-N_2 (or hydrazido(4-)) complex $[\{MCl_3(THF)_2\}_2(N_2)]$ (M = Ta, Nb) from $[M(CHBu^t)Cl_3(THF)_2]$ and PhCH=NN=CHPh [53], as well as the formation of azines and oxo complexes by treatment of the Ta μ-N_2 complexes of this type with PhCHO and Me_2CO [52,53].

The Zr complexes $[(Cp_2Zr)_2(NNCHR)_2]$ (R = aryl) and their Cp′ derivative **11** already described were prepared from reactions of [Cp_2ZrCl_2] or [Cp'_2ZrCl_2] with Li_2NNCHR generated in situ by treatment of H_2NNCHR with $LiBu^n$ [42]:

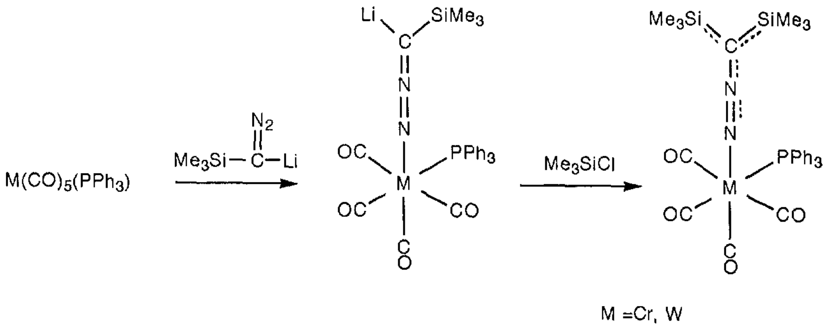
$$2\,[Cp_2ZrCl_2] + 2\,Li_2NNCHR \xrightarrow{THF} [(Cp_2Zr)_2(NNCHR)_2] \qquad (3)$$

R = aryl

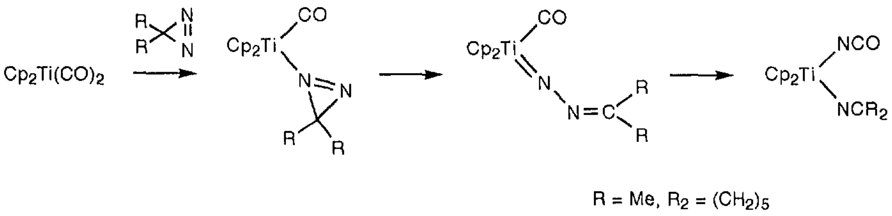
On the contrary, the W complex **6** and its Cr analogue were obtained on treatment of [$M(CO)_5(PPh_3)$] with the Li salt of trimethylsilyldiazomethane $Me_3Si(Li)CN_2$, followed by workup with Me_3SiCl [29] (Scheme 2). Free Me_3SiCHN_2 does not react with [$M(CO)_5(PPh_3)$].

Diazirines $R_2\overline{CN{=}N}$, which are the cyclic isomers of diazoalkanes, act as the σ electron donor through the N atom, forming complexes with the mononuclear η^1- and dinuclear μ-η^1:η^1-diazirine ligands [8]. Transformations of these diazirine ligands into the coordinated diazoalkanes are not observed in an unequivocal manner but are postulated to occur in the formation of the isocyanato–ketiminato complex [$Cp_2Ti(NCO)(NCR_2)$] from [$Cp_2Ti(CO)_2$] and $R_2\overline{CN{=}N}$ (Scheme 3) [8]. An analogous mechanism may be involved in the reactions of [$Fe_3(CO)_9$] or [$Ru_3(CO)_{12}$] with diazirines to give [$Fe_2(\mu$-$NCR_2)(\mu$-$NCO)(CO)_6$] [54] or [$Ru_3\{\mu_2$-$N\overline{C(CH_2)_4C}H_2\}(\mu_2$-$NCO)(CO)_9$] [55] respectively.

As already described, reactions of α-diazo ketones and esters with metal complexes have been studied in detail because these diazoalkanes are readily prepared.

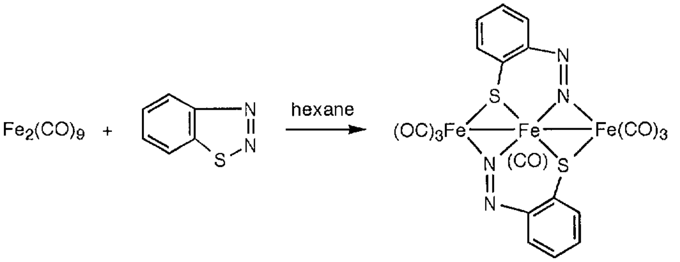


Scheme 2



Scheme 3

In contrast, few examples are known with the corresponding thiocarbonyl compounds. The reaction of 1,2,3-thiadiazole, the isomer of α-diazo thioketone (or α-thioketo diazoalkane), with $Fe_2(CO)_9$ has been investigated and the formation of a complex containing the α-diazo thioketone trapped at the linear triiron site has been clarified [56]:



(4)

The bonding parameters associated with the C–N–N moiety (C–N, 1.438(3) Å; N–N, 1.238(3) Å; C–N–N, 118.8(2)°) suggest, however, that this ligand can be considered as a bridging aryldiazenide ligand rather than a diazoalkane ligand.

4. REACTIVITY OF COORDINATED DIAZOALKANE

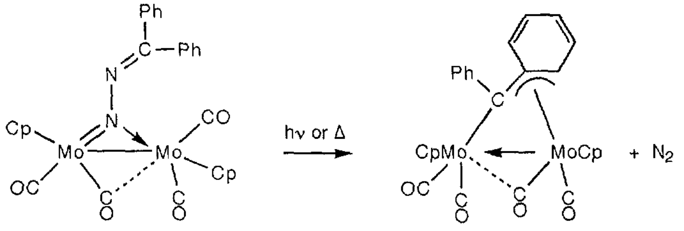
4.1 Reactions with loss of dinitrogen

As described in the introduction, reactions of diazoalkanes with metal complexes often result in the formation of carbene complexes concurrent with the liberation of N_2 [4]. This is a key reaction in catalytic reactions such as the cyclopropanation of olefins and carbene insertion into C–H bonds, which enjoy wide applicability in organic synthesis [3]. Obviously the coordination of a diazoalkane to a metal complex precedes the N_2 loss from the diazoalkane, and it is of great importance to elucidate how the N_2 extrusion from the diazoalkane ligands proceeds in these complexes. However, in many cases isolable diazoalkane complexes resist the thermal N_2 loss owing to the stabilization of the diazoalkane ligands by coordination. As a result, there have only been a few examples where well-defined diazoalkane complexes undergo clean N_2 loss to give carbene complexes or related products.

In pioneering work, thermolysis of $[Ni(diazofluorene)(Bu^tNC)_2]$ (**2**) and analogous Pd complexes in the presence of olefins such as diethyl maleate was investigated in detail in relation to catalytic cyclopropanation [11]. The corresponding cyclopropanedicarboxylate was detected in a moderate yield, but the possibility that the cyclopropane was formed from the thermal reaction of free diazofluorene dissociated from **2** with diethyl maleate could not be ruled out.

The dinuclear complex $[Cp_2Mo_2(NNCPh_2)(CO)_4]$ (**8**) undergoes clean N_2

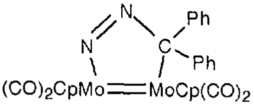
extrusion under UV irradiation or heating at 60–70 °C to give the bridging diphenylcarbene complex $[Cp_2Mo_2(CPh_2)(CO)_4]$ (**15**) [36]:



(5)

8a **15**

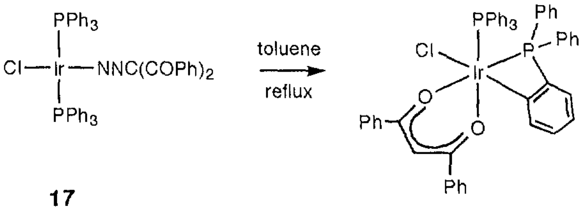
No cross-product $[Cp'_2Mo_2(CPh_2)(CO)_4]$ was observed in the thermolysis of **8** in the presence of $[Cp'_2Mo_2(CO)_4]$ and, further, a double-label thermolysis using **8** and $[Cp'_2Mo_2(NNCTol_2)(CO)_4]$ yielded only the unimolecular reaction products. Therefore this reaction was considered to proceed by an intramolecular mechanism, probably by way of a five-membered dimetallacycle **16**.



16

Similar dimetallacycles have been proposed as intermediates in other related reactions [44,57]. $[Os_3(NNCH_2)(C_2Ph_2)(CO)_9]$ is thermally stable up to 80°C, but its photolysis gives $[Os_3(CH_2)(C_2Ph_2)(CO)_9]$ [44]. This reaction is also supposed to proceed intramolecularly.

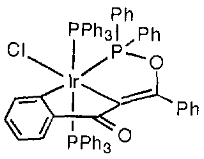
A thermal reaction of $[IrCl\{NNC(COPh)_2\}(PPh_3)_2]$ (**17**) yielded a β-diketonato complex **18** in high yield [58]:



(6)

17 **18**

The N_2 extrusion from **17** forming a carbene complex should be followed by orthometalation of one phosphine phenyl group, and hydride transfer to the carbene carbon and further rearrangement result in the formation of the β-diketonate ligand.



19

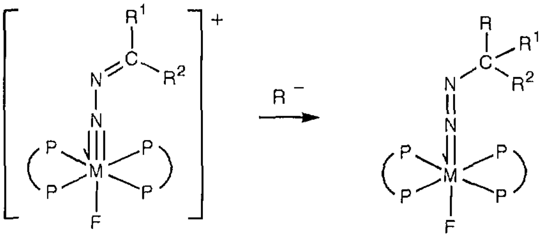
A different product **19**, accompanied by a geometric isomer of **18**, was also obtained from reaction of $[\mathrm{IrCl(PPh_3)_3}]$ with $\mathrm{N_2C(COPh)_2}$ [58].

4.2 Reactions with retention of dinitrogen

In addition to N_2 extrusion on metal complexes, diazoalkane ligands are expected to exhibit various reactivities depending on the coordination mode of the diazoalkane ligands and the electronic state of the central metals. The metal-mediated reactions of diazoalkane ligands are remarkably different from those of free diazoalkanes, and a variety of nitrogen-containing ligands have been characterized as products. However, because reactivities of only limited types of diazoalkane complexes have been investigated so far, it is not easy to systematize all the reactivities of diazoalkane ligands. Nevertheless, the coordination modes and resonance structures of diazoalkane ligands help us to understand their reactions.

4.2.1. Nucleophilic addition and substitution reactions

As described before, four-electron donating singly bent diazoalkanes coordinated to Mo or W such as found in $[\mathrm{MX(NNCR^1R^2)(dppe)_2}]^+$ (**4**) and $[\mathrm{MX_2(NNCR^1R^2)(PMe_2Ph)_3}]$ (**5**) have a contribution of the resonance structure $[\mathrm{M^-{=}N^+{=}N{-}C^+R^1R^2}]$ (vide supra). This is most typically substantiated by the fact that the diazoalkane ligands in **4** and **5** are susceptible to attack by nucleophiles such as $\mathrm{LiAlH_4}$ and Grignard reagents at the C_α atom adjacent to the diazo group. Thus, complex **4** gives the corresponding diazeniod complex **20** according to



(7)

M = Mo, W
P P = $\mathrm{Ph_2PCH_2CH_2PPh_2}$

4

20

under mild conditions [16], while the monophosphine complexes **5** undergo complete reduction to form amines by treatment with $LiAlH_4$ [49]. In a similar context, a cationic dichlorodiazomethane complex $[WBr(NNCCl_2)(dppe)_2]^+$ is subject to nucleophilic attack at the C_α atom by various amines, alkoxides, carbanions, and F^- to afford various diazoalkane or diazenido complexes [18,59].

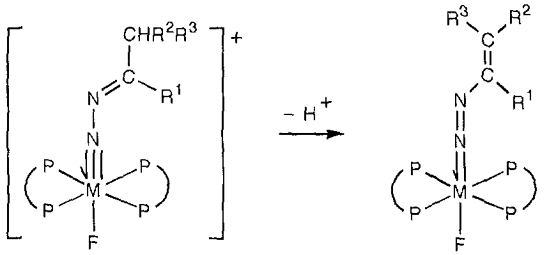
Another example of nucleophilic addition to diazoalkane ligands was found in the reaction of $[Mo(O)(NNCHPh)(S_2CNEt_2)_2]$ with $Ph_3P{=}CHBu$ [42]. The nucleophilic carbon of the phosphine ylide attacks the C_α atom leading to the Wittig-type olefin formation concurrent with N_2 evolution:

$$\mathrm{Mo(O)(NNCHPh)(S_2CNEt_2)_2 + Ph_3P{=}CHBu \longrightarrow PhCH{=}CHBu + N_2 + PPh_3 + Mo(O)(S_2CNEt_2)_2} \qquad (8)$$

The more sterically crowded diazoalkane complex $[Mo(O)(NNCPh_2)(S_2CNEt_2)_2]$ reacts at the N_α atom to give $Ph_2C{=}NN{=}CHBu$.

4.2.2 *Deprotonation of diazoalkane ligands*

As a result of the resonance effect attributed to the structure $[M^- {\leftrightharpoons} N^+{=}N{-}C^+R^1R^2]$ for the four-electron donating diazoalkane ligands in **4** and **5**, they have a tendency to be deprotonated by a strong base to give alkenyldiazenido ligands:



M = Mo, W

4

21

(9)

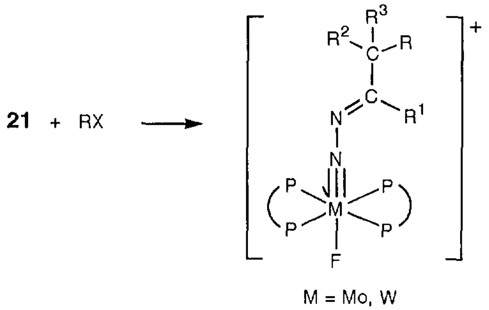
Such deprotonation was first examined in a reaction of **4a** with NaOMe, and the resulting alkenyldiazenido complex $[WF(N{=}NCMe{=}CHCOMe)(dppe)_2]$ (**21a**) regenerated **4a** on protonation [60]. The deprotonation of diazoalkane complexes without electron withdrawing functional groups was achieved by using LDA or $LiN(SiMe_3)_2$ as the base [19].

One of the interesting features of this deprotonation is the regio- and stereoselectivity with regard to the C=C double bond formed. The deprotonation product from the reaction of 1-diazopropane complex $[WF(NNCHEt)(dppe)_2][BF_4]$ (**4b**) with $NaN(SiMe_3)_2$ at room temperature was a 6:1 mixture of *Z* and *E* isomers of $[WF(N{=}NCH{=}CHMe)(dppe)_2]$ (**21b**), the *Z* isomer being predominant. Reaction at 0°C increased the stereoselectivity to 12:1. Further, the 2-diazopropane complex

$[WF(NNCMe_2)(dppe)_2][BF_4]$ (**4c**) underwent the deprotonation regioselectively at the *exo* Me group to give $[WF(N{=}NCMe{=}CH_2)(dppe)_2]$ (**21c**). This regioselectivity is particularly advantageous for the selective synthesis of functionalized diazoalkane complexes described below.

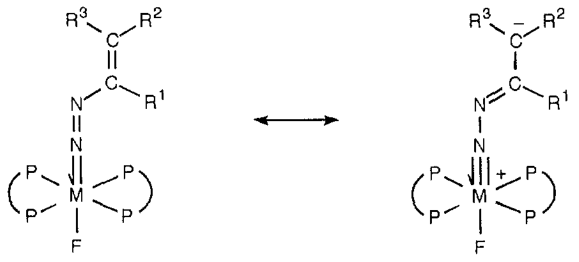
The alkenyldiazenido complexes $[WF(N{=}NCR^1{=}CR^2R^3(dppe)_2]$ (**21**) generated by the deprotonation of the diazoalkane complexes **4** show low ν(N=N) (1376–1448 cm^{-1}) and ν(C=C) (1567–1610 cm^{-1}) values in their IR spectra. The X-ray analysis of the molecular structure of an alkenyldiazenido complex $[WF(N{=}NCH{=}CMe_2)(dppe)_2]$ indicates that the N=N bond length of 1.29(3) Å is relatively long, while the N–C bond length of 1.26(3) Å is short. These data suggest that there exists a considerable contribution of the resonance structure **22**, in which the terminal carbon of the C=C bond is negatively charged. Evidently the metal centre accommodates the positive charge to stabilize the charge-separated resonance structure.

The resonance structure **22** strongly indicates that the terminal carbon of the alkenyldiazenido group is nucleophilic. Thus, the reactions of alkyl halides with complexes **21** are expected to give new diazoalkane complexes as *C*-alkylation products, although *N*-alkylation has been reported in the case of alkyldiazenido complexes [61]. In fact, treatment of **21** with an excess of an alkyl halide RX resulted in formation of the corresponding *C*-alkylated cationic diazoalkane complex $[MF(NN{=}CR^1CR^2R^3R)(dppe)_2]^+$ (**23**):



(10)

23

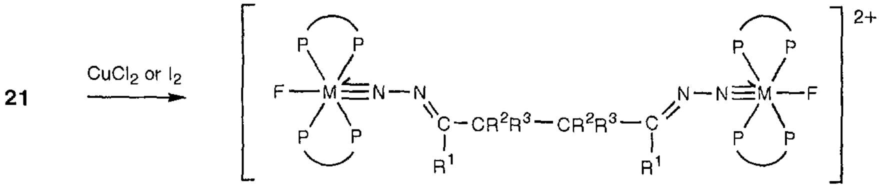


21 **22**

A similar reaction of **21** with $[Cr(FC_6H_4R)(CO)_3]$ (R = H, Me) gave a novel μ-1-aryl-2-diazopropane complex $[WF\{NNCMeCH_2[(C_6H_4R)Cr(CO)_3]\}(dppe)_2]^+$ as the *C*-arylated product. Therefore the sequential deprotonation–alkylation or –arylation of diazoalkane complexes provides a facile *C*-alkylation or arylation method for diazoalkane ligands. Moreover, the high regioselectivity in the deprotonation described above makes it possible to attain the selective α,α-dialkylation of complex **4** by repeated deprotonation–alkylation reactions. Thus, sequential methylation and ethylation of $[WF(NNCMe_2)(dppe)_2][BF_4]$ **4c** gave $[WF(NNCMeCHMeEt)(dppe)_2][BF_4]$ in 63% total yield.

Alkenyldiazenido complexes **21** also reacted with electrophilic heterocumulenes such as isocyanates, phenyl isothiocyanate, and diphenylketene to give *C*-acylated diazoalkane complexes after aqueous workup (Scheme 4). Again high *exo* regioselectivity was observed. Interestingly, in the reactions of **21c** with aryl isocyanates, the use of a controlled amount of the reagent led to the formation of the mono-*C*-acylation product **24**, while the use of an excess amount of aryl isocyanate yielded the α,α-di-*C*-acylated product **25** via the monoacylated alkenyldiazenido complex **26**. Furthermore, aldol-type condensation was observed in the reaction of **21** and aldehydes without α hydrogens such as pivalaldehyde or benzaldehyde. The isolated products were the dehydrated diazoalkane complexes.

In addition to the nucleophilic reactivities, alkenyldiazenido complexes **21** were found to undergo oxidative coupling by treatment with I_2 or $CuCl_2$ forming dinuclear μ-bis(diazo)alkane complexes **27**:

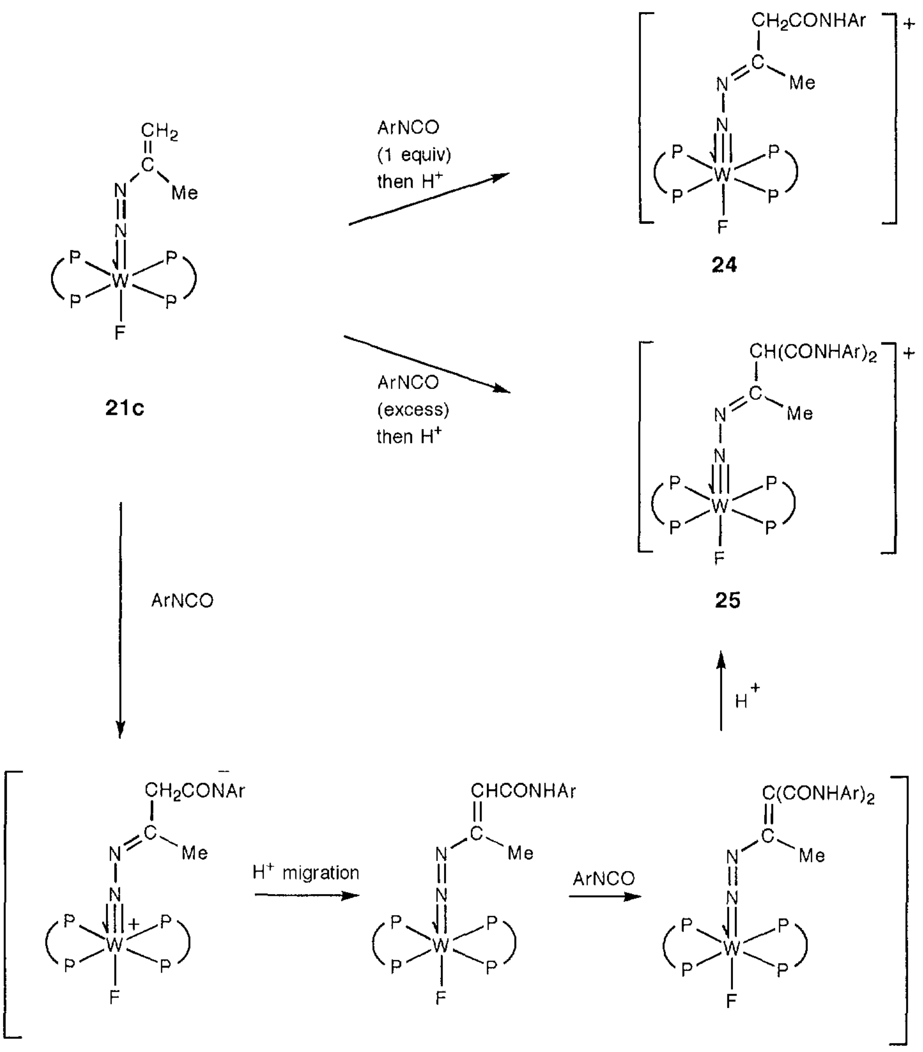


(11)

M = Mo, W

27

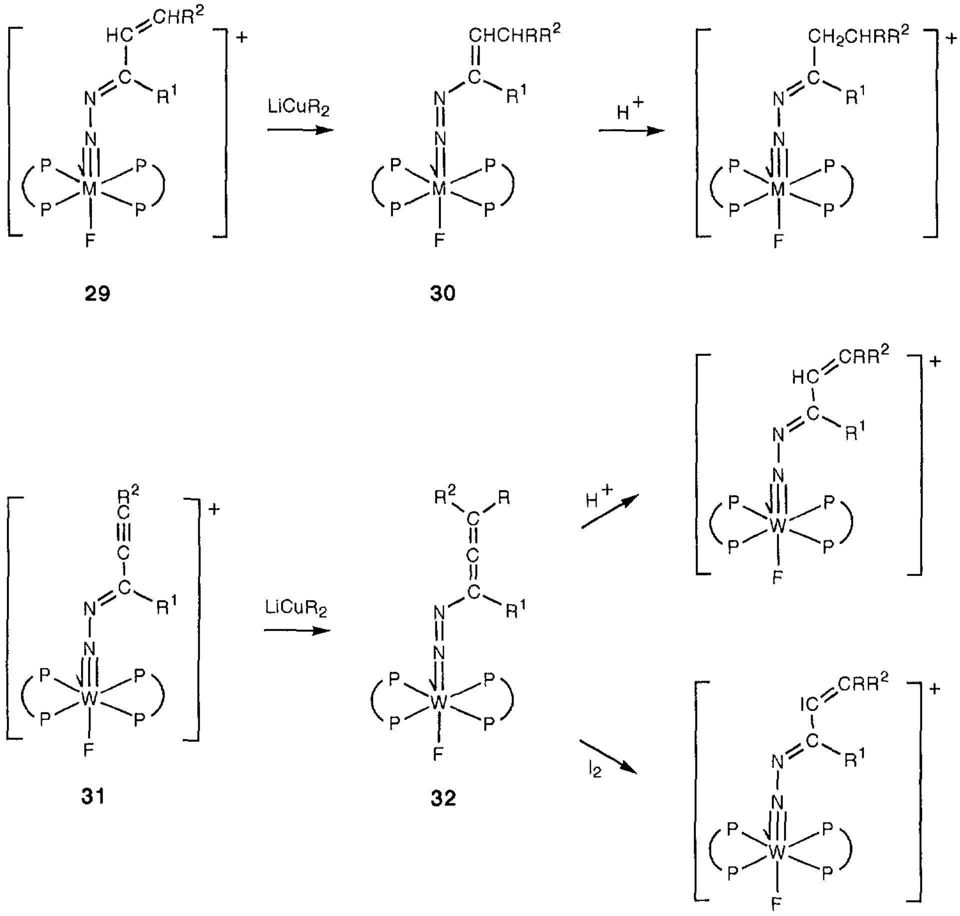
This coupling reaction exhibited some stereoselectivity; oxidation of the 1-propenyldiazenido complex **21b** yielded $[(dppe)_2WF(NN{=}CHCHMeCHMeCH{=}NN)FW(dppe)_2][BF_4]_2$ as a mixture of two stereoisomers in ratios 2.1 : 1–8.3 : 1, where the *threo* isomer was predominantly formed. Cyclic voltammetry measurement of alkenyldiazenido complexes **21** indicated that the oxidative coupling of **21** proceeds via one-electron oxidation to form a 17-electron cationic Mo(III) or W(III) species $[MF(N{=}NCR^1{=}CR^2R^3)(dppe)_2]^+$ (**28**; M = Mo, W). The terminal carbon atom of the C=C bond in **28** is considered to have radical character owing to the conjugated double-bond system including the metal atom, and the radical coupling of two molecules of **28** eventually yields the μ-bis(diazo)alkane complex **27**.



Scheme 4

4.2.3 Conjugate addition of cuprates to unsaturated diazoalkane ligands

Cationic four-electron donating diazoalkene complexes [MF(NNCR^{1}CH=CHR^2)(dppe)$_2$][BF$_4$] (**29**; M = Mo, W) react with lithium cuprates LiCuR$_2$ to give alkenyldiazenido complexes [MF(N=NCR^1=CHCHRR^2)(dppe)$_2$] (**30**) as conjugate addition products (Scheme 5) [62]. Since these alkenyldiazenido complexes are versatile precursors for the preparation of various functionalized diazoalkane complexes as described above, the conjugate addition of cuprates to diazoalkane ligands



Scheme 5

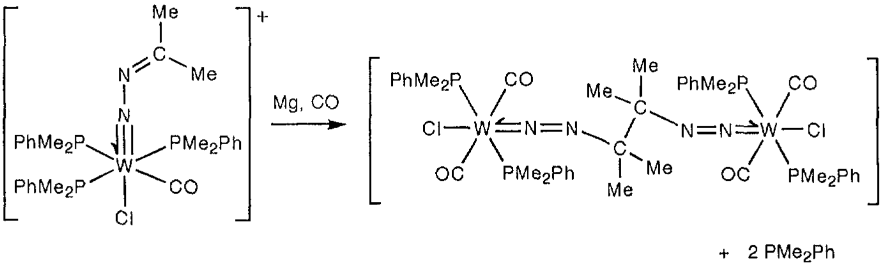
followed by workup with electrophiles such as H$^+$, alkyl halides, or isocyanates can be used as a convenient method to obtain functionalized diazoalkane ligands.

The diazoalkane ligand in $[WF(NNCR^1C{\equiv}CR^2)(dppe)_2][BF_4]$ (**31**) undergoes similar conjugate addition by $LiCuR_2$ to give reactive allenyldiazenido complexes $[WF(N{=}NCR^1{=}C{=}CRR^2)(dppe)_2]$ (**32**), which in turn are trapped to electrophiles such as H$^+$, I_2, or *N*-halosuccinimide to give the corresponding diazoalkane complexes [62].

4.2.4 Reductive coupling of diazoalkane ligands

Controlled electroreduction of a cationic diazomethane complex $[WF(NNCH_2)(dppe)_2][BF_4]$ (**4d**) affords an insoluble tungsten complex, which was formulated as a bridging diazenido complex $[(dppe)_2WF(N{=}NCH_2CH_2N{=}N)\text{-}WF(dppe)_2]$ [63]. A proposed reaction mechanism includes one-electron reduction of **4d** forming a W(III) diazomethane complex [WF(NNCH$_2$)(dppe)$_2$], in which the diazomethane ligand is supposed to have radical character on the C atom, and its dimerization gives the bridging ligand.

Recently a carbonyl diazoalkane complex [WCl(NNCMe$_2$)(CO)(PMe$_2$Ph)$_3$][ZnCl$_3$(THF)] (**33**) was prepared from the reaction of [WCl$_2$(NNCMe$_2$)(PMe$_2$Ph)$_3$] and CO in the presence of ZnCl$_2$, and its reduction with Mg under CO was examined [64]:



33 **34** (12)

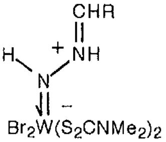
X-ray analysis of the product [WCl(CO)$_2$(PMe$_2$Ph)$_2$(N=NCMe$_2$CMe$_2$N=N)WCl(CO)$_2$(PMe$_2$Ph)$_2$] (**34**) confirmed the formation of the bridging diazenido ligand by the reductive coupling of the diazoalkane ligand.

4.2.5 Electrophilic addition to diazoalkane ligands

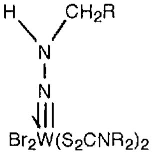
The four-electron donating diazoalkane ligand not only reacts with nucleophilic reagent as described above, but also is attacked by H$^+$. When the diazoalkane complex [WBr$_2$(NNCMe$_2$)(PMe$_2$Ph)$_3$] (**5b**) was treated with HBr, successive proton attack occurred on the diazoalkane ligand [49]. The initial product with 1 equivalent HBr in CH$_2$Cl$_2$ was assumed to be the N_α-protonation product [WBr$_3$(NHN=CMe$_2$)(PMe$_2$Ph)$_3$], but further reaction products with HBr remain unclear. A reaction of **5b** with a large excess of HBr gave NH$_2$NH$_2$, Me$_2$C=NN=CMe$_2$ and [WBr$_4$(PMe$_2$Ph)$_2$]. The primary organic product was supposed to be H$_2$NN=CMe$_2$, whose disproportionation resulted in the formation of NH$_2$NH$_2$ and the azine.

The four-electron donating diazoalkane ligand in [W(NNCHTol)(CO)(S$_2$CNMe$_2$)$_2$] (**35**) reacts with a large excess of HBr to give a complex formulated as [WBr$_2$(N$_2$H$_2$CHTol)(S$_2$CNMe$_2$)$_2$] (**36**) concurrent with evolution of CO [23]. The latter complex is considered to have a structure **36a** or **36b**. In the absence of excess HBr, **36** readily produces the hydrazone H$_2$NNCHTol and [WBr$_2$(S$_2$CNMe$_2$)$_2$]. Hydrolysis of **35** is also reported to give the hydrazone.

On the contrary, the μ-diazoacetate ligand in [Rh$_2$(NNCHCOOEt)(CO)$_2$(dppm)$_2$] was protonated by HBF$_4$ at the C$_\alpha$ atom to form a cationic diazenido complex [Rh$_2$(N=NCH$_2$COOEt)(CO)$_2$(dppm)$_2$]$^+$ [38]. This *C*-protonation is reversible and treatment of the diazenido complex with NaOEt regenerates the diazoacetate complex. Interestingly, the corresponding reaction of the diazomalonate



36a



36b

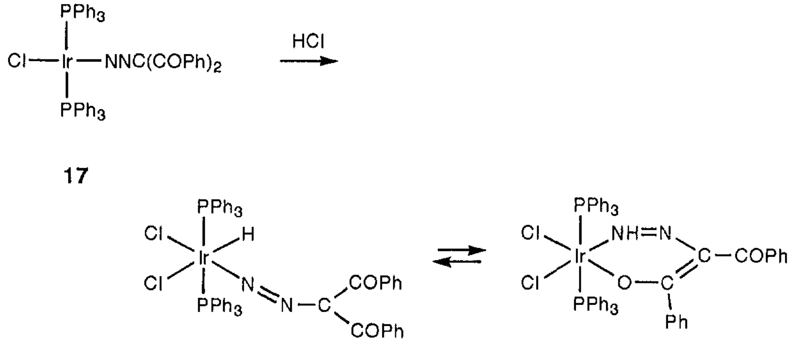
complex $[Rh_2\{NNC(COOEt)_2\}(CO)_2(dppm)_2]$ with HBF_4 brought about the dissociation of the diazomalonate ligand, and a hydrido complex $[Rh_2H(CO)_2(dppm)_2]^+$ was formed.

Reactions of diazoalkane ligands with aldehydes or ketones were observed on Zr complexes [42]. Because of the low electronegativity of Zr, the diazoalkane ligand in $[(Cp_2Zr)_2(NNCR^1R^2)_2]$ (**37**) is susceptible to electrophilic attack at the N_α or the C_α atom. As a result, reaction of **37** with aldehydes or ketones affords azines or olefins (Scheme 6). The reaction mechanism depicted in the scheme was proposed on the basis of substituent effects on the reaction rate.

4.2.6 Insertion of diazoalkanes into metal–H, –C, and –P bonds

Diazoalkanes are known to insert into metal–hydrogen bonds without extrusion of N_2. Both 1,1-insertion (at N_α,N_α) and 1,3-insertion (at N_α,C_α) are reported, which give hydrazonato(1-) and alkyldiazenido(1-) ligands respectively. Such reactions are thought to proceed via diazoalkane complexes, but only in a few examples are intermediary diazoalkane hydrido complexes observed.

A reaction of the square-planar Ir complex $[IrCl\{NNC(COPh)_2\}(PPh_3)_2]$ (**17**) with HCl afforded an equilibrium mixture of two complexes in a ratio of 1 : 15. The minor species was identified as a six-coordinate complex $[IrHCl_2\{(NN(COPh)_2\}(PPh_3)_2]$ (**38**) formed by the oxidative addition of HCl. The crystallographically characterized major species was $[IrCl_2(NH{=}NC(COPh)_2\}(PPh_3)_2]$ (**39**), resulting from the 1,1-insertion of dibenzoyldiazomethane ligand into the Ir–H bond [34]:

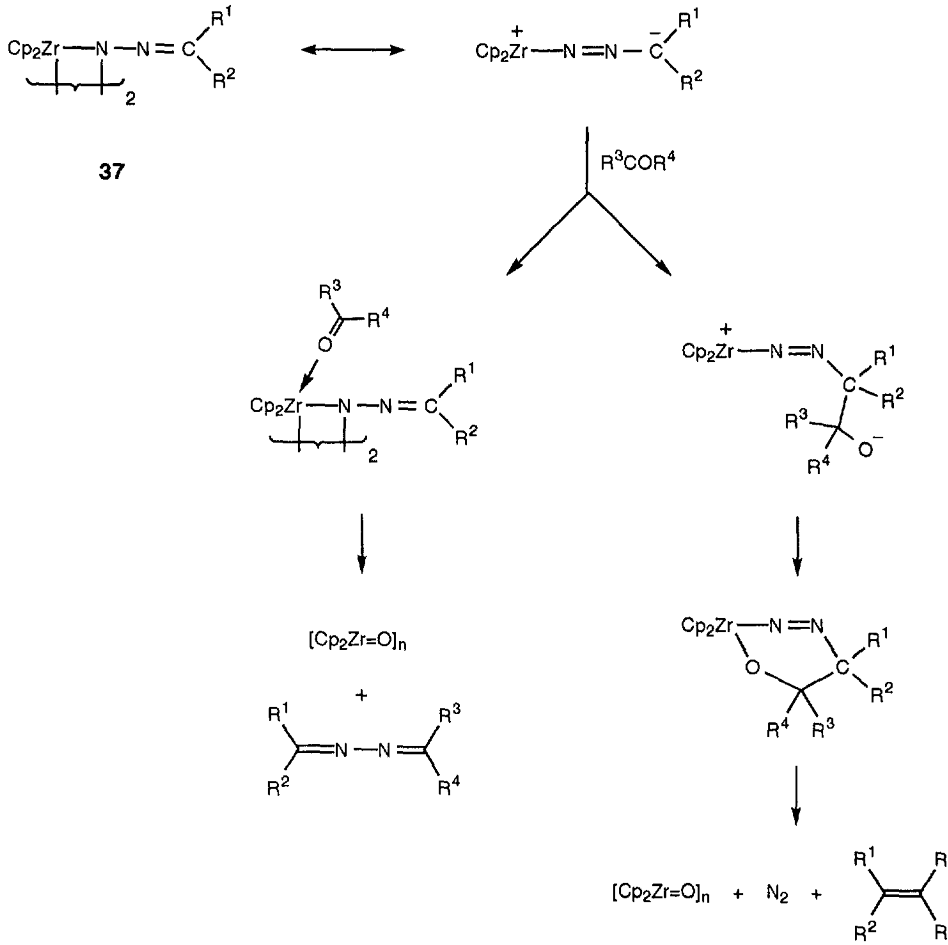


17

(13)

38

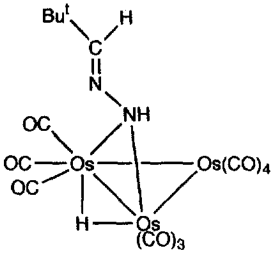
39 (major)



Scheme 6

Obviously the coordination of benzoyl group contributes to the stabilization of **39**. The observation that HBF_4 failed to react with **17** indicates that direct electrophilic attack on the diazoalkane ligand by H^+ is not an important process in the formation of **39**. A related diazoalkane complex $[IrCl(NNC_5Cl_4)(PPh_3)_2]$ also reacted with HCl. In this case, on the basis of IR and ^{31}P nuclear magnetic resonance, the product was considered to be a six-coordinate hydrido complex $[IrHCl_2(NNC_5Cl_4)(PPh_3)_2]$, which is in a rapid equilibrium with the five-coordinate 1,1-insertion product $[IrCl_2(NHNC_5Cl_4)(PPh_3)_2]$ [33].

Reactions of a diazoalkane with $[Os_3H_2(CO)_{10}]$ and $[Cp_2ZrHCl]$ were also shown to occur via the 1,1-insertion, and μ-η^1-hydrazonato(1-) complexes $[Os_3H(NHN{=}CR^1R^2)(CO)_{10}]$ (**40**) [65,66] and a η^2-hydrazonato(1-) complex $[Cp_2ZrCl(NHNCPh_2)]$ (**41**) [67] respectively were obtained. Analogous to the latter



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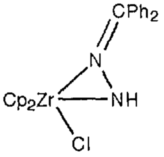
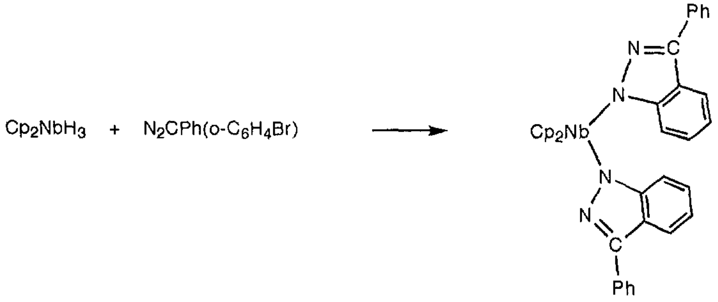


41

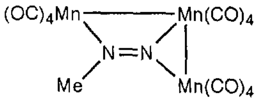
reaction, insertion of diazoalkanes into a Zr–C bond in [Cp_2ZrMe_2] [67], Ti–C bonds in [$(Cp^*_2TiMe)_2O$] and [$(Cp^*_2TiMe)_3O_3$] [68], and Zr–P bonds in [$Cp_2Zr(PPhPPhPPh)$] [69] was reported to yield the corresponding η^2-hydrazonato(1-) type complexes.

In contrast, the 1,3-insertion of diazoalkanes was observed in reactions with several carbonyl hydrides. Treatment of [$CpM(CO)_3H$] (M = Mo, W) with N_2CH_2 or $N_2CHSiMe_3$ gave a mononuclear η^1-alkyldiazenido complex [$CpM(N{=}NR)(CO)_2$] [70,71], while $N_2C(COOEt)_2$ caused the 1,1-insertion [70]. On the contrary, a trinuclear bridging methyldiazenido complex [$Mn_3(N{=}NMe)(CO)_{12}$] (**42**) was obtained from the reaction of [$HMn(CO)_5$] with N_2CH_2 [72].

Further new transformations of diazoalkanes which may include the insertion of diazoalkane ligands into metal–C bonds were observed in the reactions with [Cp_2NbH_3]. Thus, $N_2CPh(o\text{-}C_6H_4Br)$ was converted to a pyrazole type ligand, i.e.

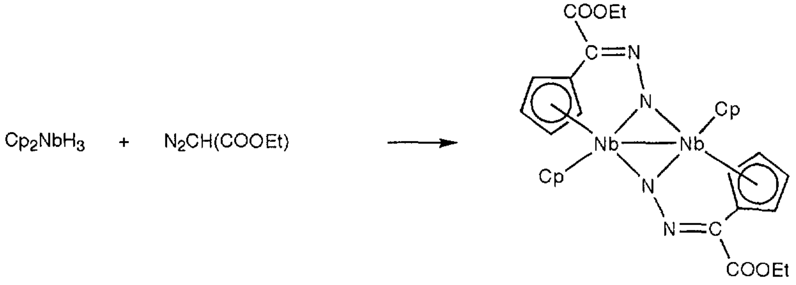


(14)



42

while $N_2CHCOOEt$ yielded an unusual bridging ligand via coupling with a cyclopentadienyl ligand [27]:

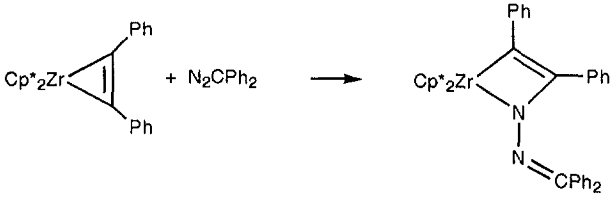


(15)

4.2.7 Coupling with CO or alkyne

Coupling reactions of diazoalkanes with coordinated alkyne or CO with retention of N_2 yield various types of bi- and multidentate ligands. Reactions both at the N_α and at the C_α have been reported.

$[Cp^*_2Zr(PhCCPh)]$ reacted with N_2CPh_2 to afford a metallacycle compound $[Cp^*_2\overline{Zr\{CPh{=}CPhN}(N{=}CPh)\}]$ (**43**). This reaction can be regarded as a 1,1-insertion of N_2CPh_2 into a Zr–C bond of a zirconacyclopropene [73]:



(16)

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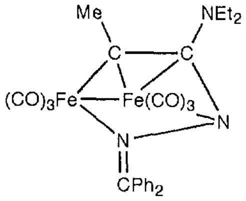
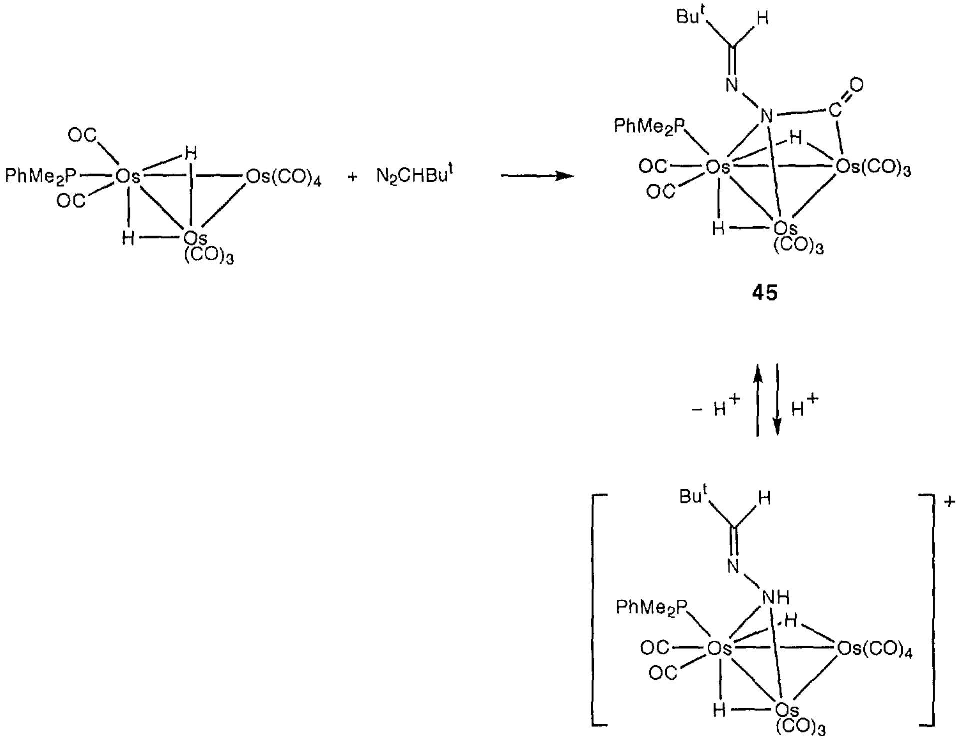
An aminoalkyne on a dinuclear iron centre in $[Fe_2(CO)_7(MeCCNEt_2)]$ also coupled with N_2CPh_2 to give $[Fe_2(CO)_6\{CMeC(NEt_2)NN(CPh_2)\}]$ (**44**) [74], which contains a μ-η^2:η^3-azaallyl type of ligand.

The one-to-one coupling reaction of N_2CHBu^t with CO on $[Os_3H_2(CO)_9(PMe_2Ph)]$ occurs at the N_α atom and forms a complex with a bridging

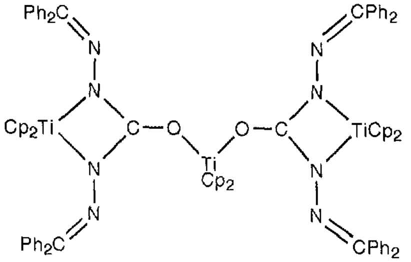


44

isocyanate type ligand, $[Os_3H_2(OCNN{=}CH^tBu)(CO)_8(PMe_2Ph)]$ (**45**). The N–CO bond can be reversibly cleaved by protonation (Scheme 7) [65]. Similar bridging isocyanate type complexes $[M_2(OCNN{=}CH_2)(CO)_9]$ (M = Mn, Re) were also obtained from the reaction of $[HM(CO)_5]$ with N_2CH_2 [72]. On the contrary, a two-to-one coupling reaction of a diazoalkane with CO at the N_α atom was found in the reaction of N_2CPh_2 with $[Cp_2Ti(CO)_2]$, where the product was a trinuclear complex $[(Cp_2Ti)_3(Ph_2CN{=}NC(O)N{=}NCPh_2)_2]$ (**46**) [13].



Scheme 7



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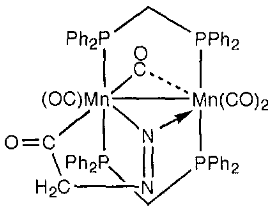

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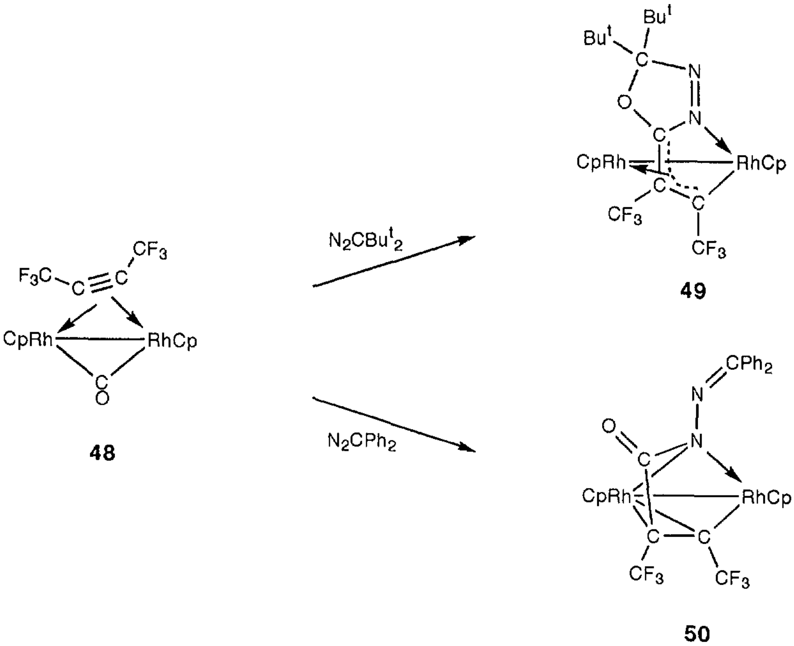
In contrast, C–C bond formation between N_2CH_2 and CO took place on $[Mn_2(dppm)_2(CO)_5]$, and a metallacyclic product $[Mn_2(\mu\text{-}COCH_2N{=}N)(CO)_4(dppm)]$ (**47**) was formed [75]. The CO–CH_2 bond in **47** is long (1.56 Å), and heating in C_6H_6 or photolysis caused regeneration of the starting carbonyl complex.

Furthermore, interesting three-component coupling reactions of a diazoalkane, CO and an alkyne were observed with $[Cp_2Rh_2(CO)(CF_3CCCF_3)]$ (**48**) (Scheme 8) [76]. Thus, when **48** was allowed to react with $N_2CBu^t_2$, a complex formulated as $[Cp_2Rh_2(N_2CBu^t_2)(CO)(CF_3C_2CF_3)]$ (**49**) was isolated, which contains a ligand formed from $N_2CBu^t_2$, CO, and CF_3CCCF_3. The new ligand has an $\overline{N{=}N{-}C{-}O{-}C}$ ring, and can be regarded as a formal 1,3-dipolar cycloaddition product of the diazoalkane to the bridging carbonyl. Complex **49** showed remarkable thermal stability (melting at 184°C without decomposition), which is in sharp contrast to the fact that the (3 + 2) cycloadduct of a diazoalkane and a organic ketone is an unstable species. Reaction of **48** with N_2CPh_2 also resulted in the formation of a complex formulated as $[Cp_2Rh_2(N_2CPh_2)(CO)(CF_3C_2CF_3)]$ (**50**) by a different type of three-component coupling on the Rh_2 centre.

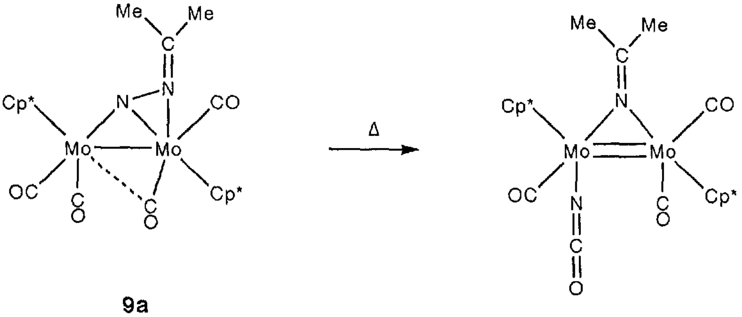
4.2.8 N–N bond fission of diazoalkane ligands

Several notable reactions including the N–N bond fission of a diazoalkane were observed on di- and multinuclear complexes.



Scheme 8

When a dinuclear complex **9a** containing a μ-η^1:η^2-NNCMe$_2$ ligand (vide supra) was heated in toluene at reflux, N–N fission of the diazoalkane ligand and the subsequent rearrangement of the intermediate nitrido complex occurred to yield [Cp*$_2$Mo$_2$(CO)$_4$(NCO)(μ-N=CMe$_2$)] (**51**) [77,78]:



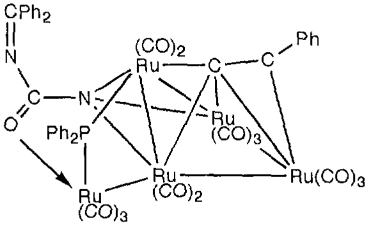
9a

51

(17)

Evidently the η^1:η^2-coordination mode plays an important role in the N–N bond cleavage, but a closely related complex [Cp$_2$Mo$_2$(CO)$_4$(NNCMe$_2$)] failed to undergo similar reactions [36]. In a thermal reaction of [Cp*$_2$Mo$_2$(CO)$_4$(CH$_2$)(NNCH$_2$)], the N–N fission led to a bis(methylene) amido complex [Cp*$_2$Mo$_2$(CO)$_3$(NCH$_2$)$_2$] [77]. Several reactions of diazirines with low valent metal carbonyls of Ti [8], Fe [54] and Ru [55] bring about similar N–N bond fission and form isocyanato complexes (vide supra).

Another example of N–N bond cleavage of a diazoalkane ligand was reported in the reaction of **14** with CO. The μ_4 coordination of N$_2$CPh$_2$ in **14** makes the N–N bond very long (vide supra) and facilitates N–N bond breaking. In this case, CO insertion into the N–N bond occurred to yield [Ru$_5$(μ_4-NCON=CPh$_2$)(μ_4-η^2-C≡CPh)(μ-PPh$_2$)(CO)$_{13}$] (**52**) [46].



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