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Coordination Chemistry Reviews
178–180 (1998) 623–663

COORDINATION
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REVIEWS

# Crystal and molecular structures of transition metal complexes with N- and C-bonded diazoalkane ligands

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Received 17 March 1998; accepted 16 April 1998

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## Abstract

The review covers structural and physicochemical studies on diazoalkanes N-coordinated to transition metals and encompasses all collected crystal structures. Our goal is to provide a classification of the complexes based on the metal, ranging from early to late transition metals, the nuclearity of the complex (mono, dinuclear, clusters), the electronic configuration

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*PII* S0010-8545(98)00117-9

of the metal ($d^0$ to $d^{10}$) and the bonding mode of the diazoalkanes. Interestingly, the variety of structures may be rationalized within the valence bond formalism, the reactions being essentially oxidative addition of diazoalkane on the metal complexes giving hydrazonido (-2-ligand). C-coordinated diazoalkyl complexes are still restricted to a few metals and a few diazosubstituents and their chemistry is not well developed. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Diazoalkanes N-Coordinated; Crystal Structures; Bonding mode; Transition metals

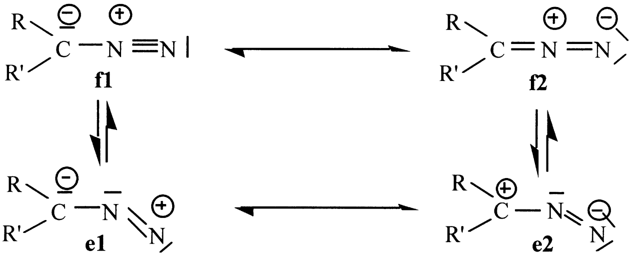
## 1. Introduction

The past decade has seen remarkable development in the chemistry of compounds containing diazoalkanes that violate the long-held view that compounds containing metal–diazo bonds would be unstable and that diazoalkanes are catalytically decomposed into carbene by transition metals.

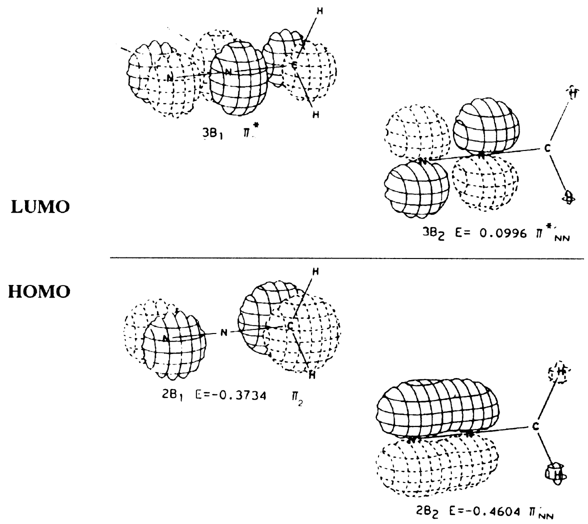
Diazoalkanes are heterocumulenes, i.e. possess lone electron pairs and unsaturated bonds. Much of the reactions of diazoalkanes can be rationalized by the valence bond formalism based on the different conformations (linear or bent) of the molecule (Scheme. 1).

Using the molecular orbital description of Jorgensen and Salem [1], the critical sets of diazoalkane orbitals playing an important role in the bonding are: two HOMO, a non-bonding π orbital $2B_1$ localized on the terminal N atom and perpendicular to the diazo molecular plane and, at higher energy, a π orbital $2B_2$, bonding with respect to the two N atoms and located in the diazo molecular plane. The LUMOs are π* antibonding orbitals: the $3B_2$ located on the two N atoms and lying in the diazo molecular plane and, at slightly lower energy, the $3B_1$ orbital located on the three N, N and C atoms and perpendicular to the diazo plane. These orbitals are shown in Scheme. 2.

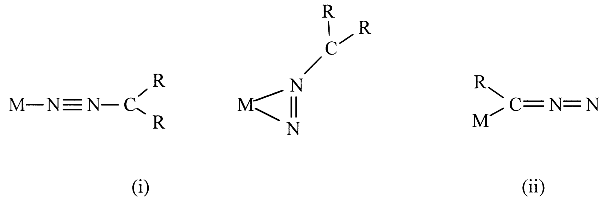
Consequently, diazoalkanes can coordinate to metals to form several types of nitrogen-bonded complex in which they are either σ-bonded through the terminal N atom or side-on coordinated via the π function of N≡N or both when coordinated to more than metal (Scheme. 3(i)). Metal complexes can also act as diazo substituents giving C-bonded diazoalkane or α-diazoalkyl complexes (Scheme. 3(ii)).



Scheme 1. Conformations of diazoalkanes according to the valence bond view



Scheme 2. HOMO and LUMO for diazoalkanes following [1]



(i)

(ii)

Scheme 3. Diazoalkane N and C bonded to a single metal fragment [M]

The synthesis of N-bonded diazoalkane complexes has been developed first in view of nitrogen activation or for studying the mechanistic aspects of the catalytic decomposition of diazoalkanes. The diazoalkanes used first were those stabilized by strongly electron-withdrawing groups, such as R = CN, $CF_3$, $CO_2R$, C(O)R, or groups which can resonance-stabilize negative charges, such as those found in diazotetrachlorocyclopentadiene, diazofluorene and diazophenylmethane.

On the other hand, reported diazoalkyl metal complexes or α-metalled diazoalkanes are quite few in number and most of them are those of non-transition metals, which will not be reviewed here.

Previous books and reviews covering the synthesis and chemistry of organic diazoalkanes and their use as precursors of carbenes have been published [2]. Synthetic and structural carbene derivatives resulting from the reaction of diazoalkanes and transition metals together with their use as one carbon fragment producers for carbon–carbon synthesis have also been summarized [3]. Besides the results described by Regitz and Maas [4], a previous, quite exhaustive, review of N-coordinated diazoalkane complexes was published by Hidai and coworkers [5] who, after describing the most important structures, focused mainly on the synthetic and reactivity aspects of the field.

This review focuses on the structural and spectroscopic studies of transition metal diazoalkane complexes and encompasses all collected molecular structures. It is meant to provide a classification of the different complexes following the metal, the electronic configuration of the metal and of the diazoalkane and the nuclearity of the complexes in order to understand the reaction of the diazoalkane with transition metals and to predict the reactivity of the resulting complexes. In Section 2 we discuss the molecules in which the diazoalkane is N-coordinated to one, two, three and four metal centers. In all these cases, several coordination modes are observed which will be indicated and discussed in terms of the valence bond formalism. Although little concerted effort has been devoted to the synthesis and reactivity of transition metal C-bonded diazoalkyl ligands, this new field will be described in Section 3.

In the valence bond formalism, the neutral diazoalkanes which possess free electron pairs located on the two N atoms and $\pi$ electrons in the double or triple bonds can be considered as two-, four- or six-electron donor ligands that may coordinate to transition metal centers. The different complexes will each be considered.

## 2. Transition metal complexes with N-coordinated diazoalkane

### 2.1. *Diazoalkane coordinated to a single metal center*

The four possible structural models are illustrated in Scheme. 4. Type **I** is an $\eta^1$ end-on N coordination; types **II** and **III** are $\eta^2$ (N,N) and $\eta^2$ (N,C) side-on coordinations respectively. Type **IV** is an $\eta^2$ metallacycle.

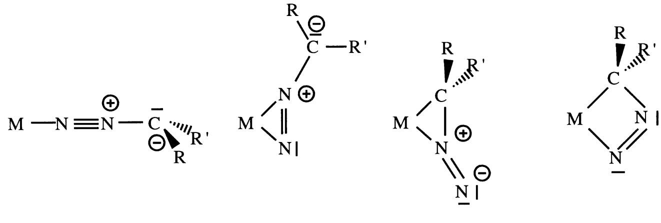
Until now, only the coordination modes **I** and **II** have been observed. The structural models **III** and **IV** have been proposed as intermediates in the mechanisms of decomposition of diazoalkanes but not yet isolated.

### 2.1.1. *Type **I** complexes: end-on $\eta^1$ N coordination*

Scheme. 5 indicates that, in fact, the end-on $\eta^1$ coordination mode of the diazo moiety may cover different electronic configurations.

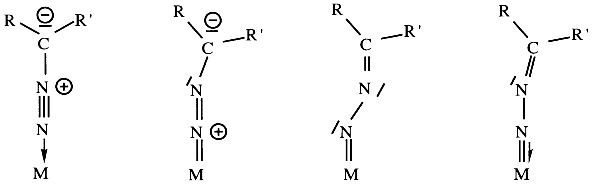
$R_2CN_2$ may act as a two- (**Ia**, **Ib** and **Ib′**) or a four-electron donor (**Ic**) making one to three bonds to a metal. In type **Ia** complexes, the terminal N atom acts as a $2e^-$ donor giving a dative bond, thus behaving as a neutral diazo ligand. In type **Ib** (singly bent) and **Ib′** (doubly bent) species, the terminal nitrogen has two covalent ($\sigma+\pi$) bonds. **Ic** is a $4e^-$ donor with two covalent bonds and one dative bond. Consequently, the diazo ligand, in the ionic formalism of electron count, may be considered as reduced by the metal center into the hydrazonido($-2$) entity. The coordination of diazoalkanes corresponds then to an oxidative addition on the metal center, which increases correlatively its formal oxidation state by $+2$ units. If type **Ia** and **Ic** complexes have been clearly characterized by X-ray structure, **Ib** and **Ib′** forms are usually involved in equilibrium with **Ia** or **Ic**.

Infrared data available for each type of complex are reported in Tables 1 and 2.



I II III IV

Scheme 4. Possible structural models for diazoalkane N-bonded to single metal fragments



**Ia** **Ib** **Ib'** **Ic**

Scheme 5. End-on $\eta^1$ coordination mode for diazoalkanes bonded to single metal fragments

*2.1.1.1. Type **Ia** complex.* There is only one example of structurally characterized coordination mode **Ia**. This totally linear coordination has been observed by Dartiguenave and coworkers [26] in $[M\{N_2C(SiMe_3)_2\}(CO)_5]$ (**1**) (M = Cr, W) and $[W\{N_2C(SiMe_3)_2\}(CO)_4(PPh_3)]$ (**2**) (Fig. 1). They were synthesized by addition of an equimolar amount of $LiC(N_2)SiMe_3$ and $Me_3SiCl$ on $[M(CO)_6]$ or $[W(CO)_5PPh_3]$.

The main bond distance and angle values in (**2**) are in good agreement with the formalism illustrated by Scheme. 5, the structure **Ia** being stabilized by the presence of the electron-withdrawing $SiMe_3$ substituents (W–N: 2.161(11) Å; N1–N2: 1.165(15) Å; N2–C: 1.34(1) Å; C–Si: 1.75(1) Å, 1.77(1) Å; W–N1–N2: 176(1)°; N1–N2–C: 170(1)°).

The diazo ligand behaves as a $2e^-$ donor and the complex is formally a neutral diazo complex of W(0). More specifically, the diazoalkane can be described as a dinitrogen molecule bridged to the W(0) center and the carbanion unit $[C(SiMe_3)_2]^-$.

*2.1.1.2. Type **Ib** complexes.* Most of these compounds have been prepared through ligand substitution reacting diazoalkanes on metal complexes under mild conditions:

$$[ML_n] + N_2CR_2 \rightarrow [L_{n-1}M{=}N_2CR_2] + L \qquad (1)$$

Examples have been reported for late transition metal complexes. Addition of $N_2C(CO_2Et)_2$ on $[Cp'Mn(CO)_2(THF)]$ at room temperature in THF allowed Herrmann and coworkers [6,7] to synthesize $[Cp'Mn(CO)_2\{N_2C(CO_2Me\}]$ (**3**), (Cp' = Cp, $MeC_5H_4$), whereas iridium complexes $[IrCl(N_2R_2')(PR_3)_2]$ (**4**)

Table 1
Type **Ib** complexes

| Compound | | No. | Diazoalkane | IR ($cm^{-1}$) | Raman ($cm^{-1}$) | $^{13}C$ (ppm) | Ref. |
|---|---|---|---|---|---|---|---|
| [Cp′Mn(CO)$_2$] | | **3** | | | | | |
| Cp′= | Cp | | $N_2C(CO_2Et)_2$ | 1951 | | | [6,7] |
| | MeCp | | $N_2C(CO_2Et)_2$ | 1948 | | | |
| [IrCl(PR$_3$)$_2$] | | **4** | | | | | |
| R= | Ph | | $N_2C_5Cl_4$ | 1858 | 1872 | | |
| | Ph | | $N_2C_5Br_4$ | | 1915 | | |
| | *p*-tol | | $N_2C_5Cl_4$ | | 1874 | | |
| | *p*-tol | | $N_2C_5Br_4$ | | 1908 | | |
| | *p*-$FC_6H_4$ | | $N_2C_5Cl_4$ | | 1858 | | |
| | *p*-$FC_6H_4$ | | $N_2C_5Br_4$ | | 1867 | | |
| [IrCl(L)(PPh$_3$)$_2$] | | **5** | | | | | |
| L= | $PMePh_2$ | | $N_2C_5Cl_4$ | 1660 | | | [8–10] |
| | $PMe_2Ph$ | | $N_2C_5Cl_4$ | | 1635 | | |
| | $PMe_3$ | | $N_2C_5Cl_4$ | | 1541 | | |
| | $^tBuNC$ | | $N_2C_5Cl_4$ | 1455 | 1520 | | |
| [IrCl(NO)(PPh$_3$)$_2$] [PF$_6$]CH$_3$CN | | **5** | $N_2C_5Cl_4$ | 1449 | 1448 | | |
| [IrCl$_2$(L)(PPh$_3$)$_2$] | | **6** | | | | | |
| L= | H | | $N_2C_5Cl_4$ | 1614 | | | |
| | NO | | $N_2C_5Cl_4$ | 1443 | 1440 | | |
| [IrCl(PPh$_3$)$_2$] | | **4** | $N_2C(CO_2Et)_2$ | 1960 | | | |
| | | | $N_2C(COMe)(COPh)$ | 1880 | | | |
| [IrCl(P$^i$Pr$_3$)$_2$] | | **5** | $N_2C(CO_2Et)_2$ | 1930 | | 68.2 | |
| | | | $N_2C_{11}H_8O$ | 1820 | | | |
| | | | $N_2C(COMe)(COPh)$ | 1860 | | 85.2 | [11] |
| [IrMe(P$^i$Pr$_3$)$_2$] | | | $N_2C(COMe)(COPh)$ | 1837 | | | |
| [IrH$_2$Cl(P$^i$Pr$_3$)$_2$] | | | $N_2C(CO_2Et)_2$ | 1950 | | | |
| | | | $N_2CPh_2$ | 1990 | | | |
| [IrCl(PPh$_3$)$_2$] | | **4** | $N_2C(COPh)_2$ | 1869 | | | [12] |
| [RhCl(P$^i$Pr$_3$)$_2$] | | **7** | $N_2CPh_2$ | 1940 | | 78.7 | |
| [RhMe(P$^i$Pr$_3$)$_2$] | | **7** | $N_2CPh_2$ | 2040 | | 69.1 | [13] |

(R′=$C_5Cl_4$, Ph, *p*-tol, *p*-$FC_6H_4$) were obtained by Schramm and Ibers [8–10] and Werner and coworkers [11].

This $\eta^1$ end-on coordination is illustrated by the X-ray structural characterization of (**4a**) (Fig. 2). The diazoalkane group is singly bent at the central N2 atom, giving the molecule a non-linear geometry (N1N2C=141.2(7)°). The Ir–N (1.824(6) Å) bond distance is shorter than expected for a single Ir–N bond: 1.93 Å in [Tp*Ir($C_6H_5$)$_2$]$_2$(μ$N_2$) (Tp*=HB(3,5-$Me_2$pz)$_3$) [27], 1.970(20) Å in $IrCl_2(HN_2C(C(O)Ph)_2)(PPh_3)_2$ [12] and longer than for a triple Ir≡N bond (1.712(7) Å) in [($C_5Me_5$)IrN$^t$Bu] [28]. The N1–N2 distance of 1.163(7) Å is interme-

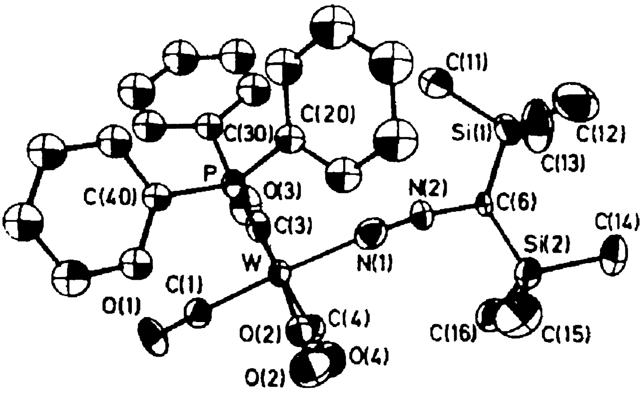


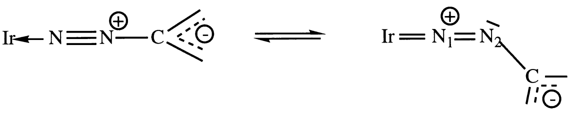
Fig. 1. ORTEP drawing of $[W\{N_2C(SiMe_3)_2\}(CO)_4(PPh_3)]$ (**2**) following Ref. [26].

diate between that of double and triple bonds. This indicates the presence of the two alternative valence bond structures **Ia** and **Ib**, which confers upon the metal a formal oxidation state +1 (neutral diazoalkane) and +3 (hydrazonido(−2) ligand) respectively (Scheme. 6).

This equilibrium reflects the metal to ligand π overlap interactions. Coplanarity of the Ir, N1, N2, C atoms and the $C_5Cl_4$ atoms of the cycle provides a very effective disposition for creation of an extended delocalized π system utilizing the carbon pπ orbitals on the Cp ring, the N–N π* orbitals and the filled $d_{xy}$ orbital of Ir, thus stabilizing the negative charge present on the C atom. According to Schramm and Ibers, this delocalization of π electrons is also responsible for the variations of $\nu(N_2C)$ stretch, which can be used as a probe. This is clearly illustrated in Table 1 where the IR data of tetracoordinated $[IrCl(N_2CR'_2)(PR_3)_2]$ (**4**), pentacoordinate $[IrX(L)(N_2CR'_2)(PR_3)_2]$ (**5**) and hexacoordinate $[IrCl_2L(N_2CR'_2)(PR_3)_2]$ (**6**) iridium complexes are reported. Structure **Ia** is favored in tetracoordinate complexes, whereas structure **Ib** is preferred in coordination 5 and 6 [9–12].

The rhodium analogue, $[RhCl(N_2CPh_2)(P^iPr_3)_2]$ (**7**), was isolated by Werner and coworkers in reacting $Ph_2CN_2$ on $[RhCl(P^iPr_3)_2]$ at room temperature [13]. When $R_2CN_2$ ($R={}^iPr$, *p*-$FC_6H_4$, Cy, $^tBu$) were used, the diazo complexes were only observed as transients at low temperature. Interestingly, diazomethane gives the ethylene complex $[RhCl(CH_2{=}CH_2)(P^iPr_3)_2]$.

The $\eta^1$ coordination mode was also observed with early transition metals. Diphenyldiazomethane reacted with the Ti(II) complexes $[Cp_2Ti(PMe_3)_2]$ and



**Ia** **Ib**

Scheme 6. Schematic illustration of the resonance forms between line 158-159 for complex [4]

Table 2
Type **Ic** complexes

| Compound | | No. | Diazoalkane | IR ($cm^{-1}$) | $^{13}C$ (ppm) | Ref. |
|---|---|---|---|---|---|---|
| $[WBr(dppe)_2][PF_6]$ | | **9** | $N_2CCl_2$ | 1535 | | [14,15] |
| $[WBr(dppe)_2]Br$ | | **9** | $N_2CH_2$ | | 155.3 | [16] |
| | | | $N_2CHMe$ | 1575 | 168.7 | |
| | | | $N_2CMe_2$ | 1580 | 174.5 | |
| | | | $N_2CHPh$ | 1530 | | |
| $[MoF(dpe)_2][BF_4]$ | | **10** | $N_2CHCH_3$ | 1575 | | [17,18] |
| | | | $N_2CHCH_2CH_3$ | 1565 | | |
| | | | $^{15}N_2CHCH_2CH_3$ | 1550 | | |
| | | | $N_2CHPh$ | 1525 | | |
| | | | $N_2CHCH_2Ph$ | 1560 | | |
| | | | $N_2CHCHCHCH_3$ | 1565 | | |
| | | | $N_2CHCHCHPh$ | 1510 | | |
| | | | $N_2C(CH_3)CH_2COCH_3$ | 1570 | | |
| | | | $N_2C(CH_3)_2$ | 1585 | | |
| | | | $N_2C_6H_{10}$ | 1575 | | |
| $[WF(dpe)_2][BF_4]$ | | **10** | $N_2CHCH_2CH_3$ | 1580 | | |
| | | | $N_2CHPh$ | 1540 | | |
| | | | $N_2C(CH_3)CH_2COCH_3$ | 1595 | | |
| $[WCl_2(PMe_2Ph)_3]$ | | **11** | $N_2CMe_2$ | 1582 | 168.7 | [19] |
| $[WBr_2(PMe_2Ph)_3]$ | | **11** | $N_2CMe_2$ | 1582 | 168.0 | |
| | | | $N_2C(CD_3)_2$ | 1570 | | |
| | | | $N_2CEtMe$ | 1572 | | |
| | | | $N_2CMePh$ | 1537–1520 | 177.6 | |
| | | | $N_2C(CH_2)_5$ | 1569–1562 | | |
| | | | $N_2CMe(CH_2COMe)$ | 1572 | | |
| | | | $N_2CMe(CH_2CH_2COMe)$ | 1577 | | |
| $[WI_2(PMe_2Ph)_3]$ | | **11** | $N_2CMe_2$ | 1583 | 163.0 | |
| $[W(8\text{-}hq)(PMe_2Ph)_3]Br$ | | **11** | $N_2CMe_2$ | 1584 | | |
| hq = hydroxyquinolato | | | $N_2C(CD_3)_2$ | 1563 | | |
| $[WCl_2L(PMe_2Ph)_2]$ | | | | | | [20] |
| L = | $C_2H_4$ | | $N_2CMe_2$ | 1582 | 175.8 | |
| | $CH_2{=}CHCO_2Me$ | | $N_2CMe_2$ | 1575 | | |
| | $CH_2{=}CHCH{=}CH_2$ | | $N_2CMe_2$ | 1575 | 177.3 | |
| | CO | | $N_2CMe_2$ | 1578 | | |
| | PhCHO | | $N_2CMe_2$ | 1580 | | |
| | $C_2H_4$ | | $N_2CMePh$ | 1525 | | |
| | CO | | $N_2CMePh$ | 1520 | | |
| | $^tBuNC$ | | $N_2CMePh$ | 1530 | | |
| | PhCHO | | $N_2CMePh$ | 1525 | | |
| | $p\text{-}CH_3C_6H_4CHO$ | | $N_2CMePh$ | 1509 | | |
| | CO | | $N_2CHPh$ | 1510 | | |

Table 2
(*continued*)

| Compound | | No. | Diazoalkane | IR ($cm^{-1}$) | $^{13}C$ (ppm) | Ref. |
|---|---|---|---|---|---|---|
| | PhCHO | | $N_2CHPh$ | 1535 | | |
| | $PMe_2Ph$ | | $N_2CHPh$ | 1535 | | |
| $[MoCl_2(CO)(PMe_2Ph)_2]$ | | **12** | $N_2CMePh$ | 1510 | | |
| $[W(CO)(S_2CNMe_2)_2]$ | | **13** | $N_2CH(p\text{-}C_6H_4Me)$ | 1530 | | |
| | | | $N_2CHPh$ | 1530 | | |
| | | | $N_2CMe(p\text{-}C_6H_4Me)$ | 1527 | | |
| $[Mo(CO)(S_2CNMe_2)_2]$ | | **13** | $N_2CH(p\text{-}C_6H_4Me)$ | 1524 | | |
| $[W(CO)(S_2CNEt_2)_2]$ | | **13** | $N_2CH(p\text{-}C_6H_4Me)$ | 1498 | | [21] |
| | | | $N_2CHPh$ | 1497 | | |
| $[W(CO)\{S_2CN(CH_2)_4\}_2]$ | | **13** | $N_2CH(p\text{-}C_6H_4Me)$ | 1494 | | |
| $[WCl_2(S_2CNMe_2)_2]CHCl_3$ | | **14** | $N_2CH(p\text{-}C_6H_4Me)$ | 1546 | | |
| $[WBr_2(S_2CNMe_2)_2]CHCl_3$ | | **14** | $N_2CH(p\text{-}C_6H_4Me)$ | 1549 | | |
| $[MoBr_2(S_2CNMe_2)_2]CHCl_3$ | | **14** | $N_2CH(p\text{-}C_6H_4Me)$ | 1543 | | |
| $[Mo_2Cp_2(CO)_3\{C(p\text{-}MeC_6H_4)_2\}]$ | | **15** | $N_2C(p\text{-}MeC_6H_4)_2$ | | 163.8 | [22] |
| | | | | | | [23] |
| $[Mo(O^tBu)_4]$ | | **16** | $N_2CPh_2$ | | 167.2 | |
| $[Mo_2(OCH_2{}^tBu)_6(HNMe_2)]$ | | **17** | $N_2CPh_2$ | | 152.2 | [24] |
| with two bonded diazos | | | | | 149.9 | |
| $[W_2(\mu\text{-}CSiMe_3)_2L_4]$ | | **18** | | | | |
| L = | $CH_2SiMe_3$ | | | | 163.1 | [25] |
| | $O^iPr$ | | | | 163.1 | |

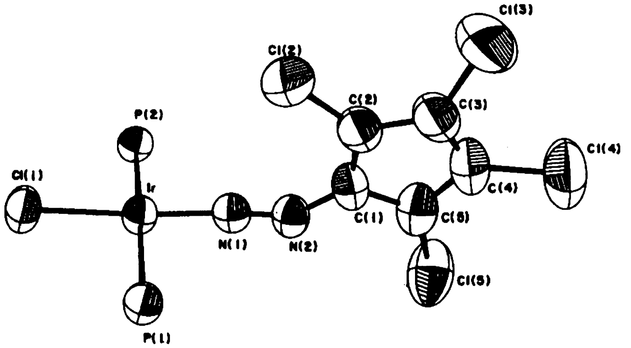
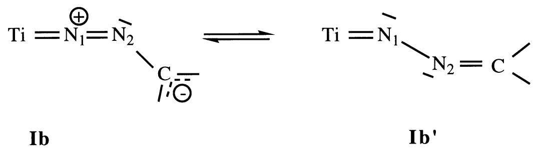


Fig. 2. ORTEP drawing of $[IrCl(N_2C_5Cl_4)(PPh_3)_2]$ (**4a**) following Refs. [9,10].

$[Cp_2Ti(CO)(PMe_3)]$ in pentane under ambient conditions to yield the stable Ti(IV) complex $[Cp_2Ti(N_2CPh_2)(PMe_3)]$ [29] (**8**) in 80% yield. The bond distance and angle values agree with a Ti(IV)–hydrazonido(−2) complex with both the N1–N2



Scheme 7. Schematic illustration of the valence bond equilibrium in [8]

(1.262(15) Å) and N2–C1 (1.311(16) Å) bond distances intermediate between single and double N–N and N–C bonds respectively. The significant bending of the molecule observed at N1 with Ti–N1–N2 = 156.8(9)° agrees with the presence of the two main valence bond structures **Ib** and **Ib**′, the amount of form **Ib**′ being not negligible. The N1–N2–C1 angle value of 126.0(9)° is as expected for the $sp^2$-hybridized N2 atom (Scheme. 7).

Bending of the M–N1–N2 fragment at N1 results from the absence of $\pi$ bonding between the metal center (Ti(IV), $d^0$) and the $\pi^*$ orbital of the multiple bonded N–N–C fragment. Such a distortion from linearity will be found in all the $\eta^1$-diazo complexes of early transition metals (Ti, V, Zr) and of the high oxidation state of molybdenum and tungsten.

However, the experimental conditions and the nature of the ancillary ligands remain important parameters. Reacting diphenyldiazomethane with $[Cp_2Ti(CO)_2]$ at room temperature in toluene yields several species, among which is $Cp_2Ti(NN(CPh_2)CO(CPh_2)NN)$ resulting from the metal-mediated coupling of CO with diazoalkane [30].

*2.1.1.3. Type **Ic** complexes.* Several examples of **Ic**-type coordination mode, where the terminal nitrogen atom N1 acts as a $4e^-$ donor, have been reported. Monometallic and bimetallic complexes have been described, but, in all cases, only middle transition metals (Mo and W) are involved with oxidation states ranging from IV to VI.

Interestingly, none of the first complexes showing **Ic** coordination mode were produced from free diazoalkane, but rather were prepared by oxidative addition of dibromocarbene on Mo(0) complexes (Eq. (2)) or by condensation of a coordinated hydrazido ligand with a carbonyl compound (Eq. (3)):

$$[M(N_2)_2(dppe)_2] + R_2CBr_2 \rightarrow [MBr(N_2CR_2)(dppe)_2]Br + N_2 \tag{2}$$

$$[MX_2(N_2H_2)L_3] + RR'_2CO \rightarrow [MX_2(N_2CRR')L_3] + H_2O \tag{3}$$

$[WBr(N_2CR_2)(dppe)_2]^+$ (**9**), with ($CR_2{=}CH(CH_2)_3OH$, $CMe_2$) [31] ($CR_2{=}$**$CCl_2$, $(Cl)C{=}C(CN)_2$, $CN(Me)CH_2CH_2NMe$**, $CNHCH_2CH_2NH$) [14,15] and ($CR_2{=}CH_2$, CHMe, $CMe_2$, CHPh) [16] were prepared via the reaction in Eq. (2).

The diphosphine complexes $[MF(N_2CR_2)(dpe)_2]BF_4$, (**10**), with (M = W, $CR_2{=}CHEt$, CHPh, $CMeCH_2COMe$, $CMeCH(CONHPh)_2$; M = Mo, $CR_2{=}CH_2$, CHMe, $CMe_2$, CHEt, CHPh, $CHCH_2Ph$, CHCH=CHMe, CHCH=CHPh,

$CMeCH_2COMe$, $C_6H_{10}$) and *t*-*t*-[$(dpe)_2WF$(**NN=CHCHMeCHMeCH=NN**) $WF(dpe)_2][BF_4]_2$, $6C_6H_6$ [17,18]; the mono tertiary phosphines [$WX_2(N_2CR_2)(PMe_2Ph)_3$], (**11**), (X=Cl, Br, I and $CR_2=CMe_2$; X=Br, $CR_2=CMeEt$, CMePh, $C(CH_2)_5$, $CMeCH_2COMe$, $CMe(CH_2)_2COMe$) [19] and [$MCl_2(N_2CR_2)(L)(PMe_2Ph)_2$], (**12**), (M=Mo, W; $CR_2=CMe_2$, **CMePh**; L=$\mathbf{C_2H_4}$, CO, $^t$BuNC, **aldehyde**) [20] were prepared via the reaction in Eq. (3).

Only those complexes with emboldened $CR_2$ substituents have been structurally characterized. The main bond and angle values are reported in Table 5. The structural analysis of $[WF(N_2CMeCH(CONHPh)_2)(dpe)_2]^+$, (**10c**) (Fig. 3), shows that the diazo ligand is singly bent and that the distance and angle values are in the range of those of the hydrazido(−2) complex $[WCl(NNH_2)(dppe)_2]^+$, indicating a W(IV) center and a hydrazonido (2−) ligand (Scheme. 8).

However, Haymore and Hillhouse [21] reported the synthesis of monometallic diazoalkane complexes of type **Ic** starting from free diazoalkane: [$M(CO)(N_2CR_2)(S_2CNR'_2)_2$], (**13**), (M=W; $CR_2$=CHtolyl, CHPh, CMetolyl or M=Mo; $CR_2$=CHtolyl); [$MX_2(CO)(N_2CHto)(S_2CNMe_2)_2$], (**14**), (M=W; X=Cl, Br or M=Mo; X=Br) [21]. $MoO(S_2CNR_2)(N_2RR')$ (M=Mo, W; $CRR'=CPh_2$, CHPh, CMePh) [32] have also been prepared.

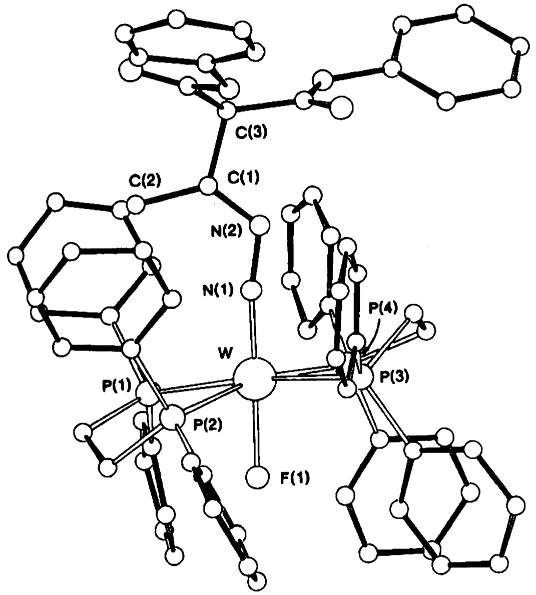
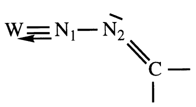


Fig. 3. ORTEP drawing of trans[$WF(NN=CMeCH(CONHPh)_2)(dpe)_2]BF_4$ (**10c**) from Refs. [17,18].



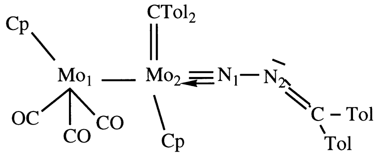
Scheme 8. Schematic illustration of the bonding for [10c]

This end-on diazo coordination mode has also been observed in some cases when diazoalkanes were reacted with electron-rich bimetallic molybdenum or tungsten complexes. One example is described by Messerle and Curtis who synthesized $[Cp(CO)_3Mo\text{–}Mo(\eta^1CR_2)(\eta^1N_2CR_2)Cp]$ ($R=CH_3C_6H_4$) (**15**), in 75% yield, by reacting $[Cp_2Mo_2(CO)_4\{\mu\text{-}C(C_6H_4Me)_2\}]$ with $N_2C(C_6H_4Me)_2$ in benzene [22,23]. This compound shows a terminal alkylidene and an N-terminal diazoalkane ligand bonded on the same Mo center (Scheme. 9).

The X-ray crystal structure indicates bond lengths of 1.741(10) Å for Mo2–N1, 1.323(12) Å for N1–N2, 1.318(13) Å for N2–C and bond angles of 174.7(9)° for Mo2–N1–N2 and 121(1)° for N1–N2–C which are consistent with a singly bent $Mo2{\equiv}N1\text{–}N2{=}C$ group (Scheme. 9). Both molybdenum atoms require an $18e^-$ configuration, Mo1 by its array of ligands and Mo2 by the donation of $4e^-$ from N1 to give the short $M{\equiv}N$ distance of 1.741(10) Å. As a consequence, each Mo formally presents a different oxidation state.

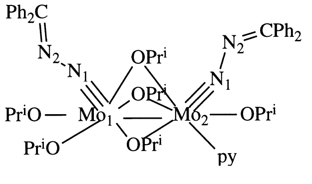
Chisholm and coworkers observed a similar reactivity by adding diazoalkane to M(VI) complexes (Mo, W) with $M{\equiv}M$ multiple bonds. A variety of products was formed, depending on M (Mo, W) and on the alkoxy ligand. In the reaction between $Mo_2(O^tBu)_6$ and $N_2CPh_2$, the $Mo{\equiv}Mo$ bond is cleaved and the mononuclear compound $Mo(O^tBu)_4(N_2CPh_2)$ (**16**) is isolated. In the presence of donor ligands (pyridine or $HNMe_2$), the less sterically demanding isopropyl and neopentyl Mo2 compounds reacted with two equivalents of $N_2CR_2$ ($CR_2=CPh_2$, CHPh) at low temperature (−78 °C) to yield $[Mo_2(O^tBu)_6(N_2CR_2)(L)]$ (L = Py, $HNMe_2$) (**17**). The X-ray structure of $[Mo_2(O^iPr)_6(N_2CPh_2)_2(Py)]$, (**17a**), shows one diazo molecule $\eta^1$-bonded on each Mo (Scheme. 10) [24].

The Mo–Mo distance of 2.662(2) Å indicates a single bond. As already observed when electron-poor metal centers are involved, the Mo–N1–N2 fragment is bent at



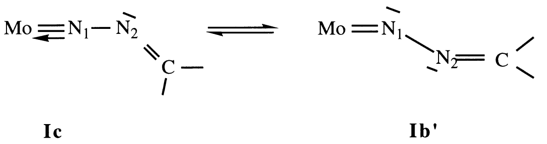
**(15)**

Scheme 9. Schematic illustration of the bonding for [15]

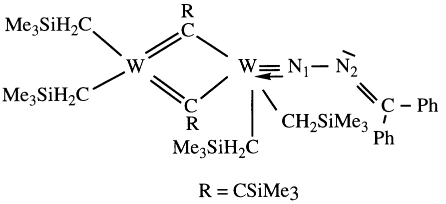


**(17a)**

Scheme 10. Schematic illustration of the bonding for [17a]



Scheme 11. Schematic illustration of the valence bond equilibrium in [17a]



**(18a)**

Scheme 12. Schematic illustration of the structure of [18a]

N1 with angle values of 164.4(8)° for Mo1 and 155.3(7)° for Mo2 centers. Both diazo molecules are $\eta^1$-bonded on each Mo center in a similar fashion which is intermediate between the two isomeric forms: singly bent **Ic** and doubly bent **Ib**′ (Scheme. 11). This complex contains $(Mo–Mo)^{10+}$ units with a single Mo–Mo bond, indicating that the two diazoalkanes have been reduced into hydrazonido (−2) ligands, the triple bond $(Mo{\equiv}Mo)^{6+}$ acting as the source of $4e^-$.

Diphenyldiazomethane is also reduced into the hydrazonido (−2) ligand by the $d^2$(M–M) electrons of the bimetallic complex $[W_2(\mu\text{-}CSiMe_3)_2X_4]$ ($X = CH_2SiMe_3$; $O^iPr$) giving quantitatively the 1:1 W(VI) adduct $[W_2(\mu\text{-}CSiMe_3)_2X_4(N_2CPh_2)]$ (**18**). The diazoalkane is coordinated through its terminal nitrogen atom and coordination occurs to one tungsten atom only (Scheme. 12). The W–W distance, 2.91 Å, is characteristic of a non-bonding distance and **18a** corresponds to a $d^0$–$d^0$ binuclear compound. Interestingly, this reaction parallels the formation of the 1:1 $\eta^2$ alkyne adduct, the alkyne acting as a $4e^-$ donor [33].

This coordination mode could result from a steric congestion between the bulky diazo group and the $\mu$-$CSiMe_3$ and $CH_2SiMe_3$ ligands which prevents either a symmetrically bridged or an asymmetric $\mu\eta^2$ N1–N2 diazoalkane coordination as observed in other cases [25]. The W–N distance of 1.767(1) Å is clearly indicative of a multiple bond character. This W–N distance, together with the W–N–N angle of 158.2(8)°, indicates that the structure is best described by a hybrid of the two formalisms described on Scheme. 11.

### 2.1.2. *Type **II** complexes: side-on $\eta^2$(N,N) coordination*

Type **II** complexes are characterized by an $\eta^2$(N,N) coordination mode (Scheme. 4). Several examples are reported in the literature, including early to late transition metals. Infrared data available for these compounds are reported in Table 3.

Complexes of electron-rich metals $[ML_2(N_2CR_2)]$ have been obtained by ligand

Table 3
Type **II** complexes

| Compound | | No. | Diazoalkane | IR (cm$^{-1}$) | Ref. |
|---|---|---|---|---|---|
| [Ni($^t$BuNC)$_2$] | | **19** | diazofluorene | 1509 | [34,35] |
| [Cp$_2$Mo] | | **20** | diazofluorene | 1510 | [36] |
| [Ni($^t$BuNC)$_2$] | | **19** | $N_2C_5Cl_4$ | 1557 | |
| | | | $N_2C_5Br_4$ | 1541 | |
| [Ru(CO)$_2$(PPh$_3$)$_2$] | | **21** | $N_2C_5Cl_4$ | 1520 | |
| | | | $N_2C_5Br_4$ | 1508 | [37] |
| | | | 9-diazofluorene | 1496 | |
| | | | 2,7 dibromo-9-diazofluorene | 1495 | |
| [Pt(PPh$_3$)$_2$] | | **22** | $N_2C_5Cl_4$ | 1496 | |
| | | | $N_2C_5Br_4$ | 1490 | |
| [CoR(PMe$_3$)$_3$] | | **23** | | | |
| R= | Me | | $N_2C_5H_4$ | 1564–1558 | |
| | Me | | $N_2CPh_2$ | 1669 | |
| | 4-$CH_3C_6H_4C_2$ | | $N_2C_5H_4$ | 1591–1545 | |
| | $C_6F_5$ | | $N_2C_5H_4$ | 1670 | |
| | $C_6F_5$ | | 9-diazofluorene | 1640–1502 | [38] |
| [CoR{MeC(CH$_2$PMe$_2$)$_3$}] | | **23** | | | |
| R= | Me | | $N_2C_5H_4$ | 1545–1525 | |
| | Me | | 9-diazofluorene | 1606–1512 | |
| | COMe | | $N_2C_{13}H_8$ | 1580–1500 | |
| [TiCp$_2$] | | **24** | $N_2C(CO_2Et)_2$ | 1695–1640 | |
| [VCp$_2$] | | **25** | $N_2C(CO_2Et)_2$ | 1670–1640 | [30] |

displacement reaction from zero-valent metal complexes under mild conditions (0 to $-78$ °C). Side-on $\pi$-bonded diazoalkane was first postulated by Otsuka and coworkers in the nickel complexes [ML$_2$(N$_2$CR$_2$)] (**19**), (L=$^t$BuNC, PPh$_3$; N$_2$CR$_2$=N$_2$CPh$_2$, 9-diazofluorene) [34,35] and molybdenum [Cp$_2$Mo(9-diazofluorene)] (**20**) on the basis of their IR spectra, which showed a strong band in the 1480–1520 cm$^{-1}$ region [36].

This $\eta^2$(N,N) coordination is illustrated in the X-ray structure of [Ni($^t$BuNC)$_2$(9-diazofluorene)] (**19a**) (Fig. 4) which shows a diazofluorene molecule singly bent, $\eta^2$-bonded to the Ni atom through the N1–N2 multiple bond. The inner coordination around Ni is nearly planar, indicating that the molecular orbitals involved in the coordination lie in the NiNNC plane.

The two significantly different Ni–N distances have been explained by the polarizability of the N1N2C entity or the differences in $\pi$ acidity of the two N atoms (Ni–N2=1.834(3) Å and Ni–N1=1.874(3) Å) and are shorter than expected for a single bond. The N2–N1 distance of 1.245(4) Å is in the range of double bonds and N2–C1=1.334(4) Å is intermediate between a single and double bond. The N1–N2–C1=133.8(3)° angle indicates bending at the central N2 atom. This coordination mode is a consequence of the electronic configuration of the metal. In these

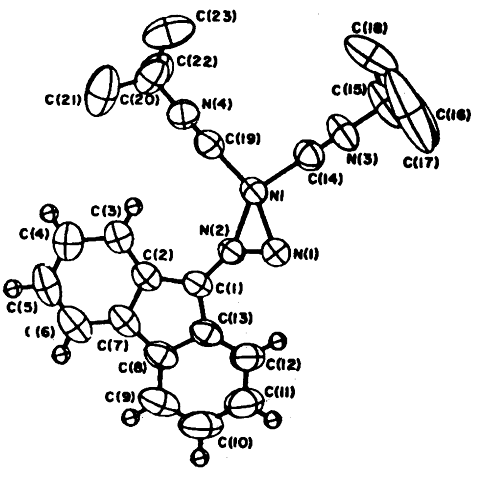
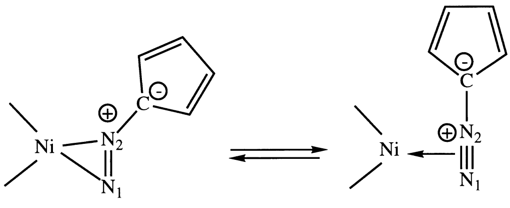


Fig. 4. [Ni($^t$BuNC)$_2$(9-diazofluorene)] (**19a**) following Refs. [34,35].

electron-rich systems, the diazo molecule acts as a π acid ligand and the formation of the 1:1 diazo adduct parallels the formation of the $\eta^2$ alkyne compound. In both cases, the electron-rich metal center serves as a reservoir of electrons for reduction of the organic molecule to a $-2$ ligand forming a metallacyclopropene unit for the alkyne and an metallacycloazirine unit for the diazoalkane. Thus, the formation of a 1:1 adduct can be viewed as an oxidative addition reaction (structure **IIa** of Scheme. 13).

Schramm and Ibers observed a similar $\eta^2$(N,N) coordination mode in [Ru(CO)$_2$(N$_2$CR$_2$)(PPh$_3$)$_2$] (**21**) ($N_2CR_2 = N_2C_5Cl_4$, $N_2C_5Br_4$, 9-diazofluorene, 2,7-dibromo-9-diazofluorene) and in [M(N$_2$CR$_2$)(PPh$_3$)$_2$] (M = Ni (**19**), Pt (**22**); $N_2CR_2 = N_2C_5Cl_4$, $N_2C_5Br_4$) [37]. These complexes have been prepared by substitution of ethylene by diazoalkane in [Ru(CO)$_2$(C$_2$H$_4$)(PPh$_3$)$_2$] and [Pt(C$_2$H$_4$)(PPh$_3$)$_2$]. Comparison of the X-ray structure of [Ru(CO)$_2$(N$_2$C$_5$Cl$_4$)(PPh$_3$)$_2$] (**21a**) with the nickel one (**19**) indicates a larger asymmetry in the Ru–N bond distances (Ru–N1 = 2.141(5) Å and Ru–N2 = 2.062(4) Å) and a diazo molecule distorted from planarity.

Klein et al. described related cobalt(I) complexes: [CoR(N$_2$CR$_2$)(PMe$_3$)$_3$] (**23**)



**IIa** **IIb**

Scheme 13. Schematic illustration of the valence bond equilibrium in [19]

($R = Me$, 4-Me–$C_6H_4$, $C_6F_5$; $CR_2 = C_5H_4$, $CPh_2$, $C_{13}H_8$). Crystal structure analysis of $[CoMe(N_2C_5H_4)(PMe_3)_3]$, (**23a**), indicates strong similarities with compound (**19**) [38].

Interestingly, the $\eta^2$(N,N) coordination mode has also been observed in early transition Ti(II) and V(II) complexes which are powerful nucleophiles. $[MCp_2(N_2CR_2)]$ (M = Ti (**24**), V (**25**); $N_2CR_2 = N_2C(CO_2Et)_2$), have been isolated by ligand exchange reaction of diethyldiazomalonate on $[MCp_2(CO)_2]$. In $[Cp_2Ti(N_2C(CO_2Et)_2)]$, (**24**), the diazo ligand is $\eta^3$-N,N,O-bonded to the metal through both nitrogen atoms and one oxygen of the ester group (Scheme. 14) [30]. The main bond distances and angle values are as expected in this coordination mode: Ti–N2 = 1.980(5) Å; Ti–N1 = 2.219(7) Å; Ti–O1 = 2.247(4) Å; N1–N2 = 1.214(7) Å; C1–N2 = 1.371(7) Å. The significant asymmetry of the two Ti–N bond distances suggests that the complex could be viewed as resulting from a [1,4] addition of the $Cp_2Ti$ carbene-like unit to the unsaturated system (Scheme. 14).

This bonding mode is highly dependent on the presence of the acetyl substituent (donor group) on the diazo skeleton. When $N_2CPh_2$ was used no $\eta^2$(N=N) complex was obtained, but instead the "$Cp_2Ti$" unit promotes the coupling of CO with two $N_2CPh_2$ molecules to give a carbohydrazido ligand.

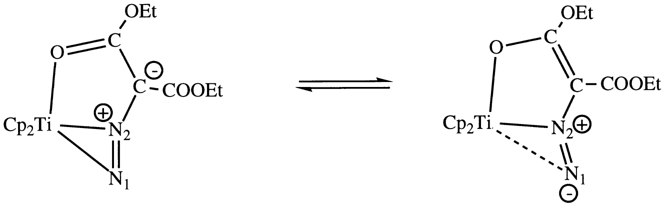
The electronic configuration of the metallic center ($d^1$ for $V^{IV}$ and $d^0$ for $Ti^{IV}$) is important because the vanadocene analogue $[Cp_2V(N_2CR_2)]$ (**25**), ($CR_2 = C(CO_2Et)_2$, $CPh_2$), presents an $\eta^2$-(N,N)-bonded diazoalkane without extra V–O stabilization. All of these $[MCp_2(N_2CR_2)]$ (M = Ti, V) complexes show strong infrared bands in the 1695–1600 $cm^{-1}$ region, which serve as a probe for this coordination mode (Table 3).

### 2.1.3. Type *III* and type *IV* complexes

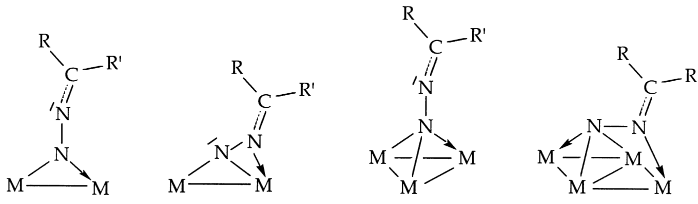
No example of $\eta^2$(C,N) coordination mode (**III**) has been reported. Similarly, no [1 + 3] cycloadduct which belongs to type **IV** has been obtained.

## 2.2. Coordination to two or more metal centers

The number of diazoalkane coordination modes increases considerably in the presence of bimetallic complexes or clusters. Besides the modes (**I** to **IV**) reported with single metal centers, four new modes (types **V** to **VIII**; Scheme. 15) may be proposed in the valence bond formalism.



Scheme 14. Schematic illustration of the valence bond equilibrium in [24]



V VI VII VIII

Scheme 15. Possible structural model for diazoalkanes N-bonded to bimetallic metal complexes and clusters

In types **V** and **VII**, the diazoalkane is bonded via its terminal nitrogen atom to bimetallic or trimetallic fragments and acts as a $4e^-$ donor giving two covalent bonds and a dative bond. In type **VI**, both N atoms are involved in the coordination ($4e^-$). Coordination mode **VIII** presents a diazoalkane bonded to four metal centers through two dative and two covalent bonds acting as a six-electron donor ligand.

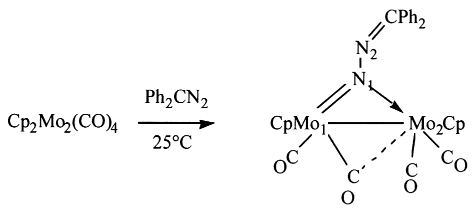
As in the case of monometallic complexes, the ionic formalism can be used for counting electrons. Then, these coordination modes are best described as a $2e^-$ oxidative addition of diazoalkane on the metallic fragment. The diazoalkane behaves as an hydrazonido ligand: $(N_2CR_2)^{2-}$ and the metallic fragment or cluster increases its formal oxidation state by two units.

### 2.2.1. *Coordination to two metal centers: type V and VI complexes*

These coordination modes have been observed with bimetallic complexes of early and late transition metals.

*2.2.1.1. Type V complexes.* Messerle and Curtis reported the first end-on $\mu\eta^2$-diazoalkane coordinated on two electron-rich metal centers [39]. $[Cp'Mo(CO)_2]_2(\mu\text{-}N_2CR_2)$ (**26**) (R = Ph, *p*-$MeC_6H_4$; Cp′ = Cp, $C_5H_4Me$) were isolated in 90% yield from addition of one equivalent of $CR_2CN_2$ on the bimetallic Mo≡Mo complex $[CpMo(CO)_2]_2$ (Scheme. 16).

The X-ray structure of **26a** (Fig. 5) shows a terminal $sp^2$ nitrogen atom asymmetrically coordinated to the two molybdenum centers. One Mo1–N1 bond is more like



**(26a)**

Scheme 16. Synthesis for complex [26a]

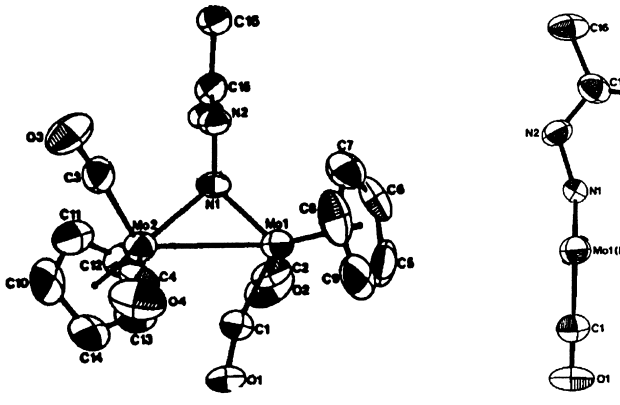


Fig. 5. ORTEP drawing of $[CpMo(CO)_2]_2(\mu\text{-}N_2CPh_2)$ (**26a**) following Ref. [39].

a double bond (1.914(8) Å) and the second one, Mo2–N1, is single (2.083(8) Å). The $Mo_1$–$Mo_2$ bond of 2.987(4) Å is single. The ionic formalism, considering the diazoalkane as a dianionic ligand $(R_2CN_2)^{2-}$, implies two metal centers formally in different oxidation states. Mo1, electron poor, is in the +3 oxidation state and Mo2, electron rich, is in the +1 oxidation state. The presence of the semi-bridging CO group, which helps to stabilize the conformation by giving electrons to the electron poor Mo1 center, is in agreement with this analysis.

In this reaction the metal–metal bond order decreases from three (Mo≡Mo) in $[CpMo(CO)_2]_2$ to one (Mo–Mo) in (**26**). Thus, the binuclear center (Mo≡Mo) provides a reservoir of electrons for reduction of diazoalkane to a dianionic ligand $(R_2CN_2)^{2-}$.

Such a type **V** coordination has also been observed with late transition metals: in $[Rh_2(\mu\text{-}N_2CRCO_2Et)(CO)_2(dppm)_2]$ (**27**) (R = H, $CO_2Et$) [40] and in $[(Cp_2)Rh_2(\mu\text{-}N_2CRR')(\mu COC(CF_3){=}C(CF_3)]$ [41] (**28**) obtained by reaction of $RR'CN_2$ (when R = R′ = Ph; R = Me, R′ = Ph or $CF_3$) with $[Cp_2Rh_2(\mu CO)(\mu CCF_3)]$, but when R = R′ = ${}^tBu$, [3+2] cycloaddition of the diazo moiety into the bridging carbonyl ligand is observed; or in the osmium cluster $[Os_3(\mu\text{-}PhC{=}CPh)(\mu\text{-}N_2CRR')(CO)_9]$ (**29**) (R = H, R′ = H, Me, Ph, $CO_2Et$, $CF_3$, CHCHMe) [42].

Similar reactivity was described for electron-poor metal complexes. Starting from the electrophilic hexaalkoxide ditungsten (W≡W) complex, Chisholm et al. isolated $[W_2(O^tBu)_6\{N_2CR_2\}]$ ($R = C_6H_5$, $CH_3C_6H_5$) (**30**), possessing a single (W–W) bond [24].

More recently, Gambarotta and coworkers reported the synthesis of $[\{2\text{-}(MeO)C_6H_4O\}_2V(\mu\text{-}N_2CHSiMe_3)]_2$ (**31**) by slow addition of $N_2CHSiMe_3$ on the monometallic vanadium(II) complex $[V\{2\text{-}(MeO)C_6H_4O\}_2(TMDA)]$ [43]. The X-ray structure of (**31**), reported in Fig. 6, shows a diazo ligand symmetrically coordinated to the two vanadium centers, with a short contact distance V–V of 2.498(1) Å. This result suggests electron delocalization within the bridge, illustrated

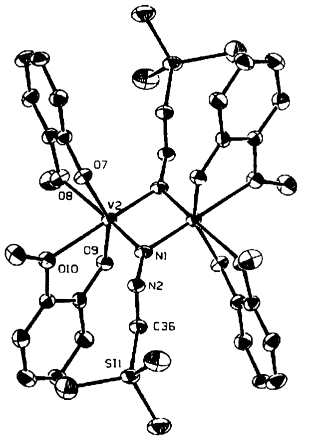


Fig. 6. ORTEP drawing of $[\{2\text{-}(MeO)C_6H_4O\}_2V(\mu\text{-}N_2CHSiMe_3)]_2$ (**31**) following Ref. [43].

by the double bond character of the V–N bonds of 1.847(3) Å. In agreement with this is the formal (+4) oxidation state of the vanadium centers and the absence of a vanadium–vanadium bond.

*2.2.1.2. Type VI complexes.* Herrmann and coworkers reported the first example of type **VI** $\mu\eta^2$-diazoalkane coordination. $[(Cp^*)_2Mo_2(CO)_4(Me_2CN_2)]$ (**32**) was synthesized via addition of 2-diazopropane on the metal–metal triple bond of $[Cp^*_2Mo_2(CO)_4]$ [44]. Its X-ray structure presents a terminal $sp^3$ nitrogen atom symmetrically bridging the Mo–Mo single bond (Mo1–Mo2: 3.050(2) Å; Mo1–N1: 2.120(12) Å; Mo2–N1: 2.126(10) Å). The second nitrogen atom is singly bound to one molybdenum (Mo2–N2: 2.134(13) Å). This complex is stabilized by a semi-bridging carbonyl group which increases the electronic density on the $Mo_1$ center.

Curtis et al. observed the same coordination by reacting diazoacetate on $Cp_2Mo_2(CO)_4$ giving $[Cp_2Mo_2(CO)_4(N_2CHCO_2Et)]$ (**33**) [45]. Its structure is reported on Fig. 7. The bond distance and angle values are reported in Table 5.

The presence of electron pairs on the nitrogen atoms together with the existence of electrophilic metal centers gives exotic coordination modes when diazoalkanes are reacted with electron-poor titanium and zirconium complexes. An example of type **VI** coordination on a zirconium dimer has been described by Herrmann et al. $[(\mu\text{-}\eta^5\text{:}\eta^5C_{10}H_8][\mu\text{-}\eta^1\text{:}\eta^2N_2CPh_2]Zr_2Cl_2Cp_2$ (**34**) results from the stoichiometric addition of $N_2CPh_2$ on the homodinuclear Zr(II) species $[(\mu\text{-}\eta^5\text{-}\eta^5C_{10}H_8)[(\mu Cl)Zr(\eta^5Cp)]_2$. The reaction can be described as an insertion of the diphenyldiazomethane into the Zr–Zr bond with concomitant opening of the chloride bridges (Scheme. 17). The Zr1–N1 distance of 2.073(2) Å is shorter than Zr2–N1 (2.209(3) Å) and Zr2–N2 (2.255(3) Å) distances which can be associated with a higher electron density on Zr2. The N2=C distance of 1.311(3) Å accounts for a normal double bond, whereas the N1–N2 distance (1.343(3) Å) is shorter than

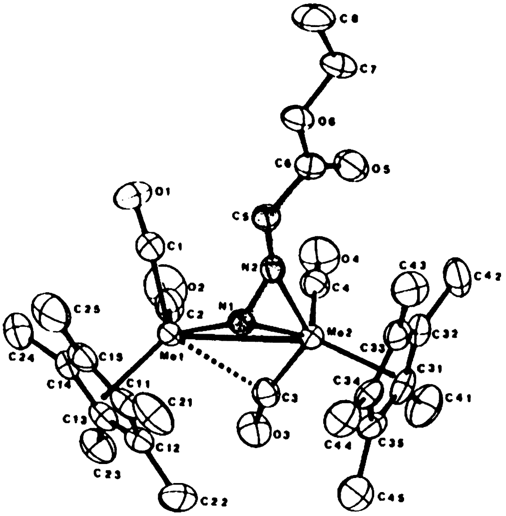
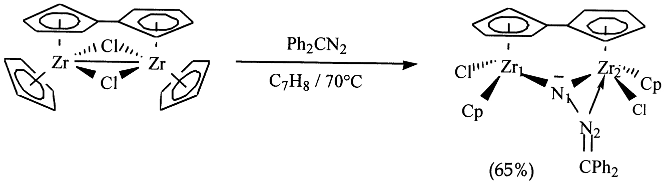


Fig. 7. ORTEP drawing of [Cp$^*_2$Mo$_2$(CO)$_4$(N$_2$CHCO$_2$Et)] (**33**) following Ref. [45].



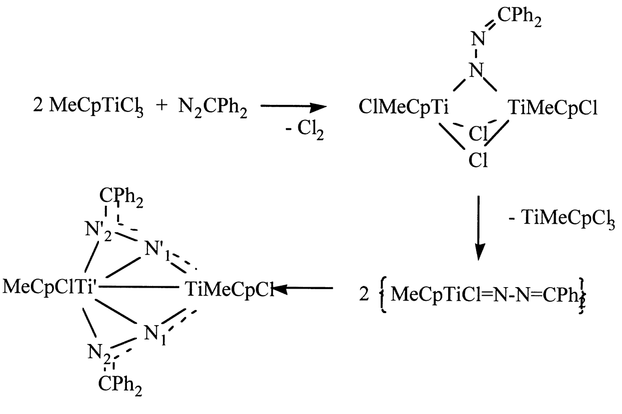
Scheme 17. Synthesis of complex [34]

expected for a single N–N bond. The N1–N2–C unit is strongly bent at N2 (129.1(2)°) [46].

Floriani and coworkers reported an example of reduction of diphenyl diazomethane to the hydrazonido (−2) ligand by the Ti(III) mononuclear complex [(MeCp)TiCl$_2$] to form [MeCpTiCl$_2$]$_2$(μN$_2$CPh$_2$). This dimer loses [(MeCp)TiCl$_3$] and evolves to a dinuclear Ti(IV) complex [{(MeCp)TiCl}$_2$(μ-N$_2$CPh$_2$)] (**35**) in which two [(MeCp)TiCl] units are bridged by two non-symmetrically bonded hydrazonido(−2) ligands [47]. A possible reaction is described on Scheme. 18.

The X ray structure of (**35**) (Fig. 8) suggests an electronic delocalization over the Ti–N–N–C units. Both hydrazonido ligands are $\eta^2$ N1–N2-bonded to the same titanium atom Ti′, with Ti–N bond distances ranging from 2.006(6) to 2.178(5) Å, whereas the second titanium Ti is bonded at very short distances (1.860(5) and 1.835(6) Å) to terminal nitrogen only.

*2.2.1.3. Type V and VI complexes.* A few examples of complexes showing type **V** and type **VI** coordination modes either in the same molecule or as an equilibrium in solution have been reported. Schwartz and coworkers have synthesized



**35**

Scheme 18. Reaction of $N_2CPh_2$ on $MeCpTiCl_3$

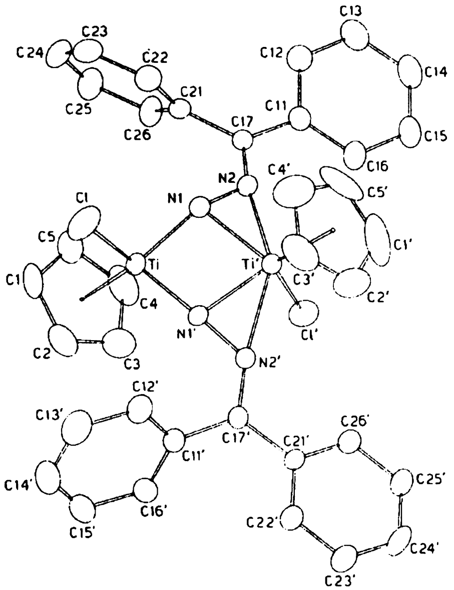


Fig. 8. ORTEP drawing of $[\{CpTiCl\}_2(\mu\text{-}N_2CPh_2)]$ (**35**) follow Refs. [48,49].

$[(CpMe)_2Zr(\mu\eta^2N_2CHR)]_2$ (**36**) as a zirconium dimer asymmetrically bridged by one type **V** and one type **VI** diazoalkane [48,49]. The X-ray structure of (**36a**) is illustrated in Fig. 9.

These compounds $[(CpMe)_2Zr(\mu\eta^2\text{-}N_2CHR)]_2$, ($R=C_6H_5$, *p*-$CH_3OC_6H_4$, *p*-$ClC_6H_4$, *p*-$NCC_6H_4$) were prepared either by ligand metathesis between a Zr(IV) complex $[(CpMe)_2ZrCl_2]$ and $Li_2N_2CHR$ (reaction in Eq. (4)) or by oxidative addi-

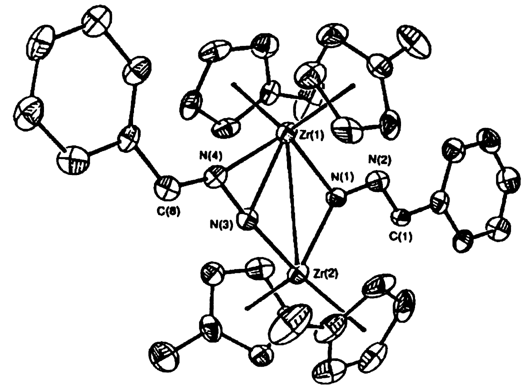


Fig. 9. ORTEP drawing of $[(CpMe)_2Zr(\mu\eta^2\text{-}N_2CHR)]_2$ (**36a**) following Refs. [48,49].

tion of diazoalkane on the Zr(II) complex $[(CpMe)_2Zr(dmpe)]$ (reaction in Eq. (5)).

$$[(CpMe)_2ZrCl_2] + Li_2N_2CHR \xrightarrow{THF/-78\ ^\circ C} [(CpMe)_2Zr(\mu\eta^2\text{-}N_2CHR)]_2 \tag{4}$$

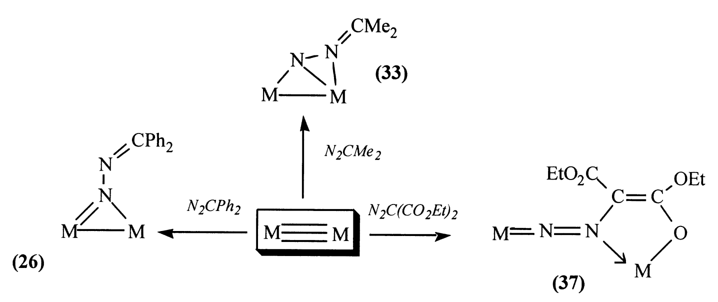
$$[(CpMe)_2Zr(dmpe)] + N_2CHPh \xrightarrow{Tol./-50\ ^\circ C} [(CpMe)_2Zr(\mu\eta^2\text{-}N_2CHPh)]_2 \tag{5}$$

Both pathways yielded the same Zr(IV) bimetallic complexes but the reaction of Eq. (4) gave a better yield.

Other examples are observed when diazoalkane are reacted on the bimetallic $[Mo{\equiv}Mo]^{2+}$ complexes: $[R_2Mo_2(CO)_4]$ ($R = Cp$, $MeC_5H_4$, Cp*). The coordination mode depends markedly on the ancillary ligands R as well as on the diazoalkanes. Moreover, it appears that neither the basicity of the internal nitrogen nor the steric bulk of the Cp* group seem to control the diazo coordination mode. Thus, at the moment, the factors determining the bonding remain unclear [22,23,45,50–54].

Scheme. 19 illustrates the diversity of adducts and the variety of bonding modes of the diazoalkanes following Refs. [50,51].

In the presence of Cp, MeCp and Cp* ligands, type **V** complexes (**26**) were obtained with $CPh_2N_2$. When $CH_2N_2$, $C_5H_5N_2$ or $CH(CO_2Et)_2N_2$, were used, coor-



Scheme 19. Reactions of diazoalkane on $[R_2M_2(CO)_4]$ ($R = Cp$, MeCp, Cp*)

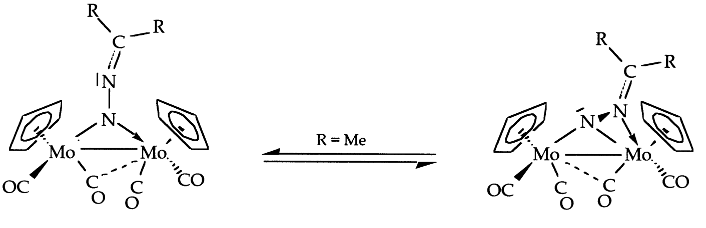
dination occurred only with the more sterically demanding Cp* ligand, giving the type **V** (**26**) and type **VI** (**33**) adducts. However, $Me_2CN_2$ reacted with both Cp and Cp* complexes to produce the type **VI** complex (**33**) which, in solution, gives a mixture of (**26**) and (**33**) isomers that interconvert within minutes but which are not fluxional on the NMR time scale. The relative amounts of these isomers, determined by NMR experiment, is temperature- and solvent-dependent (Scheme. 20).

With the Cp ligand, diethyldiazomalonate and 2-diazodimedone induced the cleavage of the Mo≡Mo triple bond to give a chelate with a diazoalkane bridge in which the diazo ligand acts as a $6e^-$ donor (**37**), a mode of coordination which is reminiscent of diazonium complexes. No adduct was obtained with 9-diazofluorene.

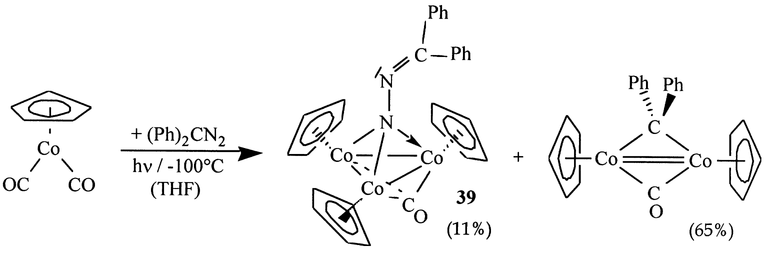
Interestingly, under similar experimental conditions, whatever the diazoalkane used was, no complex was isolated with the tungsten homologue $Cp_2W_2(CO)_4$, whereas $N_2CH_2$ reacts with $[Cp^*W(CO)_2]_2$ with clean nitrogen–nitrogen bond rupture and formation of $[Cp^*W(CO)(NCO)W(CO)_2Cp^*](\mu\text{-}NCH_2)$.

### *2.2.2. Coordination to three metal centers: type VII complexes*

The $4e^-$ donor end-on coordination mode (type **VII**), implying three metal centers, are directly derived from the precedent ones (**V** to **VI**). It has been observed in $[Fe_3(CO)_9(\mu^3\eta\text{-}N_2Ph_2)_2]$ (**38**) [55,56] and $[Co_3(CO)Cp_3(\mu^3\eta N_2CPh_2)]$ (**39**) [57] clusters (Scheme. 21). In such a coordination mode, the terminal nitrogen atom of the diazo group caps a triangular metal face. However, no crystal data are available for these compounds.



Scheme 20. Schematic illustration of the resonance equilibrium between [26] and [33]



Scheme 21. Reaction of $Ph_2CN_2$ on $CpCo(CO)_2$

### *2.2.3. Coordination to four metal centers: type VIII complexes*

Carty and coworkers reported the only example of $\mu^4\eta^2$N-coordinated diazoalkane (type **VIII**). $[Ru_5(CO)_{12}(\mu^4\eta^2C{\equiv}CR)(\mu PPh_2)(\mu^4\eta^2N_2CPh_2)]$ (**40**) has been obtained by addition of excess diphenyldiazomethane on the ruthenium cluster: $[Ru_5(CO)_{13}(\mu^4\eta^2C{\equiv}CR)(\mu PPh_2)]$ (R = Ph, $^iPr$) [58]. The reaction occurs with loss of a carbonyl group and cleavage of two Ru–Ru bonds. The X-ray structure of (**40**) (R = Ph) (Fig. 10) shows that the terminal N1 caps the inner face of the Ru2–Ru3–Ru5 triangle while the second N2 atom is connected only to Ru4. The N1–N2 distance of 1.401(13) Å indicates a significant reduction in the N–N bond order on coordination. The N2–C2 distance of 1.304(16) Å is typical for a double bond.

Thus, the $4e^-$ donor terminal nitrogen atom is implicated in two $\sigma$ bonds and one dative bond, whereas the internal nitrogen behaves as a $2e^-$ donor toward one ruthenium center. Diphenyl diazomethane acts as a six-electron donor ligand.

Interestingly, the maximum coordination mode possible for a diazoalkane ligand, i.e. $8e^-$ donor, has not been observed yet.

### *2.3. Spectroscopic characterization*

Useful spectroscopic data for characterizing diazoalkane complexes could be the infrared stretching frequency of the diazoalkane ligand $\nu(C{=}N{=}N)$. Free diazoalkanes generally have the $\nu(CN_2)$ vibrations in the 2100–2200 $cm^{-1}$ range [2]. When they are coordinated to metals, this band shifts to lower frequencies, as expected from the disappearance of the triple $N{\equiv}N$ bond and formation of $N{=}N$ and $N{=}C$ double bonds. However, caution must be exercised in using these measured values because the vibrational coupling is dependent on the diazo substituent, on the metal and on the number of ligands in the metal coordination sphere.

Infrared spectra, and Raman spectra in some cases, of the diazo complexes show absorptions characteristic of the multiple bond stretching vibrations. The data are reported in Tables 1–4 for types **Ib**, **Ic**, **II** and **V–VI** complexes respectively.

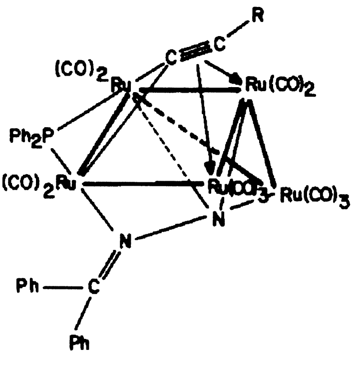


Fig. 10. Simplified ORTEP drawing of $[Ru_5(CO)_{12}(\mu^4\eta^2C{\equiv}CR)(\mu PPh_2)(\mu^4\eta^2N_2CPh_2)]$ (**40**) following Ref. [58].

Table 4
Type **V** and **VI** complexes

| Compound | | | No. | Diazoalkane | IR ($cm^{-1}$) | $^{13}C$ (ppm) | Ref. |
|---|---|---|---|---|---|---|---|
| $[Mo_2Cp'_2(CO)_4]$ | | | | | | | |
| Cp′= | Cp | **V** | **26** | $N_2CMe_2$ | | 137.3 | |
| | Cp | **VI** | **33** | $N_2CMe_2$ | | 140.4 | [39] |
| | Cp, *p*-$MeC_6H_4$ | **V** | **26** | $N_2CPh_2$ | 1535 | | |
| | | **V** | | $N_2C(C_5H_4Me)_2$ | 1535 | | |
| $[Rh_2(CO)_2(dppm)_2]$ | | **V** | **27** | $N_2CH(CO_2Et)$ | 1400 | | |
| | | | | $N_2C(CO_2Et)_2$ | 1380 | | |
| $[W_2(O^tBu)_6]$ | | **V** | **30** | $N_2CPh_2$ | | 159.2 | [24] |
| with two bonds diazos | | | | | | 159.4 | |
| $[Mo_2Cp^*_2(CO)_4]$ | | **VI** | **32** | $N_2CMe_2$ | | 133.8 | [44] |

No IR stretch was observed for complex **3** of type **Ia**. In contrast, in type Ib complexes (**1**–**7**) ν($N_2C$) frequencies occur in the range 2040 (Rh) to 1440 $cm^{-1}$ (Ir), indicating that the coordination of the diazoalkane depends markedly on the coordination number, the geometry of the complex, the nature of the ancillary ligands and on the diazo substituent. In some complexes, the $N_2C$ stretching bands are strongly IR active, but other examples have been described in which this vibration is weakly IR active but strongly Raman active. Thus the absence of an N–N stretching band in the IR spectrum does not necessarily indicate a differing mode of coordination for the diazo ligand.

Type **Ic** complexes (**9**–**18**) show absorptions at about 1600–1500 $cm^{-1}$, which is the region for ν(C=N) of C=N double bond (Table 2). The ν(N=N) stretching frequencies of type **II** complexes (Table 3) which also appear in the same range (1490 to 1670 $cm^{-1}$) are as expected.

Some data have been reported for diazo bridged complexes. However, in no cases have the frequencies been assigned to metal–nitrogen modes and no general trends have emerged. As a consequence they are not listed here.

Although the diazo carbon atom is not coordinated to the metal, its $^{13}C$ NMR chemical shift is of great interest. Even if little $^{13}C$ data are available, they are typically found in two regions: at about 70 ppm for the type **Ib** complexes **5**–**7** (nucleophilic carbon) and at 160–170 ppm for type **Ic** complexes ($sp^2$ ethylene-like carbon), that is at the two extreme parts of the $=CR_2$ range as expected. These data are consistent with the valence bond formalism described in Scheme. 5.

## *2.4. Structural X-ray characterization*

Important structural data for the diazoalkane complexes that have been characterized by X-ray diffraction studies are set out in Table 5. The data are presented in

Table 5
Structural data for N-bonded diazoalkane transition metal complexes

| Complex | Type | No. | M–N1 [M2–N1] | M1–N1 [M2–N1] | M2–N2 | N1–N2 | N2–C | M–N1–N2 | N1–N2–C | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| Type **I** complexes | | | | | | | | | | |
| $[W(CO)_4PPh_3(N_2C(SiMe_3)_2)]$ | | **2** | 2.161(11) | | | 1.165(15) | 1.34(1) | 176(1) | 170(1) | [26] |
| $[MnCp(CO)_2\{N_2C(CO_2Me)_2\}]$ | | **3** | 1.796(5) | | | 1.165(7) | 1.351(8) | 176.9(4) | 150.5(4) | [6,7] |
| $[IrCl(N_2C_5Cl_4)(PPh_3)_2]$ | | **4a** | 1.824(6) | | | 1.163(7) | 1.347(9) | 174.6(6) | 141.2(7) | [9,10] |
| $[TiCp_2(PMe_3)(N_2CPh_2)]$ | | **8** | 1.829(11) | | | 1.262(15) | 1.311(16) | 156.8(9) | 126.0(9) | [29] |
| $[WBr\{N_2CH(CH_2)_3OH\}(dppe)_2][PF_6]$ | | **9a** | 1.772(13) | | | 1.32(2) | 1.30(3) | 172.6(12) | 116.2(15) | [31] |
| $[WBr(N_2CMe_2)(dppe)_2]Br$ | | **9b** | 1.724(12) | | | 1.355(18) | 1.290(17) | 171.3(7) | 123.9(1 1) | [31] |
| $[WBr\{N_2CN(CH_3)CH_2CH_2N(CH_3)\}(dppe)_2][PF_6]$ | | **9c** | 1.776(7) | | | 1.309(9) | 1.323(11) | 163.0(5) | 123.5(6) | [14,15] |
| $[WBr(N_2CCl_2)(dppe)_2][PF_6]$ | | **9d** | 1.75(2) | | | 1.35(3) | 1.28(3) | 169(2) | 122(2) | [14,15] |
| $[WF\{N_2C(CH_3)CH_2COCH_3\}(dpe)_2][BF_4]$ | | **10a** | 1.770(17) | | | 1.317(25) | 1.300(30) | 173.8(15) | 125.2(19) | [17,18] |
| $[WF(N_2CHCMe_2)(dpe)_2][BF_4]$ | | **10b** | 1.79(1) | | | 1.29(3) | 1.26(3) | 171.0(10) | 119.6(16) | [17,18] |
| $[WF\{N_2CMeCH(CONHPh)_2\}(dpe)_2][BF_4]$ | | **10c** | 1.77(1) | | | 1.33(2) | 1.30(3) | 170.4(12) | 122.2(16) | [17,18] |
| $[(dpe)_2FW(N_2CHCHMeCHMeCHN_2)WF(dpe)2][BF_4]_2$ | | **10d** | 1.772(8) | | | 1.34(2) | 1.17(4) | 168.2(14) | 120.5(22) | [17,18] |
| $[WCl_2(C_2H_4)(N_2CMe_2)(PMe_2Ph)_2]$ | | **12a** | 1.750(6) | | | 1.34(1) | 1.29(1) | 167.3(6) | 116.7(7) | [20] |
| $[WCl_2(p\text{-}MeC_6H_4CHO)(N_2CMePh)(PMe_2Ph)_2]$ | | **12b** | 1.79(1) | | | 1.29(2) | 1.27(2) | 166(1) | 121(1) | [20] |
| $[Cp(CO)_3Mo\text{–}MoCp\{C(p\text{-tol})_2\}\{N_2C(p\text{-}MeC_6H_4)_2\}]$ | | **15** | 1.741(10) | | | 1.323(12) | 1.318(13) | 174.7(9) | 121.1(10) | [22,23] |
| $[Mo(O^tBu)_4(N_2CPh_2)]$ | | **16** | 1.797(3) | | | 1.314(4) | 1.312(5) | 168.2(3) | 122.5(3) | [24] |
| $[Mo_2(O^iPr)_6(N_2CPh_2)_2(Py)]$ | | **17a** | 1.758(9) | | | 1.319(12) | 1.287(14) | 164.4(8) | 123.8(9) | [24] |
| | | | 1.781(8) | | | 1.297(11) | 1.310(13) | 155.3(7) | 121.6(9) | |
| $[W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(N_2CPh_2)]$ | | **18a** | 1.767(10) | | | 1.355(13) | 1.291(15) | 158.2(8) | 123.0(10) | [33] |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Type **II** complexes | | | | | | | | | |
| [Ni($^t$BuNC)$_2$(diazofluorene)] | | **19a** | 1.874(3)<br>[1.834(3)] | | | 1.245(4) | 1.334(4) | 133.8(3) | [34,35] |
| [Ru(CO)$_2$(N$_2$C$_5$Cl$_4$)(PPh$_3$)$_2$] | | **21a** | 2.141(5)<br>[2.062(4)] | | | 1.224(6) | 1.372(7) | 131.6(5) | [37] |
| [CoMe(PMe$_3$)$_3$(N$_2$C$_5$H$_4$)] | | **23a** | 1.994<br>[1.914] | | | 1.244(18) | 1.367(21) | 134.2(5) | [38] |
| [Cp$_2$Ti{N$_2$C(CO$_2$Et)$_2$}] | | **24a** | 2.219(7)<br>[1.980(5)] | | | 1.214(7) | 1.371(7) | 146.7(5) | [30] |
| Type **V** and **VI** complexes | | | | | | | | | |
| [Cp$_2$Mo$_2$(CO)$_4$(N$_2$CPh$_2$)] | **V** | **26a** | | 1.914(8)<br>[2.083(8)] | | 1.352(10) | 1.279(12) | 122.4(9) | [39] |
| [W$_2$(O$^t$Bu)$_6${N$_2$C(*p*-Tol)$_2$}$_2$] | **V** | **30** | | 1.942(11) | | 1.410(16) | 1.264(18) | 121.2(13) | [24] |
| [(2-MeC$_6$H$_4$O)$_2$V(N$_2$CHSiMe$_3$)]$_2$ | **V** | **31** | | 1.847(3) | | 1.377(4) | | 117.6(3) | [43] |
| [Cp$_2^*$Mo$_2$(CO)$_4$(N$_2$CMe$_2$)] | **VI** | **32** | | 2.120(12)<br>[2.126(10)] | 2.134(13) | 1.369(18) | 1.303(22) | 133.3(13) | [44] |
| [Cp$_2^*$Mo$_2$(CO)$_4$(N$_2$CHCO$_2$Et)] | **VI** | **33** | | 2.105(4)<br>[2.109(4)] | 2.108(5) | 1.336(6) | 1.288(7) | 128.6(5) | [45] |
| [CpZrCl]$_2$(μ-η$^5$:η$^5$-C$_{10}$H$_8$)(μ-N$_2$CPh$_2$) | **VI** | **34** | | 2.073(2)<br>[2.209(3)] | 2.255(3) | 1.343(3) | 1.311(3) | 129.1(2) | [46] |
| [CpTiCl(N$_2$CPh$_2$)]$_2$ | **VI** | **35** | | 1.860(5)<br>[2.006(6)] | 2.163(6) | 1.327(7) | 1.302(8) | 125.3(5) | [47] |
| [(η$^5$-MeC$_5$H$_4$)$_4$Zr$_2$(N$_2$CHPh)$_2$] | **V** | **36** | | 2.180(7)<br>[2.063(7)] | | 1.36(1) | 1.29(1) | 119.7(7) | [48,49] |
| | **VI** | | | 2.213(7)<br>[2.004(7)] | 2.232(7) | 1.32(1) | 1.29(1) | 123.4(7) | |

eight columns, starting with the formula of the compound and its number in the text; then the main bond distances and angles are noted. The last column gives the references. Owing to the high thermal motion of the light N and C atoms, uncertainty arises in the C=N distances, which could be not very precise, and their values have to be handled with circumspection.

The property that structurally characterizes the diazoalkane complexes is the bending at internal N2 of the linear diazo ligand which reflects its coordination mode. Effectively, the N1N2C angle value ranges from 176° for type **Ia** complexes ($2e^-$ donor neutral diazoalkane) to 117° (hydrazonido $-2$ ligand), depending on the particular type of complex and emphasising the relative importance of the valence bond isomers.

The structural data of type **I** complexes show that the N=C bond lengths do not significantly change on coordination. They lie within the 1.34–1.29 Å range near to free diazoalkane (1.34 Å in $N_2CH_2$ [59] and 1.28 Å in $N_2CPh(SiPh_3)$ [60]). The lowest values correspond to diazoalkanes with the most electron-attracting substituents. In contrast, the N1–N2 bond lengths of the metal-coordinated diazo are significantly elongated from 1.11–1.13 Å in free diazoalkane. The values range from 1.165 Å (a value near to that of free diazo) in type **Ia** and **Ib** complexes (and thus intermediate between typical triple N≡N (1.10 Å) and double N=N (1.24 Å) distances) to 1.35 Å in type **Ic** complexes (a value intermediate between the double (1.25 Å) and single (1.48 Å) N–N bond distance). The bending at N2 agrees with these values, the shortest NN bond being related to an increase in linearity of the NNR moiety.

In type **II** complexes, the bonding of the diazoalkane to the metal is different and this difference is reflected in the structural parameters. Coordination of the diazo molecule through the N–N bond leads to a significant elongation of this bond, with an average of 1.23 Å for the four structurally characterized type **II** complexes, i.e. the value of an N=N double bond. Concomitantly, lengthening of the N–C distance is observed, the averaged value (1.36 Å) being intermediate between a single and double bond and thus indicating the presence of a long-range effect in the coordination. The variations observed for the bending at N2 suggest that the presence of the isomeric form **IIb** is important for titanium. As for type **I** complexes, shortening of the N–N bond is correlated to the increase in the N1N2C angle value.

In type **V** and **VI** complexes, the bonding modes of the diazo ligand to two or more metal centers are related to those already observed and suggest contributions from the different resonance forms. The N1–N2 bond lengths (average 1.37 Å) are between double and single bonds, whereas the N2–C distances (average 1.29 Å) correspond to a double bond. These data agree with the bending at N2 ($sp^2$: average N1N2C 120°). Interestingly, bending at N1 is significant and sensitive to the nature of the metal center.

The coordination mode of the diazoalkane as a $2e^-$ or $4e^-$ donor ligand (dative and covalent bonding) is reflected by the metal–N1 distances. These values depend on the metal oxidation state, which in these complexes covers a wide range from low oxidation states in W(0) or W(II) complexes to a high one in W(VI) compounds. Table 5 shows that the values are in good agreement with the literature data and, as a consequence, are important parameters in the structural assignment.

The entire range of single, double and triple metal–N bonds are observed in the monometallic metal–diazo complexes. Only one example of a single W–N bond in a W(0) complex is observed in **3**. Its value of 2.161(11) Å agrees with W–N single bond distances of low-valent Mo and W complexes [45,61]. The Ir–N distance of 1.819(6) Å in **4a** agrees with a double bond, since it lies between the 1.93 Å distance observed in the Ir–N single bond of $[Tp^*Ir(C_6H_4)_2]_2(\mu N_2)$ [27] and 1.712(7) Å in the Ir≡N triple bond of $Cp^*IrN^tBu$ [12]. Multiple Mo≡N and W≡N bond values range from 1.724(12) to 1.79(1) Å in the monometallic complexes (**9**–**18**) and at about 1.860(5) Å when the diazo is bridging two metal centers. These values also agree with the values reported in related imido and hydrazido complexes [62,63]

## 3. Diazoalkyl transition metal complexes

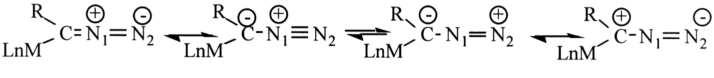
Diazoalkyl transition metal complexes $LnM–C(N_2)R$ are molecules where the diazoalkyl ligand is σ-bound to the metal fragment ($\eta^1$ mode). The four possible resonance structures are dipolar and show that the metal fragment may stabilize nucleophilic or electrophilic α-carbon atoms (Scheme. 22). The discovery of this class of transition metal compounds, characterized by a metal–carbon bond (C-coordinated diazoalkane) and a functional group ($C=N_2$), was accomplished by Murahashi and coworkers [64,65] in 1979 who synthesized the first diazoalkyl palladium complexes. Most of the recent work has been done in our group.

However, diazoalkane with metallic substituents such as Group 11 (Ag), Group 12 (Hg, Cd, Zn), Group 14 (Si, Ge, Sn, Pb) and Group 15 (P) have been known for a long time. The basic character of the C atom allows the formation of alkali metal derivatives $MCR(N_2)$ (M = Li, Na), which are stable at low temperature and used as reactants at that temperature [4], and also rare earth derivatives $Cp^*ClM[C(N_2)SiMe_3]$ (M = Y, Lu, Yb) [66].

Until now, $\eta^1$ diazoalkyl complexes have essentially been reported for late transition metal complexes of $d^8$ Pd(II), Rh(I), Rh(III), Ni(II) and $d^6$ Os(II) electronic configurations. They are reported in Table 6, together with their IR and NMR characterizations.

### 3.1. Synthesis and characterization

The palladium complexes $(PR_3)_2Pd[C(N_2)R']_2$ (41) (R′ = Et, Bu, Ph) were synthesized by reacting $LiC(N_2)R'$ (R′ = $^iPr$, $^tBu$, Ph, $MeC_6H_4$) or $Hg\{C(N_2)R'\}_2$ (R′ =



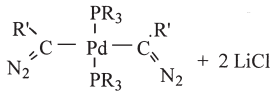
Scheme 22. Schematic illustration of the resonance forms in diazoalkyl transition metal complexes

Table 6
Infrared and $^{13}C\{^1H\}$ NMR data for diazoalkyl complexes

| Compound | No. | $\nu(CN_2)$ IR ($cm^{-1}$) | $\delta[^{13}C\{^1H\}]$ NMR (ppm) | Ref. |
|---|---|---|---|---|
| $(PPh_3)_2PdCl[C(N_2)CO_2Et]$ | **42** | 2035 | 37.63 (t,8.8) | |
| $(PPh_3)_2PdCl[C(N_2)C(O)Me]$ | | 2010 | | |
| $(PEt_3)_2PdCl[C(N_2)CO_2Et]$ | | 2030 | | |
| $(PBu_3)_2PdCl[C(N_2)CO_2Et]$ | | 2030 | | |
| $(PPh_3)_2PdB[C(N_2)CO_2Et]$ | | 2035 | | [64,65] |
| $(PPh_3)_2PdI[C(N_2)CO_2Et]$ | | 2030 | | |
| $(PBu_3)_2Pd[C(N_2)CO_2Et]_2$ | **41** | 2020 | 33.0 (t, 11.8) | |
| $(PPh_3)_2Pd[(C(N_2)CO_2Et]_2$ | | 2025 | 36.64 (t, 11.8) | |
| $(PPh_3)_2Pd[C(N_2)C(O)Me]_2$ | | 2005 | | |
| $(PEt_3)_2Pd[C(N_2)CO_2Et]_2$ | | 2025 | 32.82 (t, 11.8) | |
| $(PEt_3)_2Pd[C(N_2)Ph]_2$ | | 1975, 1966 | 37.05(t, 11.8) | |
| $(PEt_3)_2Pd[C(N_2)C_6H_4\text{-}p\text{Me}]_2$ | | 1980, 1970 | | |
| $(PEt_3)_2Pd[(C(N_2)^iPr_2]$ | | 1965, 1953 | 35.24 (t, 12.7) | |
| $(PEt_3)_2Pd[C(N_2)^tBu_2]$ | | 1960, 1950 | 35.50 (t,13.2) | |
| $[(PPh_3)2OsCl[C(N_2)CO_2Et]HgC(N_2)CO_2Et(NO)$ | | | | |
| $[(PPh_3)2OsClC(N_2)CO_2Et]HgI(NO)$ | | | | |
| $(PPh_3)_2OsICl[C(N_2)CO_2Et](NO)$ | **49** | | | [67] |
| $(PMe_3)_4Rh[C(N_2)SiMe_3]$ | **43** | 1950 | | [68] |
| $(PMe_3)_2Rh[C(N_2)SP(N^iPr_2)_2]$ | **52** | 1990 | | [66] |
| $(PMe_3)_3Rh[C(N_2)SiMe_3]IMe$ | **46** | 1955 | | [68] |
| $(PEt_3)_3Rh[C(N_2)SiMe_3]$ | **43** | 1950 | | [69] |
| $(PEt_3)_2(CO)Rh[C(N_2)SiMe_3]$ | **44** | 1961 | 11.2 (dt, $J_{PC}=14$; $J_{RhC}=28$ Hz) | |
| $(PPP)Rh[C(N_2)SiMe_3]$ | **47** | 1952 | | [70] |
| $(PPP)Ir[C(N_2)SiMe_3]$ | **48** | 1955 | | [70] |
| $(PMe_3)_2NiCl[C(N_2)SiMe_3]$ | **50** | 1955 | | [71] |

COMe, $CO_2Et$) on $(PR_3)_2PdX_2$ (X = Cl) or alternatively by oxidative addition of bis(α-diazomethyl)mercury to $(PR_3)_4Pd$ followed by reductive elimination of Hg.

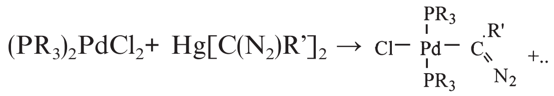
$$(PR_3)_2PdCl_2 + 2\ Li[C(N_2)R'] \rightarrow$$



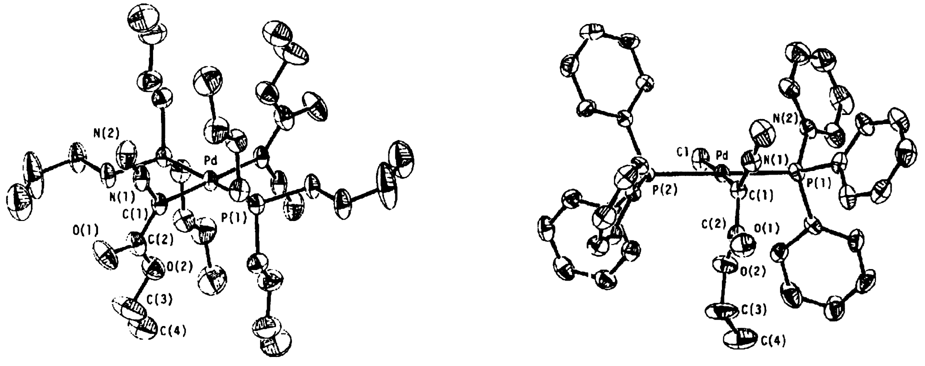
$$(PR_3)_4Pd + Hg[C(N_2)R']_2 \rightarrow$$

The mono(α-diazoalkyl)palladium compound $(PR_3)_2PdCl\{C(N_2)R'\}$ (**42**) resulted from the reaction of $(PR_3)_2PdX_2$ with $Hg\{C(N_2)R'\}_2$

The $\eta^1$ coordination mode was confirmed by the X-ray structural characterization of $(PBu_3)_2Pd\{C(N_2)CO_2Et\}_2$ (**41**) and $(PPh_3)_2PdCl\{C(N_2)CO_2Et\}$ (**42**) (Fig. 11). The M–$CN_2$ diazoalkyl group is planar and its plane is almost perpendicular to the palladium coordination plane.



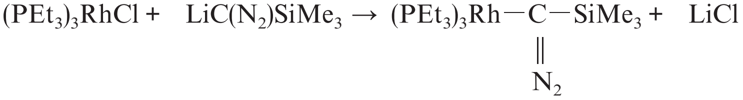
$$(PR_3)_2PdCl_2 + Hg[C(N_2)R']_2 \rightarrow Cl-\overset{PR_3}{\underset{PR_3}{Pd}}-C(R')(=N_2) + ..$$



**41** **42**

Fig. 11. ORTEP drawings of $(PBu_3)_2Pd\{C(N_2)CO_2Et\}_2$ (**41**) and $(PPh_3)_2PdCl\{C(N_2)CO_2Et\}$ (**42**) following Ref. [65].

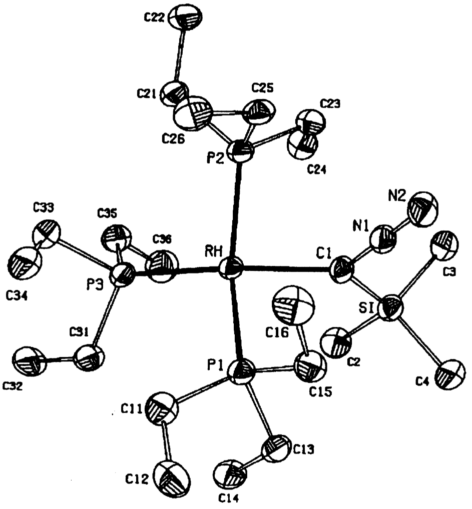
Such a planar diazo ligand located in a plane nearly perpendicular to the metal coordination plane is observed in $(PEt_3)_3Rh[C(N_2)SiMe_3]$ (**43**) (Fig. 12) and $(PEt_3)_2(CO)Rh[C(N_2)SiMe_3]$ (**44**) obtained by reacting $LiC(N_2)SiMe_3$ on $(PEt_3)_3RhCl$ and $(PEt_3)_2(CO)RhCl$ respectively at −78 °C [69]



$$(PEt_3)_3RhCl + LiC(N_2)SiMe_3 \rightarrow (PEt_3)_3Rh-\underset{\underset{N_2}{\|}}{C}-SiMe_3 + LiCl$$

Using $PMe_3$ produced the pentacoordinate $(PMe_3)_4Rh[C(N_2)SiMe_3]$ (**45**) which is stable only in solution and decomposes upon isolation. Oxidative addition of $CH_3I$ gave the Rh(III) complex $(PMe_3)_3RhIMe[C(N_2)SiMe_3]$ (**46**) characterized by X-ray crystallography [68].

The_$\eta^1$ diazoalkyl complexes $(P_3)RhC(N_2)SiMe_3$ (**47**) and $(P_3)IrC(N_2)SiMe_3$ (**48**) with the tridentate ligand $P3 = {}^tBuP(CH_2CH_2CH_2PPh_2)_2$ were synthesized



**(43)**

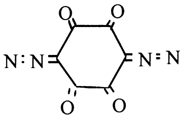
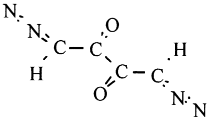
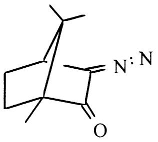
Fig. 12. ORTEP drawing of $(PEt_3)_3Rh[C(N_2)SiMe_3]$ (**43**) follow Ref. [69].

following the same procedure. Although the X-ray data of the Rh species was not satisfactory in the phosphine region, coordination of the diazo group was unambiguously observed [70].

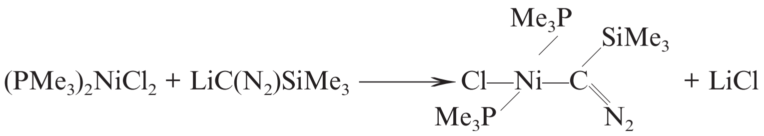
The high $\nu(CN_2)$ values of the IR bands observed for these complexes suggest the importance of the N≡N resonance form, which is confirmed by the structural data summarized in Table 7. They are informative in regard to the bonding even if, because of the thermal agitation, they are not accurate enough to allow adequate assessment of the importance of the different resonance structures. They are not significantly different from those obtained in organic diazoalkanes [73–76,72]. The N–N distances are in the range 1.09(3)–1.66(8) Å, only slightly longer than the corresponding distances in free diazoalkane, and suggest a bond between double and triple. The C–N distances of 1.275(13) Å (average) are slightly shorter than in free diazoalkane, implying a significant multiple bond. The M–C distances are typical of single bonds.

Reaction of $Hg[C(N_2)CO_2Et]_2$ on $OsCl(NO)(PPh_3)_3$ [67] illustrated the difficulty met in using mercury salts. The first step of the reaction corresponded to the oxidative addition of the bis(diazoalkane)mercury on the metal center to generate $\{OsCl[C(N_2)CO_2Et][HgC(N_2)CO_2Et](NO)(PPh_3)_2\}$. Addition of $I_2$ gave $\{OsCl[C(N_2)CO_2Et](HgI)(NO)(PPh_3)_2\}$ which reductively eliminates $HgI_2$ to produce $\{OsCl[C(N_2)CO_2Et](NO)(PPh_3)_2\}$ (**49**). The authors concluded that these multiple steps make this process not very convenient for the synthesis of diazoalkyl complexes.

Table 7
Structural data for diazoalkyl complexes and for diazolakanes for comparison

| Compound | No. | M–C (Å) | C–N2 (Å) | N2–N1 (Å) | C–N1–N2 (deg) | M–C–N1 (deg) | Ref. |
|---|---|---|---|---|---|---|---|
| $(PPh_3)_2PdCl[C(N_2)CO_2Et]$ | **42** | 2.015(10) | 1.275(13) | 1.160(15) | 177.2(12) | 121.7(8) | [65] |
| $(PBu_3)_2Pd[C(N_2)CO_2Et]_2$ | **41** | 2.078(6) | 1.279(8) | 1.130(10) | 176.3(8) | 119.5(5) | [65] |
| $(PEt_3)_3Rh[C(N_2)SiMe_3]$ | **43** | 2.156(5) | 1.276(7) | 1.166(8) | 179.7(6) | 126.6(4) | [69] |
| $(PMe_3)_3(CH_3)IRh[C(N_2)SiMe_3]$ | **46** | 2.09(2) | 1.30(3) | 1.09(3) | 175(2) | 119(2) | [68] |
| $(CO)_3Mo(\eta^5C_6H_6C(N)_2SiMe_3)$ | **53** | — | 1.295(3) | 1.136(3) | 178.6(2) | 125.0 | [72] |
| $PhC(N_2)SiPh_3$ | | | 1.280(7) | 1.130(16) | 178.1(14) | 125.7(8) | [73] |
|  | | | 1.357(10) | 1.107(10) | 177.9(9) | 129.1(7) | [74,75] |
|  | | | 1.313(2) | 1.114(2) | 176.8(1) | 116.1(3) | [72] |
|  | | | 1.296(8) | 1.325(8) | 178.8(8) | | [76] |

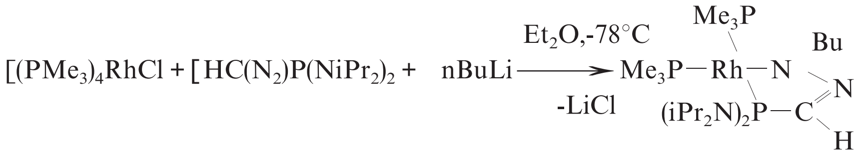
Nickel(II) complexes $(PR_3)_2NiCl\{C(N_2)SiMe_3\}$ (**50**) were synthesized as green crystals, stable only below −20 °C, by reacting $LiC(N_2)SiMe_3$ on $Ni(PR_3)_2Cl_2$ ($PR_3 = PMe_3$, $PEt_3$) [71].



$$(PMe_3)_2NiCl_2 + LiC(N_2)SiMe_3 \longrightarrow Cl{-}Ni(PMe_3)_2{-}C(N_2)SiMe_3 + LiCl$$

The organic substituent of the diazoalkyl group participated in the bonding in the case of $HC(N_2)\{P(N^iPr_2)_2\}$. When the lithium salt prepared from addition of excess $^nBuLi$ on $HC(N_2)\{P(N^iPr_2)_2\}$ at −78 °C was reacted on $(PMe_3)_3RhCl$, the heteropyrazoline (**51**) complex was isolated and characterized by X-ray crystallography [77] (Fig. 13).

The mechanism of the reaction is not clear. It may proceed via initial attack of $^nBuLi$ on the terminal N atom of $HC(N_2)P(N^iPr_2)_2$ giving with excess $^nBuLi$ a diazenido ligand which reacts then with the Rh–Cl bond. Formation of the heterocycle resulted then from coordination of the phosphorus lone pair to the rhodium,



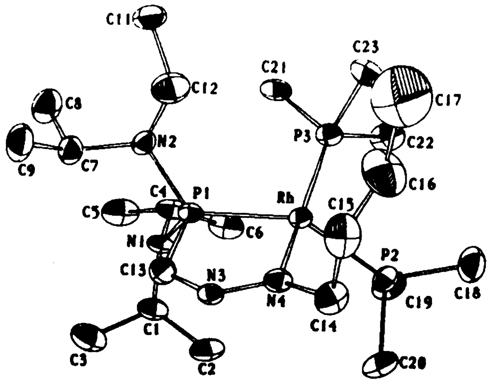
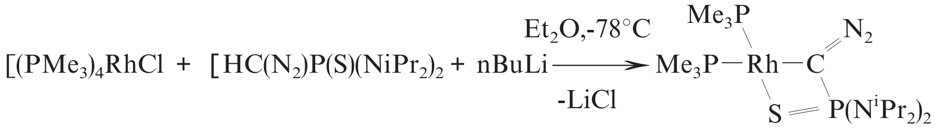


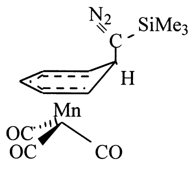
Fig. 13. ORTEP of $(PMe_3)_2Rh(N^nBuNCHP(N^iPr_2)_2$ (**51**) following Ref. [76].

one $PMe_3$ ligand being lost. Interestingly, trapping the phosphorus lone pair with sulfur in $HC(N_2)(S)P(N^iPr_2)_2$ gave the expected η$^1$-bonded diazo complex $(PMe_3)_2RhC(N_2)P(S)(N^iPr_2)_2$ (**52**).



Reacting a 1:1 mixture of $LiC(N_2)SiMe_3$ and $SiMe_3Cl$ on the carbonyl complexes $M(CO)_6$ (M = Cr, W) and $W(CO)_5PPh_3$, in a process similar to the one used for the synthesis of metal carbene compounds, did not produce the expected C-bonded diazoalkyl complexes but instead the N-bonded diazo compounds $M(CO)_5(N_2C(SiMe_3)_2)$ (M = Cr, W) (**1**) and $W(CO)_4(PPh_3)[N_2C(SiMe_3)_2]$ (**2**) [26].

Interestingly, the reaction of $LiC(N_2)SiMe_3$ on $[Mn(C_6H_6)(CO)_3]^+$ gave $[Mn(C_6H_6C(N_2)SiMe_3)(CO)_3]^+$ (**53**) resulting from the nucleophilic attack of the η$^6$-coordinated benzene ring by the diazo anion [78].



**(53)**

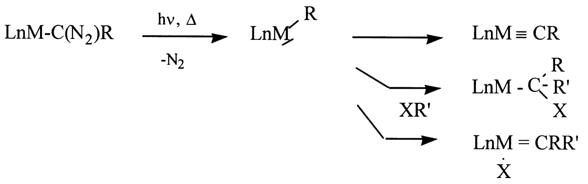
### *3.2. Reactions of diazoalkyl transition metal complexes*

The chemistry of metal-coordinated diazoalkanes is still in its infancy. These molecules are expected to display a diazo-like behavior, showing the characteristic reactions of free diazoalkane: decomposition into carbene species and dipolar reactivity. Consequently, the first interest in their chemistry is their capability to act as an $\alpha$-metallated carbene precursor, giving a new synthetic approach to metal carbene or metal carbyne chemistry (Scheme. 23).

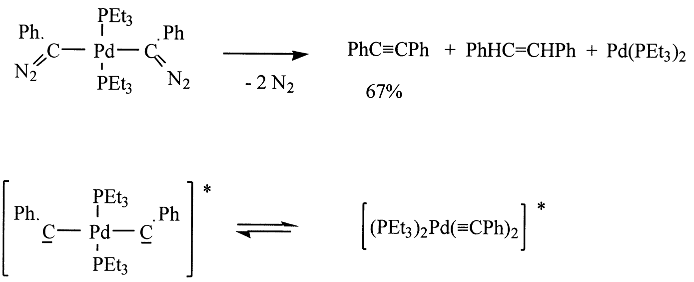
#### *3.2.1. α-Metallated carbene precursor*

Photolysis and pyrolysis of $(PEt_3)_2Pd[C(N_2)Ph]_2$ gave mainly diphenylacetylene, suggesting the intermediacy of the carbene complex $(PEt_3)_2Pd–C–Ph$, which can be considered as the isomeric form of the metal carbyne $(PEt_3)_2Pd(\equiv CPh)_2$ (Scheme. 24).

Formation of a transient metal carbyne complex was suggested to explain the formation of: (i) the metal-bridging carbyne complexes (**54**) via the reaction of $Hg[N_2C(CO_2Et)_2]_2$ on $[(CO)_4Mn\equiv C(CO_2Et)]^*$ [79,80]; (ii) the complex (**55**) by



Scheme 23. Possible thermal and photochemical reactions for diazoalkyl transition metal complexes



Scheme 24. Compounds obtained from the pyrolysis or photolysis of [41]

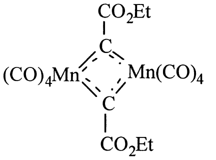
the reaction of $R_3SnC(N_2)CO_2R'$ on $Mn(CO)_5Br$ [81] and the intramolecular insertion of $[OsCl(NO)I({=}C(CO_2Et)(PPh_3)_2]^*$ into the C–H bond of a phenyl group [82] (Scheme. 25).

Whereas metal carbyne species could reasonably be invoked in the chemistry of Mn and Os complexes, they are unknown in the nickel chemistry. The reaction observed in the photolysis of $(PMe_3)_2NiCl\{C(N_2)SiMe_3\}$ proceeded via photo-induced intramolecular migration of one phosphine to the electrophilic carbon atom of the carbene ligand; this generates an unsaturated metal-substituted ylid complex which dimerizes into $[NiCl\{\eta^2\mu C(PMe_3)(SiMe_3)]_2$ (**57**) (Scheme. 26) [71].

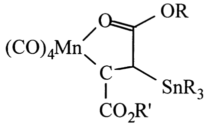
The X-ray structure of (**57**) shows the presence of $[Ni–Ni]^{4+}$ units, the two Ni atoms being bridged by the two ylid groups (Fig. 14). Although the Ni–Ni distance of 2.281 Å is short, an extended Hückel calculation indicates the absence of an Ni–Ni bond.

Interestingly, although both nickel atoms present only a $14e^-$ configuration, the complex is stable because of its compactness due to the sterically hindered $PMe_3$ and $SiMe_3$ substituents [83].

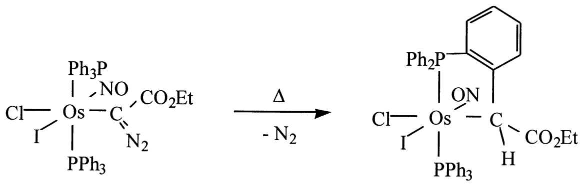
A similar reaction pathway occurred on photolysis of $(PEt_3)_2Rh\{C(N_2)SiMe_3\}$ (**43**), giving $[Rh(PEt_3)_2\{\eta^2\mu C(PEt_3)(SiMe_3)\}]_2$ (**58**) with two phosphorus ylid bridges (Scheme. 27).



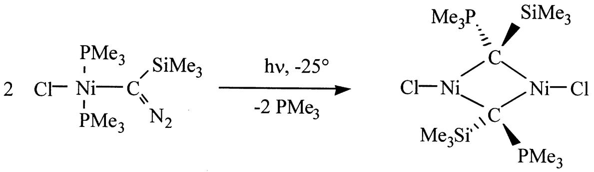
**(54)**



**(55)**



Scheme 25. Examples of metal complexes resulting from decomposition of diazoalkane suggesting the formation of transient metal carbine intermediates



**57**

Scheme 26. Photochemical activation of $(PMe_3)ClNi(CN_2SiMe_3)$

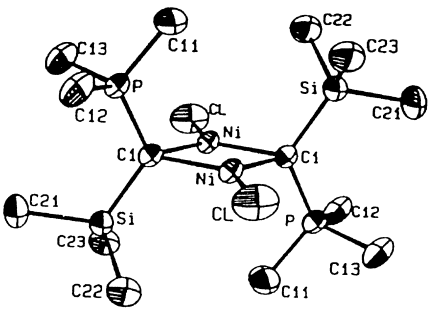
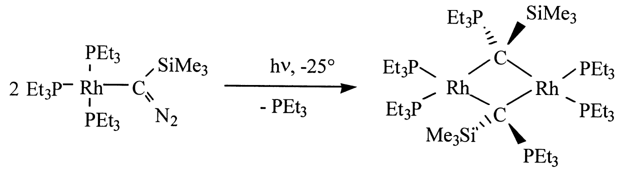
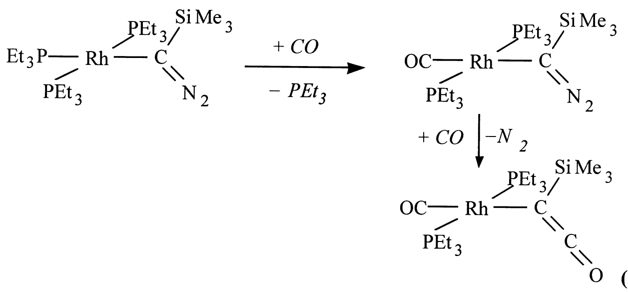


Fig. 14. ORTEP of [NiCl{$\eta^2\mu$C(PMe$_3$)(SiMe$_3$)}]$_2$ (**57**) following Ref. [71].



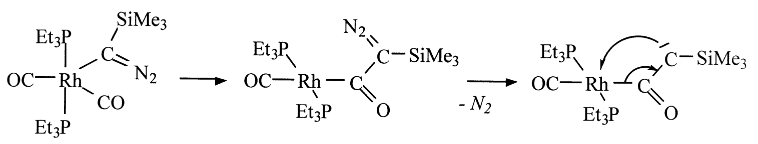
**(58)**

Scheme 27. Photochemical activation of (PEt$_3$)$_3$RhC(N$_2$)SiMe$_3$



**(59)**

Scheme 28. Reaction of CO2 on (PEt$_3$)$_3$RhC(N$_2$)SiMe$_3$



Scheme 29. Wolff-like formation of (PEt$_3$)$_2$(CO)Rh[C(CO)(SiMe$_3$)]

A remarkable reaction is the CO-induced conversion of the $\eta^1$ diazotrimethylsilylmethyl ligand of (PEt$_3$)$_3$Rh{C(N$_2$)SiMe$_3$} into the $\eta^1$ ketenyl ligand to give (PEt$_3$)$_2$(CO)Rh{C(SiMe$_3$)CO} (**59**) (Scheme. 28) [84]. Scheme. 28 was deduced from NMR and IR studies. The initial formation of monocarbonyl complex was followed by the insertion of a second CO molecule into the Rh–C diazo bond and rearrangement through a Wolff like reaction (Scheme. 29).

### 3.2.2. Dipolar addition

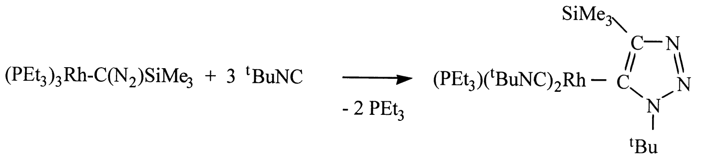
The first example of a [3+2] cycloaddition reaction involving a $\eta^1$-diazoalkyl complex was accomplished by reacting $^tBuN{\equiv}C$ or $^nBuN{\equiv}C$ on $(PEt_3)_3Rh\{C(N_2)SiMe_3\}$ (**43**) giving the cycloaddition product $(PEt_3)(^tBuN{\equiv}C)_2Rh(C{=}C(SiMe_3)N{=}NN^tBu)$ (**60**) in a high yield process (Scheme. 30). (**60**) has been structurally characterized [85].

The heterocycle is planar, perpendicular to the rhodium coordination plane. The reaction mechanism, followed by NMR and IR, indicated successive coordination of isocyanide to the metal, insertion into the Rh–C$(N_2)SiMe_3$ bond and cyclization. This result could open a profitable area of synthesis in view of the potential stereospecificity of such reactions due to the chirality developed around the metal center.

### 3.2.3. Ligand exchange

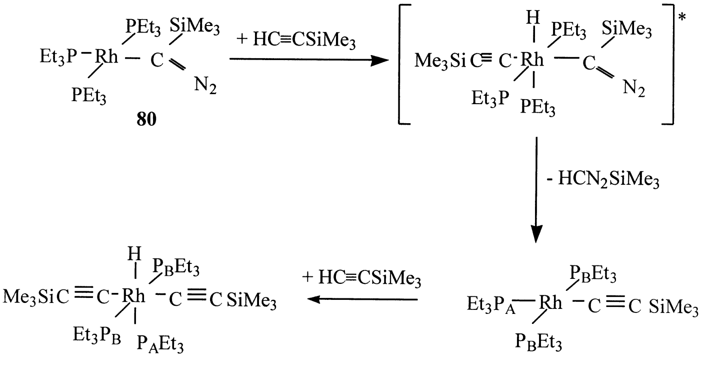
Only a ligand exchange process occurred when terminal alkynes $HC{\equiv}CR$ ($R{=}C_6H_5$, $SiMe_3$) react with $(PEt_3)_3Rh\{C(N_2)SiMe_3\}$ (**43**).

Free diazoalkane $HC(N_2)SiMe_3$ was liberated with the concomitant formation of $RhH(C{\equiv}CR)_2(PEt_3)_3$, $(PEt_3)_3Rh(C{\equiv}CR)$ acting as intermediate [86] (Scheme. 31).



**(60)**

Scheme 30. Reaction of $^t$*BuNC* on $(PEt_3)_3RhC(N_2)SiMe_3$



Scheme 31. Possible mechanism for the reaction of $^t$*BuNC* on $(PEt_3)_3RhC(N_2)SiMe_3$

## 4. Concluding remarks

This review has attempted to present a comprehensive summary of the synthesis, characterization and reactivity of transition metal N-coordinated diazoalkanes and C-coordinated diazoalkyl ligands. The field has matured now to a point where a great deal is known about the diazoalkane N coordination to transition metals. It is clear that the basic reaction is an oxidative addition of diazoalkane on the metal complex giving mainly hydrazonido(−2) ligand. As a consequence, reactions have been reported with metal complexes known to participate in oxidative addition reactions, either early or late transition metals, the electronic structure and the reactivity of the coordinated diazo being dependent on the metal center and on the diazo substituents.

However, the number of C-coordinated diazoalkyl ligands is still rather small and restricted to only a few metals and a few diazo substituents. Thus, this class of compounds is in need for more detailed investigation, including syntheses and reactivities. Moreover, the application of these compounds to synthetic chemistry is still virtually unexplored and could be useful in stereo-selective reactions.

## Acknowledgements

We thank the Ministère de l'Enseignement Supérieur et de la Recherche and the Centre National de la Recherche Scientifique from France and the CNPq from Brasil (HS) for financial support.

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