Russian Chemical Reviews **63** (3) 197 – 216 (1994)
©1994 Russian Academy of Sciences and Turpion Ltd

UDC 546.821 : 546.852

Reactions of diazoalkanes with transition metal complexes

M Putala, D A Lemenovskii

Contents

I. Introduction	197
II. Complexes with the ligand coordinated through a nitrogen atom	198
III. Complexes with the ligand coordinated through a carbon atom	206
IV. Reactions of diazoalkane complexes	210
V. Conclusion	215

Abstract. The results of studies on the interaction of diazoalkanes with transition metal complexes are presented and the successive transformations of the diazoalkane complexes formed are traced. The reactions have been classified in terms of the proposed mechanism and the structure of the products. The principal structural parameters of the diazo-ligands are presented. The bibliography includes 145 references.

I. Introduction

The reactions of diazoalkanes with transition metal complexes have become the subject of intensive study during the last 20 years. The products of these reactions are important both theoretically (for example, diazoalkanes coordinated to a metal are possible intermediates in the insertion of molecular nitrogen into organic compounds[1,2]) and synthetically (the reactions with diazoalkanes constitute the most convenient method of synthesis of bridged carbene complexes of transition metals[3,4]).

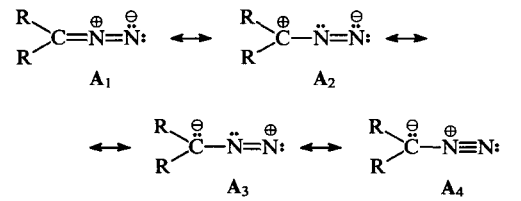
Generally speaking, several review articles have been devoted to the reactions of diazoalkanes with transition metal complexes.[5–8] In the present review, an attempt has been made to classify the available data in terms of the type of reactions or the structure of the complexes formed, mainly the interactions of diazoalkanes with mono- and bi-metallic complexes of transition metals being considered. On the other hand, the reactions of polynuclear (trinuclear and more highly condensed species) complexes are presented only in those cases where they strongly resemble the reactions of the mono- and di-nuclear complexes in terms of the mechanism or the structure of the complexes formed.

It is essential to note that a systematic approach to the consideration of the mechanisms of the processes occurring is difficult since the available literature data about them are usually restricted to the description of the structures of the complexes obtained. One should also recall that the information about the structure of the complexes can be frequently unreliable if it is based solely on data obtained by individual spectroscopic methods and not the results of X-ray diffraction studies.

M Putala Department of Organic Chemistry, Comenius University, Mlynska dolina, 84215, Bratislava, Slovakia.
D A Lemenovskii Laboratory of Physical Organic Chemistry, Lomonosov Moscow State University, Vorob'evy Gory, 119899 Moscow, Russian Federation. Fax (7-095) 939 55 46

Received 15 February 1994
Uspekhi Khimii **63** (3) 207 – 227 (1994); translated by A K Grzybowski

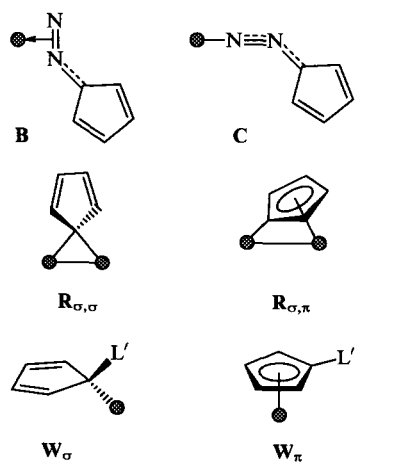
The electronic structure of diazoalkanes may be represented by the following canonical structures:[3,6]



On the basis of these structures, one can postulate that diazoalkanes enter into reactions (including those with transition metal complexes) as 1,3-dipoles (A_2, A_3), N-nucleophiles (A_1, A_2), or C-nucleophiles (A_3, A_4). Furthermore, bearing in mind the unsaturated nature of the diazoalkanes, one may also expect the formation of complexes of the π-type.

Naturally the result of the interaction of transition metal complexes with diazoalkanes depends on the nature and reactivity of the complexes. Fig. 1 presents the principal structural types of the products obtained as a result of such interaction.

It is essential to note that the simultaneous formation of several complexes of different types has been repeatedly observed in one reaction. Furthermore, the same initial complex can afford different products in reactions with different diazoalkanes and, conversely, the same diazoalkane can lead to the formation of products of a completely different type in reactions with different complexes. For example, the interaction of diazocyclopentadienes substituted in different ways with transition metal compounds afforded six types of complexes:



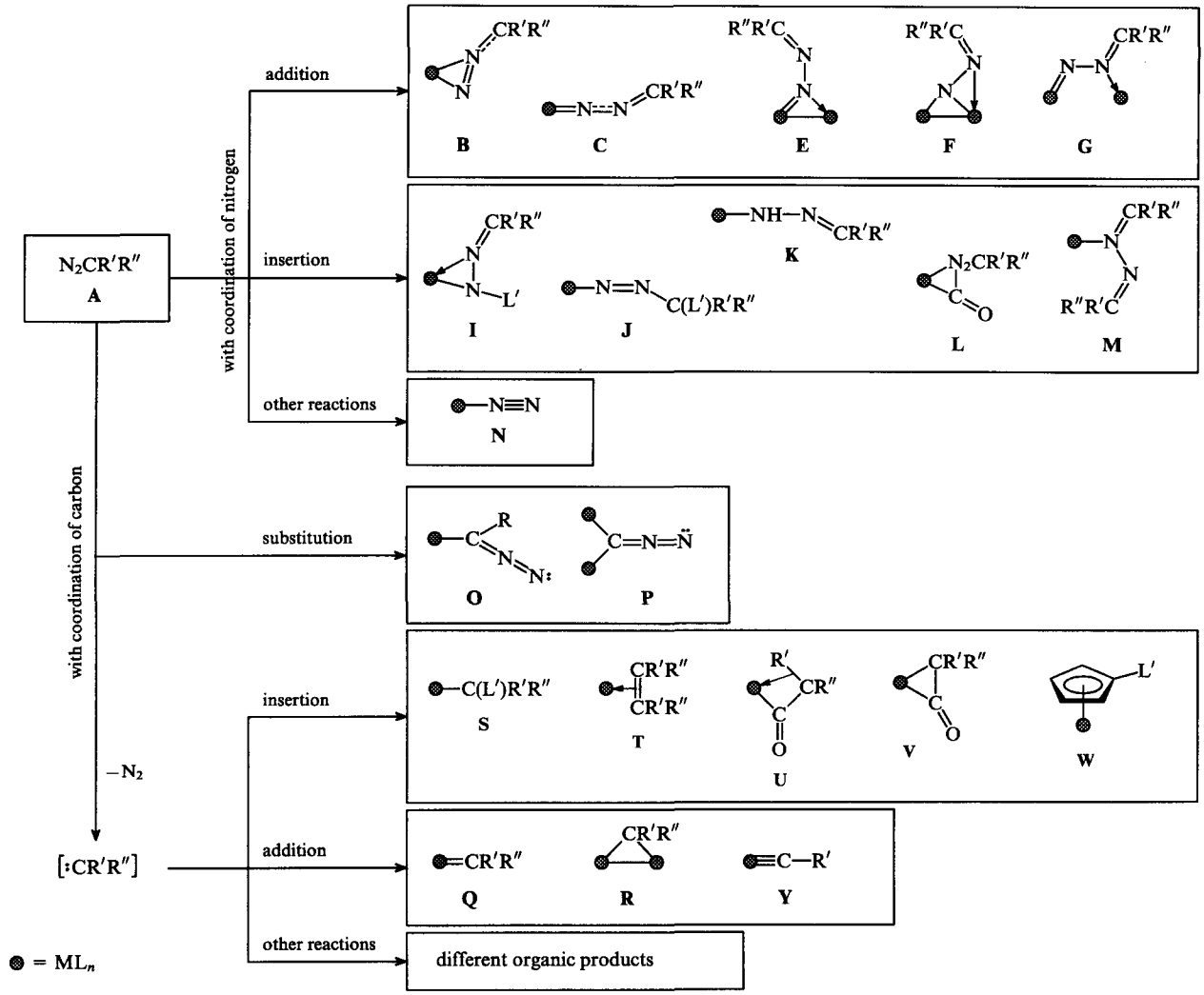


Figure 1. The principal structural types of the products of the interaction of transition metal complexes with diazoalkanes.

It follows from the wide variety of the products that the classification of reactions of diazoalkanes with transition metal complexes is by no means a trivial task. We have classified these reactions in terms of the structure of the products taking into account as far as possible the proposed reaction mechanism and the type of complex entering into the reaction.

II. Complexes with the ligand coordinated through a nitrogen atom

1. Addition reactions with formation of η^1-*N*- and η^2-*N*, *N'*-diazoalkane complexes

Coordinatively unsaturated transition metal complexes (ML_n)[9–19] or their precursors (ML_nY), containing only readily eliminated ligands Y such as hydrogen,[20–23] nitrogen,[24–29] carbon monoxide,[30–32] phosphine,[31–33] tetrahydrofuran,[34–36] or an alkene,[9,10,29,32,37] can enter into oxidative addition (or ligand exchange) reactions, which lead to the formation of η^2-*N*, *N'*-diazoalkane complexes (**B**) or η^1-*N*-diazoalkane complexes (**C**).

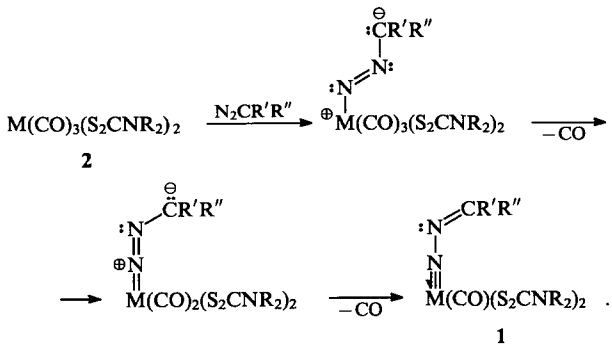
$$N_2CR'R'' \xrightarrow[(\text{or } ML_nY)]{ML_n} \longrightarrow L_nM\langle^{N}_{N}\!=\!CR'R'' \quad \text{or} \quad L_nM{=}N{=}N{=}CR'R''$$

B **C**

Y = H_2, N_2, CO, PR_3, THF, alkene.

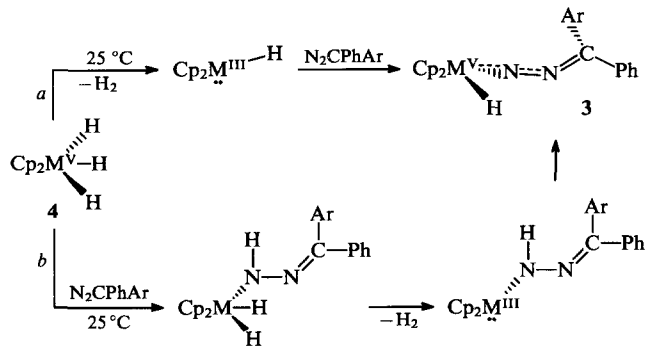
In the presence of an excess of the diazoalkane, the elimination of the phosphine ligand may be accompanied by the formation of the phosphazine $R_3PN_2CR'R''$.[32]

The mechanism of the replacement of the ligand Y can be both associative and dissociative—depending on the coordination capacity of the metal atoms and the ability of the other ligands to undergo a change in their electron-donating properties. Thus it has been suggested[17] that molybdenum and tungsten complexes of the type $M(CO)(S_2CNR_2)_2(\eta^1\text{-}N_2CR'R'')$ (M = Mo, W) **1** are formed from $M(CO)_2(S_2CNR_2)_2$ **2** and $N_2CR'R''$ in several stages, in which the diazoalkane $N_2CR'R''$ is consecutively a 0-, 2-, and 4-electron-donating ligand (the process is accompanied by the elimination of two CO molecules in successive stages:



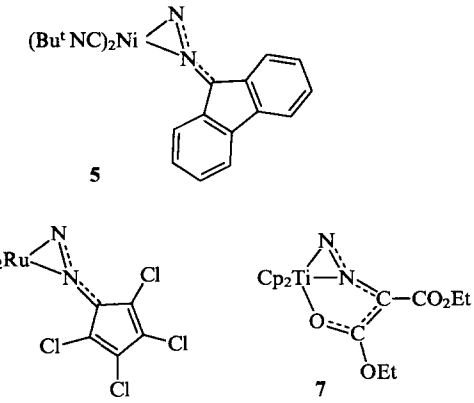
2 1

A mechanism differing from the usual one for the formation of η^1-*N*-diazoalkane complexes has been proposed for the formation of diaryldiazomethane complexes of niobocene and tantalocene $Cp_2M(H)(N_2CPh_2)$ (M = Nb, Ta) **3** [21,22] by the reaction of the corresponding metallocene trihydride **4** with the diazoalkane. Since the rate of elimination of hydrogen from Cp_2MH_3 (pathway *a*) is appreciably lower than the rate of formation of compound **3**, pathway *b*, involving the insertion of the diazoalkane in a M – H bond and only then the elimination of hydrogen, is more likely.



In the first communications [9,10,24] (up to 1975) in which the synthesis of stable monometallic diazoalkane complexes was reported, the question of the type of coordination of the diazoalkane usually remained open. The hypothesis, put forward in 1966,[38] that diphenyldiazomethane is coordinated to cyclododeca-1,5,9-trienenickel exclusively via the carbon atom can hardly be regarded as realistic in the light of present day knowledge.

The results of X-ray diffraction studies on the complexes $Ni(CNBu^t)_2(N_2Fld)$ (N_2Fld = 9-diazofluorene) **5** [14] and $Ru(CO)_2(PPh_3)_2(N_2C_5Cl_4)$ **6** [11] indicate that diazoalkanes are involved in η^2-*N,N'*-coordination (type **B**) in both complexes. The above complexes with the η^2-*N,N'*-coordination of the diazoalkane are regarded as π-type complexes. A similar type of coordination has been demonstrated by X-ray diffraction for the complex $Cp_2Ti[\eta^3$-*N,N',O*-$N_2C(CO_2Et)_2]$ **7**, [12] in which the metal atom is additionally coordinated to an oxygen atom of the carboxy-group. The displacement of the ν_{CNN} vibration band from 2050–2150 cm^{-1} for the free diazoalkanes to 1400–1600 cm^{-1} for the complexes has been observed in the spectra of the complexes. On this basis, it has been suggested that this type of coordination of the diazoalkane occurs also in many other complexes, in particular in $Cp_2V(N_2CR_2)$ (R = Ph, CO_2Et),[12,13] $Cp_2M(H)(N_2CPh_2)$ (M = Nb, Ta) **3**,[20] and $Cp_2Mo(N_2Fld)$,[23] and in certain complexes of the type $L_2M(N_2CR_2)$ (L = $CNBu^t$, PR_3; M = Ni, Pd; CR_2 = CPh_2, $C(CN)_2$, Fld, C_5X_4; X = H, Cl, Br).[9–11,14]



5 6 7

Complexes with the η^1-*N*-coordination of the diazoalkane ligand were obtained later — for example, $IrCl(N_2C_5Cl_4)(PPh_3)_2$ **8a**.[33] It was then also suggested [11] that the η^2-*N,N'*-coordination of the diazoalkane is more probable in those cases where the electron-accepting nature of the nonterminal nitrogen atom becomes enhanced under the influence of the electron-deficient CR_2 of the diazoalkane and when the *d* orbitals of the transition metal are filled to a greater extent.

Numerous data are already available on complexes for which the η^1-*N*-coordination of the diazoalkane has been postulated with a high degree of probability or reliably established:

$MClL_2(N_2CR'R'')$ — $Cp_2Ti(PMe_3)(N_2CPh_2)$ [31]

8 **9**

$Cp_2M(X)(N_2CPhAr)$ [21,22,39] — M = Nb, Ta; X = H, Cl, Br.

3, 10

$M(CO)(S_2CNR_2)_2(N_2CR'R'')$ [15,30] — M = Mo, W.

1

$MX_2(N_2CR'R'')L(PMe_2Ph)_2$ [40,41] — M = Mo, W; X = Hal, OR; L = PMe_2Ph, π-ligands.

11

$[MX(N_2CR'R'')(dppe)_2]^+Y^-$ [42–48]

12

M = Mo, W; X = Hal; dppe = $PPh_2(CH_2)_2PPh_2$; Y = Br, BF_4, PF_6.

$X_2W(\mu$-$CSiMe_3)_2WX_2(N_2CPh_2)$ [16] — X = CH_2SiMe_3, OPr^i.

13

$Mo(OBu^t)_4(N_2CAr_2)$ [18]

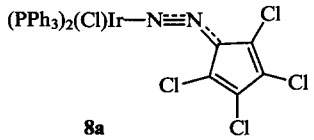
14

$Cp'Mn(CO)_2[N_2C(CO_2R')_2]$ [34,35] — Cp' = C_5H_5, C_5H_4Me.

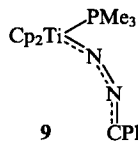
15

$MCl_{3-x}H_xL_2(N_2CR'R'')$ [26,27,29,37] — M = Ir, Rh; x = 1, 2; L = CO, PR_3.

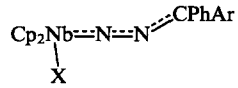
It was observed that the absorption band for the ν_{CNN} vibration in the spectra of these complexes is in the same range as for the complexes with η^2-*N,N'*-coordination of the diazoalkane, i.e. in the region 1400–1600 cm^{-1}.



8a

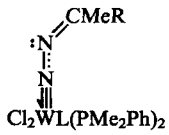


9



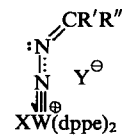
3a,10a,b

3a: X = H; Ar = Ph.
10a: X = Cl; Ar = *o*-C_6H_4Br.
10b: X = Br; Ar = *o*-C_6H_4Br.



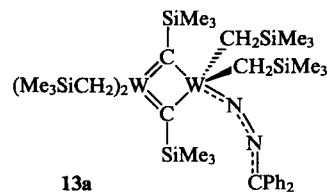
11a,b

11a: L = *p*-MeC_6H_4CHO; R = Ph.
11b: L = C_2H_4; R = Me.

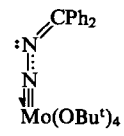


12a–c

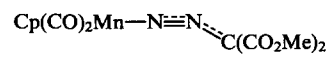
12a: X = Y = Br; R′ = R″ = Me.
12b: X = Br; Y = PF_6; R′ = H; R″ = $(CH_2)_3OH$.
12c: X = F; Y = BF_4; R′ = Me; R″ = CH_2COMe.



13a

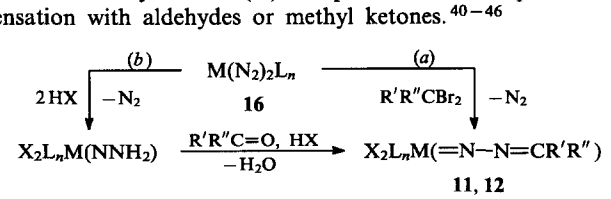


14a



15a

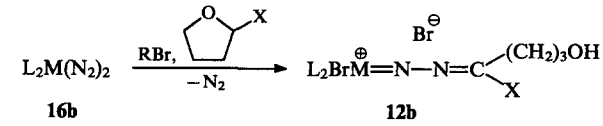
Apart from the reactions involving the addition of diazoalkanes to the coordinatively unsaturated complex or the substitution of another ligand by the diazoalkane, other methods of synthesis of η^1-*N*-diazoalkane complexes have also been discovered. Among the molybdenum and tungsten complexes $M(N_2)_2L_n$ **16** containing coordinated molecular nitrogen, the diazoalkane complexes **11** and **12** have been obtained in two ways: (*a*) by reaction with geminal dibromocompounds;[46–48] (*b*) by the protonation of the nitrogen with formation of hydrazinate(2-) complexes and subsequent condensation with aldehydes or methyl ketones.[40–46]



11, 12

M = Mo, W;
X = F, Cl, Br, I, BF_4, PF_6;
L = PMe_2Ph, dppe;
R′ = H, Me; R″ = H, R, COR, Ar.

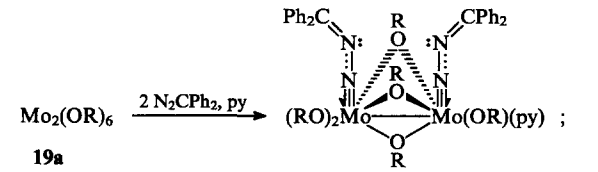
The tungsten complex of diazobutanol **12b** and the related complexes $[MBr(N_2C(X)CH_2CH_2CH_2OH)(dppe)_2]^+$ (M = Mo, W; X = H, Me)[48–50] have been obtained by the reaction of $M(N_2)_2(dppe)_2$ **16b** with 2-X-substituted tetrahydrofuran (THF) in the presence of alkyl bromides.



16b **12b**

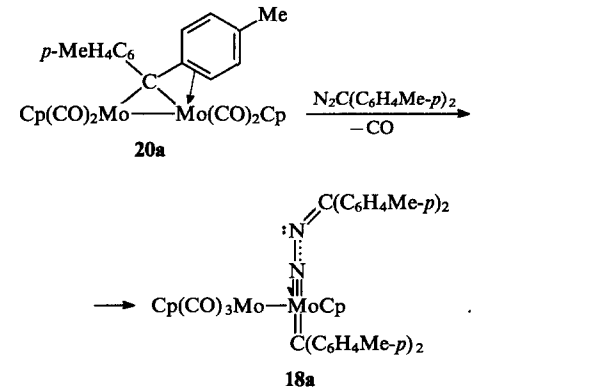
M = Mo, W; L = dppe; R = Alk; X = H, Me.

The molybdenum complexes $Mo(OBu^t)_4(N_2CAr_2)$ **14**,[18] $(RO)_2(N_2CAr_2)Mo(\mu\text{-}OR)_3Mo(OR)(N_2CAr_2)(py)$ **17**, where R = Pr^i or CH_2Bu^t,[18,51] and $Cp(CO)_3MoMoCp(CAr_2)\cdot(N_2CAr_2)$ **18**[52,53] with η^1-*N*-coordination of the diazoalkanes have been obtained from the complexes $Mo_2(OR)_6$ **19** and $Cp(CO)_2Mo(\mu\text{-}CAr_2)Mo(CO)_2Cp$ **20**. The addition of the diazoalkane molecule takes place as a result of the transformation of the coordination sphere in the initial complexes, for example:



19a **17a**

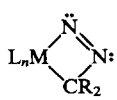
R = Pr^i.



20a **18a**

The diazoalkanes in complexes with η^1-*N*-coordination can be formally regarded as neutral diazoalkane or nitrene ligands or as hydroazonate(2-) ligands. However, the nature of the bonds in them, particularly that of the N–N bonds, differs from those in hydrazones. The N–N bond length in these complexes is close to that in a double bond, while the M–N–N angle tends to 180°. The principal structural parameters of diazoalkane and related complexes are presented in Table 1 and the average C–C and C–N bond lengths in organic molecules are shown for comparison in Table 2. On the basis of the structural data for the diazoalkane complexes, one can postulate the *sp* hybridisation of the terminal nitrogen atom. The M–N bond length is also close to that of a double bond, so that the diazoalkane ligand can be regarded as a 2-electron donor (in complexes **3**, **8**, **9**, **10**, and **15**) and a 4-electron donor (in complexes **11**–**14**, **17**, **18**) depending on the coordination capacity of the metal atom.

The formation of metallocyclobutane complexes of type **D** with 1,3-*N*,*C*-coordination of the diazoalkane has been postulated only as intermediates in the catalytic decomposition of diazoalkanes, leading to carbenes and hence to the products of the reactions of carbenes.



D

Table 1. Structural parameters of η^1-*N*- and η^2-*N,N'*-diazoalkane and related complexes.

No.	Complex	Bond lengths/Å		Bond angles/deg		Ref.
		N–N'	N'–C	M–N–N'	N–N'–C	
	Free N_2CH_2	1.12	1.32	–	180	54
	B. Complexes with η^2-*N,N'*-coordination					
5	$Ni(CNBu^t)_2(N_2Fld)$	1.25	1.34	69	134	14
6	$Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2$	1.22	1.37	70	132	11
7	$Cp_2Ti[N_2C(CO_2Et)_2]$	1.21	1.37	84	147	12
–	$CpTiCl_2(N_2Ph)$	1.22	–	71	126	55
	C. Complexes with η^1-*N*-coordination					
9	$Cp_2Ti(PMe_3)(N_2CPh_2)$	1.26	1.31	157	126	31
3a	$Cp_2Nb(H)(N_2CPh_2)$	1.29	1.31	171	124	21
10a	$Cp_2Nb(Cl)[N_2(C(Ph)(o\text{-}C_6H_4Br)]$	1.29	1.30	169	126	22
10b	$Cp_2Nb(Br)[N_2C(Ph)(o\text{-}C_6H_4Br)]$ [a]	1.20	1.31	159	126	39
		1.35	1.34	171	121	
11a	$WCl_2(N_2CMePh)(p\text{-}MeC_6H_4CHO)(PMe_2Ph)_2$	1.29	1.27	166	121	56
11b	$WCl_2(N_2CMe_2)(C_2H_4)(PMe_2Ph)_2$	1.34	1.29	167	117	56
12a	$[WBr(N_2CMe_2)(dppe)_2]Br$	1.34	1.28	171	124	57
12b	$[WBr(N_2CH(CH_2)_3OH)(dppe)_2]PF_6$	1.31	1.29	172	116	49
12c	$[WF(N_2C(Me)CH_2COMe)(dppe)_2]BF_4$	1.32	1.30	174	125	44
13a	$(RCH_2)_2W(\mu\text{-}CR)_2W(CH_2R)_2(N_2CPh_2)$ R = $SiMe_3$	1.36	1.29	158	123	16
14a	$Mo(OBu^t)_4(N_2CPh_2)$	1.31	1.31	168	122	18
17a	$(RO)_2(N_2CPh)_2Mo(\mu\text{-}OR)_3Mo(OR)(N_2CPh_2)(py)$	1.32	1.28	164	124	18
	R = Pr^i	1.30	1.31	153	122	
17a	$(RO)_2(N_2CPh)_2Mo(\mu\text{-}OR)_3Mo(OR)(N_2CPh_2)(py)$	1.30	1.30	164	124	51
	R = Pr^i	1.30	1.31	155	122	
18a	$Cp(CO)_3Mo-MoCp(CAr_2)(N_2CAr_2)$ Ar = C_6H_4Me-*p*	1.32	1.32	175	121	52, 53
15a	$CpMn(CO)_2[N_2C(CO_2Me)_2]$	1.17	1.35	177	151	34
8a	$IrCl(N_2C_5Cl_4)(PPh_3)_2$	1.17	1.35	175	141	33
–	*trans*-$WI(NNSiMe_3)(PMe_2Ph)_4$	1.24	–	168	152	58
–	*mer*-$WI_2(NNHSiMe_3)(PMe_2Ph)_3$	1.32	–	171	127	58
–	*mer*-$WI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_3$	1.36	–	173	120 126	59

[a] Two independent molecules in the unit cell of the complex.

Table 2. Average N–N and N–C bond lengths (Å) in organic compounds.[60–62]

Bond	Single	Single[a]	Double	Triple
N–N	1.40–1.45	1.37	1.22–1.25	1.12
C–N	1.47–1.49	1.33–1.35	1.28–1.33	1.14

[a] The length of a single bond conjugated with a double bond.

2. Addition (insertion) reactions with formation of bridged diazoalkane complexes

Bridged diazoalkane complexes have been obtained in several ways: (a) by addition (insertion) to multiple (Mo≡Mo, W≡W[63–69] and Os=Os[70]) or single (Zr–Zr[71] and Ru–Ru[72]) metal–metal bonds; (b) by the dimerisation of coordinatively unsaturated metal complexes (Ti,[19,36] Zr,[17] Nb,[73,74] Mn, Co[75]); (c) by the substitution of other bridging ligands (Rh[76]):

(a) $L_nM{\equiv}ML_n + N_2CR_2 \longrightarrow (L_nM)_2(\mu\text{-}N_2CR_2)$ (M–M)

$L_nM{=}ML_n + N_2CR_2 \longrightarrow (L_nM)_2(\mu\text{-}N_2CR_2)$ (M–M)

$L_nM{-}ML_n + N_2CR_2 \longrightarrow (L_nM)_2(\mu\text{-}N_2CR_2)$

(b) $2\left[L_nM{=}\ddot{N}{-}\ddot{N}{=}CR_2\right] \longrightarrow (L_nM)_2(\mu\text{-}N_2CR_2)_2$

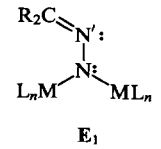
$2\,L_nM + N_2CR_2 \longrightarrow (L_nM)_2(\mu\text{-}N_2CR_2)$

(c) $(L_nM)_2(\mu\text{-}Y)_2 + N_2CR_2 \xrightarrow[-Y_2]{} (L_nM)_2(\mu\text{-}N_2CR_2)$

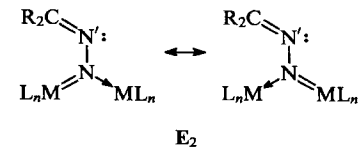
Y = H.

One can postulate at least four types of coordination of bridging diazoalkanes to a bimetallic centre (regardless of whether the direct valence metal–metal interaction is then retained):[7]

(a) A symmetrical bridge with the coordination of only the terminal nitrogen atom — with $\mu\text{-}\eta^1:\eta^1$-*N*-coordination of the diazoalkane, the diazoalkane being capable of functioning both as a 2-electron donating (E_1) or a 4-electron-donating (E_2) ligand.

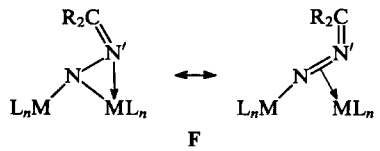


E_1



E_2

(b) An asymmetric bridge with additional coordination of the nonterminal N' atom to one metal atom (type **F**) — with μ-η^1 : η^2-*N,N,N'*- or μ-σ,π-coordination of the diazoalkane.



F

(c) A bridge where each nitrogen atom is coordinated to only one specific metal atom — with μ-η^1 : η^1-*N,N'*-coordination of the diazoalkane (type **G**).

(d) A bridge the terminal nitrogen atom of which is coordinated to one metal atom while the carbon atom is coordinated to the second metal atom — with μ-η^1 : η^1-*N,C*-coordination of the diazoalkane (type **H**).



G **H**

In bimetallic complexes, the asymmetric type **F** coordination of the diazoalkane is most often encountered. Such coordination has been established (or postulated) for the following complexes:

$CpClTi(N_2CPh_2)_2TiClCp$ [19,36]

21

$CpClZr(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(N_2CPh_2)ZrClCp$ [71]

22

$Cp'(CO)_2Mo(\mu\text{-}CO)(N_2CR'R'')Mo(CO)Cp'$ [63-65]

23

$Cp' = C_5H_5, C_5H_4Me, C_5Me_5$; $R' = R'' = Me$; $R' = H$, $R'' = CO_2Et$

$C_5Me_5(CO)_2Mo(\mu\text{-}CH_2)(N_2CH_2)Mo(CO)_2C_5Me_5$. [66]

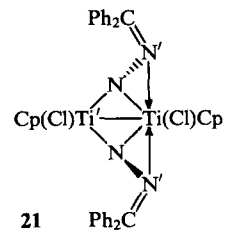
24

It has been observed (Table 3) that the N–N' bond in these complexes is intermediate between a double and single bond, while N'–C is very close to a double bond.

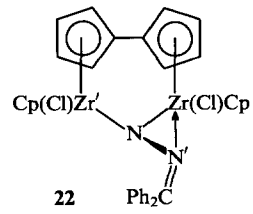
Table 3. Selected structural parameters of diazoalkane and related complexes.

No.	Complex	Bond lengths/Å		Bond angles/deg			Ref.
		N–N'	N'–C	M–N–M'	M–N–N' (M'–N–N')	N–N'–C	
	Complexes with μ-η^1 : η^1-*N*-coordination						
25a	$Cp'_2Zr(N_2CHPh)(N_2CHPh)ZrCp'_2$ $Cp' = C_5H_4Me$	1.36	1.29	100	121 (140)	120	17
26	$[CpNb(\eta^5\text{-}C_5H_4C(CO_2Et)=N_2)]_2$	1.34	1.31	93	127 (140)	118	73
27a	$(Bu^tO)_3W(N_2CAr_2)_2W(OBu^t)_3$ $Ar = p\text{-}C_6H_4Me$	1.41	1.26	[a]	[a]	137	18
28a	$Cp(CO)_2Mo(\mu\text{-}CO)(N_2CPh_2)Mo(CO)Cp$	1.35	1.28	97	130 (128)	122	65
	$CpClTi(N_2Ph_2)(N_2Ph_2)TiClCp$	1.39	1.47 1.47	95	81	[a]	78
	Complex with μ_3-*N*-coordination						
	$Fe_3(CO)_9(N_2CPh_2)$	1.40	1.26	[a]	[a]	[a]	80
	Complex with μ_4-*N*-coordination						
	$Ru_5(CO)_{12}(\mu_4\text{-}C{\equiv}CPh)(N_2CPh_2)(\mu\text{-}PPh_2)$	1.40	1.30	[a]	[a]	[a]	72
	Complexes with μ-η^1 : η^2-*N,N,N'*-coordination						
21	$CpClTi(N_2CPh_2)_2TiClCp$	1.33	1.30	94	78 (154)	[a]	19
		1.34	1.31	95	78 (157)		
22	$CpClZr(\mu\text{-}C_{10}H_8)(N_2CPh_2)ZrClCp$	1.34	1.31	131	74 (152)	129	71
23a	$Cp^*(CO)_2Mo'(\mu\text{-}CO)(N_2CMe_2)Mo(CO)Cp^*$ $Cp^* = C_5Me_5$	1.37	1.30	92	71 (113)	133	63
23b	$Cp^*(CO)_2Mo'(N_2CHCO_2Et)Mo(CO)Cp^*$ $Cp^* = C_5Me_5$	1.34	1.29	97	128 (130)	122	65
25a	$Cp'_2Zr(N_2CHPh)(N_2CHPh)ZrCp'_2$ $Cp' = C_5H_4Me$	1.32	1.29	101	74 (174)	124	17
–	$CpClTi(N_2CPh_2)(N_2Ph_2)TiClCp$	1.38	1.43 1.43	94	128 (138)	[a]	78
	Complexes μ-η^1 : η^2-*N,N',O*-coordination						
29a	$Cp(CO)_2Mo[(N_2CPh)C(O)Ph]Mo'(CO)_2Cp$	1.26	1.44	[a]	174	[a]	64
29b	$Cp(CO)_2Mo[N_2C(CO_2Et)_2]Mo'(CO)_2Cp$	1.24	1.42	[a]	[a]	122	65

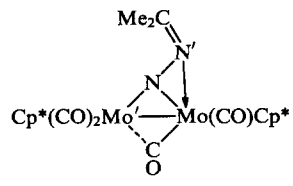
[a] The value of the given parameter is not quoted.



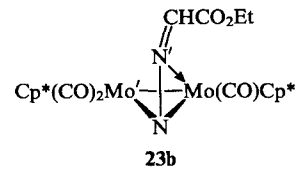
21



22



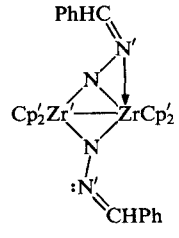
23a



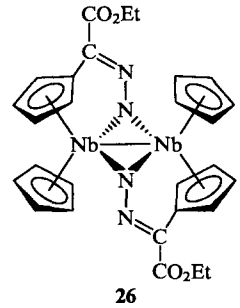
23b

Cp* = C_5Me_5.

Dimerisation of the coordinatively unsaturated complexes [$Cp'_2Zr=NN=CHAr$] generated afforded the interesting complexes $Cp'_2Zr(\mu\text{-}\eta^1:\eta^1\text{-}N\text{-}N_2CHAr)(\mu\text{-}\eta^1:\eta^2\text{-}N,N,N'\text{-}N_2CHAr).ZrCp'_2$ **25** (Cp′ = C_5H_5, C_5H_4Me),[17,76] in which the symmetrical (**E**) and asymmetric (**F**) coordination of the diazoalkane has been established. The titanium and zirconium diphenylhydrazinate(2-) complexes $CpXM(\mu\text{-}\eta^1:\eta^1\text{-}N\text{-}N_2Ph_2)(\mu\text{-}\eta^1:\eta^2\text{-}N,N,N'\text{-}N_2Ph_2).MXCp$ (M = Ti; X = Cl; M = Zr; X = Cp), similar to complexes **25**, have also been synthesised.[76,77]



25a



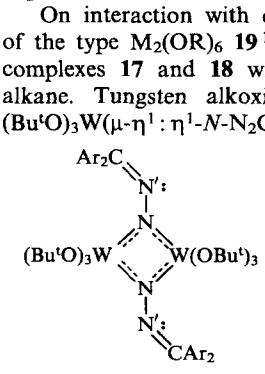
26

Cp′ = C_5H_4Me.

The interaction of the complex Cp_2NbH_3 **4a** with diazoacetate afforded the unique bimetallic complex [$CpNb\text{-}\eta^5\text{-}C_5H_4C.(CO_2Et)=N\text{-}\mu\text{-}\eta^1:\eta^1\text{-}N]_2$ **26** containing a diazoalkane ligand coordinated to the metal atom and simultaneously bound to one of the ligands.[73] The substitution of the Cp ligand in the metallocene complexes of the early transition metals is encountered extremely rarely. It has been suggested that the formation of complex **26** also includes a stage in which coordinatively unsaturated monometallic intermediates dimerise (see Section IV.1).

A bridged diazoalkane complex $[Cp_2Nb(\mu\text{-}N_2CPh_2)]_2$ [74] has been obtained from $Cp_2(Br)Nb(\eta^1\text{-}N\text{-}N_2CPh_2)$ **10c** and sodium naphthalide.

On interaction with diazoalkanes, molybdenum alkoxides of the type $M_2(OR)_6$ **19** [18] give rise to mono- and bi-metallic complexes **17** and **18** with η^1-*N*-coordination of the diazoalkane. Tungsten alkoxides afford the bridged complexes $(Bu^tO)_3W(\mu\text{-}\eta^1:\eta^1\text{-}N\text{-}N_2CAr_2)_2W(OBu^t)_3$ **27** in this reaction.



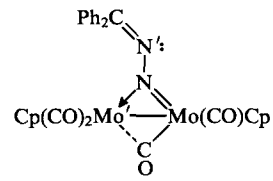
27a

Ar = C_6H_4Me-*p*.

The complexes $Rh_2(\mu\text{-}N_2CRCO_2Et)(CO)_2(dppm)_2$, where R = H or CO_2Et and dppm = $PPh_2CH_2PPh_2$,[76] have been obtained by replacing the bridging hydride atoms in $Rh_2(\mu\text{-}H)_2.(CO)_2(dppm)_2$ by the diazoalkane.

Coordination to the terminal nitrogen atom of the diazoalkane (related to type **E**) has been observed in the clusters $Os_3(CO)_9(\mu_3\text{-}PhC=CPh)(\mu_2\text{-}N\text{-}N_2CH_2)$,[70] $Fe_3(CO)_9(\mu_3\text{-}N\text{-}N_2.CPh_2)$,[80] $Co_4(CO)Cp_4(\mu_3\text{-}N\text{-}N_2CPh_2)$,[75] and $Ru_5(CO)_{12}(\mu_4\text{-}C\equiv CPh)(\mu_4\text{-}N\text{-}N_2CPh_2)(\mu\text{-}PPh_2)$,[72] the N—N′ bond being somewhat lengthened compared with that in the type **E** bimetallic complexes (Table 3).

The $\mu\text{-}\eta^1:\eta^1$-N-coordination of the diazoalkane (type **E**) has been observed in bimetallic molybdenum complexes in those cases where the groups R′ and R″ in this diazoalkane molecule are bulky and can prevent the additional coordination of the N′ atom as a consequence of steric hindrance. A coordination of this type has been observed in the complexes $Cp(CO)_2Mo(\mu\text{-}CO)(N_2CAr_2).Mo(CO)_2Cp$ **28** (Ar = Ph, C_6H_4Me-*p*).[65,66] According to spectroscopic data, at room temperature the diazoalkane bridge in complex **28** is fully symmetrical, but X-ray diffraction study of complex **28a** demonstrated some deviation from total symmetry.

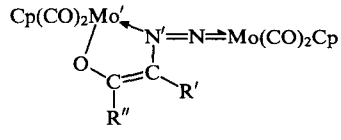


28a

It was shown later[64,65] that the ^1H NMR spectra of the complexes $Cp'(CO)_2Mo(\mu\text{-}CO)(N_2CR'R'')Mo(CO)Cp'$ **23** (Cp′ = C_5H_5, C_5H_4Me, C_5Me_5; R′ = R″ = Me; R′ = H, R″ = CO_2Et)[63,65] are only partly consistent with the structure established. In the case of the diazopropane derivative (R′ = R″ = Me), a slow isomerisation of two structures, **F** ⇄ **E**, was observed at room temperature on the basis of NMR spectroscopic data.[64] It has been suggested for the diazoacetic acid ester derivative **23b** (R′ = H, R″ = CO_2Et) [65] that thermodynamic equilibrium is established at room temperature between the complexes in which the N′ nitrogen atom is involved in type **F** coordination to one or several metal atoms.

It has been postulated that bridged type **E** and **F** complexes are formed as intermediates also in the reaction of diazoalkanes with other bimetallic complexes containing a multiple metal—metal bond. For example, in the interaction of complexes of the type $[Cp'(CO)_2W]_2$ with diazoalkanes at negative [below 0 °C (Ed.)] temperatures, the formation of type **E** and **F** complexes was observed, but only the products of the subsequent interactions, analogous to those obtained on heating the corresponding molybdenum analogues (see Section IV.1), were isolated.[81]

In the interaction of α-diazoketones with the molybdenum complex $Cp'(CO)_2Mo\equiv Mo(CO)_2Cp'$ **30** (Cp′ = C_5H_5, C_5Me_5), the Mo≡Mo bond is fully cleaved and type **G** complexes are formed with additional coordination of the oxygen atom of the oxo-group to one metal atom. The complexes $Cp'(CO)_2Mo(\mu\text{-}\eta^1:\eta^2\text{-}N,N',O\text{-}N_2C(R')=C(R'')OMo'(CO)_2Cp'$ **29** [Cp′ = C_5H_5, C_5Me_5; R′ = R″ = Ph; R′ = CO_2Et, R″ = OEt; R′—R″ = $C(O)CH_2CMe_2CH_2$] have been obtained in the same way.[64,65,69]



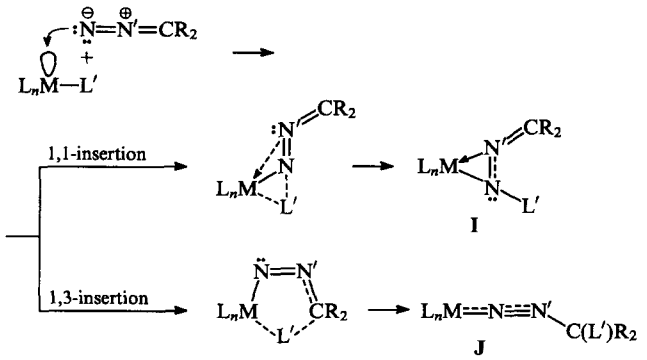
29a,b

29a: R′ = R″ = Ph.
29b: R′ = CO_2Et; R″ = OEt.

Type **H** complexes have not been isolated but it has been suggested that they are intermediates in the formation of carbenes from diazoalkanes[3,4,7] catalysed by bimetallic transition metal complexes.

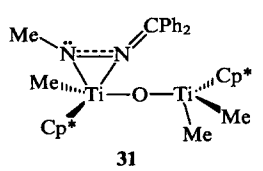
3. Reactions involving insertion in the M–L bond with formation of hydrazonate, alkyldiazene, and ketazine complexes

Diazoalkanes are capable of being inserted in highly reactive metal–ligand bonds (in the first place in M–H and M–C bonds) and the reaction can proceed as 1,1- or 1,3-insertion of the diazoalkanes. The η^2-*N,N'*-hydrazonate complexes **I** and alkyldiazene complexes **J** have been obtained in this way.

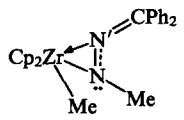


The 1,1-insertion reactions proceed as a rule more readily in those cases where the initial metal complex is coordinatively unsaturated and preliminary coordination of the diazoalkane promotes its subsequent insertion. However, the insertion product must be coordinatively unsaturated and stabilised as a result of the additional coordination of the nonterminal nitrogen atom (type **I** complex). The nonterminal nitrogen atom is not coordinated in insertion reactions with bridged complexes **K**.

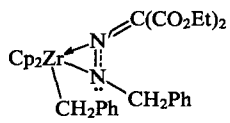
The reaction involving the insertion of N_2CPh_2 in the Ti–CH_3 bonds of the dinuclear and trinuclear titanium oxides $[Cp^*Me_2Ti]_2(\mu\text{-}O)$ and $[Cp^*MeTi(\mu\text{-}O)]_3$ ($Cp^* = C_5Me_5$) leads to the formation of hydrazonate complexes with η^2-*N,N'*-coordination (type **I**).[82] The reaction products are the following titanium complexes: $Cp^*Me_2Ti(\mu\text{-}O)TiMe(\eta^2\text{-}N,N'\text{-}NMe-N'=CPh_2)Cp^*$ **31** and $(Cp^*MeTi)_2(\mu\text{-}O)_3Ti(\eta^2\text{-}N,N'\text{-}NMe-N'=CPh_2)Cp^*$. Complex **31** can interact with another N_2CPh_2 molecule to form $(\mu\text{-}O)[TiMe(\eta^2\text{-}N,N'\text{-}NMe-N'=CPh_2)Cp^*]_2$. It has also been observed that diazoalkanes are inserted in the Zr–H, Zr–C, and Zr–P bonds of the corresponding zirconocene derivatives. The complexes $Cp_2ZrR(\eta^2\text{-}N,N'\text{-}NRN'=CR'_2)$ **32** (R = Me, CH_2Ph; R' = Ph, CO_2Et),[83,84] $Cp_2ZrCl(\eta^2\text{-}N,N'\text{-}NHN'=CPhAr)$ **33** (Ar = Ph, *o*-C_6H_4Br),[83–85] and $Cp_2Zr.[(\eta^2\text{-}N,N'\text{-}NR'N'PPh)_2PPh]$ **34** (R' = $CHCO_2Et$)[86] have been obtained similarly. Complex **33** has been synthesised also by the reaction of Cp_2ZrCl_2 with $LiHNN=CPh_2$, although the authors[17,77] assumed that only the η^1-*N*-coordination of the hydrazonate ligand takes place in it. It has been shown for complexes **32** and **33**[83–85] that only the *exo*-isomers are formed. An azametallocyclobutene derivative—the complex $Cp^*_2Zr.(\eta^2\text{-}N,C\text{-}CPh=CPh-NN'=CPh_2)$—has been obtained by inserting N_2CPh_2 in the acetylene complex $Cp^*_2Zr(C_2Ph_2)$.[87]



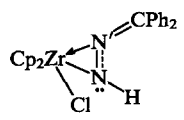
31



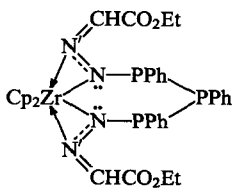
32a



32b

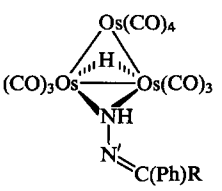


33a



34

Although the bridging hydride atoms in the rhodium complex $[Rh_2(\mu\text{-}H)_2(CO)_2(dppm)_2]$ are substituted in the reaction with diazoalkanes,[76] in the osmium cluster $(\mu\text{-}H)_2.Os_3(CO)_{10}$ the diazoalkane is inserted with formation of the complex $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}NH-N=CR'R'')$ **35** (R', R'' = H, Me, Ph).[88,89] The analogous ruthenium complexes $(\mu\text{-}H)Ru_3.(CO)_{10}(\mu_2\text{-}N\text{-}NH-N=CR'R'')$ have been obtained in the reaction of hydrazones with $Ru_3(CO)_{12}$;[90,91] when yet another CO molecule is lost, the complex $(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}N,N,N'\text{-}NH-N=CR'R'')$, with the μ_3-*N,N,N'*-coordination of the hydrazonate ligand, is formed.

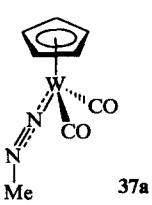


35a,b

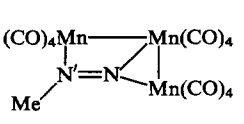
35a: R = Ph.
35b: R = Me.

1,3-Insertion has been observed only for metal hydride complexes. This is probably due to the great mobility of the H atom. The 1,3-insertion products are derivatives of alkyldiazenes $HN=N-CHR_2$, which are tautomeric forms of diazoalkanes (hydrazones) $H_2N-N=CR_2$. According to quantum-chemical calculations,[92] either one or other tautomeric form is more convenient (depending on R) for the simplest alkyl substituents R; the energy difference between them does not exceed 5 kcal mol^{-1}.

It has been found that the alkyldiazene complexes $CpM.(CO)_2(\eta^1\text{-}N\text{-}N=N-CHR'R'')$ **37** are formed as the main products in the reactions of $CpM(CO)_3H$ **36** (M = Mo, W) with the diazo-compounds $N_2CR'R''$ (R', R'' = H, Me, CO_2Et).[93–96] Under analogous conditions, the reaction of the manganese hydride $(CO)_5MnH$ with N_2CH_2 gives rise to a mixture of products,[54,97,98] from which the product of the insertion of diazomethane in the Mn–H bond, namely $(\mu_3\text{-}N,N,N'\text{-}N_2CH_3)[Mn(CO)_4]_3$ **38**, was obtained in ~10% yield.



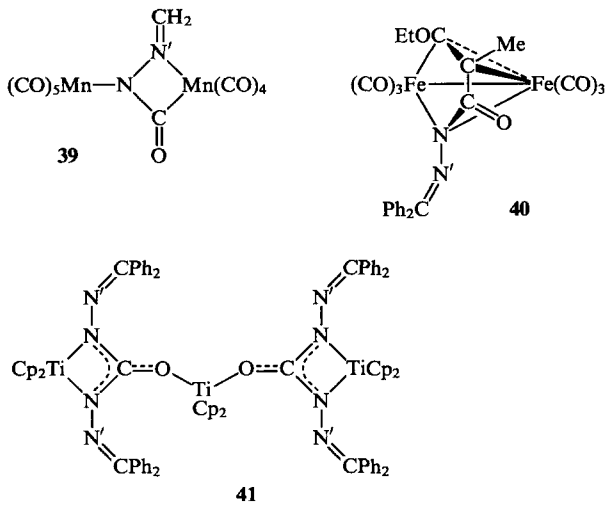
37a



38

The products of the insertion of N_2CH_2 in the M–CO multiple bond, i.e. the manganese carbohydrazonate complex $(CO)_5Mn(\mu\text{-}N,N',C\text{-}C(O)-NN'=CH_2)Mn(CO)_4$ **39**, is formed in the same reaction in 25%–30% yield.[54,98,99] The dinuclear

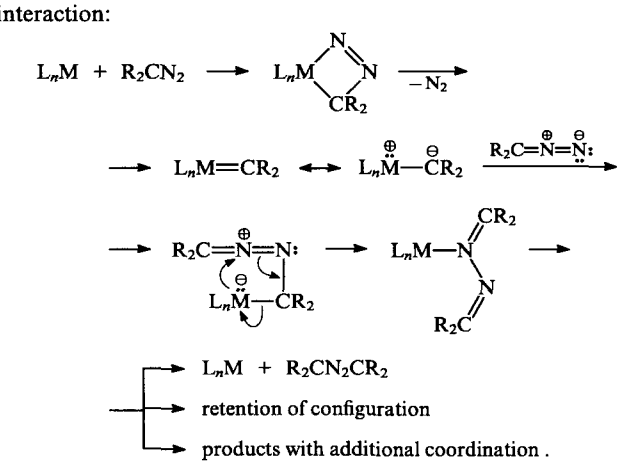
complex $Fe_2(CO)_6[Ph_2C{=}N'NC(O)C(Me)C(OEt)]$ **40**, also containing the carbohydrazonate fragment, has been obtained in the reaction of the cluster $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}COEt)$ with N_2CPh_2.[100] The double insertion of a diazoalkane in a M—CO bond has been observed in the interaction of $Cp_2Ti(CO)_2$ with N_2CPh_2. The product also contains a ligand of the carbohydrazonate type $(Cp_2Ti)_3[Ph_2CN_2C(O)N_2CPh_2]_2$ **41**.[9] On the other hand, the reaction of $Cp_2Ti(PMe_3)_{2-x}(CO)_x$ ($x = 0.1$) with N_2CPh_2 afforded a product with the η^1-*N*-coordination of the diazoalkane ligand—$Cp_2Ti(PMe_3)(N_2CPh_2)$ **9**.[31]



39 **40**

41

Diazoalkanes are capable of being inserted not only in a multiple M—CO bond in carbonyl complexes but also in a M=C double bond in carbene complexes. The products are then either ketazine complexes or a free ketazine (depending on the coordination capacity of the metal atom). The products of the interaction of diazoalkanes with transition metal complexes can also be carbene complexes (see Section III, 2). Generalising these results, a number of workers,[101—104] who observed the formation of ketazine complexes and the decomposition of diazoalkanes into a ketazine and nitrogen in the interaction of the diazoalkanes with transition metal complexes, proposed the following mechanism of this interaction:



Ketazine complexes have also been obtained by the direct interaction of ketazines with transition metal complexes, usually at elevated temperatures.[105]

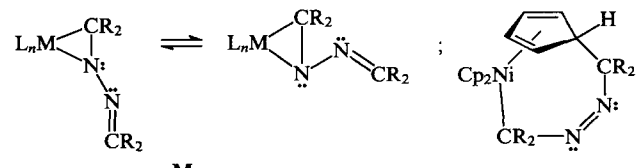
$[(\mu\text{-}OAc)_2\overline{Pd(\eta^2\text{-}N,C\text{-}Ar'_2CN'NC(Ar')\text{-}2\text{-}C_6H_3(4\text{-}OR))}]_2$

$Ar' = p\text{-}C_6H_4OR$; R = Alk.

The decomposition reactions of diazoalkanes, catalysed by transition metal complexes [for example, $Pd(OAc)_4$ [106] and $Ni(C_{12}H_{18})$ [38]] and proceeding with evolution of nitrogen, are encountered fairly often and correspond to the very simple mechanism

$$2\,N_2CR_2 \xrightarrow{ML_n} N_2 + R_2CN_2CR_2.$$

There are several ways in which ketazines may be coordinated in transition metal complexes. The π-(η^2-*N*,*C*)-coordination (type $\mathbf{M_1}$) of one of the C=N bonds of the ketazine has been proposed in studies at the beginning of the 1970s [24,101] for the complexes $L_2M(R'_2C{=}NN{=}CR'_2)$ (M = Pt, Pd, Ni; L = RNC, PR_3; $R' = CF_3$). The interaction of nickelocene with $N_2C(CF_3)_2$ afforded the compound $Cp_2Ni(C_6F_{12}N_2)$ **42**.[102] It is suggested that complex **42** has the structure $\mathbf{M_2}$. It is essential to note that the structures $\mathbf{M_1}$ and $\mathbf{M_2}$ presented have not been elucidated by objective methods.



$\mathbf{M_1}$ **42** (type $\mathbf{M_2}$)

It has been established that in ketazine complexes whose structure has been determined [these are in all cases the derivatives $N_2C(C_6H_4R\text{-}p)_2$, where R = H or Me] the transition metal atom is always coordinated solely to one nitrogen atom of the ketazine ligand. Three types of structures have been found:

(a) with η^1-*N*-coordination (type $\mathbf{M_3}$)

$Ar_2Pt(CO)(\eta^1\text{-}N\text{-}Ph_2CN_2CPh_2)$ ($Ar = C_6F_5$)[103];

(b) with η^2-*N*,*C*-coordination (type $\mathbf{M_4}$)

$(CO)_2(PPh_3)\overline{OsH[\eta^2\text{-}N,C\text{-}Ar'_2CN'NC(Ar')\text{-}2\text{-}C_6H_3(4\text{-}Me)]}$

$Ar' = C_6H_4Me\text{-}p$ [104]

$Ar\overline{Pt(CO)(\eta^2\text{-}N,C\text{-}Ph_2CN'NC(Ph)-C_6H_4\text{-}o)}$

$Ar = C_6F_5$ [103]

$[(\mu\text{-}OAc)_2\overline{Pd(\eta^2\text{-}N,C\text{-}Ar'_2CN'NC(Ar')\text{-}2\text{-}C_6H_3(4\text{-}OR))}]_2$

$Ar' = C_6H_4OR\text{-}p$; R = Alk.[105]

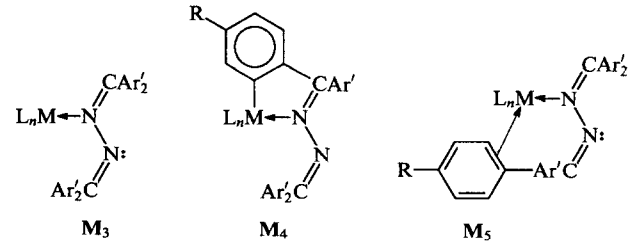
A case has also been described where the ketazine *ortho*-metallated at the benzene ring behaves as a bridging ligand, i.e. $(\mu\text{-}OAc_2)_4.Pd_3[\mu\text{-}\eta^2\text{:}\eta^2\text{-}(\text{-}NC(Ph)\text{-}C_6H_4\text{-}o)_2]$:[106]

(c) with η^2-π-coordination (type $\mathbf{M_5}$)

$Ar_2Pt(Ph_2C\text{-}\eta^1\text{-}NNC(Ph)\text{-}\eta^2\text{-}C_6H_5)$

$Ar = C_6F_5$.[103]

Thermolysis of the latter afforded the platinum complex $Ar_2Pt.[\eta^1\text{-}(C_6H_4\text{-}o)\text{-}C(Ph)\text{-}\eta^1\text{-}NNC(Ph)\text{-}\eta^2\text{-}C_6H_5)$,[103] for which both types of coordination were found simultaneously—$\mathbf{M_4}$ and $\mathbf{M_5}$.



$\mathbf{M_3}$ $\mathbf{M_4}$ $\mathbf{M_5}$

The structural parameters of a series of hydrazonate, alkyldiazene, carbohydrazonate, and ketazine complexes are presented in Table 4.

Table 4. Selected structural parameters of the hydrazonate, alkyldiazene, and ketazine complexes.

No.	Complex	Bond lengths/Å		Bond angles/deg		Ref.
		N–N′	N′–C	M–N–N′	N–N′–C	
	η^2-*N,N′*-Hydrazonate complexes					
31	$Cp^*Me_2Ti(\mu\text{-}O)TiMe(NMeN'{=}CPh_2)Cp^*$	1.33	1.30	78	126	82
	$Cp^* = C_5Me_5$		1.44[a]			
32a	$Cp_2ZrMe(NMe-N'{=}CPh_2)$	1.34	1.31	80	132	83, 84
			1.45[a]			
32b	$Cp_2ZrR(NR-N'{=}C(CO_2Et)_2)$	1.30	1.31	75	132	84
	$R = CH_2Ph$		1.47[a]			
33a	$Cp_2ZrCl(NH-N'{=}CPh_2)$	1.30	1.32	78	127	84
33a	$Cp_2ZrCl(NH-N'{=}CPh_2)$	1.35	1.30	78	126	85
34	$Cp_2Zr[(NR'-N'-PPh-)_2PPh]$	1.34	1.28[a]	83	126	86
	$R' = CHCO_2Et$	1.34	1.31[a]	80	125	
	η^3-*N,N,N′*-Hydrazonate complexes					
35a	$(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}NH-N'{=}CPh_2)$	1.43	1.29	[b]	116	88
35a	$(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}NH-N'{=}CPh_2)$	1.39	1.27	117	117	89
				116		
35b	$(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}NH-N'{=}CPhMe)$	1.42	1.28	117	118	89
				114		
	Alkyldiazene complexes					
37a	$CpW(CO)_2(\eta^1\text{-}N\text{-}N_2CH_3)$	1.22	1.48	173	117	96
38	$[Mn(CO)_4]_3(\mu_3\text{-}N,N,N'\text{-}N_2CH_3)$	1.22	1.57	146	112	54, 97
				120		
				107		
	Carbohydrazonate complexes					
39	$(CO)_5Mn(\mu\text{-}N,N',C\text{-}OCNN'CH_2)Mn(CO)_4$	1.39	1.28		124	54
40	$Fe_2(CO)_6[Ph_2CNNC(O)C(Me)C(OEt)]$	1.44	1.27	126	[b]	100
			1.41[a]	120		
41	$(Cp_2Ti)_3(Ph_2CN_2C(O)N_2CPh_2)_2$	1.38	1.31	119	114	12
		1.39	1.27	119	114	
	Ketazine complexes					
M4	$(CO)_2(PPh_3)OsH[\eta^2\text{-}N,C\text{-}Ar'_2CN'NC(Ar')\text{-}2\text{-}C_6H_3(4\text{-}Me)]$	1.41	1.27	118	120	104
	$Ar' = C_6H_4Me\text{-}p$		1.30[a]			

[a] The N–C bond length is indicated. [b] The value of the angle is not quoted.

4. Reactions with formation of other complexes

It was shown above that the diazoalkane complexes can be obtained from complexes containing coordinated molecular nitrogen.[40–50] However, there have also been cases where the opposite process — the cleavage of the diazoalkane in the coordination sphere of the metal and the coordination of the nitrogen thus produced (type **N**) — was observed in the interaction of diazoalkanes with transition metal complexes.[107,108]

$$(ON^*)Os(Cl)(PPh_3)_3 + IC(N_2)CO_2Et \longrightarrow$$

$$\longrightarrow EtO_2CCH{=}N^*(OH){-}Os(N_2)(Cl)_2(PPh_3)_2 \quad \mathbf{N}$$

$$[Ru(NH_3)_5(H_2O)]^{2+} \xrightarrow{N_2CHCO_2Et}$$

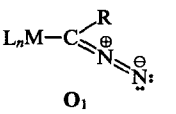
$$\longrightarrow [Ru(NH_3)_5(N_2)]^{2+} + (\mu\text{-}N_2)[Ru(NH_3)_5]_2^{4+}$$

These reactions are interesting because cleavage of the diazoalkane by transition metal complexes is accompanied much more frequently by the formation of the products of the interaction of the given metal complex with the carbene generated and the evolution of gaseous nitrogen (Section III. 2).

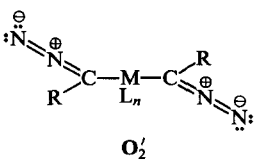
III. Complexes with the ligand coordinated through a carbon atom

1. Reactions involving the substitution of α-hydrogen or transmetallation with formation of α-diazoalkane complexes

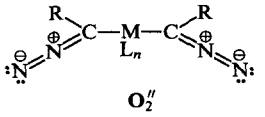
The coordination of a diazoalkane to a transition metal atom through the carbon atom attached to the diazo-group has been demonstrated only for those complexes in which the metal complex fragment (ML_n) is present as one (type **O**) or both (type **P**) substituents at the given carbon atom:



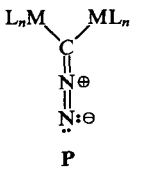
O_1



O_2'



O_2''

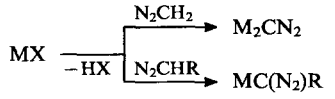


P

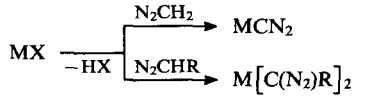
Table 5. Structural parameters of α-metallated diazoalkane complexes and free diazoalkanes.

Complex	Bond lengths/Å		Bond angles/deg		Ref.
	N–N′	N′–C	M–N–N′	N–N′–C	
Free diazoalkanes	1.12–1.13	1.28–1.32	–	–	61, 62
$(PMe_3)_3MeIRh[C(N_2)SiMe_3]$	1.09	1.30	119	175	114
$(PPh_3)_2ClPd[C(N_2)CO_2Et]$	1.16	1.28	122	177	112, 113
$(PBu_3)_2Pd[C(N_2)CO_2Et]_2$	1.13	1.28	120	176	113

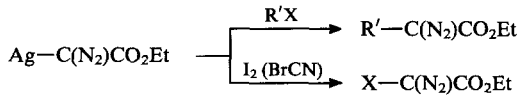
α-*C*-metallated diazoalkane derivatives of Group IB and IIB elements—silver,[109] mercury,[110,111] zinc, and cadmium[111]—have been fairly widely investigated. They have been synthesised directly from the corresponding inorganic compounds of the above metals and diazoalkanes. The compounds obtained can be used in the synthesis of substituted diazoalkanes.



M = Ag; X = $\frac{1}{2}$O.
M = RHg; X = NR_2, OR.

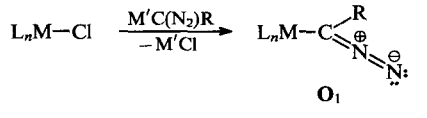


M = Hg; X = NR_2, $\frac{1}{2}$O, OR.
M = Zn, Cd; X = NR_2.



X = I, Br.

α-Metallated diazoalkane complexes of palladium,[112,113] rhodium,[114,115] yttrium, lutetium, and ytterbium[116] (type $\mathbf{O_1}$) are also known. They were obtained via a transmetallation reaction:



$\mathbf{O_1}$

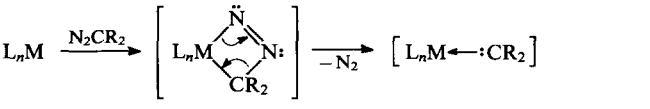
L_nM = Pd(Hal)$(PR'_3)_2$; M′ = Li, $\frac{1}{2}$Hg; R = CO_2Et, COMe, Ph.
L_nM = $Rh(PMe_3)_4$; M′ = Li; R = $SiMe_3$, $P(NR_2)S$, $P(NR_2)_2$.
L_nM = YCp^*_2, $LuCp^*_2$, $YbCp^*_2$; M′ = Li; R = $SiMe_3$.

Type $\mathbf{O_2}$ palladium complexes $(PR'_3)_2Pd[C(N_2)R]_2$ have been synthesised in a similar way.[113] Owing to the hindered rotation about the Pd–C bond in this complex, the conformational *anti*- and *syn*-isomers $\mathbf{O'_2}$ and $\mathbf{O''_2}$ were found to be present.

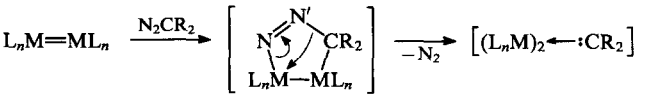
The IR spectra of the α-metallated diazoalkane complexes show a bathochromic shift of the absorption band due to the ν_{CNN} vibrations by 0–100 cm^{-1} relative to its position in the spectra of the free diazoalkanes. This finding is consistent with the observed lengthening of the N–N bond (Table 5). On the other hand, the C–N bond in α-metallated diazoalkane complexes is shorter than in the free diazoalkanes.

2. Reactions with evolution of nitrogen and the formation of carbene complexes

Apart from the coordination of the diazoalkane, the mono- and bi-metallic transition metal complexes can promote the cleavage of the diazoalkane with evolution of nitrogen and the formation of a carbene as an intermediate. It has been suggested that this stage of the interaction of the diazoalkane with the transition metal complex proceeds via a four-membered (type **D**) metallocycle in the case of monometallic complexes and a five-membered (type **H**) metallocycle in the case of bimetallic complexes.



D



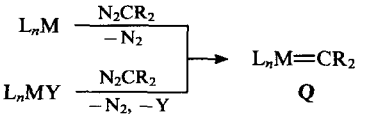
H

The intermediate coordinated carbene enters into subsequent reactions. The structure of the final product depends both on the nature of the diazoalkane itself and on the coordination capacities of the 'carbene' complexes mentioned above, on the presence in the latter of other highly reactive bonds, and also on the presence of other reactive substrates in the reaction mixture.

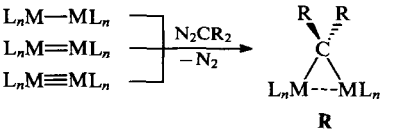
The reactions of transition metal complexes with the carbenes formed as a result of the interaction of the complexes with diazoalkanes will be examined here only to an extent sufficient to emphasise the principal features of these reactions. Since there are excellent reviews on this topic,[3,4,7] embracing the literature up to 1983, only specific studies carried out mainly since 1983 will be referred to.

a. The addition of the carbene to transition metal complexes

The simplest version of the reaction between transition metal complexes and the carbenes generated involves the addition of the latter either to a coordinatively unsaturated monometallic complex [or the substitution of another readily eliminated ligand Y with formation of carbene complexes (type **Q**)] or its addition to the metal–metal bond of a dinuclear complex with formation of methylene or other bridged complexes (Type **R**).



Q

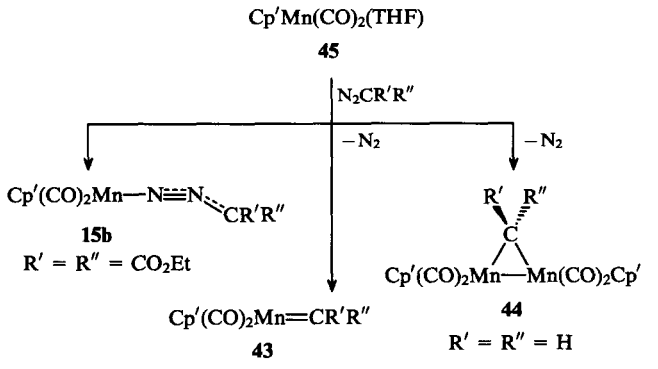


R

For example, the complex $(PPh_3)_3(NO)ClOs(=CH_2)$ has been obtained by the reaction of $(PPh_3)_3(NO)ClOs$ with N_2CH_2,[117] while the interaction of the molybdenum and tungsten complexes $M(N_2)_2(dppe)_2$ **16b** with N_2CH_2[25] leads to

the formation of $M(CH_2)_2(dppe)_2$. The products **15b**, **43**, and **44** have been synthesised by the reaction of $Cp'Mn(CO)_2(THF)$ **45** ($Cp' = C_5H_5$, C_5H_4Me) with diazoalkanes (Scheme 1).[3,34,118]

Scheme 1

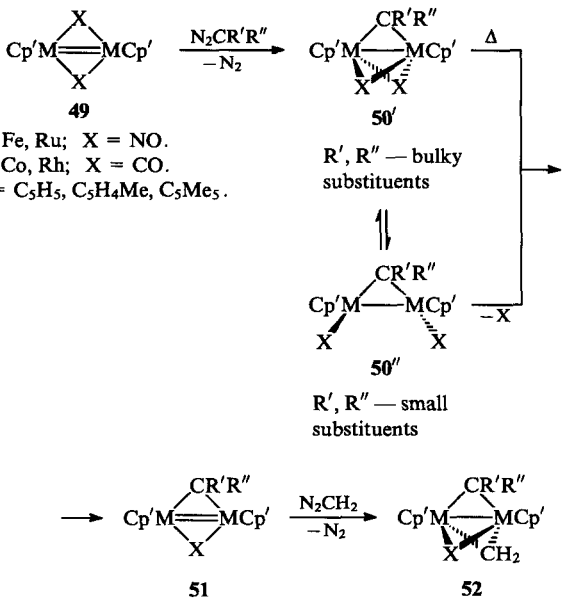


R′ = Ar; R″ = various groups.

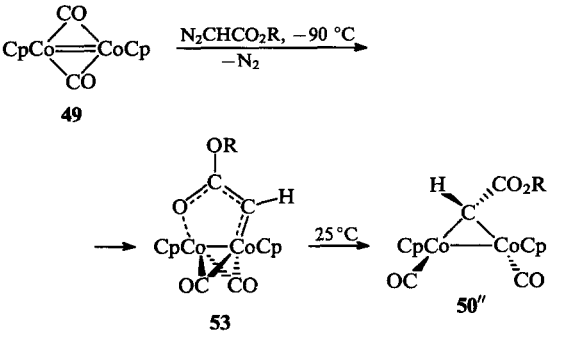
A multiplicity of various compounds have been obtained by the reaction of $Cp'_2Mo_2(CO)_4$ **46** ($Cp' = C_5H_5$, C_5H_4Me, C_5Me_5) with diazoalkanes.[65] The carbene complex **18**, the methylene-bridged complexes **24** and **47**, and the σ,π-bridged complexes **20** and **48** have been synthesised apart from the μ-η¹ : η¹-*N,N*-bridged diazoalkane complexes **18**, **24**, and **28**, the μ-η¹ : η²-*N,N,N'*-bridged diazoalkane complex **23**, and the μ-η¹ : η²-*N,N',O*-bridged diazoalkane complex **30** [Sic. Ed. possibly **29** is intended] (Scheme 2).

It is seen from Schemes 1 and 2 that the cleavage of the diazoalkane into nitrogen and a carbene is more likely when the carbon atom of the diazoalkane is more accessible (N_2CH_2) or when the substituents R′ and R″ in $N_2CR'R''$ are capable of stabilising the intermediate carbene.

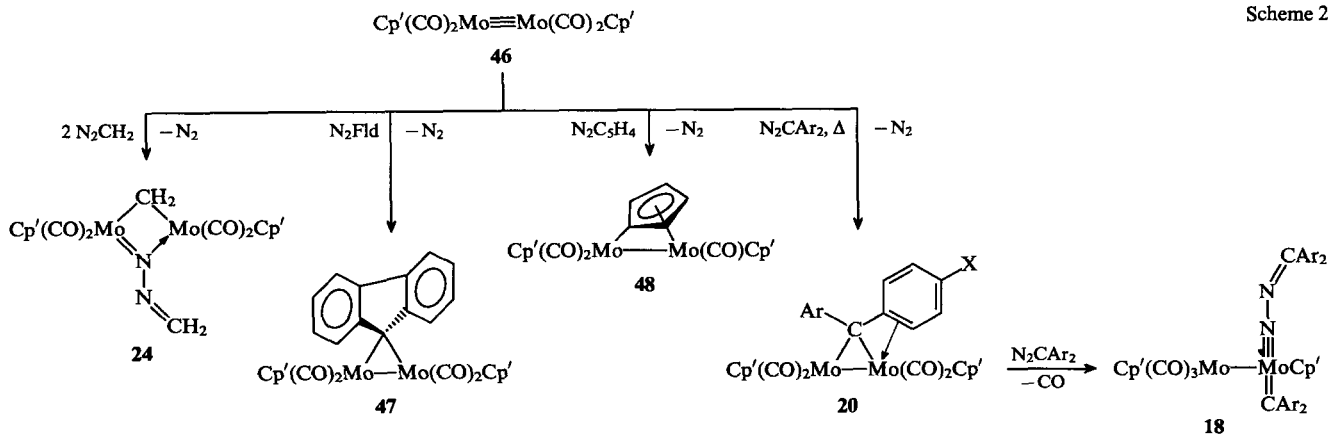
The cleavage of the diazoalkane and the formation of new bridging ligands are almost always observed in the interaction of diazoalkanes with dinuclear complexes of Group VIII transition metals $(Cp'MX)_2$ **49** (M = Fe, Ru, Co, Rh, Ni)[3,4,7,66,119–125] containing a metal–metal double bond. If the substituents R′ and R″ are relatively bulky (for example Ar), then complex **50′** with three bridging ligands obtained initially is usually the final product. If the groups R′ and R″ are small (H, n-alkyl), then the isomer **50″**, in which the ligands X (NO, CO) are terminal, is more stable. Thermodynamic equilibrium is observed between the two isomers. On heating they can both lose one molecule of X, affording complex **51**, which can react with yet another equivalent of N_2CH_2, forming thereby complex **52** with two methylene bridging ligands.

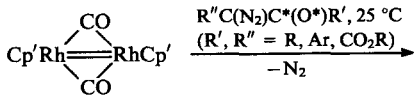


If the diazoacetic acid esters are used in the given reaction with cobalt complexes,[3] then at a reduced temperature it is possible to obtain complexes **53** with the bridging μ-η¹ : η¹-*C,O*-coordination of the carbene and, when α-diazoketones are introduced into the reaction with rhodium complexes, then more complex products **54** are formed at an elevated temperature.[3,121]

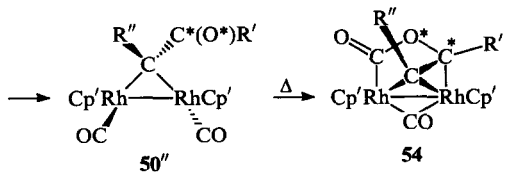


Scheme 2



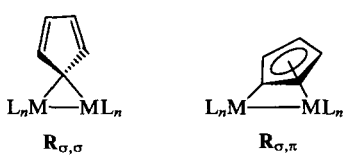


49



50″ 54

Certain carbene ligands may be coordinated in different ways in bimetallic complexes. For example, both μ-η^1: η^1- coordination (type $\mathbf{R}_{\sigma,\sigma}$) in $[CpFe(\mu\text{-}NO)]_2(\mu\text{-}C_5H_4)$, $[Cp^*Co(\mu\text{-}CO)]_2 \cdot (\mu\text{-}C_5Cl_4)$ and in all the fluorene complexes and μ-η^1: η^5-coordination (type $\mathbf{R}_{\sigma,\pi}$) in the dimeric complexes $Cp_2(CO)_3 \cdot Mo_2(\mu\text{-}C_5H_4)$ and $[Cp^*Co(\mu\text{-}CO)]_2(\mu\text{-}C_5H_4)$ have been found for the cyclopentadienylidene ligand.[3,126,127]



$\mathbf{R}_{\sigma,\sigma}$ $\mathbf{R}_{\sigma,\pi}$

It has been found that certain carbene complexes obtained from α-diazoketones may rearrange with formation of π-ketene complexes.[3]

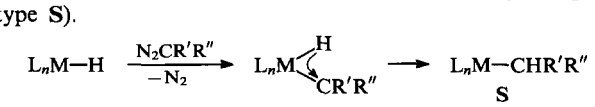
Instead of diazoalkanes, their precursors — hydrazones (in the presence of MnO_2) or *N*-alkyl-*N*-nitrosoureas — have been used successfully in the synthesis of carbene and related complexes.[3,124]

Bridged methylene complexes have also been synthesised by inserting diazoalkanes in the Pt–Pt bond in a platinum complex[128] or by substituting the bridging groups NCMe in an osmium complex[129] and CO in a palladium complex.[130]

b. Insertion of the carbene in the metal–ligand bond

Another version of the interaction of transition metal complexes with carbenes generated from diazoalkanes involves the insertion of the carbenes in metal–ligand bonds. These reactions usually take place at reduced temperatures — under conditions where the diazoalkanes themselves are stable. However, certain reactions require either elevated temperatures or UV irradiation, i.e. conditions under which the diazoalkanes themselves decompose, forming carbenes initially.[131] It is at present impossible to draw a clear-cut boundary between the thermal or photolytic decomposition of diazoalkanes and their decomposition on interaction with transition metal complexes.

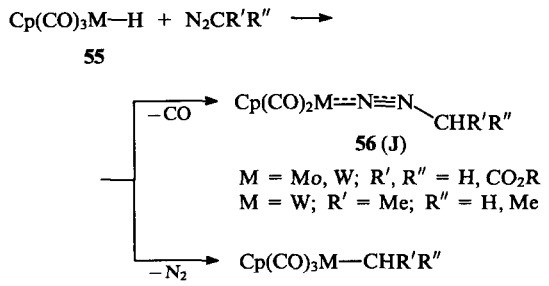
Since the M–H bond belongs to the class of the most reactive M–L bonds, it is to be expected that the carbene may be inserted in this bond too. This results in the formation of alkyl complexes (type **S**).



S

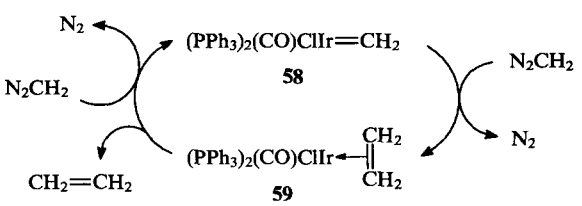
Thus the reactions of $Cp_2Zr(H)Cl$ with N_2CH_2[73] and of $(CO)_5MnH$ and $Cl(PEt_3)_2PtH$ with $N_2C(CF_3)_2$[132,133] afforded the corresponding alkyl complexes. One of the complexes of this type, namely $Fp-CH(CF_3)_2$, where Fp = $Cp(CO)_2Fe$, has been synthesised quite unexpectedly in the reaction of Fp_2 with $N_2C(CF_3)_2$ in THF.[34] The solvent served as the source of hydrogen in this process.

The interaction of molybdenum and tungsten hydride complexes $Cp(CO)_3MH$ **55** with diazoalkanes[95] leads to a mixture of products of the insertion of the diazoalkanes (compounds **56**) and carbenes (compounds **57**) in M–H bonds. The ratio of the alkyldiazene complex **56** (type **J**) and the alkyl complex **57** (type **S**) depends on the nature of the substituents R′ and R″ in the diazoalkane.



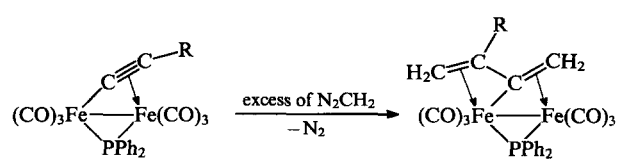
M = Mo, W; R′ = H; R″ = H, Ar.
M = W; R′ = Me; R″ = H, Me.

The insertion of the carbene has been observed also in metal–carbon multiple bonds. For example, the carbene complex of iridium **58** gives rise to the ethylene complex **59** (type **T**) on interaction with diazomethane.[134] When an excess of N_2CH_2 is used, the process proceeds as catalytic decomposition of the latter into nitrogen and ethylene.



Diazomethane diluted with an inert gas decomposes similarly on the surfaces of transition metals (Ni, Pd, Fe, Co, Ru, Cu),[136] which results in the formation of ethylene and nitrogen, while its reaction in a mixture with hydrogen affords a mixture of alkanes. A reaction mechanism involving the formation of carbenes coordinated on the surfaces of metals has been proposed[135] and the reaction has been compared with the Fischer–Tropsch reaction.

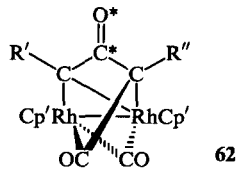
The interaction of the dinuclear iron complex **60**,[136] containing a π-bound alkyne, with diazomethane leads to the butadiene complex **61**.



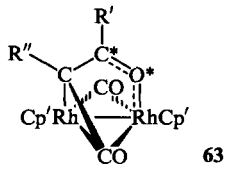
60 61

A similar reaction has been described also for a trinuclear ruthenium complex.[137]

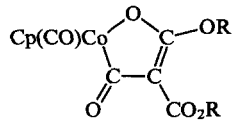
If the reaction of the rhodium complex $[Cp'Rh(\mu\text{-}CO)]_2$ (Rh = Rh) **49** ($Cp' = C_5Me_5$) described above is carried out with diazodimedone ($R'C^*(O^*)C(N_2)R''$, where R′ = R″ = Ph or R′–R″ = $-CH_2CMe_2CH_2CO-$)[3,121] or benzoylphenyldiazomethane, it is possible to obtain more involved complexes **62** and **63**, which are the products of the insertion of the carbene in the Rh–CO bond. The insertion of the carbene formed from diazomalonate in the Co–CO bond of the monomeric analogue of complex **49**,[3,7] leading to complex **64** (type **U**) with additional coordination of the oxygen atom of the carboxy-group, has also been described.



62 R′ = R″ = Ph.



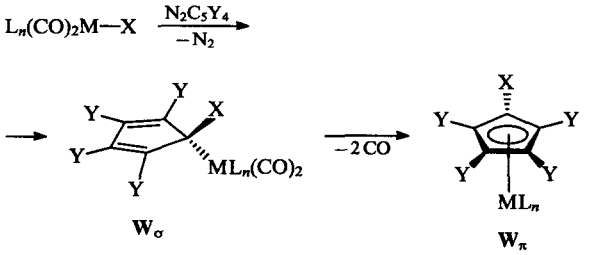
63 R′–R″ = $C(O)CH_2CMe_2CH_2$.



64 R = Me, Et.

The synthesis of the η^2-*C*,*C*-ketene complex $Cp'Mn(CO)_2.[C(O)-CR_2]$ (CR_2 = 9-anthron-10-ylidene) (type **V**) from $Cp'Mn(CO)_3$ and N_2CR_2 catalysed by the complex $CpMn.(CO)_3(THF)$ can serve as the next example of the reaction involving the insertion of the carbene in the M–CO bond.[3]

The insertion of the carbene generated from $N_2C(CF_3)_2$ in metal–halogen bonds has been described[24] for the platinum and palladium complexes $(PhCN)_2MCl_2$. The complex $(PhCN)_2.M[C(CF_3)_2Cl]_2$ (type **W**) is then formed. The carbenes obtained from substituted diazocyclopentadienes are readily inserted in metal–halogen bonds. The reaction leads to the formation of halo-substituted 5-cyclopentadienyl complexes ($\mathbf{W}_\sigma$).[3] The reactions proceed tentatively via the formation of η^1-cyclopentadienyl complexes ($\mathbf{W}_\pi$), which were successfully detected in some cases [ML_n = $Mn(CO)_3$; X = Cl, Br; Y = Cl].



ML_n = $Mn(CO)_3$, $Re(CO)_3$, $Fe(CO)_2X$, RhL_2;
X = Cl, Br, I; C_5Y_4 = C_5H_4, C_5X_4, indenyl.

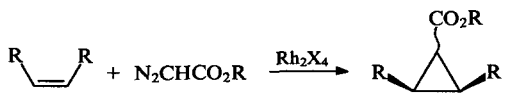
The insertion of carbenes obtained from various diazoalkanes in the Co–S and Rh–S bonds has also been observed.[138]

c. Reactions of the carbenes with other reactive substrates

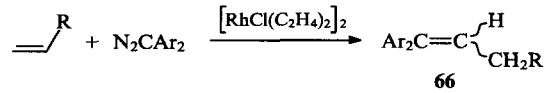
The carbenes generated from diazoalkanes can react with other reactive substrates in the reaction mixture. In such cases, the transition metal complexes behave as catalysts of the reactions.

There is in fact a large amount of information in the literature about reactions of this kind and reviews on this topic have appeared regularly (for example those of Hegedus[139] and Shapiro et al.[140]) and they will therefore not be described in this review.

We shall only note that among these processes the greatest importance attaches to the reactions of diazoalkanes with alkenes catalysed by transition metal complexes, which lead to the formation of cyclopropanes **65**[139] or substituted alkenes **66**.[29,37]



65



66

IV. Reactions of diazoalkane complexes

Diazoalkane complexes, i.e. complexes with coordinated diazoalkanes of types **B**, **C**, **E**, **F**, and **O**, are of undoubted theoretical interest as an individual class of compounds. In this sense, they have been thoroughly characterised structurally: their parameters differ from those of the free diazoalkanes. However, in order to obtain exhaustive information about such complexes, it is essential to know to what extent the coordination to the transition metal atom promotes a change in the electron density and polarity of the bonds and hence a change in the reactivity of the coordinated diazoalkane ligands compared with the free diazoalkanes.

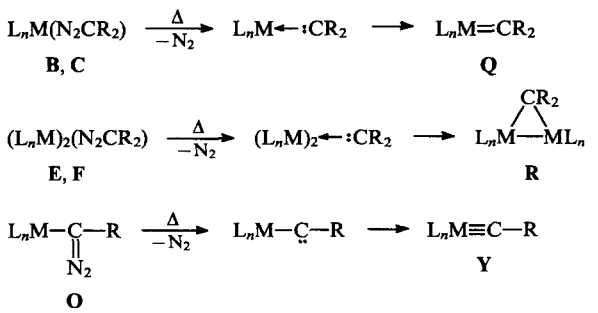
There have been few studies on the reactions of diazoalkane complexes of transition metals and they have almost all been carried out during the last decade. The diazoalkane complexes obtained were usually introduced into other reactions. Hitherto there have been no systematic studies on the reactions of diazoalkane complexes.

The available information about the reactions of diazoalkane complexes can be divided into two groups: studies involving the investigation of the products of the thermolysis of diazoalkane complexes and studies on the interaction of diazoalkane complexes with different classes of reagents.

1. Thermolysis of diazoalkane complexes

The majority of diazoalkane complexes have a limited thermal stability. When they are heated, nitrogen is usually evolved and it has been assumed tentatively that a carbene is formed and interacts with the initial complex. In principle, these are the products which have been obtained by the reaction of diazoalkanes with transition metal complexes (see Section III.2). The difference is insignificant and in essence consists only in the fact that some diazoalkane complexes decompose even below room temperature, whilst others are stable under these conditions. When the product of the reaction of the carbene with the initial complex is formed directly (sometimes at reduced temperatures), it is possible to detect diazo-complexes, which are converted into more stable products on slight heating.[6]

The thermolysis of diazoalkane complexes proceeds mainly in three ways. In the first, simplest version of the thermolysis, the evolution of nitrogen and the formation of carbene (type **Q**) or bridged methylene (type **R**) complexes is observed, while in the case of α-metallated diazoalkane complexes (type **O**) carbyne complexes are obtained (type **Y**).



For example, the carbene complex $[Cp(CO)_2Mo]_2(\mu\text{-}CPh_2)$ **20** has been synthesised from $[Cp(CO)_2Mo]_2(\mu\text{-}N_2CPh_2)$ **28a**,[65] while the complex $(PEt_3)_2Pd(CCO_2Et)_2$ has been obtained from $(PEt_3)_2Pd[C(N_2)CO_2Et]_2$.[113]

Together with the hydrazone $H_2NN=CPh_2$, the complex $Cp_2(Cl)Zr(\eta^2\text{-}NH-N=CPh_2)$ **33a**[73] gave rise to its disproportionation products—molecular nitrogen, Cp_2ZrCl_2, and the carbene complex $[Cp_2Zr(\mu\text{-}CPh_2)]_2$.

The second type of thermolysis occurs when the initial transition metal complex is insufficiently reactive in relation to the carbene or it does not form a sufficiently strong bond with the lattice. The formation of the corresponding ketazine is then observed. Ketazines are the main products of the thermolysis[104]

and photolysis[131] of the diazoalkanes themselves. In the case of α-metallated diazoalkane type **O** complexes, quantitative evolution of nitrogen is observed and the corresponding acetylenes are formed. Alkenes and alkanes may be obtained as side products in the first reaction and alkenes in the second.

$$L_nM(N_2CR_2) \xrightarrow[-N_2]{\Delta} L_nM{\leftarrow}{:}CR_2 \xrightarrow{L_nM(N_2CR_2)}$$

B, C

$$\longrightarrow L_nM + R_2C{=}N{-}N{=}CR_2$$

$$(+ R_2C{=}CR_2 + R_2HC{-}CHR_2)$$

$$L_nM{-}\underset{\underset{N_2}{\|}}{C}{-}R \xrightarrow[-N_2]{\Delta} L_nM{-}\ddot{C}{-}R \xrightarrow[-N_2]{L_nM[C(N_2)R]}$$

O

$$\longrightarrow L_nM + R{-}C{\equiv}C{-}R \ (+RHC{=}CHR)$$

For example, diphenylacetylene with an admixture of stilbene has been synthesised from the complex $(PEt_3)_2Pd[C(N_2)Ph]_2$,[113] while thermolysis of $(Bu^tNC)_2Ni(N_2Fld)$ **2** in the presence of phosphine[10] afforded fluorenone azine and $(Bu^tNC)_2Ni(PPh_3)_2$ as the main products. The formation of the products of the coupling of the carbenes to other reactive ligands is possible. For example, thermolysis of the nickel complexes $(Bu^tNC)_2.Ni(N_2CR_2)$ [CR_2 = Fld, CPh_2, $C(CN)_2$] without phosphine afforded a mixture of the corresponding azine and the ketene imine $(R_2C{=}C{=}N{-}Bu^t)$.[9,10] For CR_2 = CPh_2 or $C(CN)_2$, the latter gives rise to the complex $(Bu^tNC)_2Ni(\eta^2\text{-}N,C\text{-}(Bu^t).N{=}C{=}CR_2)$.

Ketazines have been obtained in the reaction of diazoalkane complexes **3**[21,22] and **33**[85] of the oxophilic early transition metals (Nb and Zr) with atmospheric oxygen. Oxidation of the niobium complexes **3** results in the formation also of the free diazoalkanes.

$$Cp_2Zr(Cl)(HNNCPhAr) \xrightarrow{O_2}$$

33

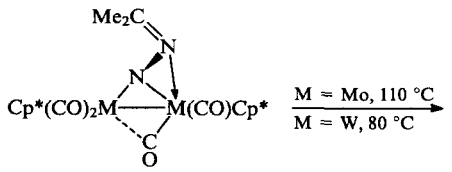
$$\longrightarrow [Cp_2ZrCl]_2O + N_2 + ArPhC{=}N{-}N{=}CPhAr$$

$$Cp_2Nb(H)(N_2CPhAr) \xrightarrow{O_2}$$

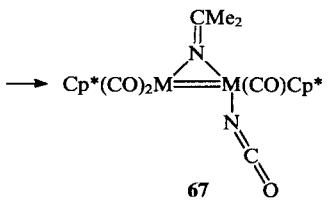
3

$$\longrightarrow (Cp_2NbO)_n + N_2 + ArPhC{=}N{-}N{=}CPhAr + N_2CPhAr$$

The third type of thermolysis comprises special cases where moderate heating can result in rearrangements or other structural changes in the molecules of the diazoalkane complexes. Thus the N–N bond is ruptured in the bridged diazopropane complexes **23a** of molybdenum[67] and tungsten[81] and in the μ-alkylideneaminometal isocyanate complex **67**.



23a

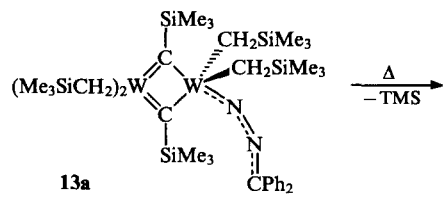


67

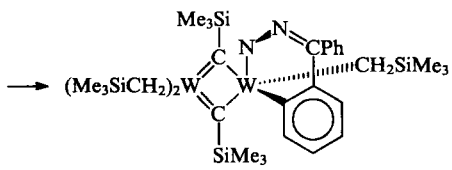
$Cp^* = C_5Me_5$.

The same process has been described also for a tungsten complex of diazocyclopentadiene,[81] but it occurs already at −10 °C. The molybdenum bimetallic complex **67** $Cp^*(CO)_2Mo.(\mu\text{-}\eta^1:\eta^2\text{-}N_2CH_2)(\mu\text{-}CH_2)Mo(CO)_2Cp^*$ of a similar type loses one CO molecule on heating and isomerises to the complex $Cp^*(CO)_2Mo(\mu\text{-}\eta^1:\eta^1\text{-}N{=}CH_2)Mo(\eta^1\text{-}N{=}CH_2)(CO)_2Cp^*$ containing two different alkylideneamino-groups.

In a crystal the M–N–N fragments of the η^1-*N*-diazoalkane ligands (Table 1) are usually almost linear (the M–N–N and N–N–C angles are 153°–177° and 117°–151° respectively). However, reactions have been discovered in which the M–N–N–C fragment is distorted, which promotes the intramolecular interaction of the reactive bonds of the CR_2 group with metallic or other reaction centres in the molecule of the complex. For example, when the diphenyldiazomethane complex of tungsten **13a** is heated, the metal is inserted in a C–H bond of the benzene ring of the diazoalkane.[17] This reaction results in the formation of the product **68** containing a metalpyridazine ring.



13a



68

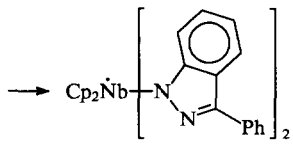
Whereas the interaction of Cp_2NbH_3 **4a** with $N_2C(Ph).(C_6H_4Br\text{-}o)$ at room temperature results in the formation of the η^1-*N*-diazoalkane complex **3b**, moderate heating of complex **4a** with an excess of the same diazoalkane afforded the bisindazole complex **69**.[22]

$$Cp_2NbH_3 \xrightarrow[25\,^\circ C]{N_2C(Ph)(o\text{-}C_6H_4Br)}$$

4a

$$\longrightarrow Cp_2Nb(H)NNC(Ph)(o\text{-}C_6H_4Br) \xrightarrow[50-60\,^\circ C]{N_2C(Ph)(o\text{-}C_6H_4Br)}$$

3b



69

In the interaction of compound **4a** with ethyl diazoacetate, the unstable η^1-*N*-diazoalkane complex **3c** is formed initially and is then slowly converted into complex **26** substituted in the Cp ring.[22,73]

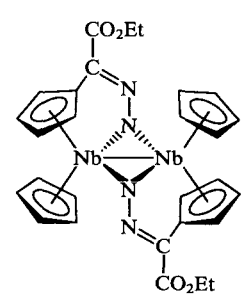
Cp_2NbH_3

4a

$\downarrow N_2CHCO_2Et$

$Cp_2Nb(H)NNCHCO_2Et$ →

3c



26

Thermolysis of the complex $(PPh_3)_2ClIr[N_2C(COPh)_2]$ afforded[140] the products of the *ortho*-metallation of the benzene ring of both the dibenzoyldiazomethane ligand and the triphenylphosphine ligand.

It has been found that, when the iridium complex $(PPr^i_3)_2.ClH_2Ir(N_2CPh_2)$ is heated,[29] a reaction which is the opposite of its formation reaction takes place—diphenyldiazomethane and the coordinatively unsaturated complex $IrH_2Cl(PPr^i_3)_2$ are formed.

When the hydrazonate complex $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}NH\text{-}N{=}CMe_2)$ obtained from $Os_3(\mu\text{-}H)_2(CO)_{10}$ and diazopropane is heated, it loses nitrogen and the 'carbene', reforming the cluster $Os_3(\mu\text{-}H)_2(CO)_{10}$.[89]

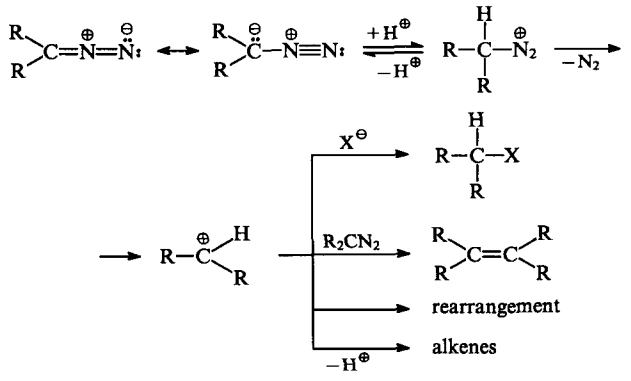
Photolytic reactions can sometimes lead to products related to the thermolysis product. As already stated above, diazoalkanes themselves usually afford ketazines in both these reactions. Unfortunately, special studies of the effect of UV radiation have been scarcely performed.

So far as we are aware, only one case of photolytic decomposition has been described in the literature, namely that of the diazoalkane complex[30] $(PPr^i_3)_2MeIr(N_2CPh_2)$, the product of which is the complex $(PPr^i_3)_2MeIr(N_2)$ with coordinated molecular nitrogen (structural type **N**).

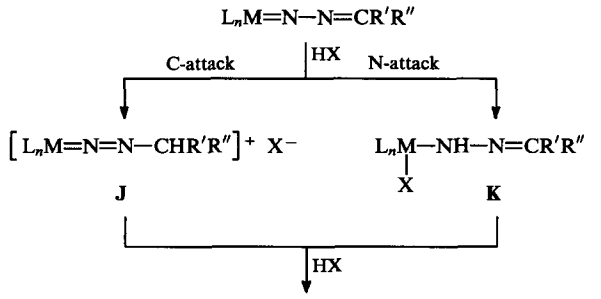
2. Interaction of diazoalkane complexes with electrophiles

In order to account for the reactions of diazoalkanes coordinated to transition metal atoms with other reagents, it is necessary to analyse the distribution of electron density in this diazo-ligand. Schwartz and coworkers,[17,77,142] claim, on the basis of reactions with the 'metalloazine' complexes of zirconium, that these compounds are exceptionally easily subjected to electrophilic attack on the carbon atom, i.e. a characteristic feature of the diazoalkane fragment in relation to this carbon atom is the repolarisation ('umpolung') of the quasi-carbonyl group of which it is a derivative.

As a consequence of the attack by a proton on the carbon atom of the diazo-group, the diazoalkanes themselves lose nitrogen in the reaction with protic acids[143] and give rise to a carbonium ion, which may be stabilised as a result of reactions with a nucleophile X and a diazoalkane, rearrangement, or deprotonation. Thus the decomposition of diazoalkanes in an acid medium can afford different products depending on the nature of the substituents R in the diazoalkane and the nucleophile present.



The protonation of the coordinated diazoalkanes can be directed both to the carbon atom and to the terminal nitrogen atom, while on treatment with a stoichiometric amount of acid the protonation products obtained initially (products of type **J** and **K**) are usually stable. Only on interaction with an excess of acid does the diazoalkane ligand decompose with formation of organic compounds.



products of the dissociation of the M − N(N − C) bonds

The above hypothesis concerning the direction of electrophilic attack on a carbon atom of the coordinated diazoalkane in the reaction with acids was confirmed directly in only one case—in the reaction of $[Rh_2(\mu\text{-}N_2CHCO_2Et)(CO)_2(dppm)_2]$ with HBF_4,[76] which leads to the formation of the cationic alkyldiazene complex $[Rh_2(\mu\text{-}N_2CH_2CO_2Et)(CO)_2(dppm)_2]BF_4$. The reaction is reversible—the initial diazoacetate complex was obtained on interaction with EtONa.

The interaction with HBF_4 resulted in the conversion of the related diazomalonate complex $[Rh_2(\mu\text{-}N_2C(CO_2Et)_2)(CO)_2.(dppm)_2]$ into $[Rh_2(\mu\text{-}H)(CO)_2(dppm)_2]BF_4$.[76]

In the remaining cases described, the site of attack by the proton is not a carbon atom but the terminal nitrogen atom of the diazo-group. The diazoalkane then undergoes a formal transformation from a hydrazonato(2-)-ligand (type **C**) into a hydroazonato(1-)-ligand (type **K**). Overall, the reaction with one equivalent of hydrogen halide proceeds as addition of HX to the metal−nitrogen bond. For example, the diazoalkanetungsten complex **11c** reacts with one equivalent of HBr via this mechanism.[42]

$$[(PMe_2Ph)_3Br_2W{=}N{-}N{=}CMe_2] \xrightarrow{1\ \text{equiv. HBr}}$$

11c

$$\longrightarrow [(PMe_2Ph)_3Br_3W{-}NH{-}N{=}CMe_2]$$

A mixture of products containing $WBr_4(PMe_2Ph)_2$ (65%), hydrazine, and acetone ketazine (25%−30%) was obtained by reaction with HBr. The cationic complex $[WBr(N_2CH_2).(dppe)_2]^+Br^-$ does not react with HBr at all.[47] The interaction of another tungsten complex **1a** with an excess of HBr afforded[30] the product of the addition of two HBr molecules (compound **70**), which slowly decomposed with formation of a hydrazone.

$$(Me_2NCS_2)_2(CO)W(=N{-}N{=}CHAr) \xrightarrow[-CO]{\text{excess of HBr}}$$

1a

$$\longrightarrow (Me_2NCS)_2Br_2W(N_2H_2CHAr) \longrightarrow$$

70

$$\longrightarrow (Me_2NCS)_2WBr_2 + ArCH{=}NNH_2$$

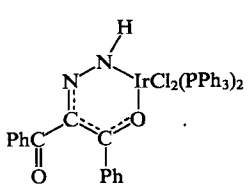
Ar = C_6H_4Me-*p*.

In the interaction of the iridium complex **8b** with HCl, the oxidative addition of hydrogen chloride takes place initially and is followed by a shift of the proton with a rearrangement of the coordination sphere.[26]

$$(PPh_3)_2ClIr[N_2C(COPh)_2] \xrightarrow{HCl}$$

8b

$$\longrightarrow (PPh_3)_2Cl_2HIr[N_2C(COPh)_2] \longrightarrow$$



The complete decomposition of the diazoalkane coordinated to a transition metal atom has been described[13] for diazoalkane complexes **71** of vanadocene.

$$Cp_2V(N_2CR'R'') \xrightarrow[-N_2]{\text{excess of HCl}} Cp_2VCl_2 + R''R'CHCl + R''R'CH{-}CHR'R''$$

71

The interaction of the dinuclear diazoalkane complex **25b** with $Et_3O^+BF_4^-$ (or EtI),[77] which resulted in the formation of a *N*-alkylated hydrazone **72** and a *N*- and *C*-alkylated hydrazone **73** (in approximately equal amounts), is an example of the reactions of diazoalkane complexes with aprotic electrophiles.

$$[Cp_2Zr(\mu\text{-}N_2CHPh)]_2 \xrightarrow[or\ EtI]{Et_3O^+BF_4^-} \text{Ph(H)C=N-N(H)Et} + \text{Ph(Et)C=N-N(H)Et}$$

25b **72** **73**

Free diazoalkanes are known to decompose on treatment with the halogens,[143] producing nitrogen and geminal dihaloalkanes. On the other hand, the interaction of the molybdenum and tungsten complexes $(R_2NCS_2)_2(CO)M(N_2CHAr)$ (**1a**) (Ar = C_6H_4Me-*p*) with an equimolar amount of chlorine or bromine[30] entails the exchange of CO for halogen atoms and the formation of the complex $(R_2NCS_2)_2X_2M(N_2CHAr)$.

Among other electrophiles, carbonyl compounds have been investigated in the reactions with diazoalkane complexes. Their interaction with the free diazoalkanes usually leads to the formation of the product of the insertion of the carbene,[140] obtained from the diazoalkane, in the C–CO bond or the products of the addition of the carbene to the C=O bond. The diazoalkane fragment in the zirconium complex **25b** behaves as both a N- and a C-nucleophile in reactions with various aldehydes and ketones,[17,77,142] which results in the formation of a mixture of the alkene **74** and the ketazine **75** in a nearly equimolar ratio.

$$[Cp_2Zr(\mu\text{-}N_2CHPh)]_2 \xrightarrow{R'C(R)=O} \text{Ph(H)C=C(R)R'} + N_2 + \text{Ph(H)C=N-N=C(R)R'} + \text{'}Cp_2ZrO\text{'}$$

25b **74** **75**

It has been observed that the enhanced electron-accepting nature of the carbonyl compounds promotes the formation of alkenes, whilst the use of substituted derivatives (steric factor) promotes the formation of ketazines. If the benzene ring in the diazoalkane fragment in complex **25b** is substituted, the rate of the second-order reaction increases with enhancement of the electron-donating nature of the substituent in the *para*-position in the benzene ring. Two mechanisms have been proposed[17,77,142] for the formation of alkenes and ketazines. They both involve the formation of an intermediate as a result of the coordination of the oxygen atom of the carbonyl compound to the oxophilic zirconium atom and the formation of a bond between the carbonyl carbon atom and the diazoalkane (with either a C- or N-nucleophile). This reaction is an analogue of the Wittig reaction and is synthetically valuable because the diazoalkane complex has also been obtained from a carbonyl compound.

In contrast to the free diazoalkanes, the diazo-ligands are resistant to the action of mild electrophiles such as alkyl halides. For example, the interaction of the niobium complex $Cp_2Nb(H).(N_2CPhAr)$ **3** with various alkyl and aryl halides involves only the substitution of the hydride atom by the halogen, which leads to the formation of the complexes $Cp_2Nb(X)(N_2CPhAr)$ **10** (X = Cl, Br, I).

3. Interaction of diazoalkane complexes with nucleophiles

Although free diazoalkanes are relatively stable in a neutral or alkaline medium, the diazoalkane complexes are appreciably more sensitive to the action of bases and nucleophiles. The attack by the nucleophile in such a reaction is usually directed to a carbon atom of the coordinated diazoalkane and leads to the formation of alkyldiazene complexes (type **J**).[46]

$$L_nM{=}N{=}N{=}CR'R'' + \ddot{X} \longrightarrow L_nM{=}N{\equiv}N{-}CXR'R''$$

J

Reactions of this type have been observed for 4-electron-donating diazoalkane complexes of tungsten and molybdenum.[2,40,42,46,47,49,144] The polarisation of the carbon atom of the diazoalkane fragment in such a reaction must be the opposite to that observed in reactions with electrophiles. On this basis, one may postulate that either the reactivities of 2- and 4-electron-donating diazoalkane ligands differ very greatly or that the diazoalkane fragment in the diazo-complexes is not markedly polar and is capable of becoming adjusted to the reagent introduced.

The neutral methyldiazene complex **76a**, the ethyldiazene complex **76b**, and the benzyldiazene complex **76c** have been obtained from the cationic diazomethanetungsten complex **12d** by its reaction with the corresponding nucleophiles.[47,49]

$$[(dppe)_2BrW(N_2CH_2)]^+ \xrightarrow{LiAlH_4} [(dppe)_2BrW(N_2CH_3)]$$

12d **76a**

$$\xrightarrow{MeLi} [(dppe)_2BrW(N_2CH_2CH_3)]$$

76b

$$\xrightarrow{PhLi} [(dppe)_2BrW(N_2CH_2Ph)]$$

76c

The analogous diazopropanetungsten complex **12a**[46] and diazobutanoltungsten complex **12b**[49] $[(dppe)_2BrW(N_2CR'R'')]^+$ [R' = R'' = Me; R' = H, R'' = $(CH_2)_3OH$] react with $LiAlH_4$ to form the alkyldiazene complexes $[(dppe)_2BrW(N_2CHR'R'')]$.

On treatment with $LiAlH_4$, the neutral diazoalkane complexes $[(PMe_2Ph)_3Br_2W(N_2CR'R'')]$ **11c,d** [R' = R'' = Me; R'–R'' = $(CH_2)_5$] decompose quantitatively to the corresponding amine R'R''CHNH$_2$ and ammonia.[42]

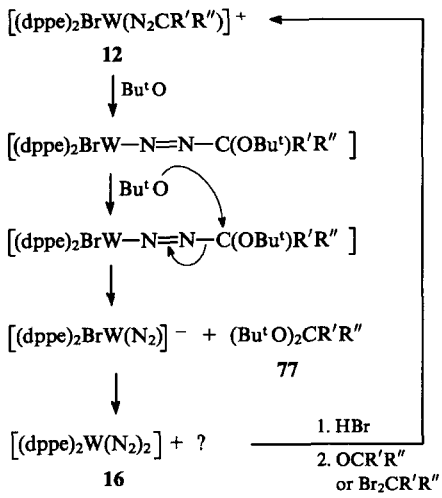
The interaction of the dinuclear rhodium complex $[Rh_2.(\mu\text{-}N_2CHCO_2Et)(CO)_2(dppm)_2]$ with $NaBH_4$ involves the substitution of the bridging dialkyl ligand by hydride atoms with formation of $[Rh_2(\mu\text{-}H)_2(CO)_2(dppm)_2]$.[76]

The attack by the nucleophile can be directed also to other highly reactive bonds of the diazoalkane complex. Thus the reaction of $Cp_2Nb(Br)(N_2CPh_2)$ **10c** with MeLi leads to the formation of the complex $Cp_2Nb(Me)(N_2CPh_2)$, while the reaction of $Cp_2Nb(H)(N_2CPh_2)$ **3a** with BuLi affords the salt $[Cp_2Nb(N_2CPh_2)]^-Li^+$.[39]

The reactions of diazoalkane complexes with oxygen-containing nucleophiles usually proceed with dissociation of metal–nitrogen or nitrogen–carbon bonds. Thus the interaction of complexes of the type $(RO)_2W(N_2CR'R'')$ with alcohols[40] led to the formation of the corresponding hydrazones $H_2NN{=}CR'R''$. On hydrolysis in air,[30] the diazoalkane complexes of molybdenum and tungsten $(Me_2NCS_2)_2(CO)M.(N_2CHC_6H_4Me\text{-}p)$ **1a** decompose, forming the hydrazone

($H_2NN=CHC_6H_4Me$-*p*), CO, and $(Me_2NCS_2)_2MO$. The complexes $Cp_2Nb(H)(N_2CPhAr)$ **3** [39] and $Cp_2Zr(Cl)(N_2CPhAr)$ **33** [85] also hydrolyse readily to the corresponding hydrazone and oxo-complex (especially in an alkaline medium).

The interaction of the cationic tungsten complexes **12** with an excess of Bu^tOK leads to the formation [46] of the initial nitrogen complex **16** (from which complex **15** was obtained) and the geminal diether **77**. It is of interest that the analogous reaction proceeds differently with MeONa.

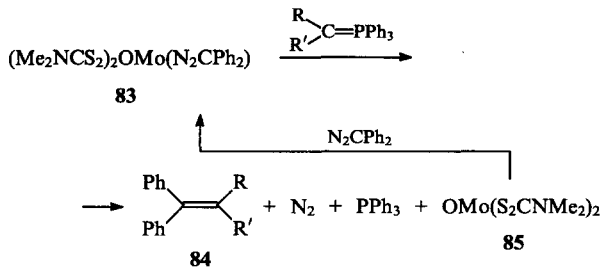


R', R'' = H, Me.

The interaction of cationic diazoalkane complexes of molybdenum and tungsten **12** with strong bases [145] entails the deprotonation of the diazoalkane ligand, leading to the alkenyldiazenide complexes **78**. Certain reactions of the alkenyldiazenide complexes, resulting in the formation of the coupling product **79** and the alkylation product **80** and in the nucleophilic addition of the α-carbon atom of the diazo-group and of H^+ to the C=N bond (compound **81**) and the C=O bond (compound **82**) (Scheme 3), have been investigated.

Schwartz and coworkers [15,17] have described another reaction of the diazoalkane complexes that is analogous to the Wittig reaction. The diazoalkanes coordinated to a molybdenum atom behave in this process as C-electrophiles, which is the opposite of the behaviour found for the diazoalkanezirconium complexes.

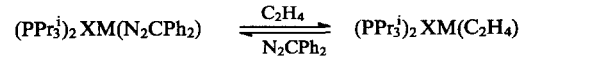
The interaction of the diazoalkane complex **83** with various alkylidenephosphines afforded the corresponding alkenes **84**. Nitrogen and the free phosphine are then evolved and the molybdenum complex **85** is formed. The initial diazoalkane complex **83** can be synthesised from it.



The olefins obtained are identical with those formed in the reaction of benzophenone with alkylidenephosphines. In the case of the analogous complex of phenylmethyldiazomethane with asymmetrically substituted alkylidenephosphines, the (*Z*)- and (*E*)-alkenes are formed in approximately the same proportions as in the classical Wittig reaction [the (*Z*)-isomer predominates]. However, in contrast to the classical Wittig reaction, the authors suggest that this reaction be regarded as an oxidation-reduction process.

The reactions of diazoalkane complexes with alkenes are in principle similar to the reactions of the carbenes (obtained from the diazoalkanes) with alkenes (Section III.2.b). The difference consists solely in the thermal stability of the diazoalkane complexes. On heating, diazoalkane complexes usually lose nitrogen and the carbene (the electrophile) formed thereby adds to the C=C double bond; the main reaction product is then a substituted cyclopropane. For example, the diazofluorene complexes $(Bu^tNC)_2M(N_2Fld)$ **5** (M = Ni, Pd) react in this way. The reactions of these complexes with dialkyl maleate afforded a mixture of the *cis*- and *trans*-isomers of the cyclopropane derivative produced thereby.[14]

Another type of reaction involves the interaction of the diphenyldiazomethane complexes of iridium and rhodium **8**, in which the diazoalkane ligand is displaced.[29,37]

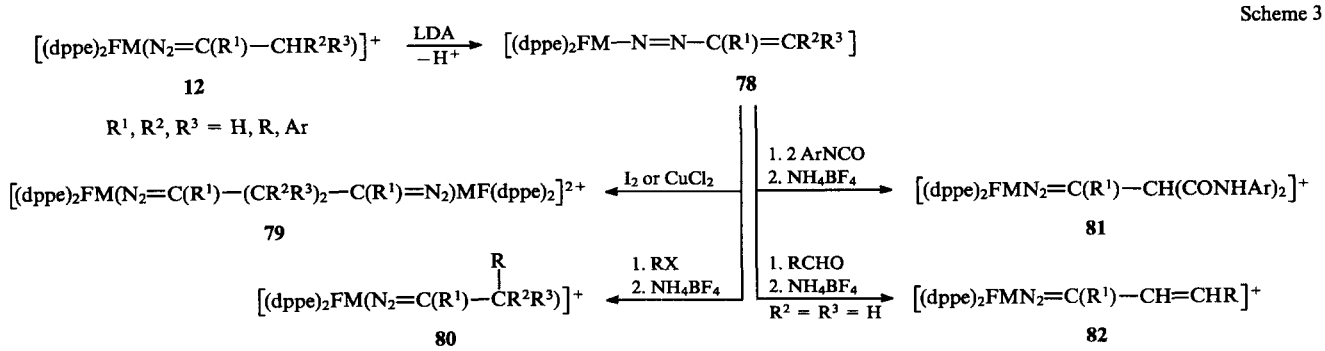


M = Ir; X = Me.
M = Ph; X = Cl.

The replacement of the diazoalkane ligand by another one has been described also in the reaction of $[Rh_2(\mu\text{-}N_2CRCO_2Et).(CO)_2(dppm)_2]$ (R = H, CO_2Et) with CO.[76]

Numerous exchange reactions of other ligands (not diazoalkanes) in the diazoalkane complexes of transition metals have also been described in the literature. However, the description of these reactions is outside the scope of the present review.

Scheme 3



V. Conclusion

The review presents and surveys the results of studies of the interaction of diazoalkanes with transition metal complexes and the reactions of the diazoalkane complexes obtained.

The results of these reactions are varied — both as regards the class of ligands formed from the diazoalkanes and as regards the type of coordination of the latter. The structure of the product depends both on the nature of the transition metal and its valence state and on the nature of the diazoalkane itself.

The interaction of a diazoalkane with a transition metal complex is usually accompanied either by the addition or insertion of the diazoalkane itself or of the carbene formed from it.

Apart from the principal structural parameters of the MN_2C fragment, the diazo-complexes have been characterised by their chemical behaviour — thermal reactions and interaction with various reagents. The principal differences between the structures and properties of the diazo-ligands and the free diazoalkanes have been elucidated.

However, it is essential to note that, as a consequence of the complexity and great variety of the reactions of diazoalkanes with transition metal complexes and the reactions of the products obtained, the studies in this field have been unsystematic and the results presented are not always sufficiently reliable.

The above reactions can serve as convenient methods of synthesis of valuable classes of complexes, in the first place hydrazonate, alkyldiazene, carbene, and alkyl complexes.

References

1. J Chatt, J R Dilworth, R L Richards *Chem. Rev.* **78** 589 (1978)
2. J Chatt, R L Richards *J. Organomet. Chem.* **239** 65 (1982)
3. W A Herrmann *Adv. Organomet. Chem.* **20** 159 (1982)
4. W A Herrmann *Pure Appl. Chem.* **54** 65 (1982)
5. A Albini, H Kisch *Top. Curr. Chem.* **65** 105 (1976)
6. H M Niemeyer, in *The Chemistry of the Diazonium and Diazo Groups, Pt 1* (Ed. S Patai) (New York: Wiley, 1978) p. 231
7. W A Herrmann *J. Organomet. Chem.* **250** 319 (1983)
8. D Sutton *Chem. Rev.* **93** 995 (1993)
9. S Otsuka, A Nakamura, T Koyama, Y Tatsuno *J. Chem. Soc., Chem. Commun.* 1105 (1972)
10. S Otsuka, A Nakamura, T Koyama, Y Tatsuno *Liebigs Ann. Chem.* 626 (1975)
11. K D Schramm, J A Ibers *Inorg. Chem.* **19** 2441 (1980)
12. S Gambarotta, C Floriani, A Chiesi-Villa, C Guastini *J. Am. Chem. Soc.* **104** 1918 (1982)
13. J Martin, C Moise *J. Organomet. Chem.* **193** C57 (1980)
14. A Nakamura, T Yoshida, M Cowie, S Otsuka, J A Ibers *J. Am. Chem. Soc.* **99** 2108 (1977)
15. J A Smegal, I K Meier, J Schwartz *J. Am. Chem. Soc.* **108** 1322 (1986)
16. M H Chisholm, J A Heppert, J C Huffman, C D Ontiveros *Organometallics* **8** 976 (1989)
17. G M Arvanitis, J Smegal, I Meier, A C C Wong, J Schwartz, D Van Engen *Organometallics* **8** 2717 (1989)
18. M H Chisholm, K Folting, J C Huffman, A L Ratermann *Inorg. Chem.* **23** 2303 (1984)
19. S Gambarotta, C Floriani, A Chiesi-Villa, C Guastini *J. Chem. Soc., Chem. Commun.* 1015 (1982)
20. J F Lebouf, J C Leblanc, C Moise *J. Organomet. Chem.* **364** C22 (1989)
21. G I Nikonov, M Putala, A I Zinin, N B Kazennova, D A Lemenovskii, A S Batsanov, Yu T Struchkov *J. Organomet. Chem.* **452** 87 (1993)
22. D A Lemenovskii, M Putala, G I Nikonov, N B Kazennova, D S Yufit, Yu T Struchkov *J. Organomet. Chem.* **454** 123 (1993)
23. A Nakamura, M Aotake, S Otsuka *J. Am. Chem. Soc.* **96** 3456 (1974)
24. J Clemens, M Green, F G A Stone *J. Chem. Soc., Dalton Trans.* 1620 (1973)
25. A J L Pombeiro, R L Richards *Monatsh. Chem.* **123** 749 (1992)
26. M Cowie, S J Loeb, I R McKeer *Organometallics* **5** 854 (1986)
27. K D Schramm, J A Ibers *Inorg. Chem.* **19** 1231 (1980)
28. K D Schramm, J A Ibers *Inorg. Chem.* **19** 2435 (1980)
29. L Brandt, J Wolf, H Werner *J. Organomet. Chem.* **444** 235 (1993)
30. G L Hillhouse, B L Haymore *J. Am. Chem. Soc.* **104** 1537 (1982)
31. B L Kool, M D Rausch, H G Alt, M Herberhold, A F Hill, U Thewalt, B Wolf *J. Chem. Soc., Chem. Commun.* 408 (1986)
32. H F Klein, H F Ellrich, B Hammerschmitt, U Koch, G Cordier *Z. Naturforsch., B Chem. Sci.* **45** 1291 (1990)
33. K D Schramm, J A Ibers *J. Am. Chem. Soc.* **100** 2932 (1978)
34. W A Herrmann, G Kriechbaum, M L Ziegler, P Wulknitz *Chem. Ber.* **114** 276 (1981)
35. W A Herrmann *J. Organomet. Chem.* **84** C25 (1977)
36. S Gambarotta, C Floriani, A Chiesi-Villa, C Guastini *J. Am. Chem. Soc.* **105** 7295 (1983)
37. J Wolf, L Brandt, A Fries, H Werner *Angew. Chem.* **102** 584 (1990); *Angew. Chem., Int. Ed. Engl.* **29** 590 (1990)
38. B Bogdanovic', M Kröner, W Günther *Liebigs Ann. Chem.* **699** 1 (1966)
39. E Stankovich, M Putala, G I Nikonov, D A Lemenovskii, E V Avtomonov *J. Organomet. Chem.* (1994) (in the press)
40. A Watakabe, T Takahashi, D-M Jin, I Yokotake, Y Uchida, M Hidai *J. Organomet. Chem.* **254** 75 (1983)
41. Y Mizobe, Y Uchida, M Hidai *Bull. Chem. Soc. Jpn.* **53** 1781 (1980)
42. P C Bevan, J Chatt, M Hidai, G J Leigh *J. Organomet. Chem.* **160** 165 (1978)
43. M Hidai, Y Mizobe, Y Uchida *J. Am. Chem. Soc.* **98** 7824 (1976)
44. M Hidai, Y Mizobe, M Sato, T Kodama, Y Uchida *J. Am. Chem. Soc.* **100** 5740 (1978)
45. Y Mizobe, R Ono, Y Uchida, M Hidai, M Tezuka, S Mone, A Tsuchiya *J. Organomet. Chem.* **204** 377 (1981)
46. R Ben-Shoshan, J Chatt, G J Leigh, W Hussain *J. Chem. Soc., Dalton Trans.* 771 (1980)
47. R Ben-Shoshan, J Chatt, W Hussain, G J Leigh *J. Organomet. Chem.* **112** C9 (1976)
48. R A Head, P B Hitchcock *J. Chem. Soc., Dalton Trans.* 1150 (1980)
49. J Chatt, P C Bevan, R A Head, P B Hitchcock, G J Leigh *J. Chem. Soc., Chem. Commun.* 509 (1976)
50. P C Bevan, J Chatt, A A Diamantis, R A Head, G A Heath, G J Leigh *J. Chem. Soc., Dalton Trans.* 1711 (1977)
51. M H Chisholm, K Folting, J C Huffman, A L Ratermann *J. Chem. Soc., Chem. Commun.* 1229 (1981)
52. M D Curtis, L Messerle *Organometallics* **6** 1713 (1987)
53. L Messerle, M D Curtis *J. Am. Chem. Soc.* **104** 889 (1982)
54. K Weidenhammer, M L Ziegler *Z. Anorg. Allg. Chem.* **457** 174 (1979)
55. I A Latham, G J Leigh, G Huttner, I Jibril *J. Chem. Soc., Dalton Trans.* 385 (1986)
56. T Aoshima, A Tamura, Y Mizobe, M Hidai *J. Organomet. Chem.* **435** 85 (1992)
57. J Chatt, R A Head, P B Hitchcock, W Hussain, G J Leigh *J. Organomet. Chem.* **133** C1 (1977)
58. M Hidai, K Komori, T Kodoma, D-M Jin, T Takahashi, S Sugiura, Y Uchida, Y Mizobe *J. Organomet. Chem.* **272** 155 (1984)
59. H Oshita, Y Mizobe, M Hidai *Organometallics* **11** 4116 (1992)
60. F H Allen, O Kennard, D G Watson, L Brammer, A G Orpen, R Taylor *J. Chem. Soc., Perkin Trans. 2* S1 (1987)
61. J B Moffat, in *The Chemistry of the Diazonium and Diazo Groups, Pt 1* (Ed. S Patai) (New York: Wiley, 1978) p. 1
62. S Sorriso, in *The Chemistry of the Diazonium and Diazo Groups, Pt 1* (Ed. S Patai) (New York: Wiley, 1978) p. 95
63. L K Bell, W A Herrmann, G W Kriechbaum, H Pfisterer, M L Ziegler *J. Organomet. Chem.* **240** 381 (1982)
64. J J D'Errico, L Messerle, M D Curtis *Inorg. Chem.* **22** 849 (1983)
65. M D Curtis, L Messerle, J J D'Errico, W D Butler, M S Hay *Organometallics* **5** 2283 (1986)
66. W A Herrmann, L K Bell *J. Organomet. Chem.* **239** C4 (1982)
67. W A Herrmann, L K Bell, M L Ziegler, H Pfisterer, C Pahl. *J. Organomet. Chem.* **247** 39 (1983)
68. L Messerle, M D Curtis *J. Am. Chem. Soc.* **102** 7789 (1980)
69. W A Herrmann, G W Kriechbaum, M L Ziegler, H Pfisterer *Angew. Chem.* **94** 713 (1982)
70. A D Clauss, J R Shapley, S R Wilson *J. Am. Chem. Soc.* **103** 7387 (1981)
71. W A Herrmann, B Menjón, E Herdtweck *Organometallics* **10** 2134 (1991)

72. D Nucciarone, N J Taylor, A J Carty *Organometallics* **5** 2565 (1986)
73. G I Nikonov, M Putala, G P Brusova, N B Kazennova, D A Lemenovskii *Izv. Akad. Nauk, Ser. Khim.* (1994) (in the press)
74. M Putala, D A Lemenovskii, unpublished results
75. W A Herrmann, I Schweizer *Z. Naturforsch., B Chem. Sci.* **33** 911 (1978)
76. C Woodcock, R Eisenberg *Organometallics* **4** 4 (1985)
77. G M Arvanitis, J Schwartz, D Van Engen *Organometallics* **5** 2157 (1986)
78. D L Hughes, I A Latham, G J Leigh *J. Chem. Soc., Dalton Trans.* 393 (1986)
79. P J Walsh, M J Carney, R G Bergman *J. Am. Chem. Soc.* **113** 6343 (1991)
80. M M Bagga, P E Baikie, O S Mills, P L Pauson *J. Chem. Soc., Chem. Commun.* 1106 (1967)
81. W A Herrmann, G Ihl *J. Organomet. Chem.* **251** C1 (1983)
82. R Serrano, J C Flores, P Royo, M Mena, M A Pellinghelli, A Tiripicchio *Organometallics* **8** 1404 (1989)
83. S Gambarotta, M Basso-Bert, A Chiesi-Villa, C Guastini *J. Chem. Soc., Chem. Commun.* 374 (1982)
84. S Gambarotta, C Floriani, A Chiesi-Villa, C Guastini *Inorg. Chem.* **22** 2029 (1983)
85. E V Avtomonov, D A Lemenovskii, unpublished results
86. E Hey, F Weller *Chem. Ber.* **121** 1207 (1988)
87. G A Vaughan, G L Hillhouse, A L Rheingold *J. Am. Chem. Soc.* **112** 7994 (1990)
88. M R Churchill, H J Wasserman *Inorg. Chem.* **20** 2905 (1981)
89. K Burgess, B F G Johnson, J Lewis, P R Raithby *J. Chem. Soc., Dalton Trans.* 263 (1982)
90. T Jenke, H Stoeckli-Evans, G Süs-Fink *J. Organomet. Chem.* **391** 395 (1990)
91. T Jenke, U Bodensieck, H Stoeckli-Evans, G Süs-Fink *J. Organomet. Chem.* **414** C28 (1991)
92. M L McKee *J. Am. Chem. Soc.* **112** 7957 (1990)
93. M L Lappert, J S Poland *J. Chem. Soc., Chem. Commun.* 1061 (1969)
94. W A Herrmann *Angew. Chem.* **87** 358 (1975); *Angew. Chem., Int. Ed. Engl.* **14** 355 (1975)
95. W A Herrmann, H Biersack *Chem. Ber.* **110** 896 (1977)
96. G L Hillhouse, B L Haymore, W A Herrmann *Inorg. Chem.* **18** 2423 (1979)
97. W A Herrmann, M L Ziegler, K Weidenhammer *Angew. Chem.* **88** 379 (1976)
98. W A Herrmann, H Biersack, K K Mayer, B Reiter *Chem. Ber.* **113** 2655 (1980)
99. W A Herrmann, M L Ziegler, K Weidenhammer, H Biersack, K K Mayer, R D Minard *Angew. Chem.* **88** 191 (1976); *Angew. Chem., Int. Ed. Engl.* **15** 164 (1976)
100. D Nuel, F Dahan, R Mathieu *Organometallics* **5** 1278 (1986)
101. J Clemens, R E Davis, M Green, J D Oliver, F G A Stone *J. Chem. Soc., Chem. Commun.* 1095 (1971)
102. J Clemens, M Green, F G A Stone *J. Chem. Soc., Dalton Trans.* 93 (1974)
103. J Formiés, B Menjón, N Gómez, M Tomás *Organometallics* **11** 1187 (1992)
104. M A Gallop, C E F Rickard, W R Roper *J. Organomet. Chem.* **395** 333 (1990)
105. P Espinet, E Lalinde, M Marcos, J Perez, J L Serrano *Organometallics* **9** 555 (1990)
106. I N Busygina, T A Stromnova, S B Katser, A S Antsyshkina, M A Porai-Koshits, S G Sakharov, I I Moiseev *Metalloorg. Khim.* **3** 312 (1990)
107. M A Gallop, C E F Rickard, W R Roper *J. Organomet. Chem.* **269** C21 (1984)
108. I A Tikhonova, V B Shur, M E Vol'pin *Izv. Akad. Nauk SSSR, Ser. Khim.* **25** 229 (1976)
109. M Schöllkopf, N Rieber *Chem. Ber.* **102** 488 (1969)
110. J Lorberth *J. Organomet. Chem.* **27** 303 (1971)
111. J Lorberth, F Schmock, G Lange *J. Organomet. Chem.* **54** 23 (1973)
112. S-I Murahashi, Y Kitani, T Hosokawa *J. Chem. Soc., Chem. Commun.* 450 (1979)
113. S I Murahashi, Y Kitani, T Uno, T Hosokawa, K Miki, T Yonezava, N Kasai *Organometallics* **5** 356 (1986)
114. M J Menu, P Desrosiers, M Dartiguenave, Y Dartiguenave *Organometallics* **6** 1822 (1987)
115. M J Menu, G Crocco, M Dartiguenave, Y Dartiguenave *Organometallics* **7** 2231 (1988)
116. H Siebald, M Dartiguenave, Y Dartiguenave *J. Organomet. Chem.* **438** 83 (1992)
117. A F Hill, W R Roper, J Waters, A H Wright *J. Am. Chem. Soc.* **105** 5939 (1983)
118. W A Herrmann, J Plank, G W Kriechbaum, M L Ziegler, H Pfisterer, J L Atwood, R D Rogers *J. Organomet. Chem.* **264** 327 (1984)
119. W Kalcher, W A Herrmann, C Pahl, M L Ziegler *Chem. Ber.* **117** 69 (1984)
120. W A Herrmann, C Weber, M L Ziegler, C Pahl *Chem. Ber.* **117** 875 (1984)
121. W A Herrmann, G W Kriechbaum, C Bauer, B Konmbours, H Pfisterer, E Guggolz, M L Ziegler *J. Organomet. Chem.* **262** 89 (1984)
122. W A Herrmann, C Bauer, J M Huggins, H Pfisterer, M L Ziegler *J. Organomet. Chem.* **258** 81 (1983)
123. W A Herrmann, M Flöel, C Weber, J L Hubbard, A Schäfer. *J. Organomet. Chem.* **286** 369 (1985)
124. W A Herrmann, C Weber, M L Ziegler, O Serhadli *J. Organomet. Chem.* **297** 245 (1985)
125. M J Chetcutti, B E Grant, P E Fanwick *Organometallics* **9** 1345 (1990)
126. W A Herrmann, G W Kriechbaum, C Bauer, E Guggolz *Angew. Chem.* **93** 838 (1975); *Angew. Chem., Int. Ed. Engl.* **20** 815 (1975)
127. W A Herrmann, J M Huggins, B Reiter, C Bauer *J. Organomet. Chem.* **214** C19 (1981)
128. A A Kazi, A A Frew, B R Lloyd, L Manojlovic'-Muir, K W Muir, R J Puddephatt *J. Chem. Soc., Chem. Commun.* 614 (1982)
129. J R Shapley, A C Sievert *J. Am. Chem. Soc.* **103** 6975 (1981)
130. I N Busygina, T Stromova, D I Kochubei, M Ya Botnikov, I I Moiseev *Metalloorg. Khim.* **4** 69 (1991)
131. W Ando, in *The Chemistry of the Diazonium and Diazo Groups, Pt 1* (Ed. S Patai) (New York: Wiley, 1978) p. 366
132. J Cooke, W R Cullen, M Green, F G A Stone *J. Chem. Soc., Chem. Commun.* 170 (1968)
133. J Cooke, W R Cullen, M Green, F G A Stone *J. Chem. Soc., A* 1872 (1969)
134. F D Mango, I Dvoretzky *J. Am. Chem. Soc.* **88** 1654 (1966)
135. R C Brady, R Pettit *J. Am. Chem. Soc.* **102** 6181 (1980)
136. S M Breckenridge, S A McLaughlin, N J Taylor, A J Carty *J. Chem. Soc., Chem. Commun.* 1718 (1991)
137. D Nucciarone, N J Taylor, A J Carty *Organometallics* **3** 177 (1984)
138. M Sakurada, M Kajitani, K Dokhi, T Akiyama, A Sugimori *J. Organomet. Chem.* **423** 141 (1992)
139. L S Hegedus *J. Organomet. Chem.* **422** 301 (1992)
140. E A Shapiro, A B Dyatkin, O M Nefedov *Usp. Khim.* **62** 485 (1993) [*Russ. Chem. Rev.* **62** 447 (1993)]
141. M Cowie, I R McKeer, S J Loeb, M D Gauthier *Organometallics* **5** 860 (1986)
142. J M Arvanitis, J Schwartz *Organometallics* **6** 421 (1987)
143. A F Hegarty, in *The Chemistry of the Diazonium and Diazo Groups, Pt 1* (Ed. S Patai) (New York: Wiley, 1978) p. 571
144. F N N Carvalho, A J L Pombeiro, O Orama, U Schubert, C J Pickett, R L Richards *J. Organomet. Chem.* **240** C18 (1982)
145. Y Ishii, H Miyagi, S Jitsukuni, H Seino, B S Harkness, M J Hidai *J. Am. Chem. Soc.* **114** 9890 (1992)