

Recueil Review

of progress in current research

Interaction of metal centres with the 1,4-diaza-1,3-butadiene (α -diimine) ligand. Versatile coordination chemistry and applications in organic synthesis and catalysis

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Introduction

A challenging new aspect in organometallic chemistry is the study of the interaction and conversion of heteroolefins with metal centres. Heteroolefins are molecules containing, for example, N=C, N=S, N=O, C=O, C=S or S=O groups as parts of their molecular skeletons. In addition to metal coordination *via* the π system, which is analogous to the single coordination possibility of olefins (η^2 -C=C), the heteroolefins may also coordinate *via* lone pairs localized on the heteroatoms. The resulting, versatile coordination possibilities of heteroolefins are illustrated by two examples in Fig. 1 which are selected from our previous review on the coordination and activation of the N=S bond in RN=S=NR and RN=S=O molecules by metal atoms¹⁻³:

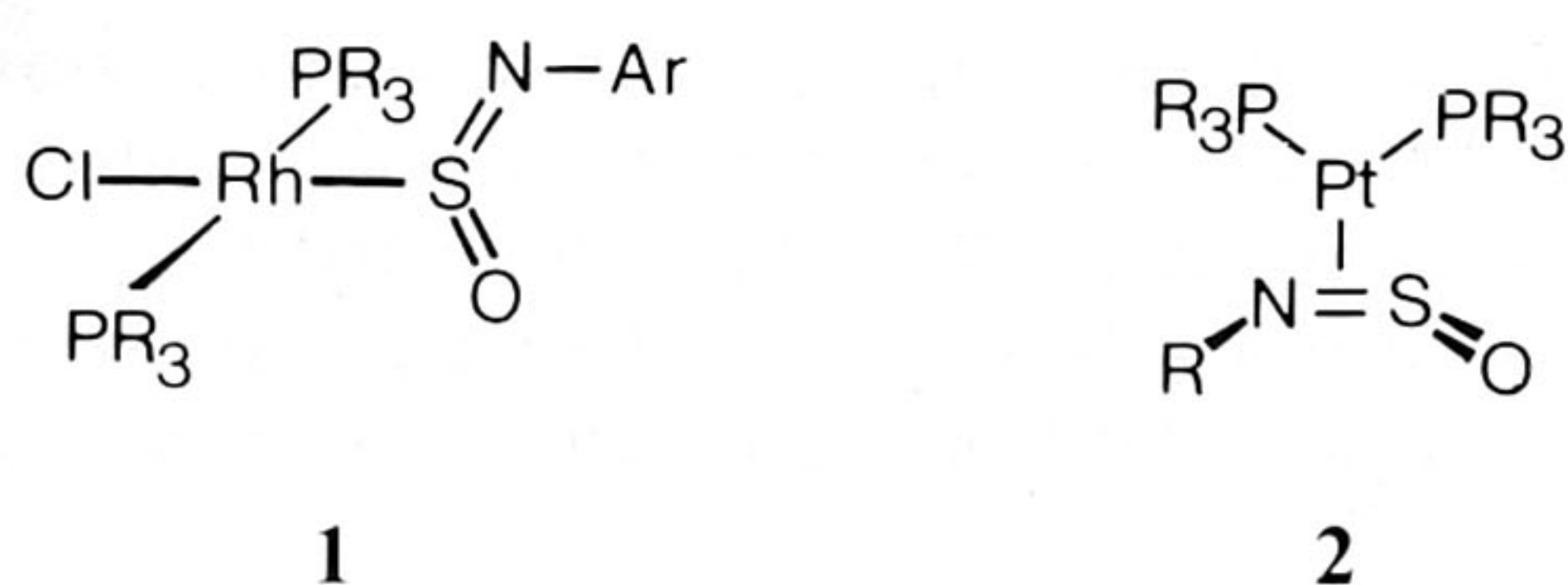


Fig. 1. Examples illustrating two of the coordination possibilities of RN=S=O heterocumulenes: **1** η^1 -S mode and **2** η^2 -N=S mode.

In **2** the N-S bond is weakened by π bonding. This weakening of the N-S bond seems to be a prerequisite for the subsequent rupture of this bond in selective conversion of RN=S=NR molecules on iron carbonyl dinuclear species and zerovalent platinum centres, see ref. 1.

In this review we will discuss the chemistry of the 1,3-butadiene analogues, RN=C(R')-C(R'')=NR*, which belong to the large group of α -diimines, and are called glyoxal diimine (R' = R'' = H), ethanediimines** or 1,4-diaza-1,3-butadienes.

* The 1,4-diaza-1,3-butadiene ligand will be abbreviated as R-DAB in which R represents the substituent on the N atom.

** Chemical Abstracts name.

*** The list of references provides a good entrance into the literature of α -diimine chemistry. An extensive review of the coordination and chemistry of 1,4-diaza-1,3-butadienes is in preparation⁴.

Rather than providing the reader with a detailed review of what has been found we will restrict ourselves to a general outline of the versatile coordination properties of this ligand system with particular emphasis on the research carried out in our laboratory. Moreover, we will discuss some of the highlights of the chemistry of the 1,4-diaza-1,3-butadienes insofar as this is based on activation by metal centres***.

Metal- α -diimine complexes: bonding and stereochemistry

α -Diimines make up a large family of compounds which all have the N=C-C=N skeleton in common. In Fig. 2 the 1,4-diaza-1,3-butadiene molecular skeleton is compared with those of two other representatives of this class of compounds, namely the 2-pyridinecarbaldehyde imines and the 2,2'-bipyridines.

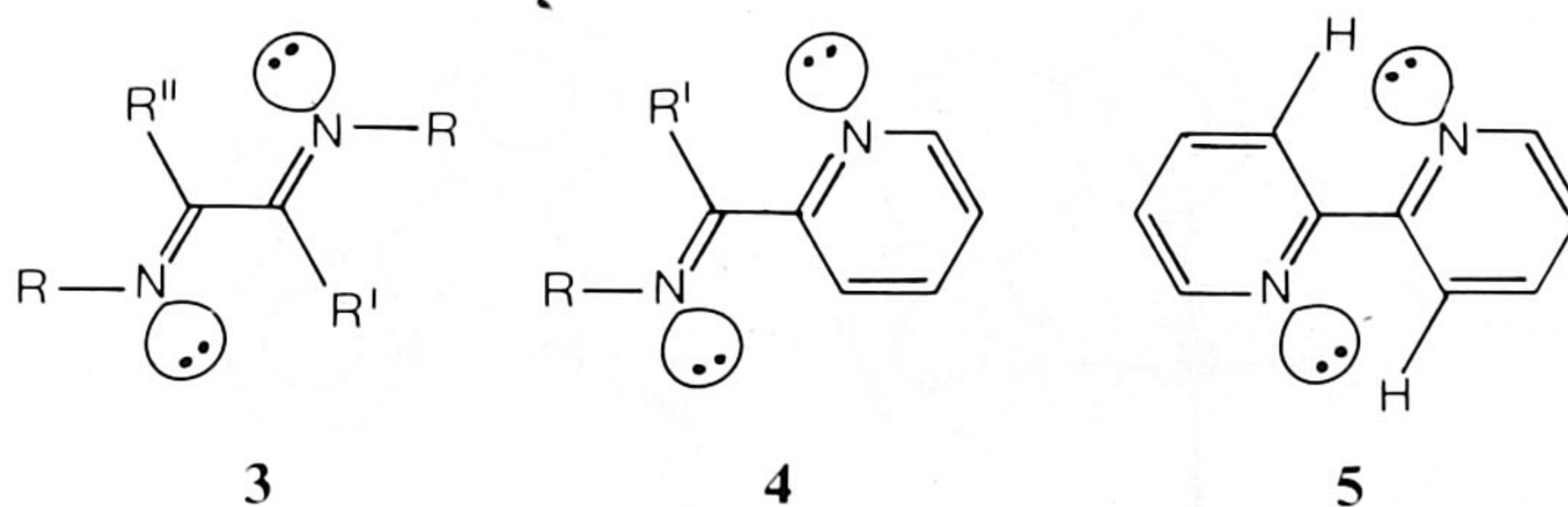


Fig. 2. Three typical representatives of the α -diimines: **3** 1,4-diaza-1,3-butadienes (R-DAB), **4** pyridinecarbaldehyde imines, **5** 2,2'-bipyridine.

1,4-Diaza-1,3-butadienes are generally derived⁵ from the condensation reaction of glyoxal or α -diketone with a primary amine RNH₂. In some instances, depending on

¹ K. Vrieze and G. van Koten, Recl. Trav. Chim. Pays-Bas **99**, 145 (1980).

² R. A. Love, T. F. Koetzle, G. J. B. Williams, L. C. Andrews and R. Bau, Inorg. Chem. **14**, 2653 (1975).

³ M. Chatt and L. A. Duncanson, J. Chem. Soc. 2519 (1960); M. J. S. Dewar, Bull. Soc. Chim. Fr. **18**, C79 (1953).

⁴ G. van Koten and K. Vrieze, Adv. Organometal. Chem., to be published.

⁵ V. C. Barnay and P. W. D. Mitchell, J. Chem. Soc. (London) 3610 (1953); L. Horner and E. Jürgens, Chem. Ber. **90**, 2184 (1957); J. F. Carson, J. Am. Chem. Soc. **75**, 4337 (1953); J. M. Kliegman and R. K. Barnes, J. Org. Chem. **35**, 3140 (1970); J. M. Kliegman and R. K. Barnes, Tetrahedron **26**, 2555 (1970).

the nature of this amine, the α -imino ketones, which are precursors of **3**, can be isolated⁶. Subsequent conversion of these α -iminoketones with a second primary amine affords the mixed 1,4-diaza-1,3-butadiene compounds⁷ in which the two R groups in Fig. 2 are inequivalent.

As with 1,3-butadiene itself, simple α -diimine ligands exist in the free state in an *s-trans* conformation with dihedral angles N=C-C=N between 90 and 140° ****. This has been concluded from extensive NMR, IR and dipole moment studies^{8,9}. In particular, no interaction between the lone pairs on the N atoms is observed in photoelectron spectra⁸ as would have been expected for the ligand in the *s-cis* conformation.

Of the aromatic α -diimines **5**, 2,2'-bipyridine (2,2'-bipy) has been extensively investigated¹⁰.

Whereas the free ligand exists predominantly in the *s-trans* conformation, 2,2'-bipy-metal complexes have only been found containing the 2,2'-bipy ligand in a nearly planar cisoid conformation. The ligand behaves as a bidentate, *i.e.* the lone pairs on both N atoms interact with empty metal *d* orbitals, thus forming a planar five-membered chelate ring. Interaction of metal *d_π* orbitals with ligand π^* orbitals is significant, but not exceptional, in cases where the metal is in its normal oxidation state. However, 2,2'-bipy is particularly suited for the stabilization of metals in low oxidation states. In such complexes the ligand π^* orbitals are extensively used as a result of charge transfer from the metal to the ligand. Various complexes can be better formulated as having radical anion ligands, *i.e.* the unpaired electrons are extensively delocalized on the ligands¹².

Tom Dieck and his coworkers, who were amongst the very first to study the coordination properties of the 1,4-diaza-1,3-butadienes in detail, found that these ligands are even superior to the 2,2'-bipy system in accepting electron density from the metal into π^* ligand orbitals^{12,13}. These conclusions were based on the results of ESR studies of $[M(CO)_4(R-DAB)]$ ($M = Cr, Mo, W$) complexes reduced with potassium in ethers, as well as on the results of $[K(R-DAB)]$ itself^{8,14}.

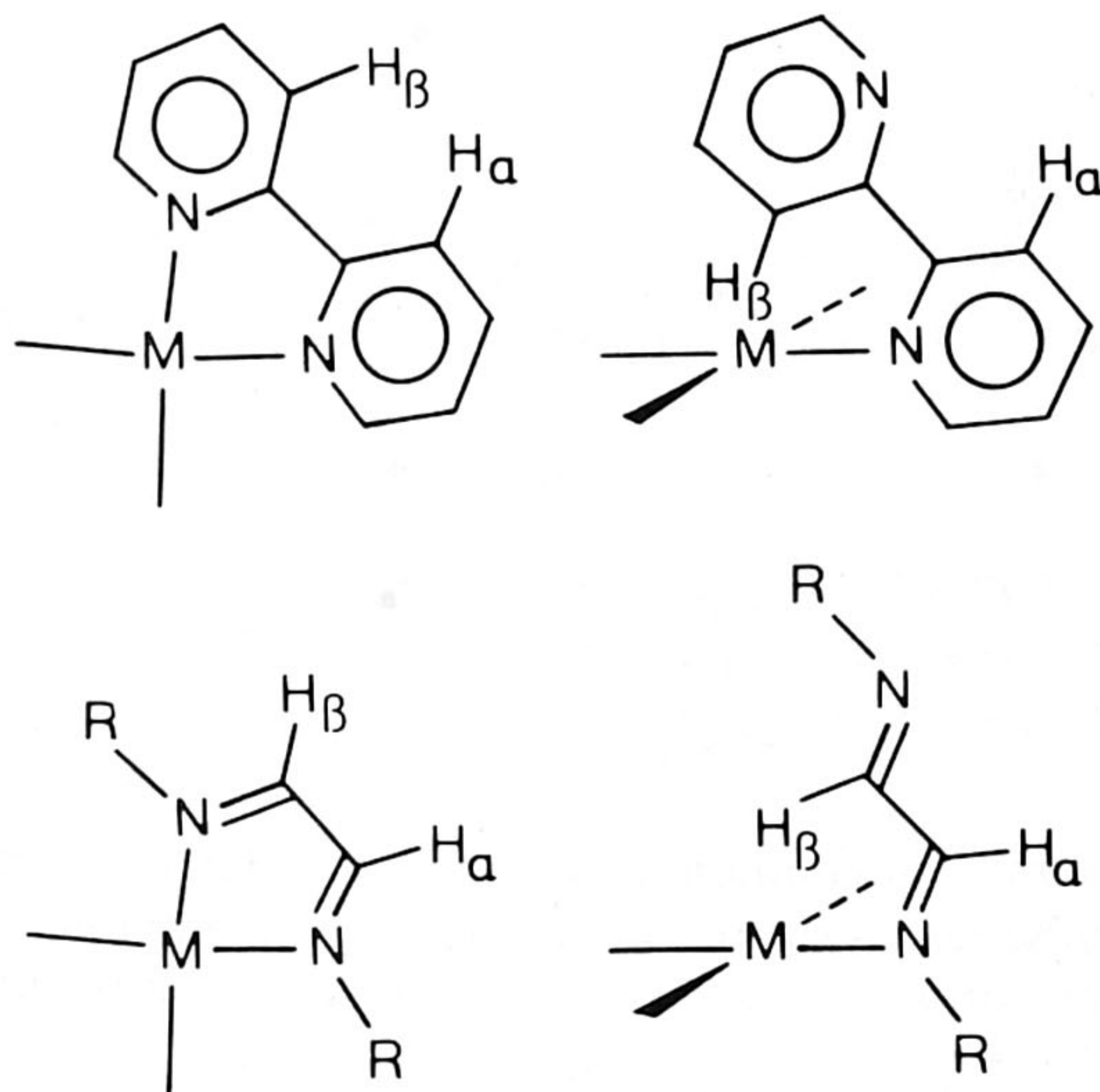


Fig. 3. Comparison of the stereochemistry of the $\sigma, \sigma-N, N'$ and $\sigma-N$ coordinate 1,4-diaza-1,3-butadiene and 2,2'-bipy ligands¹⁵.

**** Gaseous electron diffraction analysis of *t*-Bu-DAB pointed to a *gauche* conformation for the majority of the molecules characterized by a rotation of 65° from the *s-cis* form. A minor amount of the *s-trans* form is also calculated to be present^{11a}. For the results of theoretical studies of the conformations of 1,4-diaza-1,3-butadienes see ref. 11b.

It is interesting to compare the structural features and coordination possibilities of the 1,4-diaza-1,3-butadienes **3** with those of the related α -diimines **4** and **5**. Until recently complexes were found containing the ligands **3-5** bonded exclusively *via* the two lone pairs on the N atoms (see Fig. 3).

Since the free ligands **3-5** exist in the *s-trans* conformation it requires rotation around the central C-C bond to produce the *s-cis* conformation realized in the α -diimine-metal complexes. In this situation the ligand behaves as a 4e donor.

This was in fact the situation at the start of our research. However, considering the stereochemistry of the various N=C-C=N ligands **3-5** we concluded that the 1,4-diaza-1,3-butadiene ligand in particular would be capable of other types of interactions with metal centres¹⁵.

Fig. 3, for example, illustrates the coordination of **3** and **5** *via* a single lone pair on one N atom. This comparison of the two rotational isomers of monodentate-bonded 2,2'-bipy and a 1,4-diaza-1,3-butadiene shows that in the 2,2'-bipy-M complex the H ^{β} atom represents steric bulkiness in the absence of a M-H interaction. Of course this steric bulkiness can be diminished, at the cost of resonance stabilization, by a small rotation around the central C-C bond. By comparison with the 2,2'-bipy-M interaction, in the monodentate R-DAB-M interaction H ^{β} is further away from the metal, even when the two N=C systems of the R-DAB ligand are coplanar. H ^{β} in this case is part of a five-membered atom arrangement which, from a steric point of view, would be more stable than the six-membered arrangement present in the monodentate bipy-M isomer having coplanar aromatic rings. It is worth noting that this monodentate coordination mode is obtained on direct coordination of the free ligand in its more stable *s-trans* conformation. Another conclusion which emerges from this comparative study is that the coordination geometry around the metal centres must also be important. In the case of the monodentate coordination for R-DAB (**3**) it may be anticipated that a square planar configuration with a *d*⁸ metal should result in stable isolable complexes¹⁵. One can also anticipate the existence of further coordination possibilities; *e.g.*, starting from the monodentate bonded form, a bridging structure is reached by σ -coordination of the free C=N site to a second metal centre and structures appear to be feasible in which the π systems are

⁶ H. van der Poel and G. van Koten, *Synth. Commun.* **8**, 305 (1978).

⁷ M. Svoboda, H. tom Dieck, C. Krüger and Y.-H. Tsay, *Z. Naturforsch.* (1981) in the press.

H. tom Dieck, M. Svoboda and Th. Greiser, *Z. Naturforsch.* (1981) in the press.

⁸ H. tom Dieck and K.-D. Franz, *Angew. Chem. Int. Ed.* **14**, 249 (1975) and references cited therein.

⁹ O. Exner and J. M. Kliegman, *J. Org. Chem.* **36**, 2014 (1971); J. M. Kliegman and R. K. Barnes, *Tetrahedron Lett.* 1953 (1969).

¹⁰ L. F. Lindoy and S. E. Livingstone, *Coord. Chem. Rev.* **2**, 173 (1967).

^{11a} I. Hargittai and R. Seip, *Acta Chem. Scand.* **A30**, 540 (1976).

^{11b} O. Borgen, B. Mestvedt and I. Skanvik, *Acta Chem. Scand.* **A30**, 43 (1976); R. Benedix, P. Birner, F. Birnstock, H. Hennig and H. J. Hofmann, *J. Mol. Struct.* **51**, 99 (1979).

^{12a} H. tom Dieck, K.-D. Franz and F. Hohmann, *Chem. Ber.* **108**, 163 (1975);

^b J. Reinhold, R. Benedix, P. Birner and H. Hennig, *Inorg. Chim. Acta* **33**, 209 (1979).

¹³ K.-D. Franz, H. tom Dieck, K. A. Ostoja Starzewski and F. Hohmann, *Tetrahedron* **31**, 1465 (1975).

¹⁴ K.-D. Franz, H. tom Dieck, U. Krynitz and I. W. Renk, *J. Organometal. Chem.* **64**, 361 (1974).

¹⁵ H. van der Poel, G. van Koten and K. Vrieze, *Inorg. Chem.* **19**, 1145 (1980).

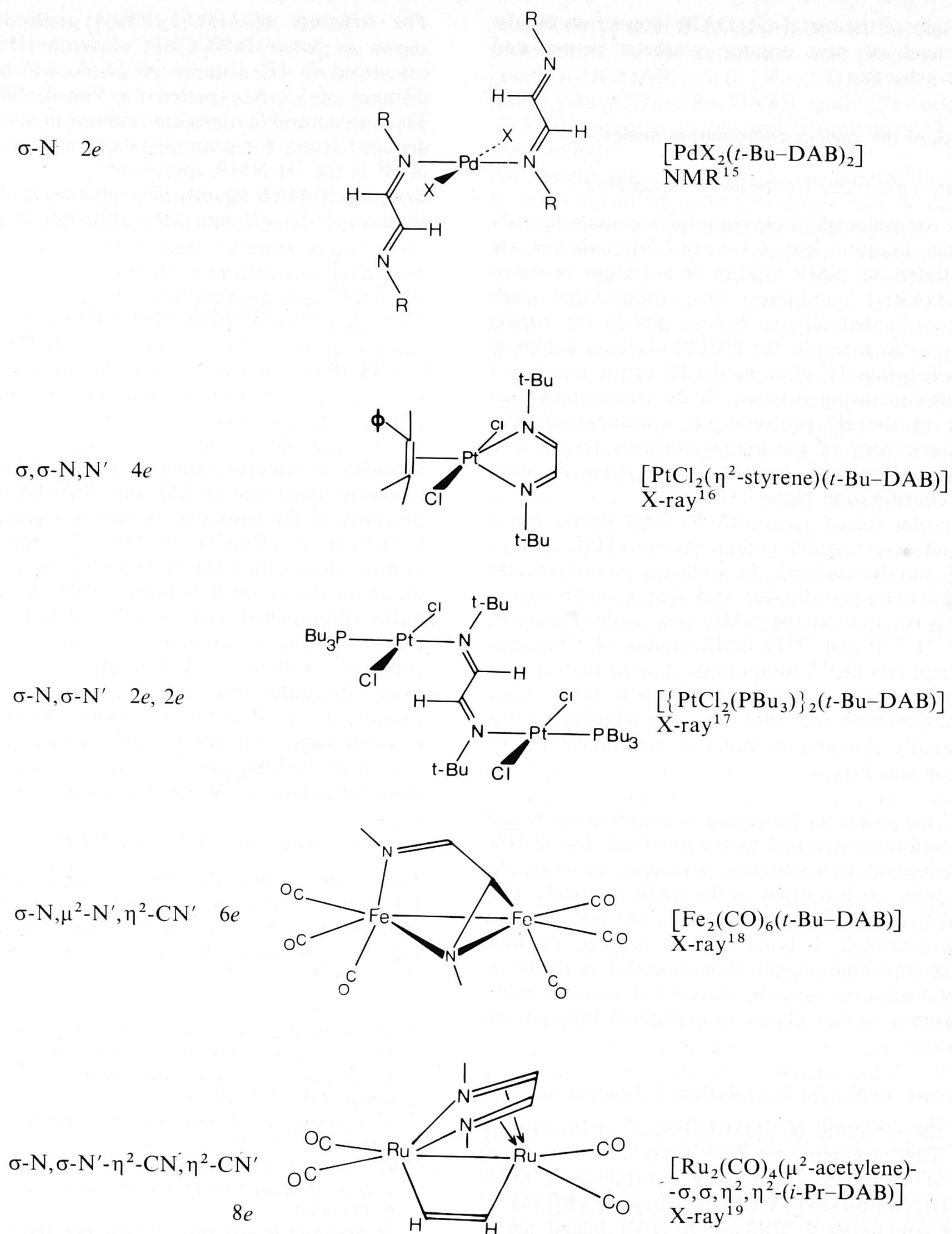


Fig. 4. Examples of 1,4-diaza-1,3-butadiene-metal complexes illustrating the versatile coordination behaviour of the R-DAB ligand.

also involved in the bonding. In particular the latter possibility is exciting, because now the R-DAB ligand may interact with metal centres using up to a maximum of eight electrons (two lone pairs on the N atoms and two pairs of π electrons from the C=N bonds). Mononuclear complexes containing purely $\eta^2\text{-C=N}, \eta^2\text{-C=N}'$ -bonded 1,4-diaza-1,3-butadiene ligands are unlikely to exist, since in the *s-cis* conformation the two lone pairs on the N atoms are unfavourably positioned pointing towards each other. However, involvement of either one or two of the π electrons of the CN bonds is fully possible when both σ lone pairs are first involved in bonding to either one or two metal centres¹⁹.

In this review we present examples of a number of these novel coordination modes (see Fig. 4). A further fascinating aspect of this versatile coordination behaviour is that, depending on the coordination mode, the metal can adjust its electron density. This is clearly an important factor when reactions take place at the metal centre.

Reversing this line of argumentation one can expect that the metal should be able to activate the 1,4-diaza-1,3-butadiene molecular skeleton for further reaction by changing its point of attachment to the system.

In the following sections we will briefly discuss:

1. Examples of the various coordination modes.
2. Examples demonstrating the flexibility in the number of electrons donated by the R-DAB ligand.

¹⁶ H. van der Poel, G. van Koten, K. Vrieze, M. Kokkes and C. H. Stam, *J. Organometal. Chem.* **175**, C21 (1979).

¹⁷ H. van der Poel, G. van Koten, K. Vrieze, M. Kokkes and C. H. Stam, *Inorg. Chim. Acta* **39**, 197 (1980).

¹⁸ H.-W. Frühauf, A. Landers, R. Goddard and C. Krüger, *Angew. Chem.* **90**, 56 (1978).

¹⁹ L. H. Staal, L. H. Polm, K. Vrieze, F. Ploeger and C. H. Stam, *J. Organometal. Chem.* **199**, C13 (1980); L. H. Staal, G. van Koten, K. Vrieze, F. Ploeger and C. H. Stam, *Inorg. Chem.* (1981) in the press.

3. Application of the metal-(R-DAB) interaction for the development of new organic synthetic routes and catalytic processes.

1. Examples of the various coordination modes

Monodentate-(σ -N; 2e) 1,4-diaza-1,3-butadienes

Only a few examples of stable complexes containing σ -N monodentate mononuclear 1,4-diaza-1,3-butadienes are known¹⁵. Extensive NMR studies on solutions of *trans*-[PdX₂(R-DAB)₂] complexes have shown that each ligand is coordinated *via* one N lone pair in the *s-trans* conformation. As a result, the NCCN skeleton is almost planar which brings H ^{β} close to the Pd centre (*cf.* Fig. 3 and 4). This conclusion is based on the tremendous low-field shift of the H ^{β} proton upon coordination. The magnetic anisotropy of the planar complex results in a deshielding of H ^{β} which is located close to the metal atom above the coordination plane.

When the *trans* ligand is not an R-DAB ligand but a phosphine or arsine, stable complexes *trans*-[PtCl₂(PR₃)₂(R-DAB)] can be isolated. In solution, intermolecular exchange between coordinated and free R-DAB ligand appeared to be slow on the NMR time scale. However, ¹H, ¹³C, ¹⁵N, ³¹P and ¹⁹⁵Pt NMR studies of ¹⁵N-labelled²⁰ and non-labelled¹⁵ compounds showed that only at low temperature (slow exchange limit) is the R-DAB ligand monodentate-bonded and rigid. At room temperature the metal is rapidly changing its point of attachment by the process shown in Fig. 5.

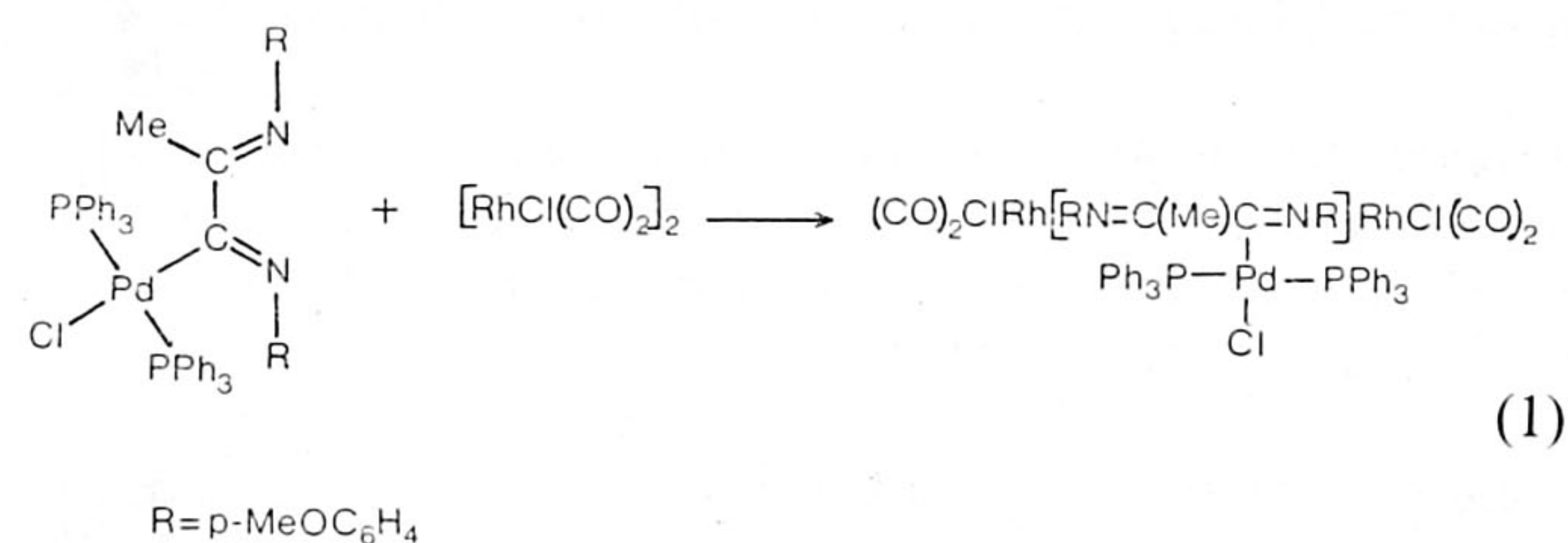
At -55°C the spectrum belonging to enantiomers A and A' is observed (characterised by the low-field shift of H ^{β}). At room temperature a situation is reached in which the process A \rightleftharpoons A' *via* B is rapid on the NMR timescale. This process involves inversion at the free-N site and rotation around the central C-C bond in order to bring the lone pair into the coordination sphere of the metal. In the intermediate or transition state B, the central metal is rehybridized from a square planar to a trigonal bipyramidal configuration.

Bridging (σ -N, σ -N'; 2e, 2e) 1,4-diaza-1,3-butadienes

In Fig. 4 the structure of [$\{PtCl_2(PBu_3)\}_2(t-Bu-DAB)$] is shown. This represents the first X-ray structure determination of a complex containing a bridging R-DAB ligand¹⁷. The complexes [$\{MCl_2(PR'_3)\}_2(R-DAB)$] (M = Pd or Pt) containing a bridging R-DAB ligand are a logical extension of the complexes containing a monodentate R-DAB ligand¹⁵.

The structure of [$\{PtCl_2(PBu_3)\}_2(t-Bu-DAB)$] clearly shows a planar PtNCCNPt skeleton. H ^{β} resides at a calculated Pt-H ^{β} distance of 2.6 Å, which is within the distance of 3.2 Å expected for Van-der-Waals contacts. These structural features are retained in solution as can be deduced from, for example, the low-field chemical shift of H ^{β} in the ¹H NMR spectrum¹⁷.

Bridging R-DAB ligands have also been observed in Rh^I chemistry^{21,22}, *cf.* eqn. 1²²; although in solution these



rhodium complexes undergo inter- and intramolecular exchange reactions of CO and R-DAB ligands²³. The positions of the equilibria, which in some cases comprise formation of [Rh(CO)₂(R-DAB)]⁺ intermediates containing chelate bonded R-DAB ligands, depend on the nature of the group R bonded to N²³. In the case of very bulky (β -branched, *vide infra* Table I) R groups the cationic structure is stabilized, *cf.* solid state structure of the complex²⁴ with R = -C(H)(i-Pr)₂.

Other structures, probably containing bridging R-DAB ligands, are [$\{Mo(CO)_3(R-DAB)\}_2(R-DAB)$] in which R-DAB is a 2,3-butanedione hydrazone²⁵, [$\{PdCl(\text{methallyl})\}_2(t-Bu-DAB)$] and [$\{Pd(\eta^2\text{-olefin})\}_2(R-DAB)$]²⁶; these formulations are based on elemental analytical data.

Chelate-bonded (σ, σ -N, N'; 4e) 1,4-diaza-1,3-butadienes

This is the commonly observed coordination mode for 1,4-diaza-1,3-butadienes. However, in view of the above mentioned σ -N \rightleftharpoons σ, σ -N, N' fluxional processes (see Fig. 5), it is interesting to mention the five-coordinate

²⁰ H. van der Poel, G. van Koten, P. S. Pregosin and K. A. Ostoja Starzewski, *Helv. Chim. Acta* (1981) in the press.

²¹ H. van der Poel, G. van Koten and K. Vrieze, *J. Organometal. Chem.* **135**, C63 (1977).

²² B. Crociani, U. Belluco and P. Sandrini, *J. Organometal. Chem.* **177**, 385 (1979).

²³ H. van der Poel, G. van Koten and K. Vrieze, to be published.

²⁴ J. Kopf, J. Klaus and H. tom Dieck, *Cryst. Struct. Commun.* **9**, 783 (1980).

²⁵ H. Bock and H. tom Dieck, *Chem. Ber.* **100**, 228 (1967).

²⁶ K. J. Cavell, D. J. Stufkens and K. Vrieze, *Inorg. Chim. Acta* **47**, 67 (1980).

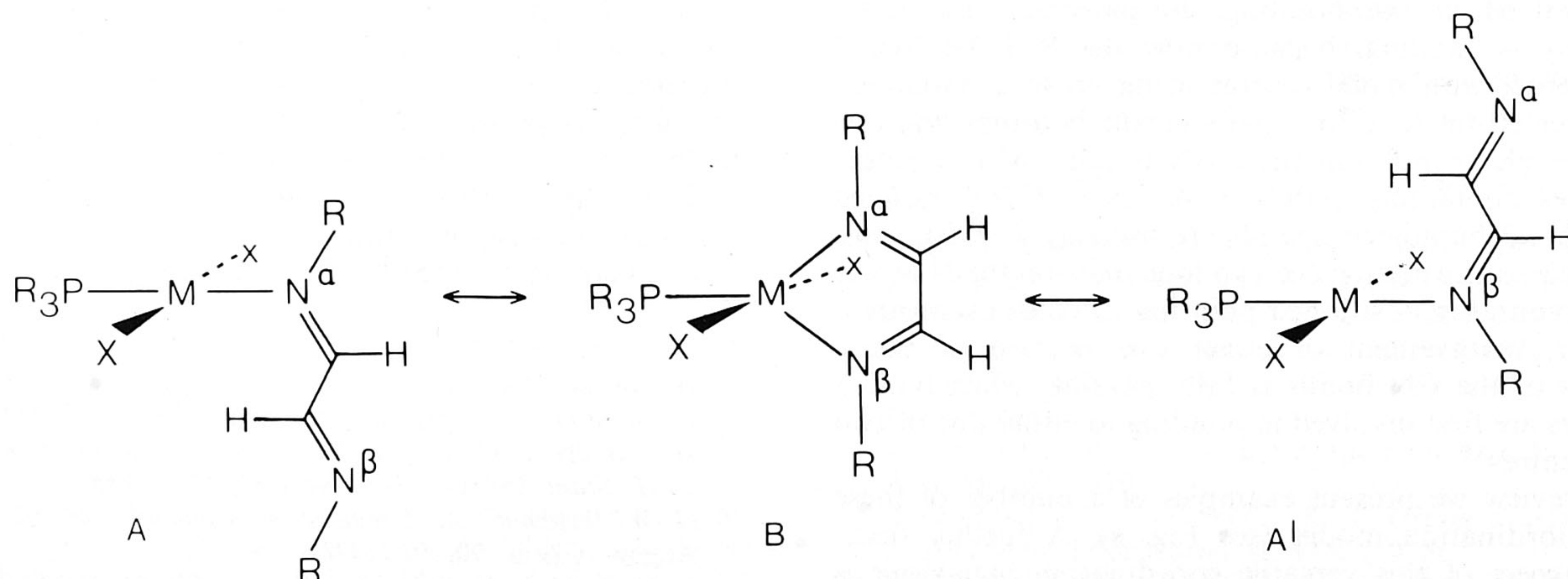


Fig. 5. Proposed mechanism for the fluxional behaviour of [MCl₂(PR₃)(R-DAB)] (M = Pt, Pd) compounds in solution (σ -N \rightleftharpoons σ, σ -N, N' rearrangement)¹⁵.

olefin-Pt^{II} complexes, $[\text{PtCl}_2(\eta^2\text{-olefin})\text{R-DAB}]^{16,27,28}$. In the case of $[\text{PtCl}_2(\eta^2\text{-ethene})(t\text{-Bu-DAB})]$ the intermediate B (Fig. 5) becomes the groundstate structure as a result of the replacement of the *trans* phosphine ligand by an olefin^{16,27}. As such, this observation demonstrates the stabilizing influence of the olefin on the $\sigma, \sigma\text{-N, N}'$ chelate bonding mode.

The five-coordinate $[\text{PtX}_2(\eta^2\text{-olefin})(\text{R-DAB})]$ and analogous $[\text{RhX}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{R-DAB})]$ complexes have been studied in detail since they represent model compounds for the five-coordinate intermediates (activated complexes) found in ligand displacement reactions from four-coordinate complexes: *i.e.* $\text{trans-}[\text{MX}_2\text{A}(\eta^2\text{-olefin})] + \text{B} \rightleftharpoons \text{trans-}[\text{MX}_2\text{B}(\eta^2\text{-olefin})] + \text{A}^{27,29}$. Moreover, the barrier to rotation of the olefin around the olefin-Pt axis in $[\text{PtX}_2(\eta^2\text{-olefin})(\text{R-DAB})]$ was studied²⁷ and found to be similar to that observed in square planar Pt-olefin complexes. This has been attributed to the planarity of the five-membered chelate ring which lowers the barrier for bending of the Cl atoms towards the R-DAB ligand when the olefin passes through an upright conformation, see Fig. 6.

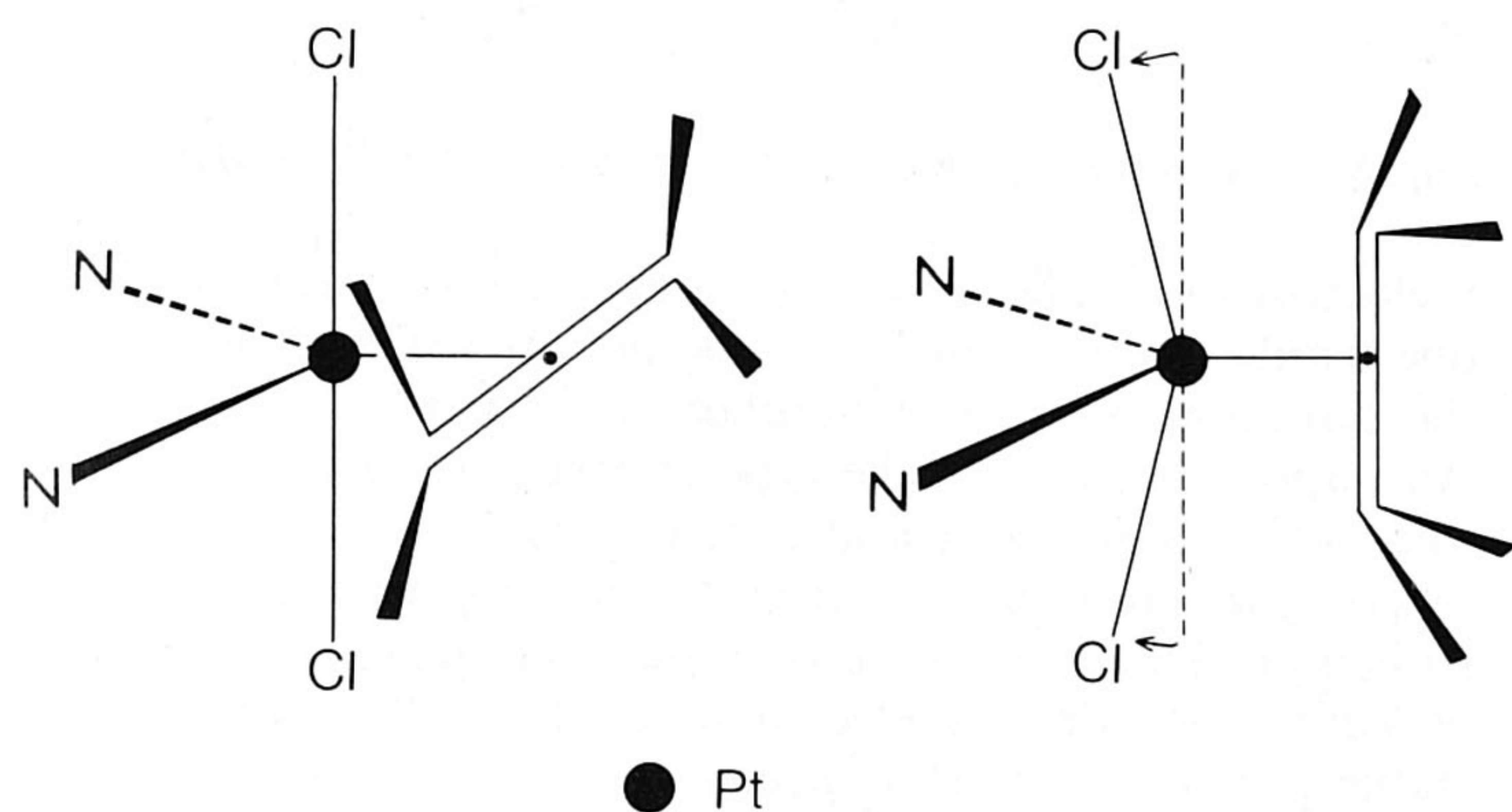


Fig. 6. Bending back of the Cl atoms in the TBP structure of $[\text{PtCl}_2(\eta^2\text{-olefin})(\text{R-DAB})]$ when the olefin passes the upright conformation during the rotation process²⁷.

Closely related to these complexes are the iso-electronic $[\text{Pt}^0(\text{L}_2)(\text{R-DAB})]$ ($\text{L}_2 = \text{COD}$; $\text{L} = t\text{-Bu-N}\equiv\text{C}$)³⁰ and $[\text{Pd}^0(\eta^2\text{-olefin})(\text{R-DAB})]^{26}$, which while lacking the two axial ligands have the same stereochemistry in the trigonal plane.

$\sigma\text{-N}, \mu^2\text{-N}', \eta^2\text{-CN}'$ ($6e$)-bonded 1,4-diaza-1,3-butadiene

When the configuration of the d^8 -metal centre changes from square planar or trigonal to octahedral geometry the steric interactions along the $\text{N}=\text{C}-\text{C}=\text{N}$ chain will increase. Accordingly, other coordination modes will become more stable.

This is reflected in the structure of $[\text{Fe}_2(\text{CO})_6(t\text{-Bu-DAB})]^{18}$ which was synthesized from the reaction of $[\text{Fe}_2(\text{CO})_9]$ with $t\text{-Bu-DAB}$. The results of a reinvestigation of the σ, π interaction in $[\text{Fe}(\text{CO})_3(\text{R-DAB})]$ given by *tom Dieck* et al.⁵⁷ are discussed in section 3c. The structure of this compound (*cf.* Fig. 4) reported by *Frühaufl* et al. shows that the $t\text{-Bu-DAB}$ ligand provides the $\text{Fe}_2(\text{CO})_6$ unit with $6e$ by donating $2e$ via one $\text{N}=\text{C}$ side and $4e$ via the other $\text{N}=\text{C}$ side of the ligand. The $4e$ donation is effected firstly by a bridge bond between two Fe centres, emanating from the lone N pair, and secondly by an interaction of the π system of the $\text{C}=\text{N}$ bond with one Fe centre. This latter η^2 bonding results in a lengthening of the $\text{C}-\text{N}$ bond from $1.280(5)$ Å ($\sigma\text{-N}$ -coordinated side) to $1.397(4)$ Å. The consequences of this weakening will be outlined in section 2.

It is interesting to note that the corresponding $[\text{Ru}_2(\text{CO})_6(\text{R-DAB})]$ compounds can be obtained *via* the reaction of

$[\text{Ru}_3(\text{CO})_{12}]$ with R-DAB (*e.g.* $\text{R} = t\text{-Bu}$) (see section 3) while mixed Fe-Ru complexes were prepared by mixing $[\text{Fe}(\text{CO})_3(\text{R-DAB})]$ and $[\text{Ru}_3(\text{CO})_{12}]$ in a 3/1 molar ratio. $[\text{Ru}_2(\text{CO})_6(t\text{-Bu-DAB})]$ and $[\text{FeRu}(\text{CO})_6(t\text{-Bu-DAB})]$ appeared to be isostructural with $[\text{Fe}_2(\text{CO})_6(t\text{-Bu-DAB})]^{31}$.

An insight into the possible mechanism by which the R-DAB ligand becomes a $6e$ donor may be derived from a comparison of the structures established for a series of other dinuclear metal complexes containing various R-DAB ligands. For example, the *i*-Pr-DAB ligand in $[\text{Mn}(\text{CO})_5\text{Mn}(\text{CO})_3(i\text{-Pr-DAB})]$ is $\sigma, \sigma\text{-N, N}'$ chelate bonded to one Mn centre³². A similar species is formed in the reaction of $[\text{Co}(\text{CO})_4]^-$ with $[\text{Mn}(\text{CO})_3(\text{DAB})\text{Br}]$. The $[\text{MnCo}(\text{CO})_7(\text{R-DAB})]$ species contain a Mn-Co bond and a $\sigma, \sigma\text{-N, N}'$ chelate-bonded R-DAB ligand. However, these species are only slightly stable in the case of 2,3-butanedione bis(cyclopropylimine). In general, they react further by cleavage of one CO ligand and concomitant change of the $\sigma, \sigma\text{-N, N}'$ coordination mode to $\sigma\text{-N}, \mu^2\text{-N}', \eta^2\text{-CN}'$ ($6e$) bonding to the Mn-Co unit³³. This process is shown in Fig. 7. The X-ray structure of $[\text{MnCo}(\text{CO})_6(t\text{-Bu-DAB})]$ has been determined and has, as notable structural features, a Mn-Co single bond ($2.639(3)$ Å) and a semi-bridging CO group leaning over from the Co to the Mn centre.

$\sigma\text{-N}, \sigma\text{-N}', \eta^2\text{-CN}, \eta^2\text{-CN}'$ ($8e$)-bonded 1,4-diaza-1,3-butadienes

Recently, two X-ray structure determinations were reported for polynuclear Ru species containing the 1,4-diaza-1,3-butadiene ligand which uses all of its available electrons ($8e$) for bonding¹⁹. The structural features of $[\text{Ru}_2(\text{CO})_4(\mu^2\text{-acetylene})(\sigma, \sigma, \eta^2, \eta^2\text{-i-Pr-DAB})]$ are shown in Fig. 4. The structure contains a *cis*-dimetallo ethene ligand, while the *i*-Pr-DAB ligand is coordinated to one of the Ru atoms *via* the lone pairs of the N atoms and to the other Ru atom *via* the π -electrons of the two C-N double bonds. The consequences of this extensive use of all the available electrons for the bonding to metal centres will be outlined in section 3. Let it suffice here to remark that now both C-N bonds are extensively lengthened [$1.395(10)$ and $1.451(9)$ Å, respectively] by coordination to the Ru centre. The structure, furthermore, shows that the repulsive forces of the lone pair electrons on the N atoms, when the ligand is in the *s-cis* conformation, are ineffective because the lone pairs take part in coordination to a second metal centre. This type of bonding of the heteroolefinic $\text{N}=\text{C}-\text{C}=\text{N}$ ligand has striking similarities with the bonding of 1,3-butadiene in $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{R})=\text{C}(\text{R})-\text{C}(\text{R})=\text{C}(\text{R})\}]$. In this compound the diolefin is bonded *via* C to one Fe atom, thus forming a five-membered chelate ring, and π bonded, *via* the $\text{C}=\text{C}$ entities, to the second Fe atom³⁴.

²⁷ H. van der Poel, G. van Koten, M. Kokkes and C. H. Stam, *Inorg. Chem.* (1981) in the press.

²⁸ L. Cattalini, F. Gasparrini, L. Maresca and G. Natile, *J. Chem. Soc. Chem. Commun.* 369 (1973); L. Maresca, G. Natile, M. Galligaris, P. Delise and L. Randaccio, *J. Chem. Soc. Dalton Trans.* 2386 (1976).

²⁹ H. van der Poel and G. van Koten, *J. Organometal. Chem.* **187**, C17 (1980).

³⁰ P. Overbosch, G. van Koten and O. Overbeek, *J. Am. Chem. Soc.* **102**, 2091 (1980).

³¹ L. H. Staal, L. H. Polm, G. van Koten and K. Vrieze, *Inorg. Chim. Acta* **37**, L485 (1979).

³² L. H. Staal, G. van Koten and K. Vrieze, *J. Organometal. Chem.* **175**, 73 (1980).

³³ L. H. Staal, J. Keijsper, G. van Koten and K. Vrieze, *Inorg. Chem.* (1981) in the press.

³⁴ F. A. Cotton, *Prog. Inorg. Chem.* **21**, 1 (1976).

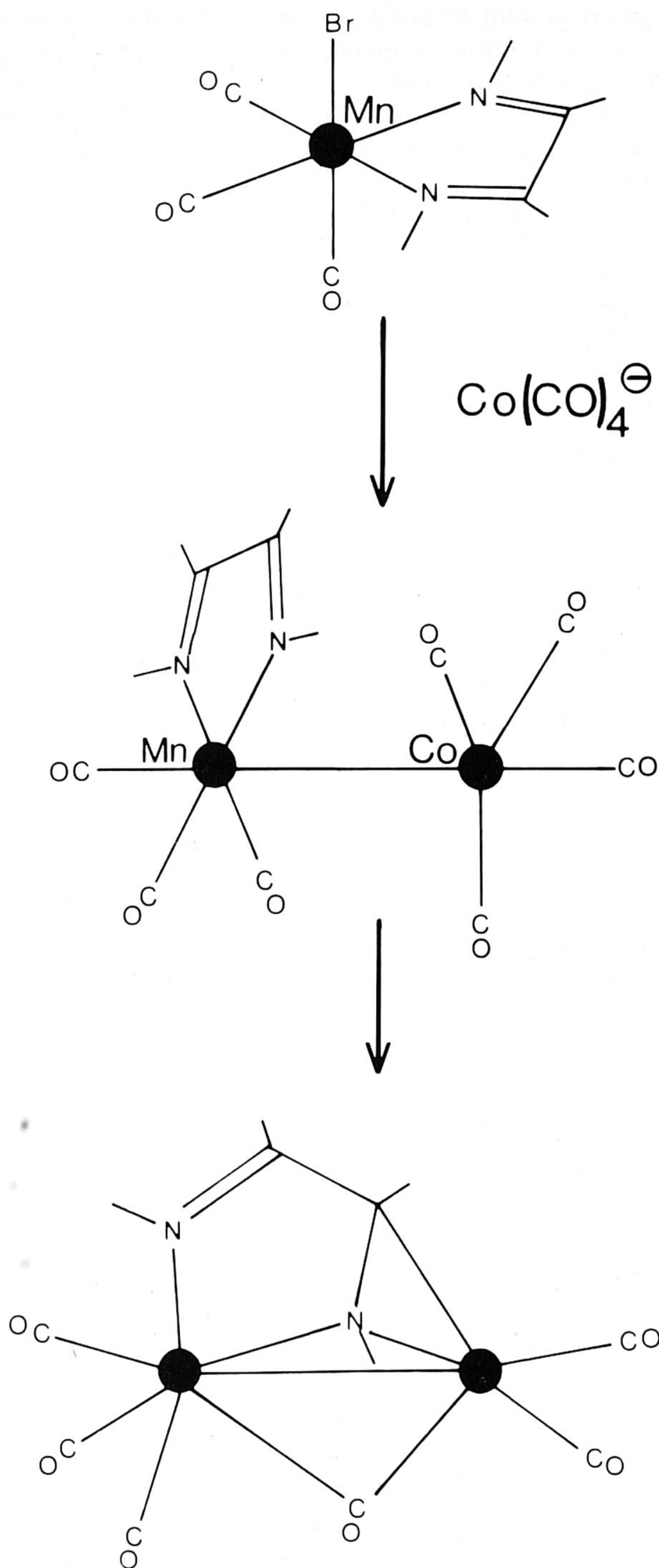


Fig. 7. Reaction pathway of the formation of $[MnCo(CO)_6(R-DAB)]$ demonstrating the change of $\sigma, \sigma-N, N'$ ($4e$) to $\sigma-N, \mu^2-N', \eta^2-CN'$ ($6e$) bonding mode of the R-DAB ligand³³.

In the second example, $[Ru_4(CO)_8(\sigma, \sigma, \eta^2, \eta^2-i-Pr-DAB)_2]$, this type of bonding leads to the structure shown in Fig. 8. The interesting point in this structure is the fact that one Ru atom is exclusively bonded to the π system of two five-membered $Ru-N=C-C=N$ chelate rings. This gives rise to a striking similarity between this part of the molecule and $[M(C_5H_5)_2]$ complexes^{19,35}.

2. The interaction of the 1,4-diaza-1,3-butadiene ligand with $[Ru_3(CO)_{12}]$ as an example of the flexibility of the ligand to donate either 2e, 4e, 6e or 8e

In the previous section a variety of bonding modes of the 1,4-diaza-1,3-butadiene ligands with metal centres have been discussed. Although the observation that the 1,4-diaza-1,3-butadiene ligand can donate either 2, 4, 6 or

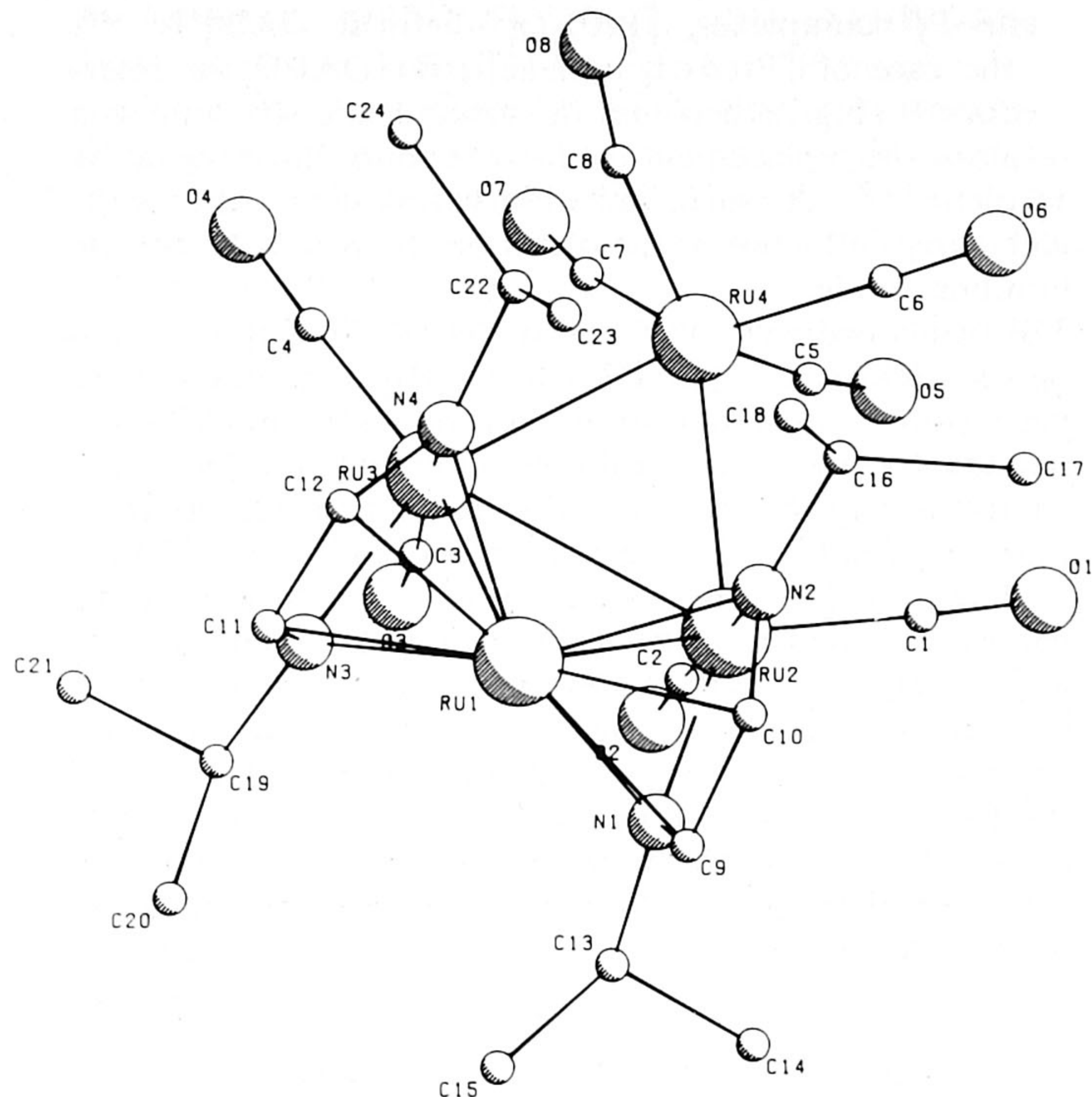


Fig. 8. Structure of $[Ru_4(CO)_8(\sigma, \sigma, \eta^2, \eta^2-i-Pr-DAB)_2]^{19}$.

8 electrons to metal entities is interesting in its own right, one would like to understand the factors which determine the donation of a given number of electrons.

An important factor is the type of metal to which the 1,4-diaza-1,3-butadiene ligand coordinates. This is illustrated by comparison of the structures found for platinum(II) and ruthenium (see Fig. 4) which reflect the greater tendency of ruthenium (by its electronic configuration) to form stable polynuclear metal species.

In a comparative study of the reactivity of the metals of the iron triad towards R-DAB it appeared that the greatest variety of products was obtained for ruthenium carbonyl derivatives due to a favourable balance between the strength of the Ru-Ru bond and the ability to eliminate or substitute CO ligands. With iron carbonyl derivatives there was a strong tendency to produce mononuclear species. This can be ascribed to the fact that Fe-Fe bonds are relatively weak compared to either Ru-Ru or Os-Os bonds³⁶.

A further factor determining the various coordination modes, which is strongly connected to the tendency of metal carbonyl fragments to eliminate CO groups, is the geometry of the coordination polyhedron. In $[Mn(CO)_5-Mn(CO)_3(R-DAB)]$ the five-membered chelate ring is perpendicular to the Mn-Mn axis. Intramolecular attack of the π system of a C=N bond, which would lead to substitution of one CO and formation of a $6e$ -bonded R-DAB ligand, does not occur because of the stability of the Mn-CO bond. In contrast, substitution takes place in $[MnCo(CO)_6(t-Bu-DAB)]$ (cf. Fig. 7). Also in this case the $\sigma, \sigma-N, N'$ -chelate-bonded R-DAB ligand is suitably positioned for intramolecular π -attack. This is, however, not the case in $[Co_2(CO)_6(R-DAB)]$ ³⁷. In this complex the five-membered chelate ring is not perpendicular to the Co-Co bond being, in fact, bent away from the Co centre to which it is not bonded but with which it would need to

³⁵ L. H. Staal, L. H. Polm, K. Vrieze, F. Ploeger and C. H. Stam, J. Organometal. Chem. **199**, C13 (1980).

³⁶ L. H. Staal, G. van Koten and K. Vrieze, J. Organometal. Chem. **206**, 99 (1981).

³⁷ L. H. Staal, P. Bosma and K. Vrieze, Inorg. Chim. Acta **43**, 125 (1981).

interact (via the π -C=N system) to become a 6e donor. The R-DAB ligand is actually locked in this position by the two bridging CO groups which are at the intersections of the dioctahedral arrays.

The nature of the other ligands bound to the metal will also play an important role. This effect of co-ligands can be deduced from the behaviour of *trans*-[PtCl₂L{*t*-Bu-NC(H)C(H)N-*t*-Bu}] in which L is either PBu₃ or C₂H₄ (see Fig. 4). The coordination mode of *t*-Bu-DAB here depends on the type of the ligand L *trans* to *t*-Bu-DAB ligand. In the case of PBu₃ we observed a groundstate structure having a 2e-bonded *t*-Bu-DAB ligand, whereas with ethene a trigonal bipyramidal structure is stabilized in which the *t*-Bu-DAB ligand donates 4e to the platinum centre. This can be explained by the greater electron-accepting properties of the olefinic system compared to those of the phosphine. This allows extensive back-bonding from the platinum *d* orbitals into π^* orbitals of the olefin, thus compensating for the increase in donation by the *t*-Bu-DAB ligand from 2 to 4 electrons.

Throughout our studies, however, a picture has slowly started to develop which reveals another factor connected with the 1,4-diaza-1,3-butadiene ligand itself, namely the nature of R. This can best be illustrated by discussing the reaction of [Ru₃(CO)₁₂] with various 1,4-diaza-1,3-butadiene ligands.

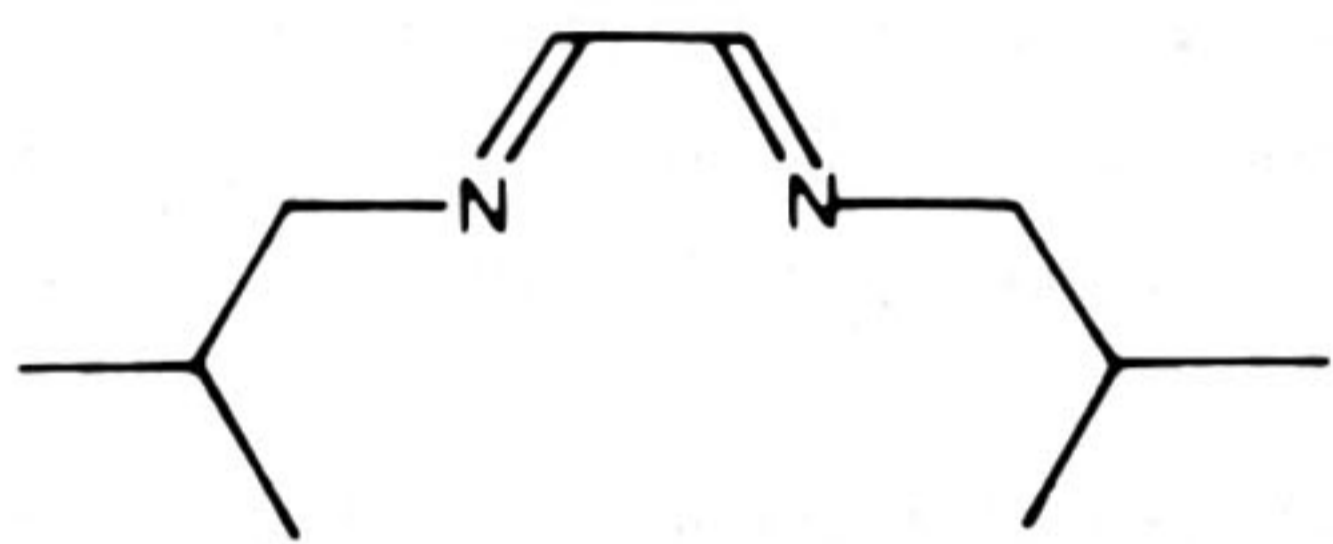
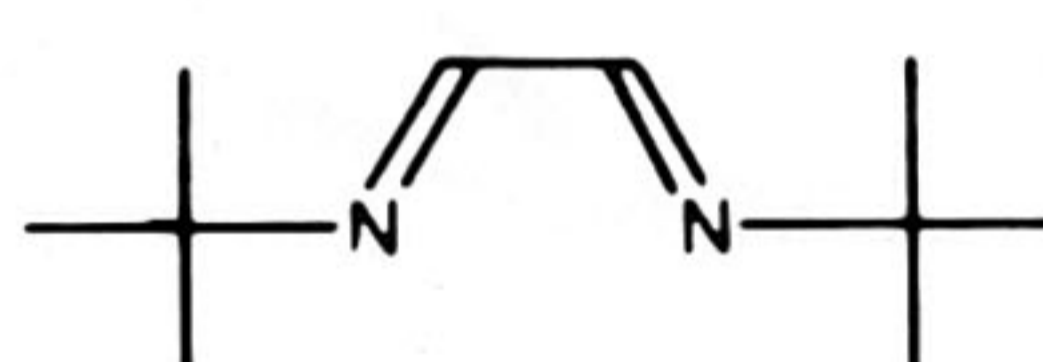
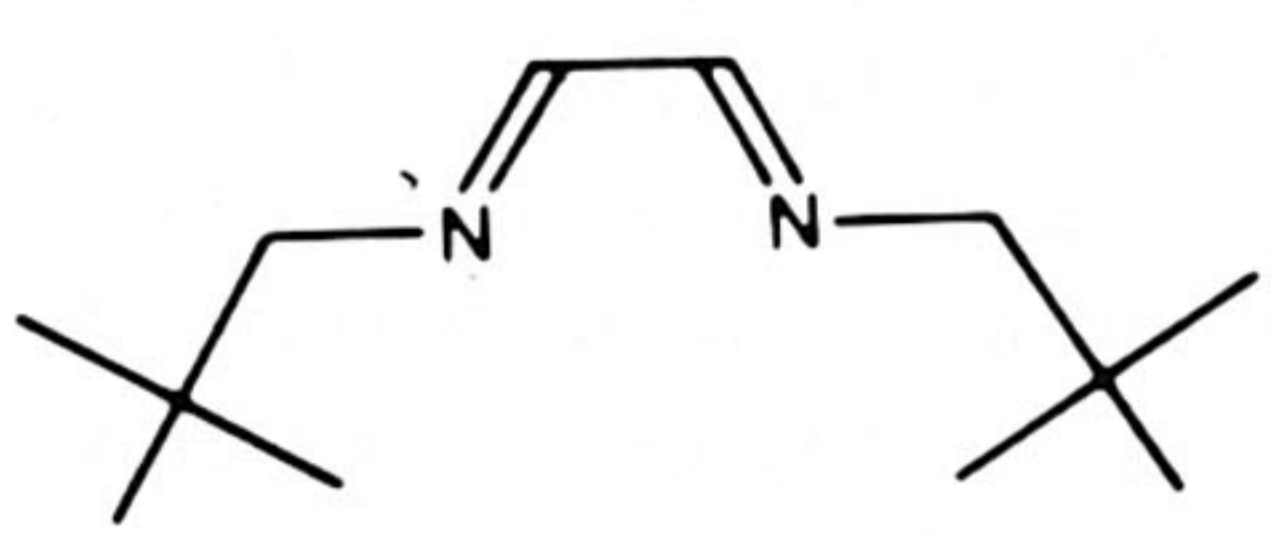
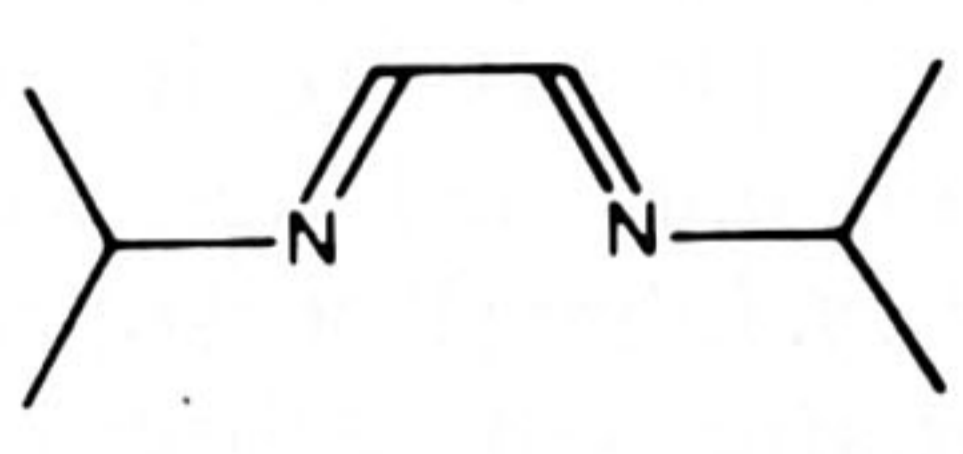
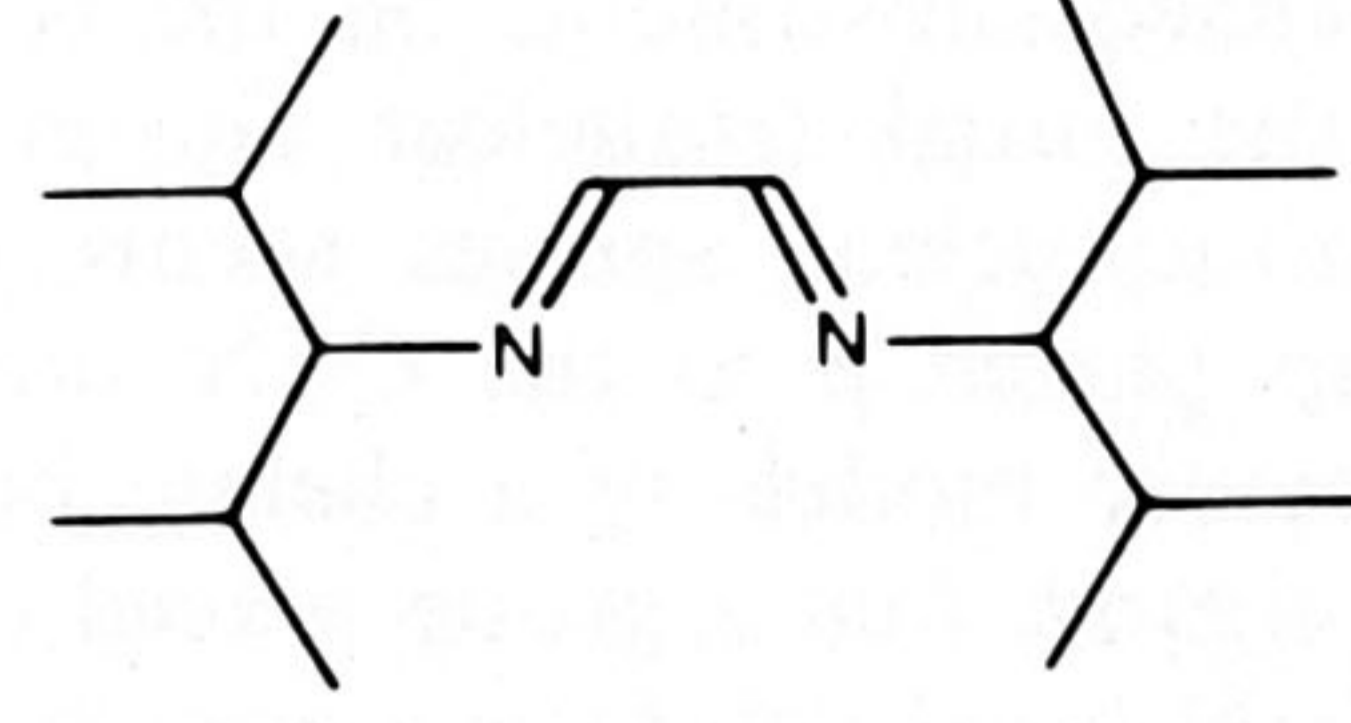
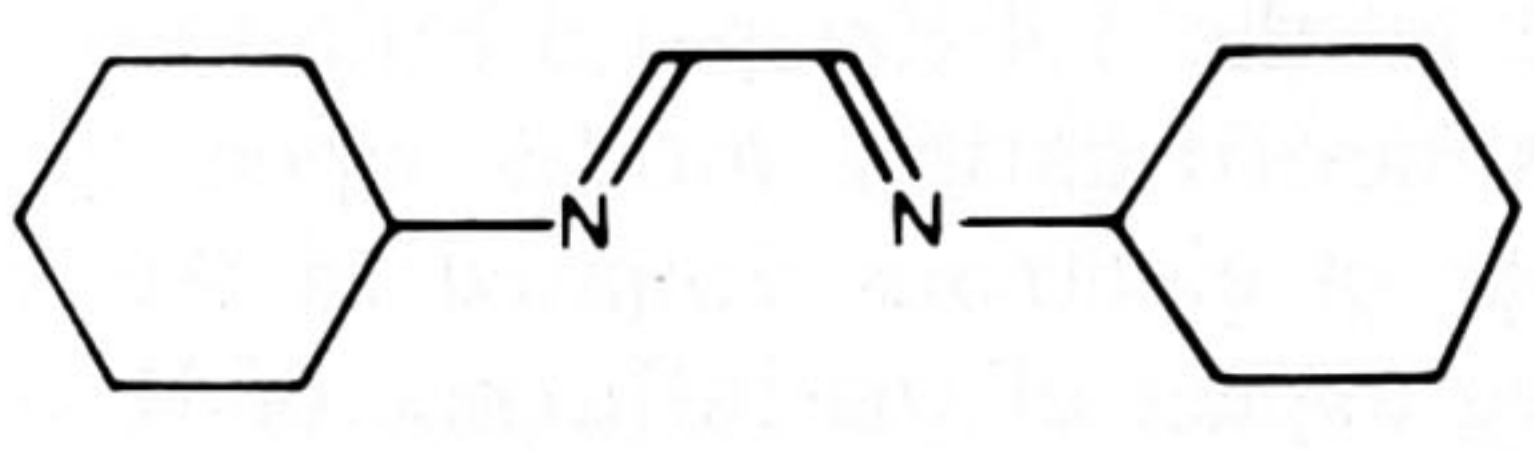
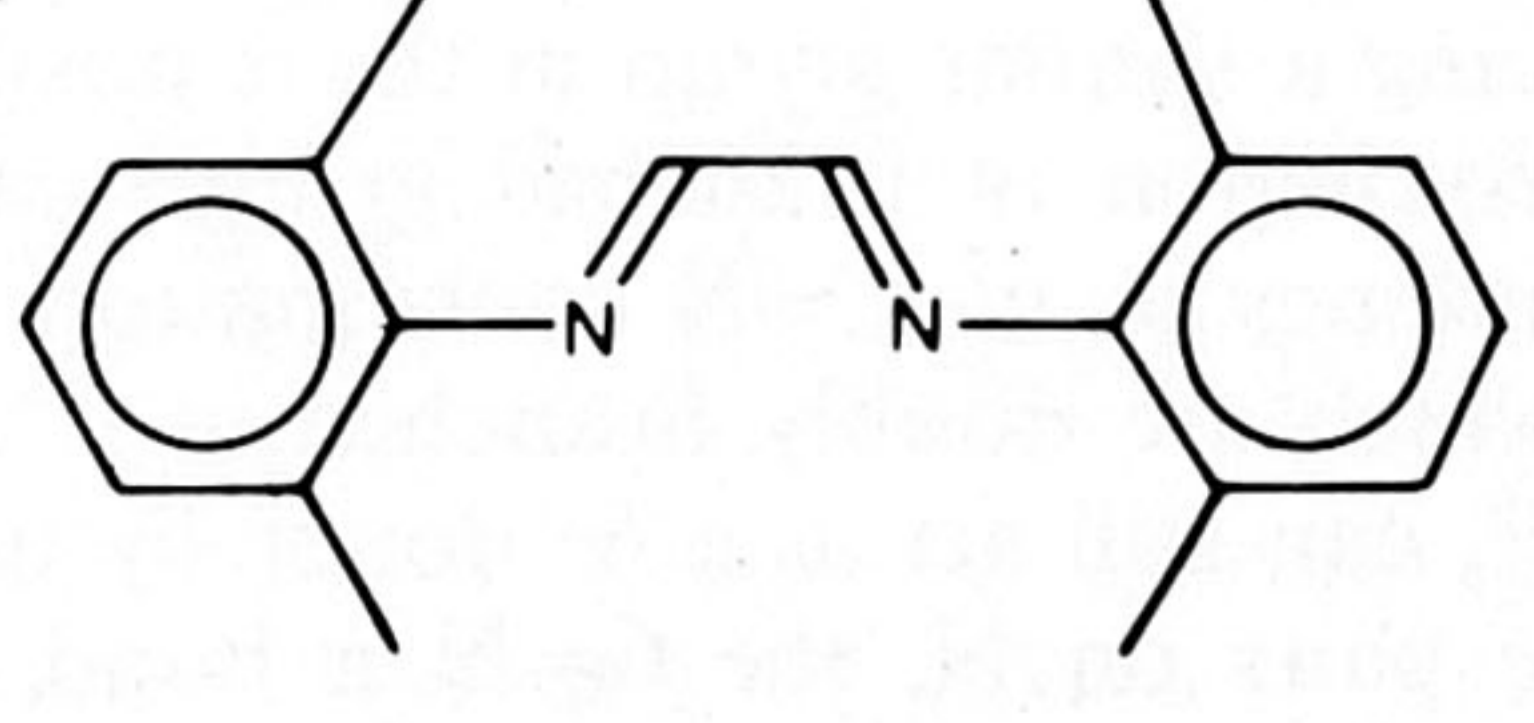
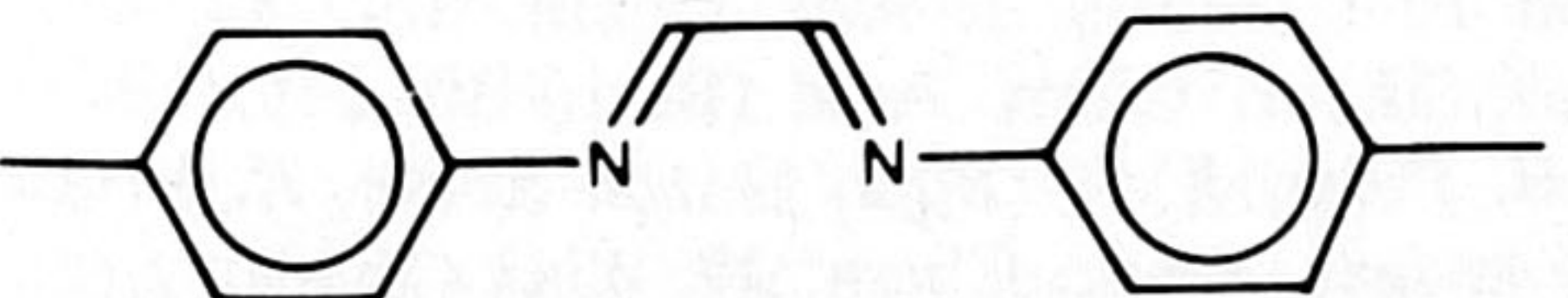
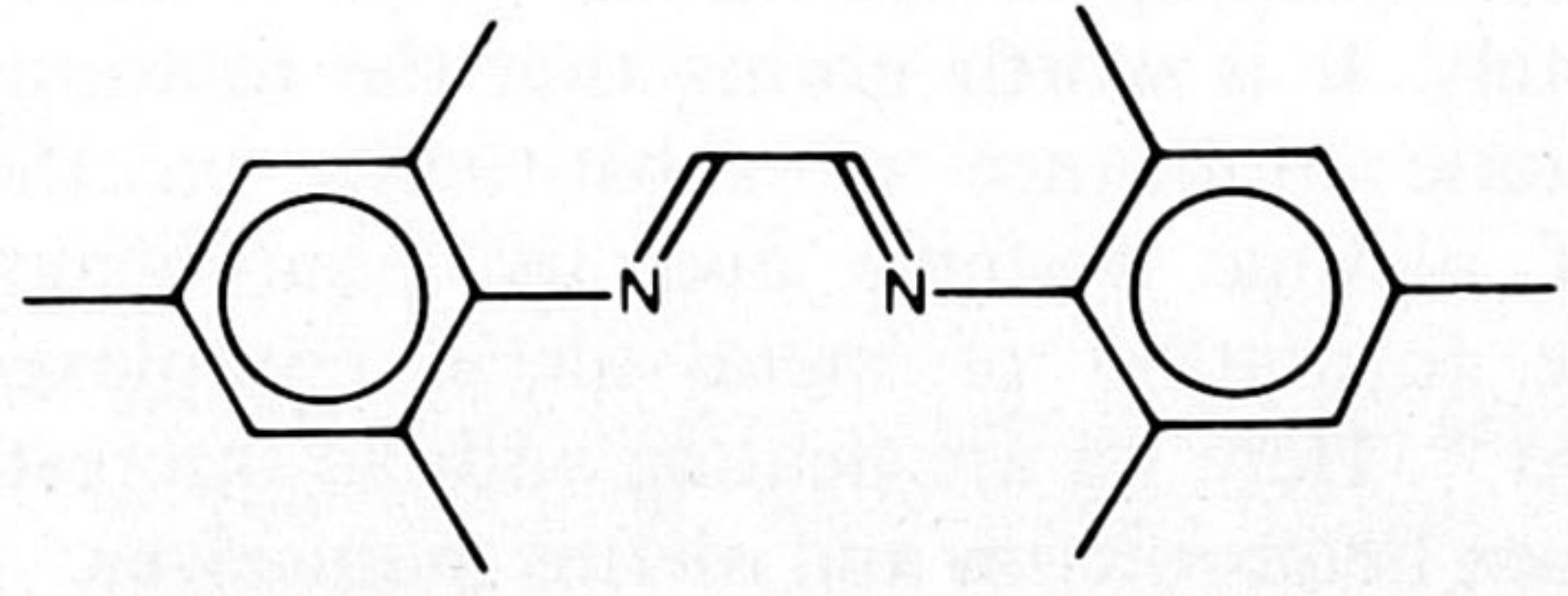
The influence of R in RN=C(H)-C(H)=NR

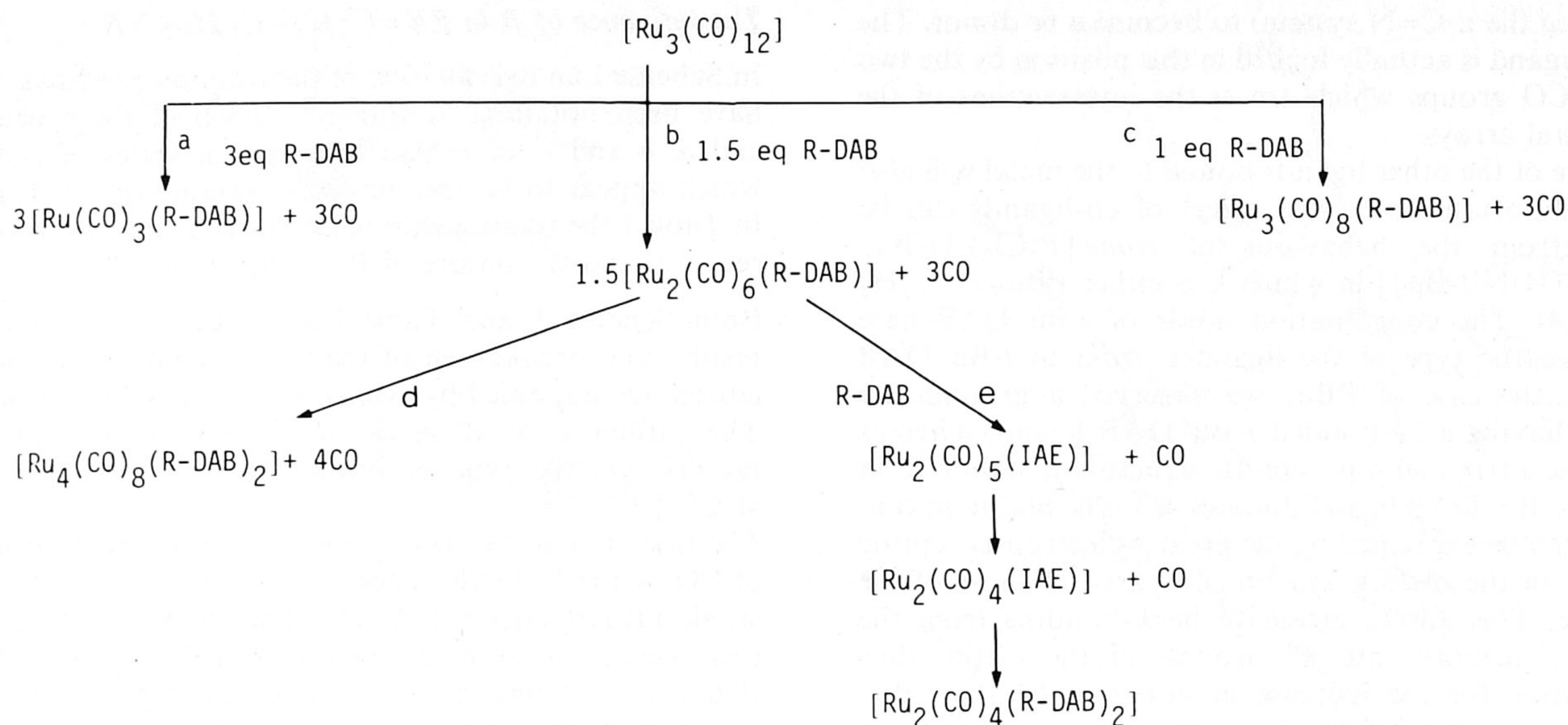
In Scheme 1 an overall view of the reaction products, which have been obtained, is shown³⁵. Each of the routes *a*, *b* and *d*, *b* and *e*, or *c* lead to a special series of products which appear to be specific for a certain type of R group. In Table I the relationship between the route chosen by the reaction and the nature of R is presented.

Both Scheme 1 and Table I show that most complexes result from breakdown of the initial trinuclear ruthenium cluster accompanied by extensive rearrangement processes. The influence of R seems to depend mainly on steric factors, *i.e.* the type of branching at C^α and even that at C^β.

The first step in the cluster breakdown will be substitution of CO by the R-DAB ligand (route *c*) leading ultimately to stable [Ru₃(CO)₈(R-DAB)]. That the R-DAB ligand in this case acts as an 8e donor can be deduced from the fact that four CO ligands, *i.e.* four electron pairs have been substituted. It is very likely that this substitution of CO groups involves a stepwise process including successive formation of 2e σ -N monodentate-, 4e σ, σ -N,N' chelate- and 6e σ -N, μ^2 -N', η^2 -CN'-bonded R-DAB ligand. The isolation of [Os₃(CO)₉(R-DAB)] from the related reaction of [Os₃(CO)₁₂] with R-DAB, in which the R-DAB ligand acts as a 6e donor, supports this assumption³⁶.

Table I Products obtained from the reaction of [Ru₃(CO)₁₂] with 1,4-diaza-1,3-butadienes.

singly branched at C _α		triply branched at C _α	
	[Ru ₃ (CO) ₈ (R-DAB)] [Ru ₄ (CO) ₈ (R-DAB) ₂]		[Ru ₂ (CO) ₆ (R-DAB)]
			
doubly branched at C _α singly branched at C _β		doubly branched at C _α doubly branched at C _β	
	[Ru ₂ (CO) ₆ (R-DAB)] [Ru ₂ (CO) ₄ (R-DAB) ₂] [Ru ₄ (CO) ₈ (R-DAB) ₂]		[Ru(CO) ₃ (R-DAB)]
			
	[Ru ₂ (CO) ₄ (R-DAB) ₂]		



Scheme 1. Overall view of the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with 1,4-diaza-1,3-butadienes, see also Table I

The trinuclear Ru complexes have been exclusively isolated (in high yields) for the R-DAB ligands in which R is single branched at C^α . This is most probably due to the fact that a singly branched R group can orientate itself in such a way that the α substituent (*i*-Pr or *t*-Bu) points away from the cluster with the two, small H atoms facing towards it. Two possible structures are shown in Fig. 9.

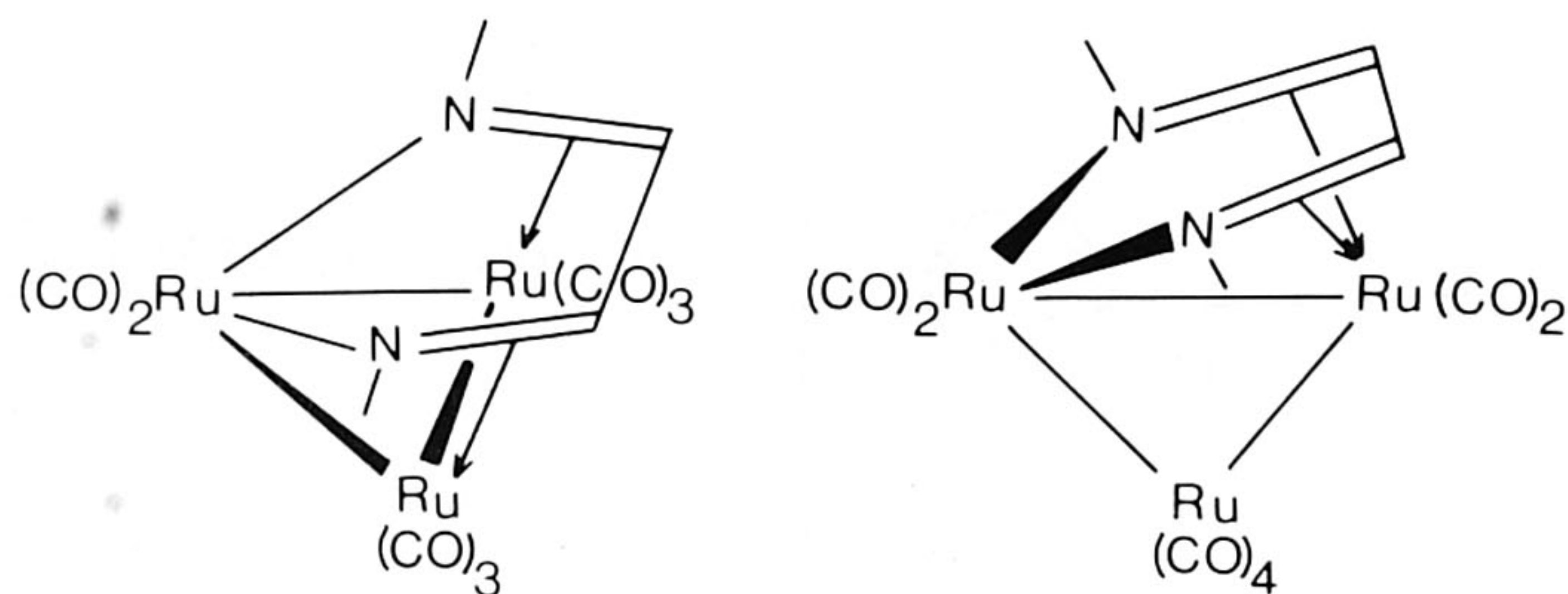


Fig. 9. Proposed³⁵ structures of $[\text{Ru}_3(\text{CO})_8(\text{R-DAB})]$; R is an alkyl group which is singly branched at C^α .

This figure reveals that these R groups do not interfere with the attack of the $\text{C}=\text{N}$ π -system on the Ru centres, leading to η^2 bonding, neither during the substitution process (via $[\text{Ru}_3(\text{CO})_9(\text{R-DAB})]$) nor in the final product³⁵.

The use of further branched substituents on the N atom causes breakdown of the initial trinuclear cluster. The total breakdown to mononuclear species seems to be dependent on the group placed β to the $\text{C}=\text{N}$ bond. It can be seen, from molecular models of a chelate bonded 1,4-diaza-1,3-butadiene ligand, that a group placed on the carbon atom β to the $\text{C}=\text{N}$ bond will have a greater effect in blocking the approach of a second metal centre to the $\text{C}=\text{N}$ bond than placing a similar group in the α position. This means that introduction of branched groups causes a reduction in the tendency to η^2 - $\text{C}=\text{N}$ coordination.

Whereas R groups which are doubly branched at C^α , but singly branched at C^β , can still act as a 6e donor by using, in addition to the 2e pairs on N, the $\text{C}=\text{N}$ π bond, it is clear that double branching at C^β blocks η^2 - $\text{C}=\text{N}$ coordination completely. It is worth noting that the relationship between steric hindrance of substituents on the double bond of olefinic systems and the equilibrium constant for the formation of metal-olefin complexes is well-established³⁸. Here we are dealing with an interesting parallel between heteroolefins and olefins themselves.

This line of argumentation can explain the formation of the $[\text{Ru}_3(\text{CO})_8(\text{R-DAB})]$, $[\text{Ru}_2(\text{CO})_6(\text{R-DAB})]$ and $[\text{Ru}(\text{CO})_3(\text{R-DAB})]$ species. Steric arguments also provide an explanation for the observation that introduction of a CH_3 group at one of the imino-C atoms causes a regioselective coordination behaviour in the $[\text{Ru}_2(\text{CO})_6(\text{R-DAB})]$ complexes, *i.e.* the $\text{R}-\text{N}=\text{CXCH}_3$ side of the R-DAB ligand will σ -N coordinate, while the $\text{R}-\text{N}=\text{C}(\text{H})$ half of the ligand provides 4e for the bonding (σ -N' and η^2 -CN'). An additional factor may be that the methyl groups cause a further increase in the electron density in the already slightly polarized $\text{C}=\text{N}$ bonds, which results in a decrease in the π -acceptor properties of the imine fragments³³.

Scheme 1 shows that tetranuclear species and even species containing two R-DAB ligands can also be formed. In separate experiments it could be demonstrated that $[\text{Ru}_4(\text{CO})_8(\text{R-DAB})_2]$ species (R = *i*-Pr or cyclohexyl) are formed *via* $[\text{Ru}_2(\text{CO})_6(\text{R-DAB})]$ ³⁵. The formation of these clusters by dimerization requires the occurrence of a variety of rearrangement and bond breaking processes. The efficiency of the, as yet unelucidated, reaction process is demonstrated by the fact that these tetranuclear clusters are formed in nearly quantitative yields.

So far, the inductive influence of the R groups has not been taken into account, this being justified by the observation that mononuclear Ru complexes are formed when R is either an aryl or alkyl substituent. However, when the R group is doubly branched at C^α , but not at C^β , a considerable difference in the type of species formed is observed. When R is *p*-tolyl, $[\text{Ru}_2(\text{CO})_4(\text{R-DAB})_2]$ is directly formed³⁹. The various intermediates, which could be isolated when R is either cyclohexyl or isopropyl (*vide infra*), are obviously too unstable with respect to the final product when R is *p*-tolyl. The exact nature of these intermediates, which is related to the activation of the R-DAB molecule by η^2 -CN coordination, is discussed in section 3.

In this section we have briefly discussed the influence of the organic group bound to the 1,4-diaza-1,3-butadiene skeleton on the various coordination modes open to this ligand (*i.e.* the number of electrons donated to the metal entity). One interesting aspect of the influence of R which

³⁸ M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.* **84**, 4697 (1962); S. Sakati, *Theor. Chim. Acta (Berl.)* **30**, 159 (1973).

³⁹ L. H. Staal, L. H. Polm, R. W. Balk, G. van Koten, K. Vrieze and A. M. F. Brouwers, *Inorg. Chem.* **19**, 3343 (1980).

still has to be discussed is its effect on the intramolecular mobility of the other ligands bound to the metal centre.

Extensive investigations by *tom Dieck* et al.⁴⁰ have shown that in $[M(CO)_4(R-DAB)]$ complexes containing a $\sigma, \sigma-N, N'$ R-DAB ligand the CO groups can change positions in the octahedral array *via* a so-called stereoisomerization process. The energy of this process depends on the steric hindrance exerted by the R groups. An R group which is triply branched at C^α (e.g. *t*-Bu) blocks this process on the NMR time scale. However, introduction of an aryl group lowers the activation barrier for an intramolecular CO rearrangement *via* an "umbrella mechanism" ($C_{2v} \rightleftharpoons C_{4v}$), because the aryl groups can minimize the steric interaction with the equatorial CO groups by taking a perpendicular position with respect to the chelate plane. This position is favoured by the presence of large *ortho* substituents. These conformational changes have also been studied by absorption and resonance Raman spectroscopy⁴¹.

Finally, in $[Fe_2(CO)_6(R-DAB)]$, intramolecular exchange of the CO groups takes place in such a way that they scramble in the coordination sphere of the Fe centre to which they are bound, but not between the two Fe centres (local scrambling)⁴².

3. Application of the metal-(R-DAB) interaction to the development of new organic synthetic routes and catalytic processes

In organic chemistry a tremendous number of routes have been made available, and are still being developed, for the conversion of organic molecules. *Via* such routes small entities are assembled into larger, sometimes very complex structures, or large molecules are broken down into smaller ones. Important aspects of such conversions are yields and selectivity. A recent development is the use of metals, either as a catalyst for a particular conversion, or in the form of an organometallic reagent in a stoichiometric reaction. This is not surprising since research in the organometallic field has shown that groups on metal centres can come together, oriented in a specific way with respect to each other, and that they may be induced to couple in the ligand sphere. Furthermore, the metal centre can activate a particular site in the organic molecule for further reaction by coordination to that site. In the case of heteroolefins this can lead to the synthesis of organic skeletons containing heteroatoms (*cf.* ref. 1).

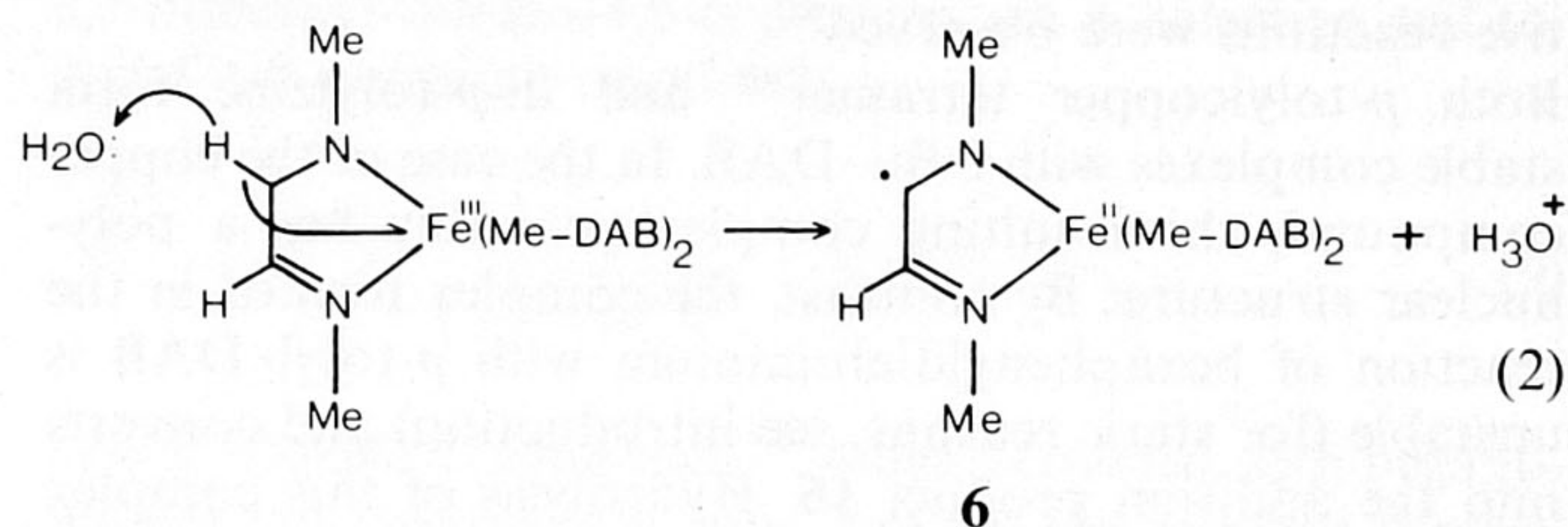
In the previous sections we have seen that the metal can interact in various ways with the 1,4-diaza-1,3-butadiene skeleton. In this section we will discuss examples in which this skeleton is converted selectively either in a stoichiometric or in a catalytic fashion.

Stoichiometric reactions

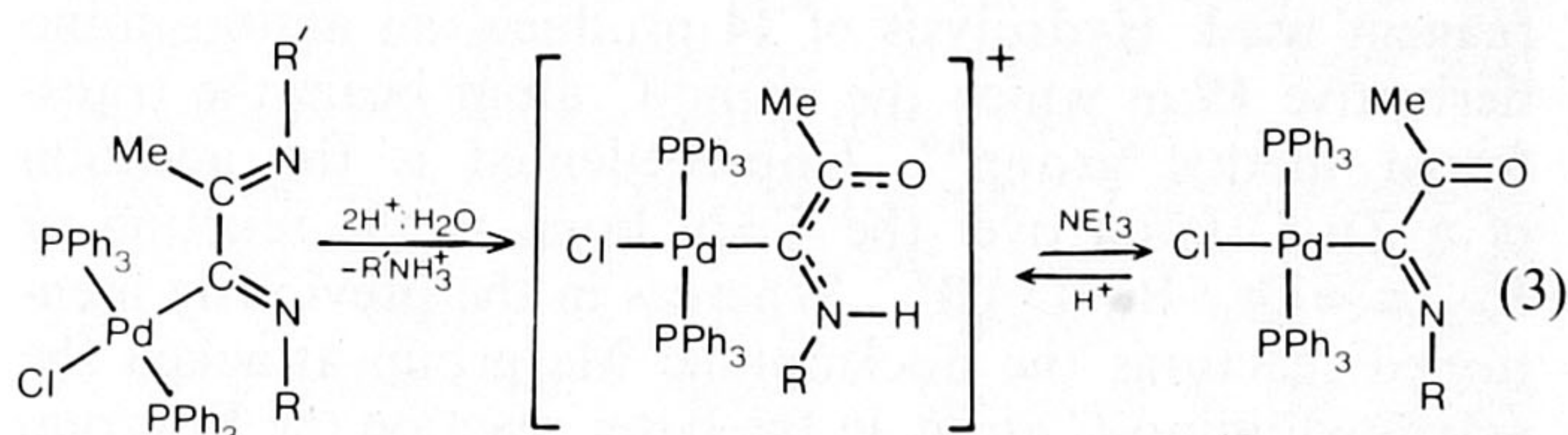
The common aspect of these reactions is that the 1,4-diaza-1,3-butadiene skeleton is converted while coordinated to the metal centre. The end-product is again an organometallic complex from which the converted R-DAB ligand can only be obtained by a subsequent cleavage reaction. Activation of a particular site in the R-DAB skeleton can be accomplished *via* coordination of the metal with the lone pairs on the N atoms, as well as by additional $\eta^2-C=N$ coordination.

a. Activation by $\sigma, \sigma-N, N'$ or $\sigma-N$ coordination. *Krumholz* and *Li Chum*⁴³ reported the oxidation of $[Fe^{II}(Me-DAB)_3]^{2+}$, with Ce^{IV} in 10M H_2SO_4 , to $[Fe^{III}(Me-DAB)_3]^{3+}$ which, *via* a disproportionation reaction, reacts to afford two new ligand-oxidized complexes, *i.e.* $[Fe(Me-DAB)_2(MeN=CHC(O)N(H)Me)]^{3+}$ or $[Fe(Me-DAB)_2(MeN=CHC(OH)=NMe)]^{3+}$ and $[Fe(Me-DAB)_2(MeN=CHCH=NCH_2OH)]^{2+}$. It has been pro-

posed that the radical complex **6**, which is formed by intramolecular electron transfer assisted by nucleophilic attack of a H_2O molecule, is the key-step in the reaction⁴⁴.

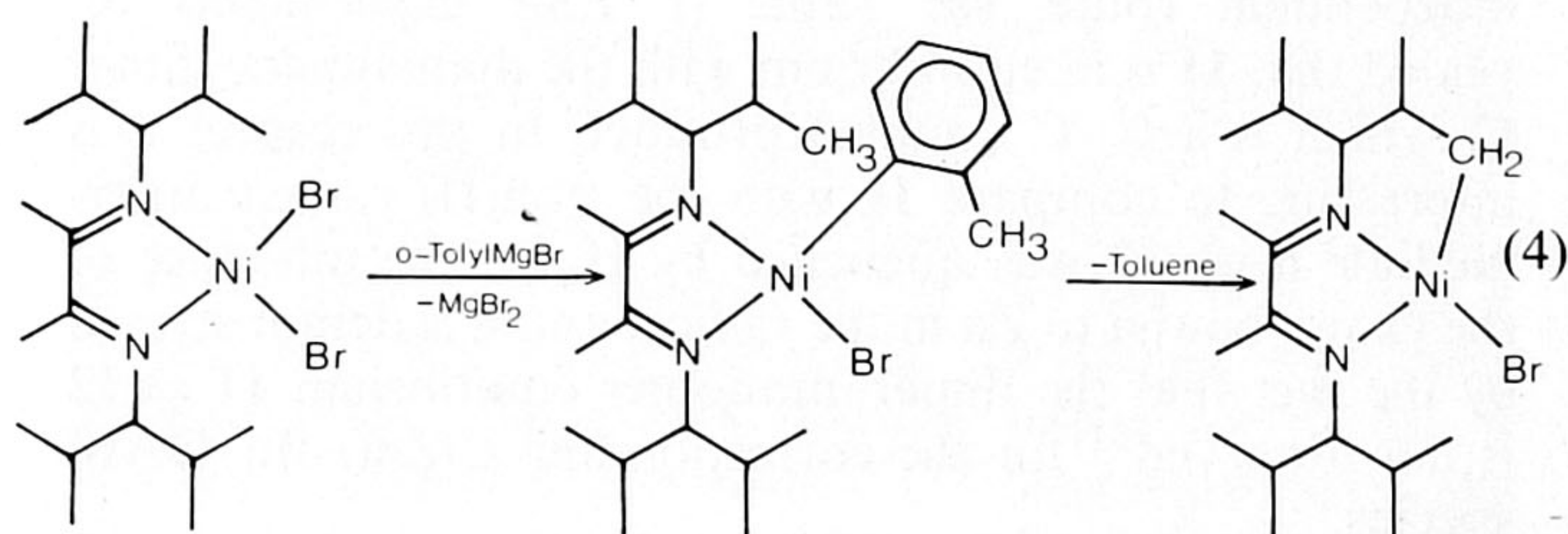


A very special case of activation is the hydrolysis reaction shown in eqn. 3:



In this reaction the R-DAB skeleton is activated by a Pd-C σ bond. The hydrolysis takes place exclusively on the C=N group not bound to the Pd atom.

Tom Dieck and *Svoboda* reported the reaction of $[NiBr_2\{i-Pr_2C(H)-DAB\}]$ with *p*-tolylmagnesium bromide⁴⁶:



Although the mechanism of the reaction is at present unclear⁴⁶, it seems plausible that initially an *o*-tolylnickel intermediate is formed from which toluene subsequently eliminates with formation of a new Ni-C bond. In such an intermediate the R substituent of the $\sigma, \sigma-N, N'$ bonded R-DAB is brought into close proximity of the reactive Ni-*o*-tolyl bond, thus facilitating the intramolecular elimination reaction.

Similar arguments play an important role in the reactions of R_3Al , R_2Zn , RCu , RLi and $RMgX$ compounds with 1,4-diaza-1,3-butadiene ligands. In addition to coordination, very selective conversions of the R-DAB skeleton have been observed which, based on the almost quantitative yields of the products, have real synthetic importance. Examples are shown in Table II.

⁴⁰ *W. Majunke, D. Leibfritz, T. Mack and H. tom Dieck, Chem. Ber.* **108**, 3025 (1975).

⁴¹ *L. H. Staal, A. Terpstra and D. J. Stufkens, Inorg. Chim. Acta* **34**, 97 (1979).

⁴² *L. H. Staal, J. Keijsper, L. H. Polm and K. Vrieze, J. Organometal. Chem.* **204**, 101 (1981).

⁴³ *H. Li Chum and P. Krumholz, Inorg. Chem.* **13** 514 (1974); *Inorg. Chem.* **13**, 519 (1974).

⁴⁴ *H. Li Chum, T. Rabockai, J. Phillips and R. A. Osteryoung, Inorg. Chem.* **16**, 812 (1977).

⁴⁵ *B. Crociani, Inorg. Chim. Acta* **23**, L1 (1977).

⁴⁶ *H. tom Dieck and M. Svoboda, Chem. Ber.* **109**, 1657 (1976); *H. tom Dieck, M. Svoboda and J. Kopf, Z. Naturforsch* **33b**, 1381 (1978).

The reaction of RLi, RMgX and R_2CuLi (cuprate) reagents with R-DAB followed by hydrolysis gave rise to the formation of extremely complex reaction mixtures. However, with RCu, R_3Al and R_2Zn reagents very selective reactions were observed⁴⁷.

Both *p*-tolylcopper tetramer⁴⁸ and di-*p*-tolylzinc form stable complexes with *t*-Bu-DAB. In the case of the copper compound, the resulting complex probably has a polynuclear structure. By contrast, the complex formed in the reaction of hexaphenyldialuminium with *p*-tolyl-DAB is unstable (for steric reasons, see introduction) and converts into the addition product **16**. Hydrolysis of this complex produces the imino-amino derivative **17** in almost quantitative yield⁴⁹. This conversion is analogous to the reaction reported by Pasykiewicz et al.⁵⁰.

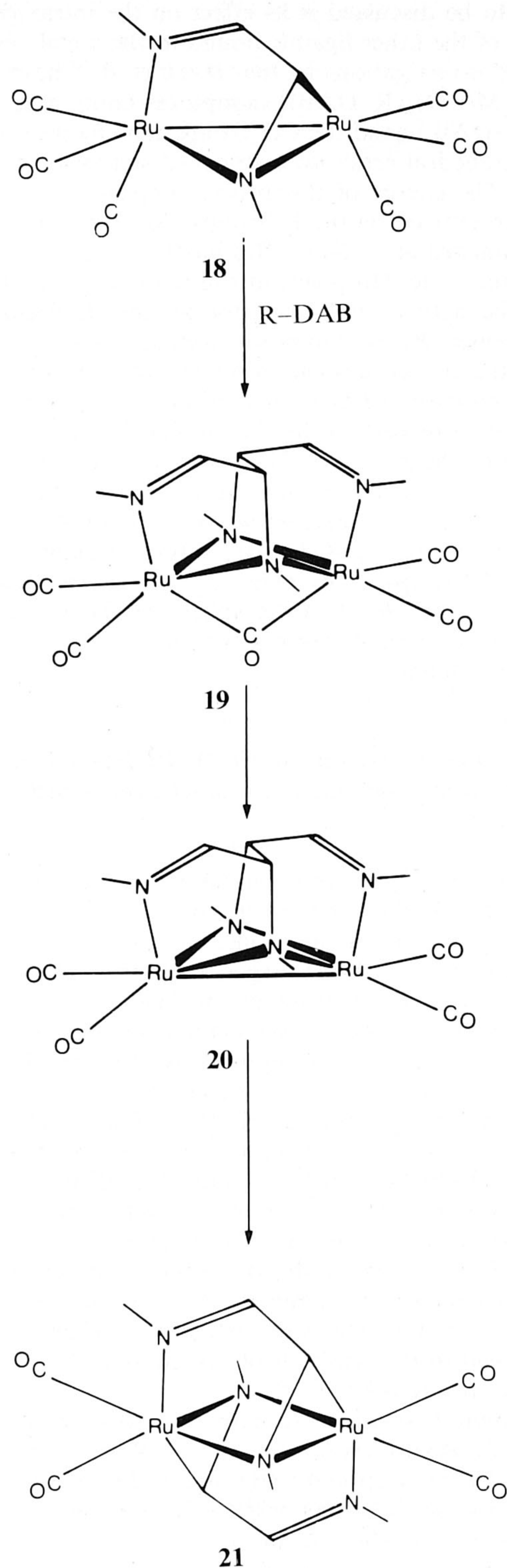
Even more interesting is the subsequent intramolecular hydride shift (**13** \rightarrow **14**) observed when Me_6Al_2 is the reagent used. Hydrolysis of **14** produces an amino-imino derivative **15** in which the imino-C atom bears the transferred methyl group⁴⁹. Unprecedented is the addition of a Zn-C bond over the C=N bond in the reaction of Et_2Zn with *t*-Bu-DAB⁴⁷. Whereas in the previously mentioned reactions the nucleophilic Me group attacked the activated imino-C atom, in the latter reaction the Et group attacks the N atom. Most probably, as a first step, $Et_2Zn(t$ -Bu-DAB) is formed (*cf.* ref. 8), followed by an intramolecular process involving either *e*-transfer/ethyl transfer or a radical cage. In this respect the presence of **11** in trace amounts is interesting because this species could result from an escape of Et from the initially formed $Et_2Zn(t$ -Bu-DAB) complex.

Compound **11** has been quantitatively prepared *via* an independent route, see Table II. ESR experiments revealed that **11** is in equilibrium with the diamagnetic dimer **12** which is a C-C coupled product. In this respect it is interesting to compare **11** with the iron(II) radical intermediate **6** which was quenched by H_2O . The influence of the group bound to Zn in the radical anion is demonstrated by the fact that the dimer-monomer equilibrium **11** \rightleftharpoons **12** is not observed⁵¹ for the corresponding $ClZn(t$ -Bu-DAB) species.

From a synthetic point of view it is interesting to note that upon hydrolysis **9** produces the novel enediamine **10** in nearly quantitative overall yield.

Tom Dieck and Bruder⁵² studied the reaction of $[K(t$ -Bu-DAB)] with alkyl halogenides (RX) and thus isolated the species, *t*-Bu-N=C(H)-C(R)=N-*t*-Bu, which results from the addition of the R group on the imino-C atom. In contrast, reaction of Me_3SiCl with $[K(t$ -Bu-DAB)] resulted in formation of *N*-silylated *cis*-enediamines and bis-*N*-silylated *trans*-enediamines, albeit in very low yields.

b. Activation by η^2 -CN coordination. An essential structural feature of the interaction and activation of 1,4-diaza-1,3-butadienes with the iron-triad metals appears to be η^2 -C=N coordination. So far we have not discussed route *e* of Scheme 1. This part of the scheme is visualized³⁹ in terms of the structures shown in Scheme 2.



Scheme 2. Reaction sequence of the reaction of $[Ru_3(CO)_{12}]$ with R-DAB showing the isolated products; $[Ru_2(CO)_6(R-DAB)]$ **18**; $[Ru_2(CO)_5(IAE)]$ **19**; $[Ru_2(CO)_4(IAE)]$ **20** and $[Ru_2(CO)_4(R-DAB)_2]$ **21**.

Each of the steps shown could be demonstrated in separate reactions. The reaction of R-DAB (R = *i*-Pr or cyclohexyl) with $[Ru_2(CO)_6(R-DAB)]$ resulted in a C-C coupling reaction. The activating step is the η^2 -CN coordination of a C=N moiety followed by insertion of an unsaturated C=N moiety of a second R-DAB ligand. The new ligand thus formed, [1,2-bis[(alkylimino)methyl]ethylene]bis(alkylamino) (IAE), which acts as a 10e donor, could not be isolated as a free molecule.

Complex **19** is analogous to $[Mo_2(CO)_6(IAE)]$ studied earlier, the structure of which was established by X-ray analysis⁵³. The C-C bond formation between two R-DAB molecules has its counterpart in the C-C bond formation

⁴⁷ J. T. B. H. Jastrzebski, J. M. Klerks, G. van Koten and K. Vrieze, *J. Organometal. Chem.* (1981) in the press.

⁴⁸ G. van Koten, J. T. B. H. Jastrzebski and J. G. Noltes, *J. Org. Chem.* **42**, 2047 (1977).

⁴⁹ J. M. Klerks, D. J. Stufkens, G. van Koten and K. Vrieze, *J. Organometal. Chem.* **181**, 271 (1979).

⁵⁰ R. Griezyski, S. Pasykiewicz and A. Serwatowska, *J. Organometal. Chem.* **69**, 345 (1974).

⁵¹ P. Clopath and A. von Zelewsky, *Helv. Chim. Acta* **55**, 52 (1972).

⁵² B. Bruder, Ph.D. Thesis, University of Frankfurt, 1979.

⁵³ L. H. Staal, A. Oskam, K. Vrieze, E. Roosendaal and H. Schenk, *Inorg. Chem.* **18**, 1634 (1979).

observed between the two N=C–C=O skeletons of ethyl (α -methylbenzylimino)acetate bound to a $[\text{Fe}_2(\text{CO})_6]$ unit⁵⁴. When $[\text{Ru}_2(\text{CO})_5(\text{IAE})]$, **19**, is heated, loss of a CO ligand takes place with formation of stable **20**. On prolonged heating the latter compound undergoes a C–C bond cleavage reaction in the IAE ligand resulting in formation of the bis(1,4-diaza-1,3-butadiene) compound **21**, $[\text{Ru}_2(\text{CO})_4(\text{R-DAB})_2]$. This complex, the structure of which was determined by X-ray methods, contains two 6e-donating R–DAB ligands³⁹.

The effect of the group R on the reactivity and stability of the complexes (*i.e.* *i*-Pr vs. *p*-tolyl) is remarkable and points to a delicate balance of the electronic distribution in the ligand system. It is important to note that the C–C coupling reaction takes place exclusively between imino-C atoms bearing a H atom. So far no coupling has been observed between methyl-substituted imino-C atoms. Accordingly, the R–DAB ligand R–N=C(H)–C(Me)=NR undergoes regio-selective coupling at the N=C(H) side (η^2 -CN-coordinated, *vide supra*) of the molecule.

The role of the metal is demonstrated by the fact that whereas C–C coupling has been observed for Ru and Mo, no coupling takes place in the analogous Fe and W compounds.

c. Catalytic reactions. The α -diimine ligands, 2,2'-bipy and 2-pyridinecarbaldehyde imines, which may be considered to contain, in a formal sense, 1,4-diaza-1,3-butadiene as part of their skeleton (see Fig. 2), are frequently used as coligands in catalytic systems. In such processes the 1,4-diaza-1,3-butadiene system functions as a modifier of the processes taking place at the active site of the metal catalyst.

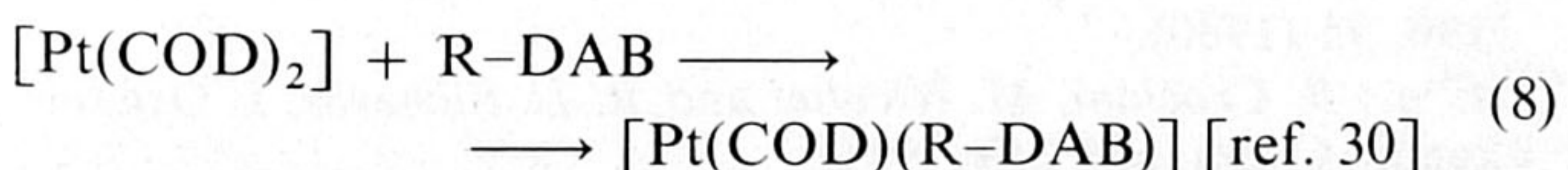
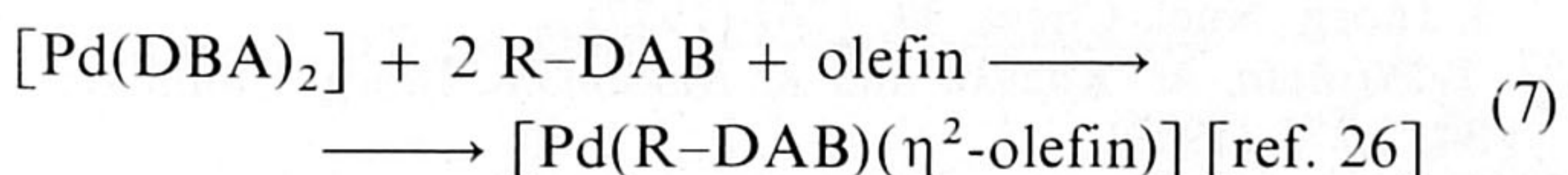
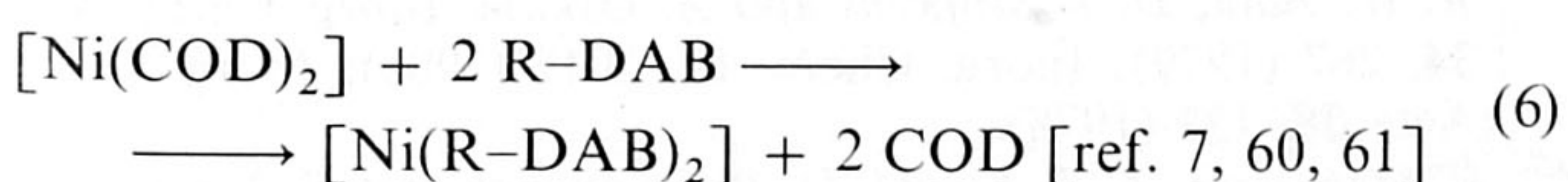
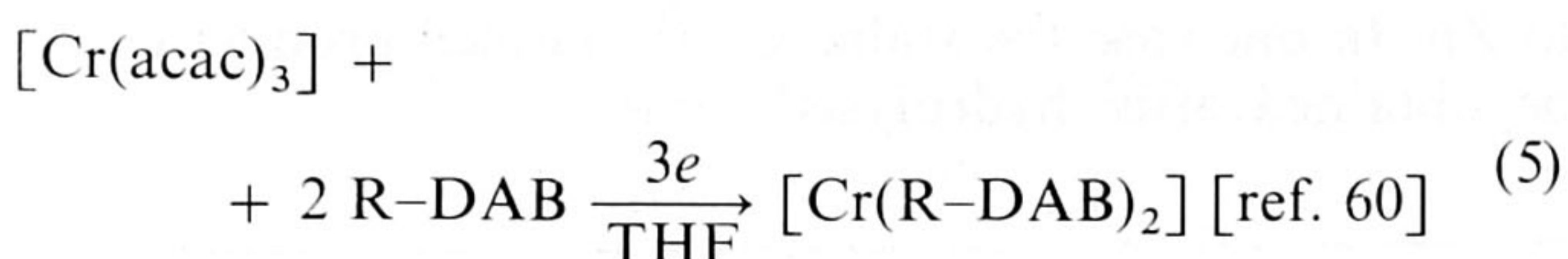
In this section we will discuss a few of the recent developments in this area. However, before doing so, one example in which R–DAB itself is converted to 2-imidazolinone in a catalytic cycle will be considered.

A reinvestigation⁵⁵ of the metal–(R–DAB) bonding in $[\text{Fe}(\text{CO})_3(\text{R-DAB})]$ complexes revealed that:

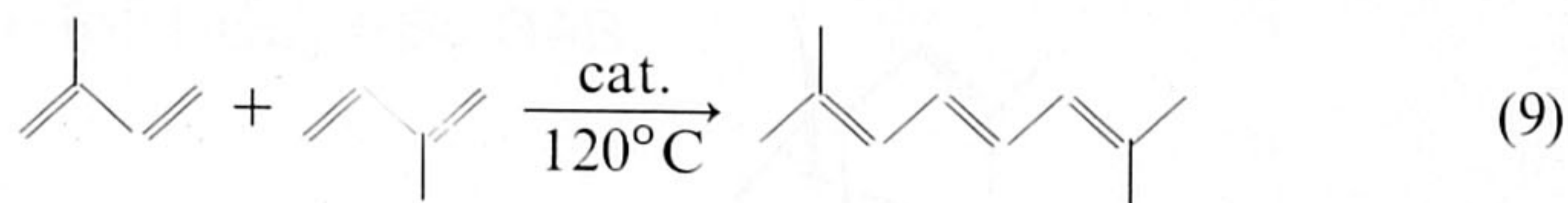
i. the R–DAB ligand is σ, σ -N,N' chelate-bonded (*cf.* ref. 56) and not σ, π , as proposed earlier by *tom Dieck* et al.⁵⁷⁻⁵⁸ and,

ii. $t\text{-Bu-NCH=CHN-(t-Bu)CO}$ (**22**) can be prepared by reacting *t*-Bu–DAB with CO in a pressure vessel using $[\text{Fe}_2(\text{CO})_9]$ as catalyst⁵⁵. Only three catalytic cycles could be obtained [*p*-(CO) 2.5–60 atm] because the 2-imidazolinone formation is blocked by formation of catalytically inactive $[\text{Fe}(\text{CO})_3(t\text{-Bu-DAB})]$ or $[\text{Fe}(\text{CO})_5]$.

An interesting class of zerovalent metal–1,4-diaza-1,3-butadiene compounds, which have been used as catalysts, has been developed independently by *Walther* and *tom Dieck* et al. It appeared that a large number of $[\text{Ni}(\text{R-DAB})_2]$, $[\text{Fe}(\text{R-DAB})_2]$ and $[\text{Cr}(\text{R-DAB})_2]$ complexes are accessible *via* the reactions of either zerovalent metal–ligand complexes, or *via* reduction of R–DAB/metal salt mixtures with Grignards or aluminium compounds⁵⁹⁻⁷². Examples are shown in eqns. 5–8:



The influence of the R–DAB ligands on the reactivity of the M–(R–DAB) catalysts is tremendous. $[\text{Cr}(\text{R-DAB})_2]$ [$\text{R} = -\text{C}(\text{H})(i\text{-Pr})_2$], activated by Et_2AlOEt (1 : 2 molar ratio), catalyses the conversion of isoprene to 2,7-dimethyl-2-*trans*-4,6-octatriene *via* a selective tail-to-tail C–C coupling reaction⁶¹.



$[\text{Fe}(\text{R-DAB})_2]$ complexes⁵⁹, when activated with organo-aluminium compounds, also catalyse the selective dimerization of 1,3-dienes. Depending on R in R–DAB, 1,5-cyclooctadienes or vinylcyclohexenes, in addition to dimers, are formed from butadiene and $[\text{Fe}(\text{R-DAB})_2]/\text{AlR}_3$ mixtures (300 : 1 : 2). The authors mention that the temperature dependence and product distribution are different from those reported for related 2,2'-bipy and 2-pyridinecarbaldehyde imine–iron systems⁵⁹.

It has to be noted that the catalytic activity is not exhibited by the zerovalent metal–(R–DAB) complexes themselves but by a $[\text{M}(\text{R-DAB})_n]/\text{AlR}_3$ complex. The $[\text{M}(\text{R-DAB})_n]$ compound is clearly a precursor to the actual catalytic species. In connection with the $\text{R}_3\text{Al}-(\text{R-DAB})$ reactions we have studied (see Table II), it is likely that the original R–DAB ligand is no longer present but is converted to either an aluminium-bonded imino-amino ligand or a diamino ligand. A further possibility is that true metal atom clusters M_n , with low *n* values, are produced. Such clusters would be expected to be catalytically extremely active⁶³.

Finally, we should like to mention the results which have been obtained by studying the reaction of the $[\text{Ru}_2(\text{CO})_6(\text{R-DAB})]$ complexes with acetylenes⁶⁴. It appeared that the η^2 -CN bond of the $\sigma\text{-N}, \mu^2\text{-N}', \eta^2\text{-CN}'$ -coordinated R–DAB ligand is not only activated to react with a second R–DAB ligand (see Scheme 2) but can also react with a variety of other small molecules containing triple and double bonds. The overall reaction routes are shown in Scheme 3. Reaction starts with C–C coupling between the alkyne ligand and the η^2 -CN-coordinated side of the R–DAB ligand. Formally, this is an insertion of an alkyne into a Ru–C bond.

With monosubstituted alkynes, *e.g.* $\text{PhC}\equiv\text{CH}$, $\text{MeO}_2\text{CC}\equiv\text{CH}$, this reaction occurs with complete regio-selectivity. The nature of the product **23** has been established by an X-ray structure determination which showed the complex to have interesting features as regards the bonding of the newly formed AIB (3-aminylo-4-imino-1-buten-1-yl) ligand to the $\text{Ru}_2(\text{CO})_5$ fragment⁶⁴.

$[\text{Ru}_2(\text{CO})_5(\text{AIB})]$, **23**, reacts further with alkynes to form $[\text{Ru}_2(\text{CO})_4(\text{AIB})(\text{alkyne})]$, probably by η^2 coordination which converts the bridging CO into a terminal CO. This

⁵⁴ A. DeCian and R. Weiss, J. Chem. Soc. Chem. Commun. 249 (1976).

⁵⁵ L. H. Staal, L. H. Polm and K. Vrieze, Inorg. Chim. Acta **40**, 165 (1980).

⁵⁶ S. Otsuka, T. Yoshida and A. Nakamura, Inorg. Chem. **6**, 21 (1967).

⁵⁷ H. tom Dieck and A. Orlopp, Angew. Chem. **87**, 246 (1975).

⁵⁸ D. Leibfritz and H. tom Dieck, J. Organometal. Chem. **105**, 255 (1976).

⁵⁹ H. tom Dieck and H. Bruder, J. Chem. Soc. Chem. Commun. 24 (1977).

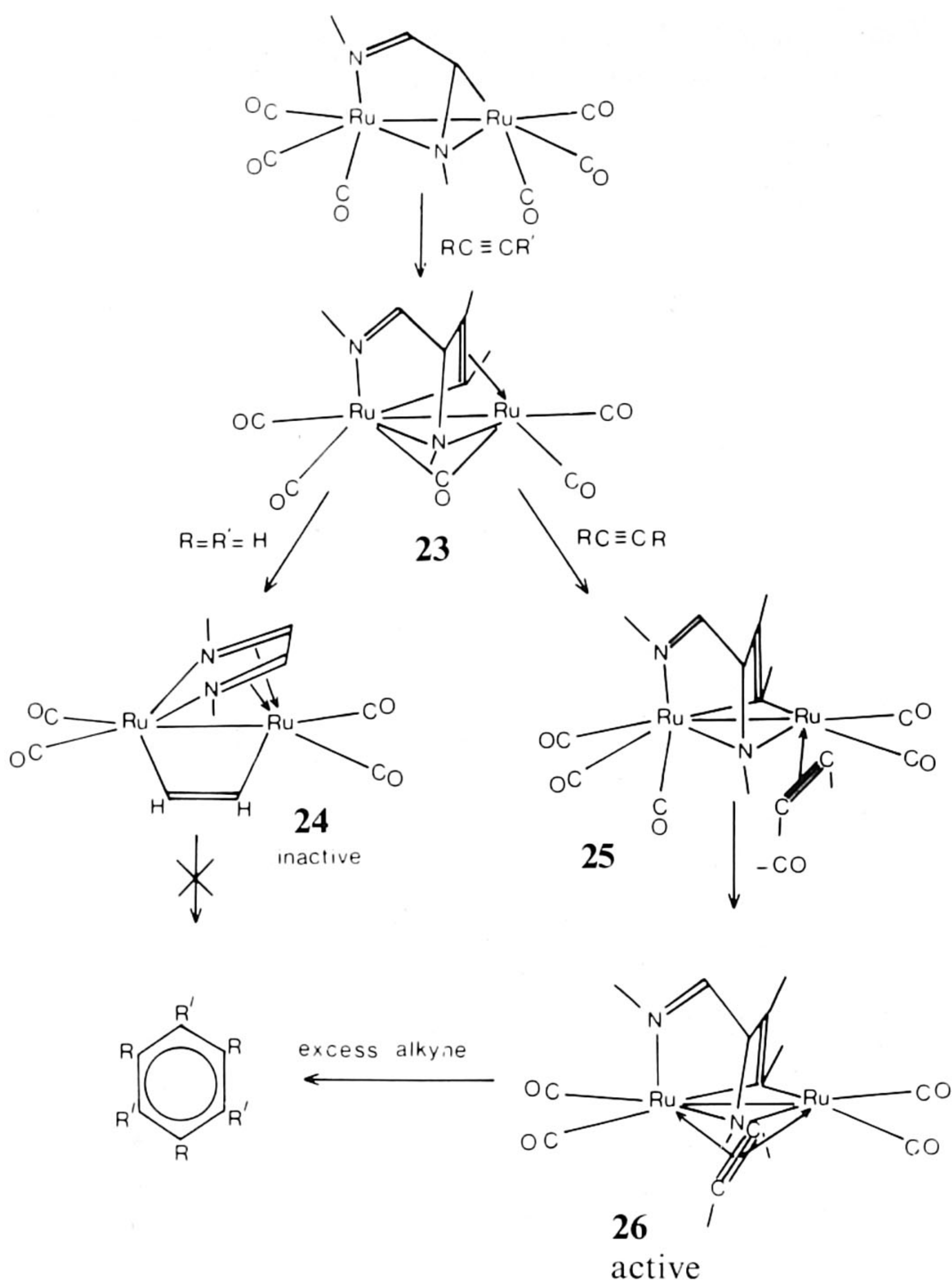
⁶⁰ D. Walther, Z. Chem. **15**, 72 (1975).

⁶¹ H. tom Dieck and A. Kinzel, Angew. Chem. **91**, 344 (1979).

⁶² D. Walther, Z. Anorg. Allg. Chem. **431**, 17 (1977).

⁶³ M. C. Cohen, J. G. Noltes and G. van Koten, U.S. Pat. 4.152.303 (1979).

⁶⁴ L. H. Staal, G. van Koten, K. Vrieze, B. van Santen and C. H. Stam, J. Am. Chem. Soc. (1981) in the press.



Scheme 3. Reactions of small molecules containing triple bonds with $[\text{Ru}_2(\text{CO})_6(\text{R-DAB})]$. The catalytic reaction for the cyclotrimerization of acetylenes⁶⁴.

complex can lose a CO which turns the formally $\eta^2\text{-C}\equiv\text{C}$ -bonded alkyne ligand into a μ^2, η^2 -bonded one (**26**).

When acetylene is used, the ultimate product is complex **24** in which the R-DAB ligand acts as a 8e donor and in which the acetylene has been converted into a *cis*-dimetallated ethene. A possible route to **24** includes formation of the C-C-coupled product, $[\text{Ru}_2(\text{CO})_5(\text{AIB})]$, which then, by analogy with the C-C-coupling/cleavage reactions observed for R-DAB (see Scheme 1 route *e* and Scheme 2), undergoes a subsequent C-C-bond cleavage.

It is interesting that the $[\text{Ru}_2(\text{CO})_4(\text{AIB})(\text{alkyne})]$ (**26**) clusters may be used for the efficient catalytic cyclotrimerization of acetylenes to benzenes. In the case of monomethyl acetylenecarboxylate the 1,3,5-trisubstituted isomer is formed exclusively; a feature which is very uncommon in catalytic alkyne trimerization reactions. Furthermore, the trimerization occurs when R is either a donor (*t*-Bu) or an acceptor (aryl or methoxycarbonyl). The rate, however, is observed to increase with increasing acceptor strength of R.

Conclusions

The 1,4-diaza-1,3-butadiene (R-DAB) chemistry described above is not intended as an extensive review of the literature (see ref. 4). In view of our own interest in the chemistry of heteroolefins we have laid emphasis on a discussion of the present state of knowledge concerning the various ways in which a R-DAB ligand can interact with metal entities together with their activation and subsequent conversion to organic molecules.

Aspects such as the detailed investigations of the bonding features of R-DAB ligands to metal centres by molecular

orbital calculations¹¹, Resonance Raman Spectroscopy⁶⁵⁻⁶⁷, and NMR and ESR spectroscopy¹³ have not been discussed. It must be noted that these studies have so far been restricted to $\sigma, \sigma\text{-N, N'}$ -bonded R-DAB ligands, since it is only during the last three years that the other bonding modes have been realized.

The chemistry of the 1,4-diaza-1,3-butadiene ligands with transition metal carbonyls is interesting because it has now been demonstrated that the N=C-C=N fragment can use, in addition to the two lone pairs on the N atoms, its π electrons for bonding. This ability contrasts with that of the 2,2'-bipy and 2-pyridinecarbaldehyde imine systems. The latter can only use the two lone pairs on the N atoms for bonding.

There is strong evidence to suggest that the imino-C atom is highly activated for further reaction as soon as the C=N system is not only σ - but also η^2 -bonded. The C-C coupling reactions with unsaturated small molecules ($\text{-C}\equiv\text{C-}$, Scheme 3, as well as C=N, *e.g.* in $\text{RN}=\text{CHCH}=\text{NR}$, Scheme 2) illustrate this. The reaction sequences in Schemes 2 and 3 in fact can be viewed as an organic synthesis of an IAE or AIB ligand on a metal surface. On the other hand, in the mononuclear $[\text{Fe}(\text{CO})_4(\text{R-DAB})]$ intermediate, formed in the catalytic reaction of $[\text{Fe}_2(\text{CO})_9]$ with R-DAB, the $\sigma\text{-N}$ -bonded R-DAB ligand is activated for CO insertion into the N-Fe bond which finally leads, *via* a second C-N bond formation, to 2-imidazolinone.

It is interesting to note that even R-DAB ligands themselves can be synthesized on metal centres. There is a very recent report by Alper et al.⁶⁸ of the synthesis of the R-DAB ligand *via* a C-C coupling reaction involving the reaction of $[\text{RC}(\text{O})\text{Ni}(\text{CO})_3]^-$ with $\text{RC}(\text{Cl})=\text{NR}$. Crociani produced a metallo-substituted R-DAB ligand *via* an insertion of one RNC molecule into a Pd-CH₃ bond, followed by insertion of a second RNC molecule into the newly formed MeC(NR)-Pd bond⁶⁹. Both the synthesis of R-DAB and the conversion of R-DAB ligands on metal centres points to the possibility of selectively assembling larger molecules from small molecules by a series of consecutive steps on mono- and polynuclear metal entities. Unfortunately, attempts to separate the organic ligand from the $[\text{Ru}_2(\text{CO})_5(\text{IAE})]$ and $[\text{Ru}_2(\text{CO})_5(\text{AIB})]$ molecules without disrupting the organic fragment failed. One factor contributing to this failure is undoubtedly the intrinsic instability of the free H₂IAE or HAIB ligands.

The flexibility in the number of electrons which can be donated by the R-DAB ligand to the metal entity is an important feature determining the catalytic activity of the M-(R-DAB) complex. However, care is needed when interpreting the results obtained with these catalytic systems. So far these systems comprise combinations of $\text{M}^0\text{-(R-DAB)}$ with R₃Al species. There is now ample evidence that organo-lithium, -aluminium, -zinc and -copper reagents do react in a variety of ways with the 1,4-diaza-1,3-butadiene system. Very unusual reactions include the production of IAE ligand systems starting from R-DAB radicals stabilized by $\sigma, \sigma\text{-N, N'}$ coordination to Zn. In one case the stable C-C-coupled product could be obtained after hydrolysis⁴⁷: *i.e.*

⁶⁵ R. W. Balk, D. J. Stufkens and A. Oskam, *Inorg. Chim. Acta* **34**, 267 (1979); *Inorg. Chem.* **19**, 3015 (1980); *Inorg. Chim. Acta* **28**, 133 (1978).

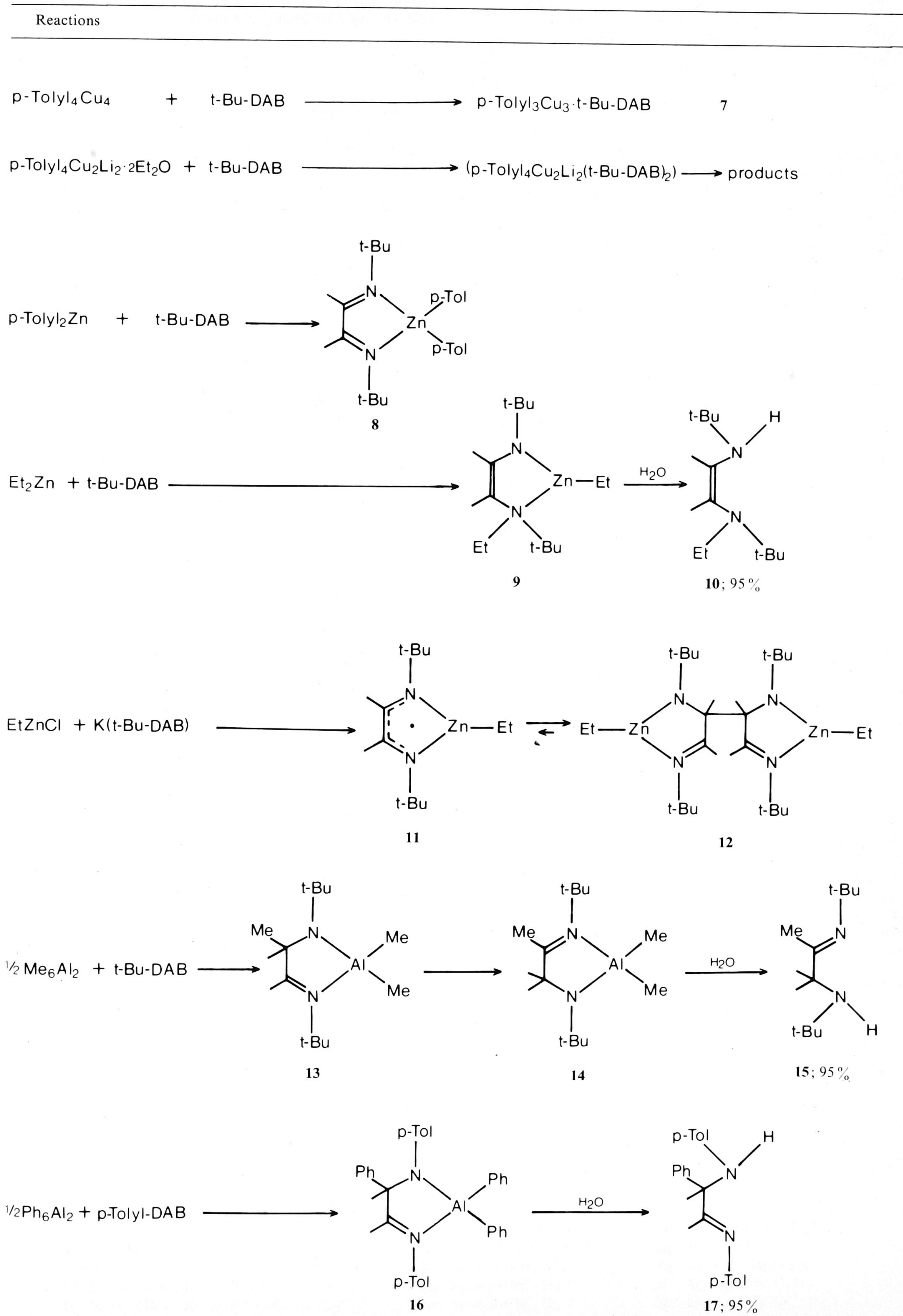
⁶⁶ B. Streusand, A. T. Kowal, D. P. Strommen and K. Nakamoto, *J. Inorg. Nucl. Chem.* **39**, 1767 (1977).

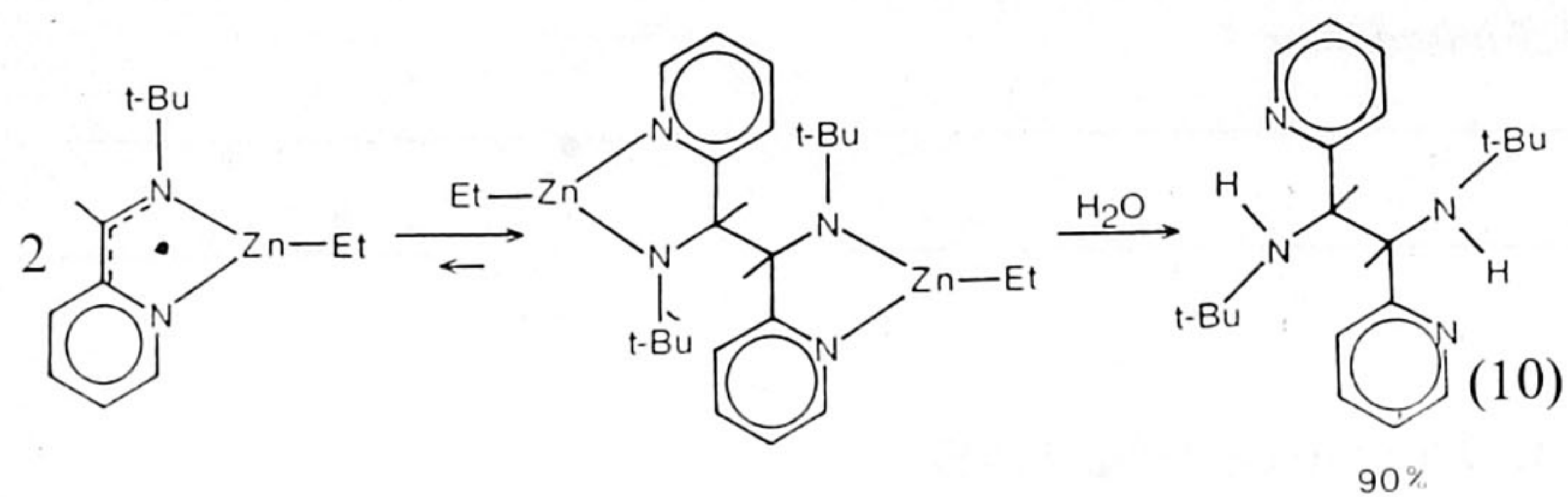
⁶⁷ Y. Nishida, M. Kozuka and K. Nakamoto, *Inorg. Chim. Acta* **34**, L273 (1979).

⁶⁸ H. Alper, M. Tanaka and K. Hachem, *J. Organometal. Chem.* **190**, 95 (1980).

⁶⁹ *E.g.*; B. Crociani, M. Nicolini and R. L. Richards, *J. Organometal. Chem.* **104**, 259 (1976).

Table II Reactions of various organometallic reagents with 1,4-diaza-1,3-butadienes.





In general, the reactions of the Zn and Al reagents seem most promising for organic synthesis (Table II). Further study is necessary to develop these findings which will undoubtedly lead not only to useful applications in organic synthesis but also to new insights into the interaction between heteroolefins and metals. It is particularly

this surprising versatility of the 1,4-diaza-1,3-butadiene system that makes its study such a fascinating area in the field of organometallic chemistry.

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