



# A QUALITATIVE $\pi$ — MOLECULAR ORBITAL RATIONALE FOR HEXACOORDINATED DINITROGEN — AND ISONITRILE-DERIVED COMPLEXES WITH METAL-NITROGEN AND METAL-CARBON MULTIPLE BONDS

*The application of Walsh type diagrams to the ligating moieties L and L' in complexes of the general types  $trans-[MLL'P_4J^{n+}]$  ( $M = Mo, W$ ;  $L$  and/or  $L' = N_2, CNR, CNHR, CNR'R$ ) and  $trans-[MXLP_4J^{n+}]$  ( $M = Mo, W$ ;  $L = N_2H, N_2R', N_2HR', N_2H_2$ ;  $X = \text{monoanionic ligand such as halide or } HSO_3^-$ ,  $P = \text{phosphine or arsine ligand}$ ) allows the prediction of their geometries and the building up of  $\pi$ -MO schemes for these and related complexes with dinitrogen and/or other isoelectronic ligands ( $CO, CN, NCR$ ). They provide a rationalization for the chemical and physical properties of those ligands and for the variable multiple bond characters of the metal-carbon and metal-nitrogen bonds.*

## 1 — GEOMETRY PREDICTIONS

The geometry of simple molecules in their ground and excited states has been rationalised by the semi-empirical and semi-quantitative Mulliken-Walsh model [1,2] which uses the basic assumption that molecular geometry is mainly determined by the number of valence electrons occupying the molecular orbitals. Tests have been made on this model, refinements proposed [3,4], and its usefulness is still widely recognised. A plot of a loosely defined function (canonical orbital energies of *ab initio* SCF type calculations, Hückel eigenvalues and other quantities have been proposed) which may have the general designation of «orbital energy»[3] against an angular variable which characterises the geometry of each class of molecules (*e.g.*,  $H\hat{A}B$  angle in HAB,  $A\hat{A}H$  in HAAH, angle of HAH plane with AB direction in  $H_2AB$ , etc.) constitutes the respective correlation diagram, the basis for the geometrical predictions.

Related diagrams have been presented more recently by GIMARC [5] for the hydrogenated species HAB and  $H_2AB$  (figs. 1-4), based on three main rules [molecular shape depends only on the number of valence electrons; an increased in-phase AO overlapping lowers the energy of the MO (AO overlap maximisation rule); orbitals of the same symmetry cannot cross during a change in geometry (noncrossing rule)] which allows one to predict conceivable shapes of 3 and 4 element groups pertinent to the present study. Replacement of H by an alkyl group may have a relatively small effect on the qualitative shape of the diagrams. In this case the  $s(H)$  orbital will be simply substituted by an  $sp^3(C)$  (without needing to consider the individual p-orbitals and p-electrons of C, at least as a first approach), thus keeping the same number of valence electrons in the ABX skeleton [ $X = s(H), sp^3(C)$ ].

We have applied these diagrams to the prediction of both ground and excited electronic state geometries of pertinent groups and the results are summarized in Table 1. Excitations have been chosen from a filled  $\sigma$ -orbital to the empty (or singly occupied)  $\pi^*$ -orbitals in an attempt to simulate the effects of coordination to a metal.

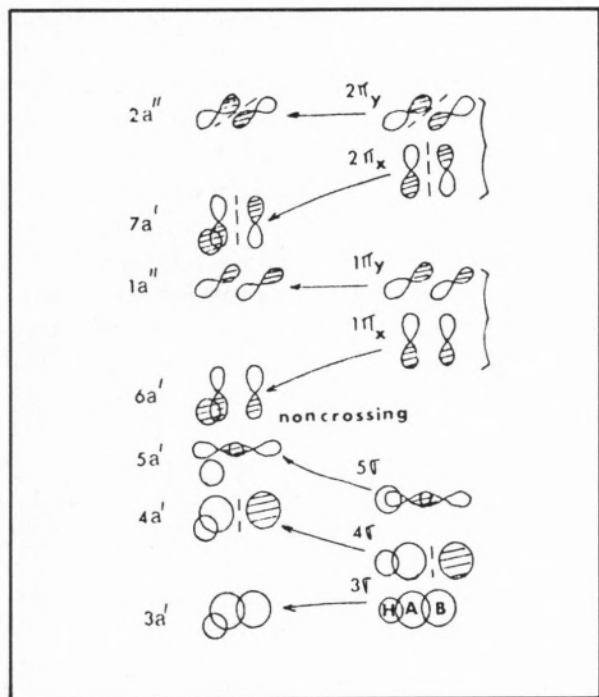


Fig. 1

MO scheme for bent and linear HAB molecules [5].  $a'$ ,  $a''$  - MO symmetric and antisymmetric, respectively, with respect to the plane of the molecule

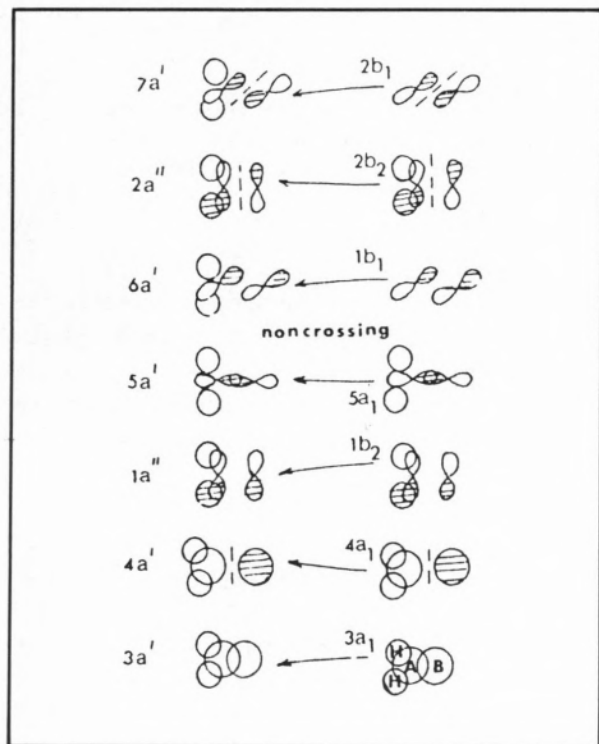


Fig. 3

MO scheme for nonplanar and planar  $H_2AB$  molecules [5]

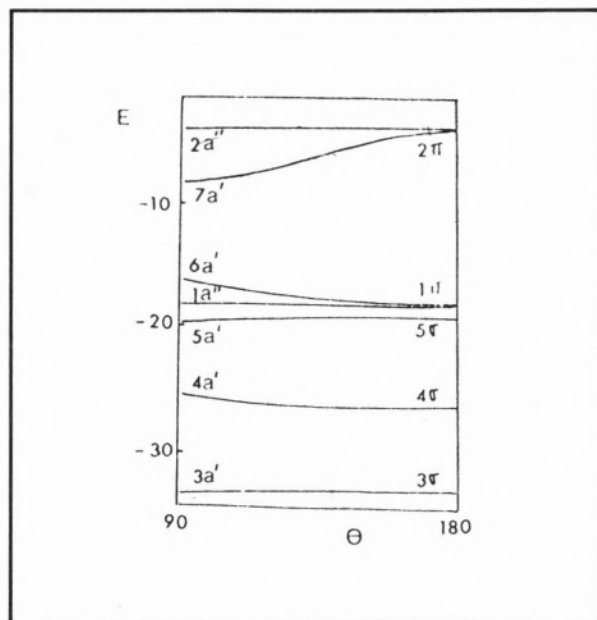


Fig. 2

Energy ( $E$ ) vs bending angle  $\theta$  for HAB molecules [5]

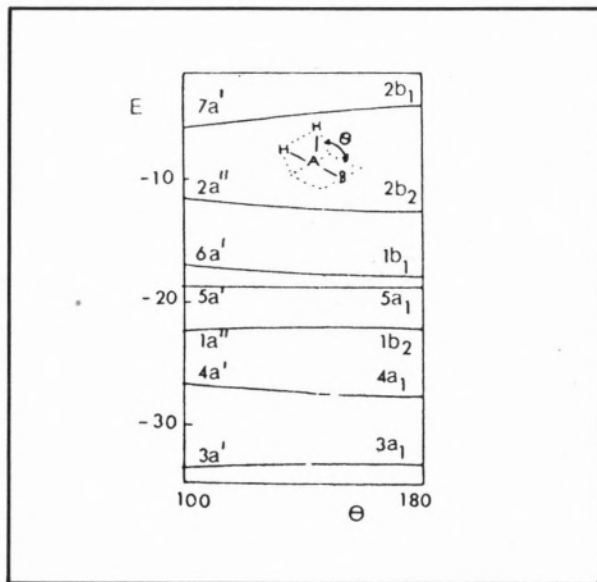


Fig. 4

Energy vs bending angle  $\theta$  for  $H_2AB$  molecules [5]

### 1.1 — CNR AND CNR'R

In the CNR  $5\sigma \rightarrow 7a'$  excitation, an electron is being removed from an orbital with energy nearly independent of the bending angle to another one which is strongly stabilised upon bending, thereby resulting in a bent excited state. This excitation may be

considered as corresponding to a hypothetical co-ordination of CNR to a metal according to the expected type of bonding: donation from a filled  $\sigma$ -orbital ( $5\sigma$ ) to a metal empty one, and  $\pi$ -acceptance by  $7a'$  (and  $2a''$ ) from  $d$  filled metal orbitals, as both  $5\sigma$  and  $7a'$  (and  $2a''$ ) appear to have the appropriate symmetry and direction to overlap with the corresponding metal orbitals. According to these assumptions, CNR is expected to bend upon co-ordination when it behaves as a strong backbonding acceptor, although a linear configuration will be followed

when it acts as a dominant  $\sigma$ -donor. This prediction has been recently fully verified by the X-ray structure determination [6] of *trans*-[Mo(CNMe)<sub>2</sub>(dppe)<sub>2</sub>] whose isonitriles display a considerable bending at nitrogen ( $156^\circ$ ) which is believed to be derived from electronic effects (strong backbonding from the electron rich metal) and which contrasts with most instances of isonitrile complexes which exhibit linear geometries which are found when the isonitrile  $\rightarrow$  metal  $\sigma$ -donation is supposed to have the pre-dominant role.

Table 1  
Shape predictions for RAB and RR'AB groups based on Gimarc's correlation diagrams<sup>(a)</sup>

Group	No. valence electrons	Ground state		Excitation <sup>(b)</sup>	
		HOMO	shape	$\sigma \rightarrow \pi^*$	$\sigma \rightarrow \pi^*$
RNC	10	$1\pi$ (DO)	linear	bent	linear
RNN <sup>+</sup>	10	$1\pi$ (DO)	linear	bent	linear
RNN	11	$7a'$ (SO)	weakly bent	bent	weakly bent
RNN <sup>-</sup>	12	$7a'$ (DO)	bent	—	bent
RR'NC <sup>+</sup>	10	$1b_1$	planar	more strongly planar	nonplanar
RR'NN <sup>2+</sup>	10	$1b_1$	planar	more strongly planar	nonplanar
RR'NC	11	$2b_2$ (SO)	planar	more strongly planar	(c)
RR'NN <sup>+</sup>	11	$2b_2$ (SO)	planar	more strongly planar	(c)
RR'NN	12	$2b_2$ (DO)	planar	—	(c)
RR'NC <sup>-</sup>	12	$2b_2$ (DO)	planar	—	(c)

(a) R, R' = hydrogen or alkyl. SO = singly occupied. DO = doubly occupied. HOMO = highest occupied molecular orbital.

(b)  $\sigma$  denotes  $5\sigma$ ,  $5a'$ ,  $5a_1$  and  $5a'$  for linear RAB, bent RAB, planar RR'AB and nonplanar RR'AB, respectively.  $\pi^*$  denotes  $2\pi$ ,  $7a'$ ,  $2b_2$  and  $2a''$  for linear, bent RAB, planar and nonplanar RR'AB, respectively.  $\pi^*$  denotes  $2\pi$ ,  $2a''$ ,  $2b_1$  and  $7a'$  for linear, bent RAB, planar and nonplanar RR'AB, respectively.

(c) A tendency to the nonplanarity is expected.

These facts constitute an important confirmation of the previous assumptions and encourage other applications.

Let us consider a protonation (or alkylation) at N of a co-ordinated isonitrile (this has been achieved by us recently)[7]. If the positive charge is regarded as being localised on the ligand,  $:C \equiv \dot{N}HR$ , it will be a 10-electron group, formally losing one electron through the  $\sigma$ -bond to the metal, and accepting another one by  $\pi$ -backbonding into the empty  $2b_2$  and  $2b_1$  antibonding orbitals. Filling of  $2b_2$  favours the planar geometry but filling of  $2b_1$  favours the nonplanarity; hence, a slight nonplanar geometry probably results. A still weaker tendency to the nonplanarity would be expected for RR'NC and RR'NC<sup>-</sup> on account of the higher filling of  $2b_2$ , and planar

geometries would not be unexpected; however, the relative importance of the driving forces for planarity and bending is not easy to evaluate from these arguments and a doubtless conclusion cannot be reached.

## 1.2 — NNR' AND NNHR'

Reaction of coordinated dinitrogen with organohalides, R'X, may result in the formation of organodiazenido (NNR') complexes [8a] whose structure has been authenticated by X-ray data, in a number of cases, e.g., [MoCl{NN(COPh)}(dppe)<sub>2</sub>][9] and [ReCl<sub>2</sub>(NNCOC<sub>6</sub>H<sub>5</sub>)(PMe<sub>2</sub>Ph)<sub>3</sub>][10]. A considerable bending at the *exo* nitrogen atom, indicative of a substantial degree of backbonding, agrees with the

Mulliken-Walsh-Gimarc model and has always been observed, these ligands being formally considered as  $\text{NNR}^+$  (in a VB representation,  $\text{M} \leftarrow \ddot{\text{N}} = \ddot{\text{N}}_{\text{R}}$ ) and as 3-electron donors. Organodiazenido ligands may also show a doubly bent structure and are then considered to be formally negatively charged,  $\text{NNR}^-$  (in a VB representation,  $\text{M} \leftarrow \ddot{\text{N}} \backslash \ddot{\text{N}}_{\text{R}}$ ) and 1-electron donors; however, this structure has not yet been proved for dinitrogen derived organodiazenidos and it is not included in the present models as the  $\text{sp}^2$  hybridisation on the coordinated N considerably changes the molecular orbitals which are used in the elaboration of the diagrams.

Application of similar arguments to the lesser known diazenido ligand  $\text{NNH}$  — which has not yet been prepared from direct protonation at  $\text{N}_2$ , but from reversible deprotonation of the hydrazido ( $2-$ )  $\text{NNH}_2$  or diazene  $\text{NHNH}$  ligand, e.g., by reaction of  $\text{NEt}_3$  with  $\text{trans-[MX(NNH}_2\text{)(dppe)}_2\text{]}$  or  $\text{[MX}_2\text{(NHNH)(dppe)}_2\text{]}$  (7-coordinated), respectively, yielding  $\text{trans-[MX(N}_2\text{H)(dppe)}_2\text{]}$  ( $\text{M} = \text{Mo, W}$ ;  $\text{X} = \text{F, Cl, Br}$ ) — would lead to the prediction of a bent geometry, either  $\text{NNH}^+$  or  $\text{NNH}$  are considered to be formed, although a linear geometry has been suggested based mainly on the observed high  $\nu(\text{NN})$  [*ca.*  $1890\text{ cm}^{-1}$  in  $\text{[WX(N}_2\text{H)(dppe)}_2\text{]}$  ( $\text{X} = \text{Cl, Br}$ )] [8b]. This value is however lower than in the parent dinitrogen complex ( $1940\text{ cm}^{-1}$ ) and a considerable bending, although not very extensive, may well be present.

The planarity of the  $\text{NNH}_2$  or  $\text{NNHR}'$  ligand has been proved by X-ray data on  $\text{trans-[MoF(NNH}_2\text{)(dppe)}_2\text{]BF}_4$  (derived from reaction of  $\text{trans-[Mo(N}_2\text{)}_2\text{(dppe)}_2\text{]}$  with excess of  $\text{HBF}_4$ ) [11] and on other related species such as  $\text{trans-[MoI(NNHC}_8\text{H}_{17}\text{)(dppe)}_2\text{]I}$  (formed by monoprotonation of  $\text{trans-[MoI(NNC}_8\text{H}_{17}\text{)(dppe)}_2\text{]}$  by  $\text{HI}$ ) [12]. This is not unexpected from the Mulliken-Walsh-Gimarc model by considering the formal structures  $\text{NNHR}$  (12-electron) or  $\text{NNHR}^+$  (11-electron) ( $\text{M} \leftarrow \text{N} = \ddot{\text{N}}\text{HR}$ ); the effect of filling the  $2b_2$  orbital (which favours a planar geometry) appears to predominate over the destabilizing effect on this geometry of the  $2b_1$  filling.

## 2 — QUALITATIVE $\pi$ -MO SCHEMES

Proposals for MO diagrams of any complexes must

account for the known physical features and chemical behaviour experimentally observed. The symmetry of the molecule is an important parameter to consider and thus the aforementioned geometry considerations appear to play a useful role.

### 2.1 — $\pi$ -MO SCHEMES FOR $\text{trans-[MLL'(dppe)}_2\text{]}$ (A) ( $\text{L, L}' = \text{CNR, CO, N}_2$ )

X-ray data [6] for  $\text{trans-[Mo(CNMe)}_2\text{(dppe)}_2\text{]}$  show a *trans* bent geometry for  $\text{R/NCMCN/R}$ , implying a  $\text{C}_{2v}$  point group symmetry for this grouping. The Mo-C (isonitrile) bond length is  $2.091(5)\text{\AA}$ , well below the expected value ( $2.28 \sim 2.38\text{\AA}$ ) [13, 14] for a single bond, thus substantiating a considerable double bond character (from the graphic correlation proposed by COTTON *et. al.* [13], a 1.4 bond order is expected).

A strengthening of the CN bond is observed [ $\nu(\text{CN})$  increases] upon chemical oxidation [14a], whereas in cyclic voltammetry the values of  $E'(1)$  (taken half-way between the first anodic oxidation and cathodic reduction potential) correlate with the electronic affinity of R (Hammett  $\sigma_p$  values for the *para* substituents of R when this is an aryl group) [15]; a correlation with the  $\text{M} \rightarrow \text{L}$  charge transfer energy is also observed [14a]. Hence it is conceivable to suppose a HOMO with ligand antibonding character and formed with R orbital participation.

The  $\pi$ -molecular orbitals are derived from the overlap of  $\pi$ -ligand orbitals with  $d_{xz}$  and  $d_{yz}$  metal orbitals and a considerable stabilization of the molecular orbitals in the  $xz$  plane relative to those in the  $yz$  plane should occur in the bent CNR complexes due to the in-phase atomic orbital overlap involving the  $\text{sp}^3(\text{C})$  orbital. Hence, the simplified scheme of fig. 5, which has been suggested [14a] for  $\text{trans-[M(CNR)}_2\text{(dppe)}_2\text{]}$  in a more simplified way, is presented now in more detail and is also applied to analogous [16] monophosphine complexes. In its derivation, ungerade molecular orbitals were believed to have an energy similar to that in the free ligands; they are ligand localised, but a nodal plane at the metal must be taken into account if they are considered to be derived from overlap of the corresponding ligand ungerade orbitals with metal d gerade ones.



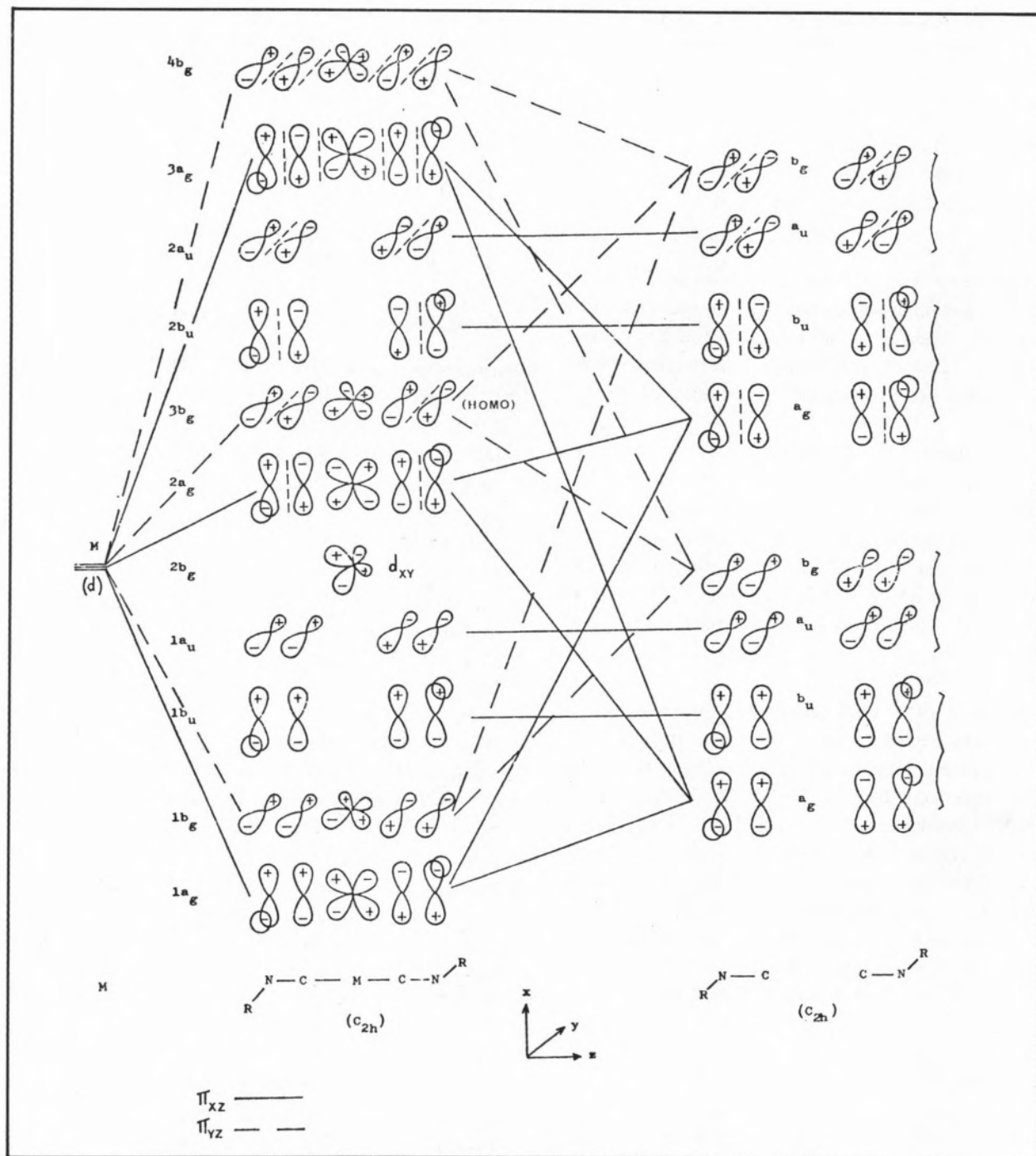


Fig. 5

Simplified  $\pi$ -MO scheme for  $\text{trans-[M(CNR)}_2\text{P}_2]$ 
 $[P = \frac{1}{2} (\text{dppe}) \text{ or monophosphine; } M = \text{Mo, W}]$ 

The HOMO has ligand antibonding character as desired and, for aryl isonitrile complexes, it involves the participation of  $\pi$  ring orbitals as it may be concluded by considering the conjugation of the  $\pi$  aryl ring orbitals with the  $\pi$ -CN orbitals; hence, e.g., if

the ring lies in the  $\text{C-N}_R$  plane, the  $a_u$  and  $b_g$  orbitals will have  $\pi$ -aryl character and will be subjected to a stabilizing effect which will be dependent on the *para* substituent of the ring.

Bending at the electron rich nitrogen atom of coor-

minated isonitrile accounts for the protonic and alkylating attack which this atom undergoes, whereas the absence of direct metal protonation in the bisisonitrile complexes may be due to the strong competition of the two nitrogens for the proton, to steric interference of the two dppe ligands with the  $d_{xy}$  metal orbital, or even to orbital overlap between P-orbitals and metal  $d_{xy}$ , in as much as some degree of  $\pi$ -backbonding from M to P is believed to occur in these species as deduced from the observed Mo-P distances in *trans*-[Mo(CNMe)<sub>2</sub>(dppe)<sub>2</sub>] [2.441(2) and 2.457(2) Å][6] which are considerably below the predicted value from the sum (2.58 Å) of the radii [17] of the two atoms involved.

Simplified  $\pi$ -MO schemes for *trans*-[MLL'L<sub>4</sub>] with other ligands L and L' which are isoelectronic with isonitriles [P<sub>4</sub> may stand for (dppe)<sub>2</sub> or other diphosphine, diarsine, mixed phosphine-arsine or monophosphine ligands][18], may be derived in a similar way as for the bisisonitrile complexes. Hence, e.g., for [L = L' = N<sub>2</sub> or CO; 18f.]P<sub>4</sub> = (dppe)<sub>2</sub>] the scheme of fig. 6(a) may be proposed; the stabilizing effect due to bending at the ligand is obviously not present and two degenerate sets of molecular orbitals occur (one in the  $\pi_{xz}$  plane and the other in the  $\pi_{yz}$  one). This scheme is in agreement with the known properties which are exhibited by *trans*-[M(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] as it has already been reported [19].

If one of the ligands (L or L') behaves as a considerable stronger  $\pi$ -acceptor than the isoelectronic ligand (L' or L, respectively) which is in *trans* position, the latter may be involved in  $\pi$ -donation to the former — «push-pull» type effect as described in other complexes with bridging end-on N<sub>2</sub> such as the metallocene type species [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>MN<sub>2</sub>]<sub>2</sub>N<sub>2</sub>] (M = Ti, Zr) [20a, 20b] and [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti]<sub>2</sub>N<sub>2</sub>][20c] — and a related  $\pi$ -MO scheme [fig. 6(b)] may be drawn including the MO  $\pi_{xz}$  (2e) instead of  $1e_u$  of fig. 6(a) where the antibonding moiety refers to the stronger  $\pi$ -acceptor. Such a situation may occur in the complexes *trans*-[Mo(N<sub>2</sub>)(NCR)(dppe)<sub>2</sub>] [9] and *trans*-[Mo(CN)(N<sub>2</sub>)(dppe)<sub>2</sub>]<sup>-</sup> [21], in which the N<sub>2</sub> behaves as a better  $\pi$ -acceptor than the nitrile and cyanide ligands, exhibiting  $\nu(\text{NN})$  values in the i.r. which are lower than in the parent *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>][e.g.,  $\nu(\text{NN}) = 1910 \text{ cm}^{-1}$  for the nitrile complex (NCMe) and  $1972 \text{ cm}^{-1}$  for

the parent bisdinitrogen species], whereas in *trans*-[Mo(N<sub>2</sub>)(CO)(dppe)<sub>2</sub>][18h,i] the N<sub>2</sub> ligand behaves as a considerable weaker  $\pi$ -acceptor than CO as evidenced by i.r. data [ $\nu(\text{NN})$  is at 2080, 2110  $\text{cm}^{-1}$  which is higher than in the bisdinitrogen species].

## 2.2 — $\pi$ -MO SCHEME FOR *trans*-[M(CNHR)<sub>2</sub>(dppe)<sub>2</sub>]<sup>2+</sup>(B)

The electron rich bent isonitrile ligands in *trans*-[M(CNR)<sub>2</sub>(dppe)<sub>2</sub>] undergo protonation reactions with acids, and *trans*-[M(CNHR)<sub>2</sub>(dppe)<sub>2</sub>]<sup>2+</sup>(B) are the species derived upon proton attack at both isonitriles [7].

The  $\pi$ -MO diagram of these complexes (which may be called dicarbenes corresponding to the VB formulation  $\text{RH}\dot{\text{N}} = \text{C} = \text{M} = \text{C} = \dot{\text{N}}\text{HR}$ ) may be handily derived from that of the parent species (fig. 7) by considering a further stabilization effect of the s(H) orbital on the  $\pi_x$  orbitals; this effect appears to be maximum for the antibonding  $\pi_x^*(\text{CN})$  orbital [e.g., compare the lowering in energy of  $\pi_x^*(\text{BA})$  and of  $\pi_x(\text{BA})$  when going from bent BAH (156°) to planar BAH<sub>2</sub> molecules: 8 eV and 4 eV, respectively — see Gimarc's diagrams — figs. 1-4]. Hence, within the filled MO's, a considerable lowering in energy of  $2a_g$ , relative to the parent bisisonitrile complexes, is expected. The high energy lowering of  $\pi_x^*(\text{CN})$  in the CNHR moiety favours its combination with the metal  $d_{xz}$  orbital of lower energy and the resulting  $2a_g$  molecular orbital (which has CN antibonding and metal-ligand bonding characters) will have an enhanced contribution for the bond what explains the weakening of the CN bond when going from [(A), L = L' = CNR] to (B) [as evidenced by the lowering in  $\nu(\text{CN})$ , e.g., from 1857  $\text{cm}^{-1}$  to 1645  $\text{cm}^{-1}$  for M = Mo, R = Me]. Moreover, an increase in the metal-carbon multiple bond character is expected and an enhancement towards carbene (and carbyne) character is thus occurring.

The  $3b_g$  orbital is derived from  $\pi_x^*$  orbitals of the ligands CNHR which are stabilized by a nonplanar geometry (see figs. 3 and 4). Hence filling of this MO favours the nonplanarity of the CNHR ligands which may then show a slight bending at N (as previously deduced by considering these ligands as 10-electron systems) which rationalizes the further

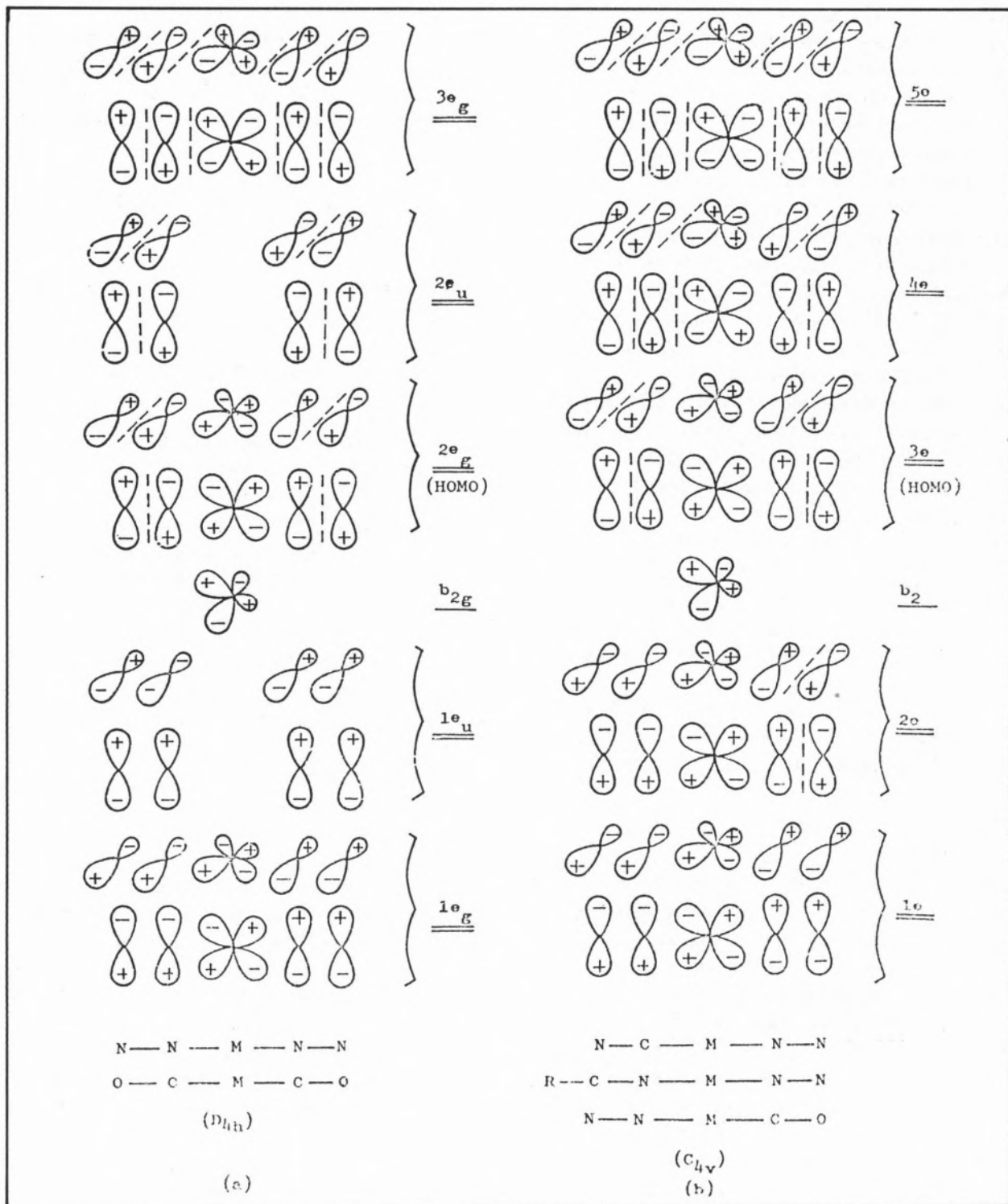


Fig. 6

Simplified  $\pi$ -MO scheme for  $\text{trans-[MLL}'P_4]$  [ $P_4 = (\text{dppe})_2$ , other disphosphine, diarsine, mixed phosphine-arsine or monophosphine ligands;  $M = \text{Mo}, W$ ] (A).

(a)  $L = L' = N_2, CO$ . (b)  $L = N_2$  as a considerable stronger or weaker  $\pi$ -acceptor than  $L'$

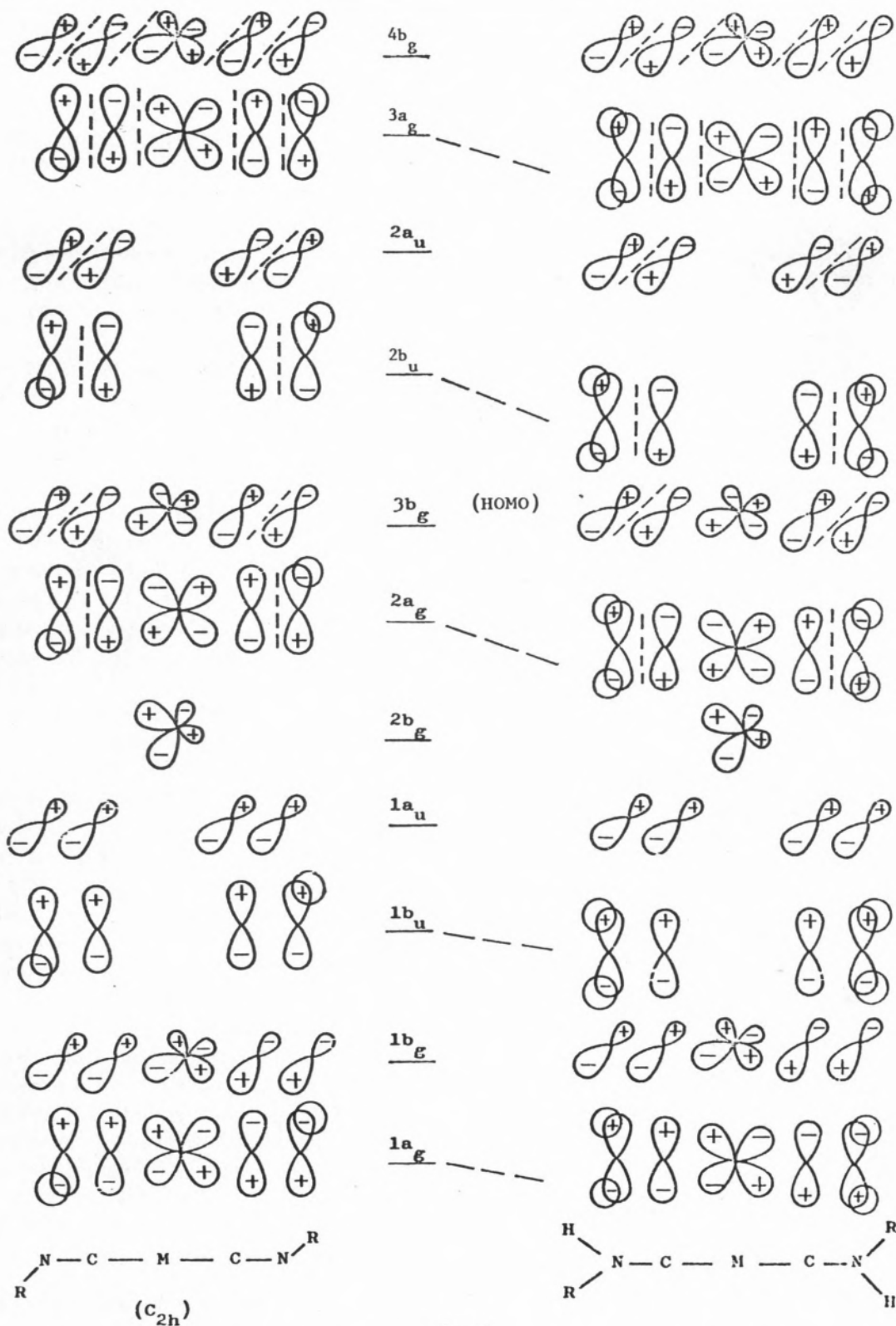


Fig. 7

(a) Derivation of a  $\pi$ -MO scheme for  $\text{trans-[M(CNHR)}_2(\text{dppe})_2]$  (b)  
 (b) from the  $\pi$ -MO scheme for  $\text{trans-[M(CNR)}_2(\text{dppe})_2]$



protonation at N which the complexes (B) undergo yielding  $\text{trans-[M(CNH}_2\text{Me)(CNHMe)(dppe)}_2\text{]}^{3+}$  [14b]. The greater electronegativity of N compared to C may account for the nucleophilic attack (by  $\text{LiAlH}_4$ ) at the electron deficient carbyne carbon of CNHMe in (B) yielding  $\text{trans-[M(CHNHMe)(CNHMe)(dppe)}_2\text{]}^+$  [14b].

### 2.3 — $\pi$ -MO SCHEME FOR $\text{trans-[M(CNR}'\text{R)(CNR)(dppe)}_2\text{]}^+$ (C)

Protonation or alkylation at one isonitrile ligand in [(A),  $\text{L} = \text{L}' = \text{CNR}$ ] leads to the monocarbyne

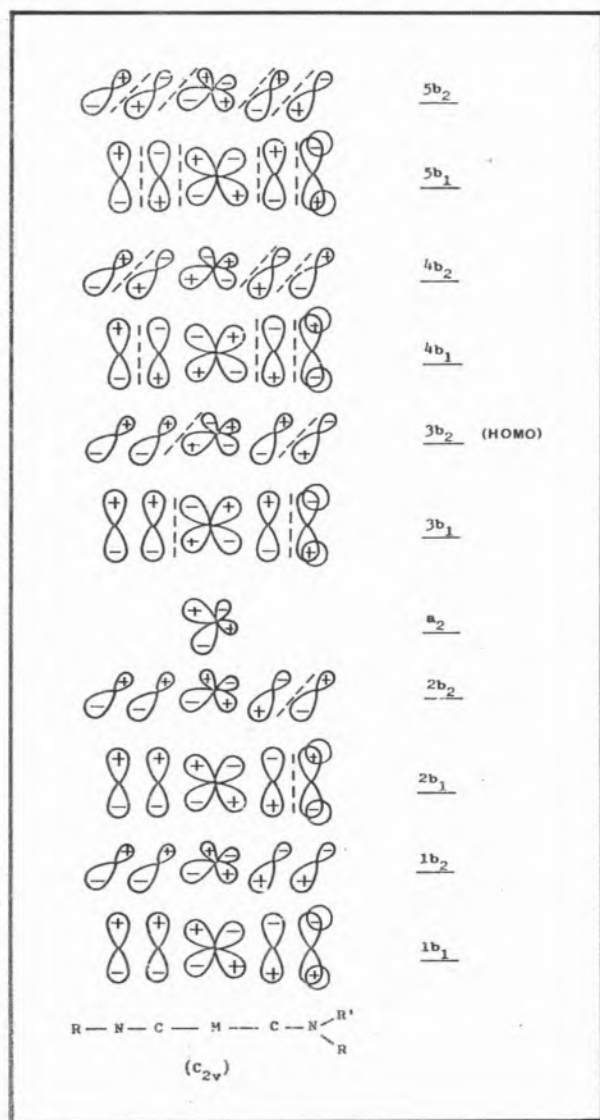
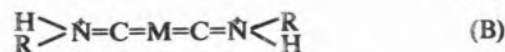
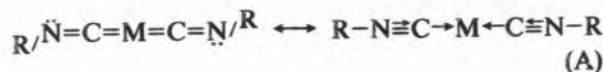


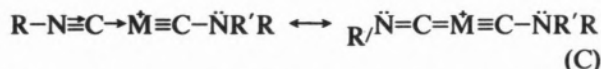
Fig. 8

Simplified  $\pi$ -MO scheme for  $\text{trans-[M(CNR}'\text{R)(CNR)(dppe)}_2\text{]}^+$  (C) ( $\text{R}' = \text{H, Me, Et}$ )

complexes  $\text{trans-[M(CNR}'\text{R)(CNR)(dppe)}_2\text{]}^+$  (C) [7, 14b]. The latter display the following pertinent features which must be rationalized by any proposed MO scheme:  $\nu(\text{CN})$  of  $\text{CNR}'\text{R}$  in (C) is lower than in (B) and than  $\text{CNR}$  in (A) [e.g., for  $\text{M} = \text{Mo}$ ,  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{H}$ :  $1518\text{ cm}^{-1}$  (C),  $1645$  (B),  $1857$  (A)] thus evidencing a decrease in the CN bond order, whereas the unreacted isonitrile exhibits an increase in  $\nu(\text{CN})$  relative to (A) as a result of a decrease in its  $\pi$ -acceptance. Another basic difference between the monocarbyne complexes and the previous ones lies in the lower symmetry of the former.

The  $\pi$ -MO scheme of fig. 8 (where a slight bending at isonitrile nitrogen — see below — has not been represented) accounts for all the abovementioned features as deduced from Table 2 which has been obtained from figs. 5, 7, 8. Hence, the weakening of the  $\text{C-NR}'\text{R}$  bond from (B) to (C) is due to the filling of 4  $\pi$  orbitals with C-N antibonding character (2 other  $\pi$  MO's have CN bonding character) in the latter, whereas in (B) only 2  $\pi$  CN antibonding orbitals (and 4 with CN bonding character) are filled. The unreacted isonitrile in (C) has a stronger CN bond than in (A) since 6  $\pi$  MO's with bonding CN character are filled in the former, whereas only 4 (and also 2 with CN antibonding character) are filled in the latter; the expected weakening of the  $\text{M-C(isonitrile)}$  bond from (A) to (C) also agrees with the filling in (C) of two  $\pi$  MO's with M-C antibonding character. In (C) the  $\text{CNR}'\text{R}$  ligand exhibits the greatest carbyne character with 6 filled  $\pi$ -MO's with M-C (carbyne) bonding character, also in agreement with the lowest field of  $\text{CNR}'\text{R}$  resonance in the  $^{13}\text{C}$  n.m.r. spectra — e.g., compare  $247.8$  ppm [(C),  $\text{M} = \text{Mo}$ ,  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{H}$ ],  $257.5$  ppm [(C),  $\text{M} = \text{Mo}$ ,  $\text{R} = \text{R}' = \text{Me}$ ] and  $204.7$  ppm [(B),  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{H}$ ] downfield from TMS. The isonitrile in *trans* position relative to the carbyne in (C) adapts itself to the strong electron withdrawing ability of the carbyne by decreasing its  $\pi$ -acceptance. These features may also be interpreted by considering the following canonical forms as those with heavier weight in the VB representations of complexes (A), (B) and (C):





Although being a weaker  $\pi$  acceptor than in (A), the unreacted isonitrile in (C) still shows a considerable degree of  $\pi$  backbonding acceptance (4 $\pi$  MO's with M-C bonding character are filled) and a slight bending at N probably occurs which may account for the possibility of proton attack at this atom, thus forming the dicarbene (B).

Complexes (C) are also less thermodynamically stable than (B) what may be a consequence of the higher energy level of the  $\pi$ -MO's: in the former the stabilization of the  $\pi_x$  orbitals due to the abovementioned in-phase atomic overlap is probably less pronounced than in the latter.

Table 2

Numbers of  $\pi$  filled MO's with M-C and C-N bonding ( $\pi$ ) and antibonding ( $\pi^*$ ) character in complexes of types (A), (B) and (C)

	type(A)	type(B)	type(C)
$\pi$ (M-CNR)	4	—	4
$\pi^*$ (M-CNR)	0	—	2
$\pi$ (M-CNR'R)	—	4	6
$\pi^*$ (M-CNR'R)	—	0	0
$\pi$ (MC-NR)	4	—	6
$\pi^*$ (MC-NR)	2	—	0
$\pi$ (MC-NCR'R)	—	4	2
$\pi^*$ (MC-NR'R)	—	2	4

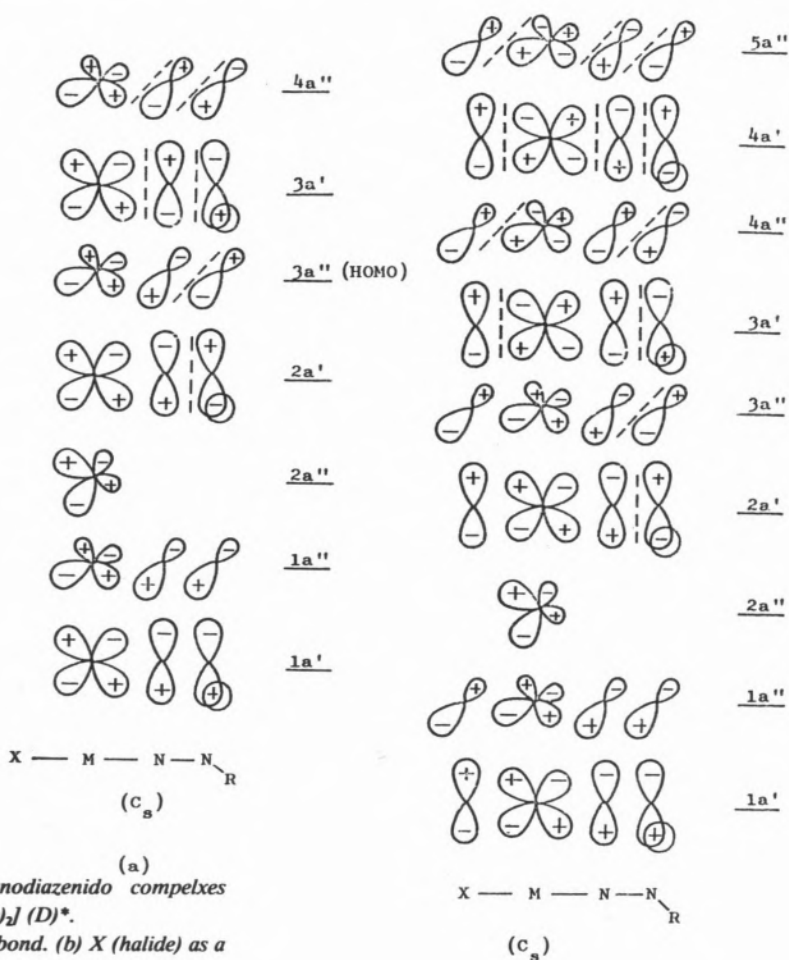


Fig. 9

Simplified  $\pi$ -MO schemes for organodiazenido complexes  $\text{trans-[MX(NNR')(dppe)_2]}$  (D)\*.

(a) Without involvement of X in the  $\pi$  bond. (b) X (halide) as a  $\pi$ -donor

(\*) Analogous schemes are also valid for the hydrazido(2-) complexes  $\text{trans-[MX(NNHR')(dppe)_2]}$  (E) (see text).

## 2.4 — $\pi$ -MO SCHEMES FOR $\text{trans-[MX(NNR') (dppe)}_2\text{] (D)}$ AND RELATED HYDRAZIDO(2-) AND DINITROGEN COMPLEXES

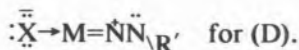
Reaction of  $\text{trans-[M(N}_2)_2(\text{dppe})_2]$  ( $\text{M} = \text{Mo, W}$ ) with organic halides,  $\text{R}'\text{X}$ , yields organodiazenido complexes (D)[8a] by a mechanism which is believed to involve  $\text{N}_2$  evolution upon oxidation or photoexcitation as rationalized by the  $\pi$ -MO scheme of fig. 6: electron removal from a MO (HOMO) with M-N bonding character weakens this bond allowing  $\text{N}_2$  to be evolved [19,22]. The final complexes (D) have an halide in *trans* position relative to the organodiazenido ligand whose bent structure is in agreement with the Mulliken-Walsh-Gimarc model.

Fig. 9(a) shows a simplified  $\pi$ -MO scheme which represents the XMNNR group if the halide is not appreciably involved in the  $\pi$  bonding. Comparison between this scheme and that for the parent bisdinitrogen complex [fig. 6(a)] allows us to explain some structural features (Table 3) of these species. Upon electrophilic attack at terminal nitrogen a N-N bond elongation is observed (the number of filled orbitals

diazenido ligand and species such as  $\text{trans-[M(N}_2)(\text{NNR}')(\text{dppe})_2]^+$  are not known. The following main VB representations may also account for the observed features:



for the bisdinitrogen and



If the halide behaves as an appreciable  $\pi$ -donor through its  $p_x$  and  $p_y$  orbitals, fig. 9(b) may be considered, the HOMO orbital now being above  $3a''$  due to the greater number of electrons involved. This scheme also explains the abovementioned features, the N-N elongation and the M-N strengthening being greater than in fig. 9(a), as expected, due to the enhancement of the  $\pi$ -acceptance of the organodiazenido ligand by the halide  $\pi$ -donation. This argument may also be used to explain the greatest lowering in  $\nu(\text{NN})$  for  $[\text{MX}(\text{NNH})(\text{dppe})_2]$  [8b] which is observed when the halide X is fluoride.

The bending at the electron rich *exo* nitrogen atom of the organodiazenido moiety accounts for the

Table 3  
X-ray data<sup>(a)</sup> on  $\text{trans-[Mo(N}_2)_2(\text{dppe})_2]$  and some organodiazenido and hidrazido(2-) derivatives

	M-N(1)	N(1)-N(2)	$\angle$ M-N(1)-N(2)	Ref.
$\text{trans-[Mo(N}_2)_2(\text{dppe})_2]$	2.014(5)	1.118(8)	176.58(53)	[23]
$\text{trans-[MoCl(NN(COPh))}_2(\text{dppe})_2]$	1.813(7)	1.255(10)	172.1(6)	[9]
$\text{trans-[MoF(NNH}_2)_2(\text{dppe})_2]$ $\text{BF}_4$	1.762(12)	1.333(24)	176.4(13)	[11]
$\text{trans-[MoI(NNHCH}_9\text{H}_{17})_2(\text{dppe})_2]\text{I}$	1.801(11)	1.259(14)	174.1	[12]

(a) Distances are expressed in angstrom.

with N-N bonding character decreases whereas the number of those filled with N-N antibonding character remains the same) concomitantly with a M-N bond strengthening due to the increase in  $\pi$ -back-bonding once the  $\pi$ -acceptor  $\text{N}_2$  is replaced by a nonacceptor (halide). A decrease in  $\nu(\text{N}_2)$  is also observed in the i.r. (e.g.,  $1972\text{ cm}^{-1}$  for  $\text{trans-[Mo(N}_2)_2(\text{dppe})_2]$  and  $1330\text{ cm}^{-1}$  for  $\text{trans-[MoCl(NNCOEt)(dppe)}_2\text{] [8a]}$ ). Hence, a close resemblance to the bisisonitrile (A) and derived carbyne (C) complexes is observed. However since  $\text{N}_2$  is a poor  $\sigma$  donor and always needs a strong metal  $\pi$  donation to coordinate, it cannot adapt itself to the electron withdrawing ability of the organo-

ready protonation which this ligand undergoes yielding *hydrazido(2-)* complexes  $\text{trans-[MX(NNHR') (dppe)}_2\text{]}^+(\text{E})$  which may also be represented by simplified  $\pi$ -MO schemes analogous to those of fig. 9 although considering a further stabilizing effect due to the in-phase overlap of  $p_x(\text{N})$  with  $s(\text{H})$  (a  $\text{C}_2$ , symmetry may be considered for the group

$\text{X-M-N-N}(\text{H})_{\text{R}'}$ ). An increase of the M-N multiple bond character and an elongation of the N-N bond relative to the bisdinitrogen complex is also observed (Table 3) as expected from those  $\pi$  schemes. Electrophilic attack at the *endo* nitrogen atom of

the organodiazenido ligand is also known [8] to occur yielding the 2-electron moiety  $\text{NHNR}'$ , but 7-coordinated species are involved —  $[\text{MX}_2(\text{NHNR}')(\text{dppe})_2]$  are the final products — and the abovementioned  $\pi$ -MO schemes do not apply; a 7-coordinated intermediate doubly bent organodiazenido (1-electron donor) may be formed upon halide attack at the metal —  $[\text{MX}_2(\ddot{\text{N}}\text{N}-\text{R}')(\text{dppe})_2]^-$  — thus allowing the observation of the ef-

fective atomic number rule and accounting for the protonation at the ligating nitrogen atom as it is known [24] to occur in doubly bent organodiazenidos.

A considerable number of fourfold symmetry *dinitrogen complexes* of the type  $\text{trans-}[\text{MX}'(\text{N}_2)\text{L}_4]$  (F) where  $\text{X}'$  is not a  $\pi$ -acceptor are known — e.g.,  $[\text{MoX}(\text{N}_2)(\text{dppe})_2]^-$  ( $\text{X} = \text{SCN}, \text{N}_3$ ) [21],  $[\text{ReX}(\text{N}_2)\text{L}_4]^{+x}$  ( $\text{X} = \text{halide}, \text{L} = \text{various monophos-}$

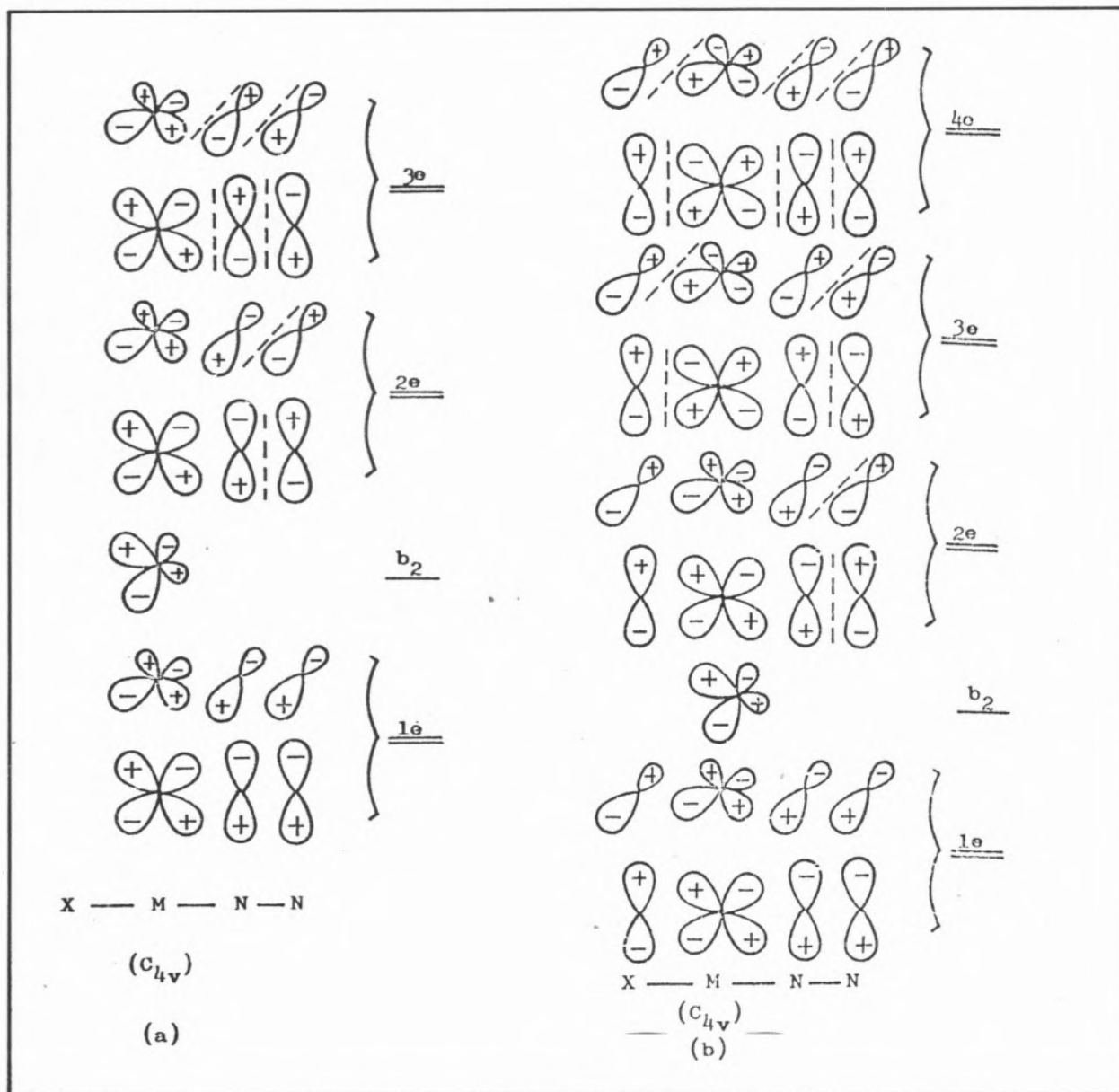


Fig. 10

Simplified  $\pi$ -MO schemes for  $\text{trans-}[\text{MX}(\text{N}_2)\text{L}_4]$  (F).

(a) With involvement of X in the  $\pi$  bonding. (b) X (halide) acting as a  $\pi$ -donor



phines,  $L_2$  = various diphosphines or mixed phosphine-arsine chelated ligands;  $x = 0, 1$ ) [25],  $[MH(N_2)(depe)_2]^+$  ( $M = Fe, Ru, Os$ ) [26],  $[M(NH_3)_5(N_2)]^{2+}$  ( $M = Ru$  [27],  $Os$  [28]) and  $[Os(N_2)(thf)(L)]$  [ $L$  = octaethylporphinato [29a], tetra(p-tolyl)porphinato [29b]] — and the bonding may be described by  $\pi$ -MO schemes similar to those of fig. 9, although consisting of two degenerate sets of orbitals (one set in the  $xz$  plane and the other in the  $yz$  one (fig. 10). All these examples involve metal  $d^6$  centres except the  $Re(II)$  species ( $d^5$ ). The former have  $10\pi$  electrons and the  $2e$  orbitals [Fig. 10(a)] are fully filled, but the latter has one  $2e$  orbital only half filled; the M-N and N-N bonding and antibonding character, respectively, of these orbitals explain the less thermal stability and the higher  $\nu(CN)$  values observed for the  $Re(II)$  complexes relative to the related  $Re(I)$  species.

### 3 — FINAL REMARKS

Isonitriles and dinitrogen behave as strong  $\pi$ -acceptors when ligating the electron rich metal site  $'M(dppe)_2'$  ( $M = Mo, W$ ) and the M-C and M-N bonds show a considerable degree of double bond character. These ligands undergo electrophilic attacks, the former at N and the latter at the *exo*-N atom with concomitant C-N and N-N bond weakening and M-C and M-N bond strengthening yielding carbene ( $:CNR'R$ ), carbyne ( $:CNR'R$  and  $:CNH_2R$ ), organodiazenido (NNR) and hydrazido ( $2-$ ) (NNHR) ligands. These structural and other physical (geometric, spectroscopic) changes which result from coordination and electrophilic attack, as well as the chemical reactivity of those moieties are explained on the basis of qualitative  $\pi$ -MO schemes of the corresponding complexes in which the HOMO orbitals have M-C (or M-N) bonding character and C-N (or N-N) ligand antibonding character.

These schemes show a considerable generality and are also applied to other fourfold symmetry complexes of dinitrogen and other related ligands such as carbonly, cyanide and nitriles.

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# RESUMO

A aplicação de diagramas de Walsh aos ligandos L e L' (diazoto, isonitrilo e seus derivados) presentes nos complexos de fórmulas gerais trans-[MLL'P<sub>4</sub>]<sup>2+</sup> (M = Mo, W. L e/ou L' = N<sub>2</sub>, CNR, CNHR, CNR'R) e trans-[MXLP<sub>4</sub>]<sup>2+</sup> (M = Mo, W. L = N<sub>2</sub>H, N<sub>2</sub>R', N<sub>2</sub>HR', N<sub>2</sub>H<sub>2</sub>; X = ligando aniônico tal como halogeneto ou HSO<sub>3</sub><sup>-</sup>. P = fosfina ou arsina) torna possível a previsão da sua geometria bem como a elaboração de diagramas simplificados de orbitais moleculares π para estes e outros complexos análogos de diazoto e/ou de outros ligandos isoelectrônicos (CO, CN<sup>-</sup>, NCR).

As propriedades físicas e químicas destes ligandos, bem como os caracteres variáveis de ligação múltipla metal-carbono e metal-a-zoto, são interpretados com base nos referidos diagramas de orbitais moleculares.