

## COMPARISON OF FREE AND METAL COORDINATED 1,4-DISUBSTITUTED-1,4-DIAZA-1,3-BUTADIENES

### CRYSTAL AND MOLECULAR STRUCTURES OF 1,4-DICYCLOHEXYL-1,4-DIAZA-1,3-BUTADIENE AND TRANS-[DICHLORO(TRIPHENYLPHOSPHINE)(1,4-DI-TERT-BUTYL- 1,4-DIAZA-1,3-BUTADIENE)PALLADIUM(II)]

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**Abstract**—The crystal and molecular structures of *c*-Hex-DAB (*c*-hexyl-N=C(H)-C(H)=N-*c*-hexyl; DAB = 1,4-diaza-1,3-butadiene) and of *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)(*t*-Bu-DAB)] are reported. Crystals of *c*-Hex-DAB are monoclinic with space group *C*<sub>2/c</sub> and cell constants: *a* = 24.70(1), *b* = 4.660(2), *c* = 12.268(3) Å, β = 107.66(4)°, *Z* = 4. The molecule has a flat *E-s-trans-E* structure with bond lengths of 1.258(3) Å for the C=N double bond and 1.457(3) Å for the central C-C' bond. These bond lengths and the N=C-C' angle of 120.8(2)° indicate that the C- and N-atoms are purely *sp*<sup>2</sup>-hybridized and that there is little or no conjugation within the central DAB skeleton. Crystals of *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)(*t*-Bu-DAB)] are triclinic with space group *P*1 and cell constants: *a* = 17.122(3), *b* = 18.279(3), *c* = 10.008(5) Å, α = 96.77(2), β = 95.29(3), γ = 109.79(2). *Z* = 4. The *t*-Bu-DAB ligand is coordinated to the metal via one lone pair only. In this *2e*; σ-N coordination mode the *E-s-trans-E* conformation of the free DAB-ligand is still present and the bonding distances within the DAB-ligand are hardly affected. [C=N: 1.261(10) Å; C-C': 1.479(10) Å (mean).] The Pd-N-, N=C- and central C-C'-bond lengths are compared with those found in other metal-R-DAB complexes.

During the last few years much attention has been paid to the coordination properties of cumulated and conjugated hetero double bond systems such as:

pseudo allenes, e.g. (R)N=C(H)-N(R)<sup>-</sup>,<sup>1a,2</sup>  
O=C(R)-O<sup>-</sup>,<sup>1a,2</sup> (R)N=N-N(R)<sup>-</sup>,<sup>1a,2</sup> (R)(R')C=S=O,<sup>1b</sup> (R)N=S=O,<sup>2c</sup> (R)N=S=N(R);<sup>2c</sup>

pseudo butadienes, e.g. (R)N=C(H)-C(OEt)=O,<sup>1c</sup>  
(R)N=N-N=N(R),<sup>1d,2a,b</sup> (R)N=C(H)-C(H)=N(R).<sup>2a,2b,3</sup>

The use of 1,4-disubstituted-1,4-diaza-1,3-butadiene (R-DAB), a member of the group of α-diimines (see Fig. 1), has been especially successful and many new R-DAB-metal complexes have been synthesized.<sup>3,4,8,9</sup>

If one compares R-DAB with other α-diimines, it is clear that the R-DAB ligand is much more versatile in coordination behaviour. It is not only possible to donate the free electron pair on each of the nitrogen atoms, but also to use the π-electrons for coordination. As expected this use has not been observed for 2,2'-bipyridine and 1,10-phenanthroline, because here the π-electrons are part of an aromatic system. With R-DAB as a ligand, changes on the metal centre can be accommodated by changing the coordination

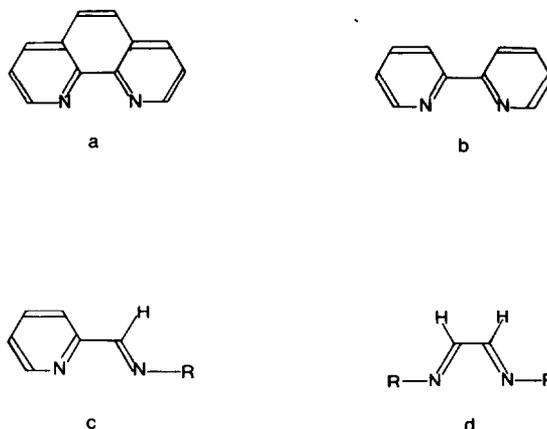


Fig. 1. Some well known α-diimines. 1,10-phenanthroline (a), 2,2'-bipyridine (b), pyridinealdimine (c), R-DAB (d).

mode of R-DAB. For example, loss of a CO-group from CoMn(CO)<sub>7</sub>(R-DAB) results in a change of the R-DAB coordination from the 4e; σ-N, σ-N'- to the 6e; σ-N, σ-N', η<sup>2</sup>-C=N'-coordination mode.<sup>3</sup>

The various coordination modes of R-DAB are shown in Fig. 2. Figure 2(a) illustrates the σ-N monodentate (*2e* donor mode) which has been postulated in

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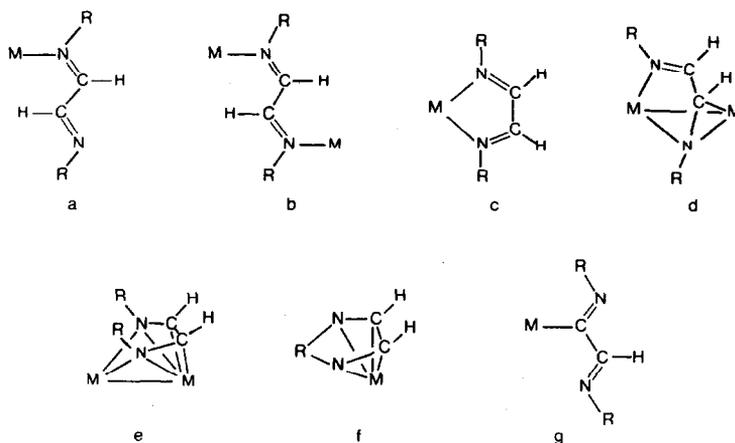


Fig. 2. The coordination modes of the R-DAB ligand: 2e;  $\sigma$ -N (a), 4e;  $\sigma$ -N,  $\sigma$ -N' bridging (b), 4e;  $\sigma$ -N,  $\sigma$ -N' chelating (c), 6e;  $\sigma$ -N,  $\sigma$ -N',  $\eta^2$ -C=N' or  $\sigma$ -N,  $\mu$ -N',  $\eta^2$ -C=N' (d), 8e;  $\sigma$ -N,  $\sigma$ -N',  $\eta^2$ -C=N,  $\eta^2$ -C=N' (e), 4e;  $\eta^2$ -C=N,  $\eta^2$ -C=N' (f), 2e;  $\sigma$ -C (g).

e.g. *trans*-[PdCl<sub>2</sub>(*t*-Bu-DAB)]<sup>5</sup> and is found in *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)(*t*-Bu-DAB)] (this report). Until now the  $\sigma$ -N,  $\sigma$ -N'-bridging (4e donor) mode (Fig. 2b) has only been found in *d*<sup>8</sup>-metal complexes of Pt(II), Pd(II), Rh(I), e.g. in [(PtCl<sub>2</sub>(PBU<sub>3</sub>))<sub>2</sub>(*t*-Bu-DAB)].<sup>4</sup> The  $\sigma$ -N,  $\sigma$ -N'-chelate (4e donor) mode (Fig. 2c) is the most common one and has been found in many low-valent metal complexes.

Relatively few examples are known in which the R-DAB also uses its  $\pi$ -electrons for coordination, though in the last few years the number has been growing rapidly. The  $\sigma$ -N,  $\sigma$ -N',  $\eta^2$ -C=N' or  $\sigma$ -N,  $\mu$ -N',  $\eta^2$ -C=N' coordination (6e donor) mode, depicted in Fig. 2(d), has been observed in MM'(CO)<sub>6</sub>(DAB) (M=M'=Fe, Ru, Os; M=Mn, Re; M'=Co) and Ru<sub>2</sub>(CO)<sub>4</sub>(DAB)<sub>2</sub> complexes.<sup>3,6,7</sup> The  $\sigma$ -N,  $\sigma$ -N',  $\eta^2$ -C=N,  $\eta^2$ -C=N' coordination (8e donor) mode (Fig. 2e) in which the DAB uses its maximum number of 8 electrons for coordination has been found in Ru<sub>2</sub>(CO)<sub>4</sub>( $\mu$ -C<sub>2</sub>H<sub>2</sub>)(DAB), Ru<sub>4</sub>(CO)<sub>8</sub>(DAB)<sub>2</sub> and Mn<sub>2</sub>(CO)<sub>6</sub>(DAB).<sup>8-10</sup>

The bonding situation recently found in Ru<sub>3</sub>(CO)<sub>9</sub>(*c*-Hex-DAB) can best be described as being intermediate between the 6e- and 8e-donor mode<sup>11</sup> because one C=N side of the DAB is strongly  $\eta^2$ -C=N bonded, while the other side is bonded only very weakly.†

In the free R-DAB ligand the conformation at the C=N bonds is the *E*(*anti*) one. This conclusion was based on IR, NMR, and dipole-moment measurements<sup>14-16,19</sup> and on an electron diffraction study in the gas phase on *t*-Bu-DAB.<sup>17</sup> This configuration is also found in all metal-R-DAB complexes. The conformation of the C-C'-bond is not quite clear. In the gas phase 20% of the *t*-Bu-DAB molecules has a *s-trans* conformation (torsion  $\tau = 180^\circ$ ), while 80% has a *gauche* conformation

( $\tau = 65^\circ$ ).<sup>17</sup> In solution conformations are present with torsion angles between 90 and 140° according to dipole-moment measurements.<sup>16</sup> Such a torsion around the C-C' bond is also found in diketones.<sup>18</sup> IR, Raman, UV and PES measurements on the other hand support the conclusion that the free R-DAB molecule predominantly exists in a *s-trans* conformation.<sup>14,19,20</sup> MO calculations on R-DAB and related hetero-butadienes such as biacetyl<sup>21</sup> and 2,2'-bipyridine<sup>22</sup> also give the *s-trans* conformer as the most stable one.<sup>23</sup>

In order to obtain both the conformation of the free ligand in the solid state, as well as precise bond lengths and angles, we have carried out an X-ray study of *c*-Hex-DAB: *c*-Hex-N=C(H)-C(H)=N-*c*-Hex. The data on bond lengths and angles obtained are more precise than those obtained earlier via a diffraction study in the gas phase on *t*-Bu-DAB.<sup>17</sup> Accordingly we have now a better point of reference for the interpretation of the molecular distances in the R-DAB ligand in a great number of metal-R-DAB complexes for which the crystal structures are known.

In order to see if 2e;  $\sigma$ -N-coordination affects the geometry of, or bonding distances within the R-DAB ligand, we have also completed an X-ray investigation on *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)(*t*-Bu-DAB)]. This compound's crystal structure also represents the first example in which the R-DAB ligand is bonded in the 2e;  $\sigma$ -N bonding mode fashion (Fig. 2a). This coordination mode as well as the dynamic properties of *trans*-[MCl<sub>2</sub>(PR<sub>3</sub>)(*t*-Bu-DAB)] (M = Pt, Pd; R = aryl) in solution have already been put forward on basis of <sup>1</sup>H-, <sup>13</sup>C-, <sup>31</sup>P-, <sup>15</sup>N- and <sup>195</sup>Pt-NMR measurements.<sup>5,24</sup>

## EXPERIMENTAL

### Syntheses

Synthesis of *c*-Hex-DAB,<sup>24</sup> and *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)(*t*-Bu-DAB)]<sup>5</sup> have been carried out according to literature methods. Recrystallization from diethyl ether and dichloromethane/pentane, respectively, yielded single crystals suitable for X-ray measurements.

†Other bonding possibilities are:  $\eta^2$ -C=N,  $\eta^2$ -C=N' coordination mode (4e-donor) (Fig. 2f), which has been proposed for cyclic  $\alpha$ -diimine systems,<sup>12</sup> while in 1,4-diaza-1,3-butadiene-2-yl-complexes there is a bond between a central C-atom of the R-DAB and the metal (Fig. 2g).<sup>13</sup>

Data collection and structure determination of 1,4 - di-cyclohexyl - 1,4 - diaza - 1,3 - butadiene,  $C_{14}H_{24}N_2$

Crystals of *c*-Hex-DAB are monoclinic with space group  $C_{2/c}$  with 4 molecules in a unit cell of dimensions  $a = 24.70(1)$ ,  $b = 4.660(2)$ ,  $c = 12.268(3)$  Å and  $\beta = 107.66(4)^\circ$ . A total of 1150 intensities were measured on a NONIUS CAD 4 diffractometer using graphite monochromated  $CuK_\alpha$  radiation, 326 of which were below the  $2.5\sigma(I)$  level and were treated as unobserved. No absorption correction was applied (crystal dimensions  $0.3 \times 0.3 \times 0.05$  mm;  $\mu = 4.54$  cm $^{-1}$ ). The structure was solved by means of the symbolic addition programme set SIMPEL.<sup>25</sup> Refinement proceeded by block-diagonal least-squares calculations, anisotropic for C and N, isotropic for H. The H-atoms were located in a  $\Delta F$ -synthesis. The final R value for the 824 observed reflexions was 0.055. A weighting scheme  $\omega = (0.66 + F_0 + 0.011 F_0^2)^{-1/2}$  was used and extinction corrections

$$F^{\text{corr}} = F \left( 1 + g \frac{1 + \cos^4 2\theta}{1 + \cos^2 2\theta / \sin 2\theta} \right)^{-1/4}$$

with  $g = 1.2 \times 10^{-5}$  were applied.†

*trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](*t*-Bu-DAB)],  $C_{28}H_{35}Cl_2N_2PPd$

Crystals of the title compound are triclinic with space-group  $P\bar{1}$  and cell constants  $a = 17.122(3)$ ,  $b = 18.279(3)$ ,  $c = 10.008(5)$  Å,  $\alpha = 96.77(2)$ ,  $\beta = 95.29(3)$ ,  $\gamma = 109.79(2)$ . There are four molecules in the unit cell, that is two in the asymmetric unit. A total of 7979 reflexions were measured on a NONIUS CAD 4 diffractometer using graphite mono-chromated  $MoK_\alpha$  radiation, 1762 of which were less than  $2.5\sigma(I)$  and were treated as unobserved. No absorption correction was applied (crystal dimensions  $0.4 \times 0.2 \times 0.25$  mm;  $\mu = 8.90$  cm $^{-1}$ ). The positions of the two Pd-atoms in the asymmetric unit were derived from an  $E^2$ -Patterson synthesis. A  $\Delta F$ -synthesis based on the contributions of the Pd-atoms revealed the remaining non-hydrogen atoms except those of the methyl groups. These showed up in a subsequent  $\Delta F$ -synthesis as rather diffuse peaks. Anisotropic block-diagonal least-squares refinement reduced R to 0.057. A  $\Delta F$ -synthesis at this stage indicated the hydrogen atoms, except those of the tert-butyl groups, and made clear that these methyl groups are subject to disorder. Since it was not possible to devise a satisfactory description for this disorder we have not introduced it in the model. Continued refinement with 34 non-methyl hydrogen atoms fixed at their calculated positions, converged to  $R = 0.049$  for the 6217 observed reflexions. A weighting scheme  $\omega = (1.0 + F_0 + 0.018 F_0^2)^{-1/2}$  was used and the anomalous scattering of Pd was taken into account. Computer programmes were taken from the X-RAY system<sup>26</sup> and PLUTO.<sup>27†</sup>

## RESULTS AND DISCUSSION

The molecular geometries of *c*-Hex-DAB and *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](*t*-Bu-DAB)] are depicted together with the atomic numbering in Figs. 3 and 4 respectively.

†Supplementary Material consists of a list of the final coordinates and equivalent isotropic thermal parameters and anisotropic thermal parameters of *c*-Hex-DAB and of *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](*t*-Bu-DAB)]. Copies are available on request from the Editor at Queen Mary College. Atomic coordinates have also been deposited with the Cambridge Crystallographic Centre.

## Molecular geometry of *c*-Hex-DAB

The bond distances and angles of *c*-Hex-DAB are listed in Table 1. In the solid state the molecular geometry of the R-DAB molecule is centrosymmetric with a flat *E-s-trans-E* conformation; deviations from the least-squares plane through  $C(2)-N(1)=C(1)-C(1')=N(1')-C(2')$  are less than 0.002(2) Å. This conformation is different from that found in the gas phase<sup>17</sup> (*vide supra*), but corresponds well with that predicted by MO-calculations.<sup>23</sup> The bond distances of  $C(1)-C(1')$  and  $C(1)-N(1)$  (1.457(3) and 1.258(3) Å respectively) are very near to the  $C(sp^2)-C(sp^2)$  and  $C(sp^2)=N(sp^2)$  standard single and double bond lengths (1.48 and 1.27 Å, respectively)<sup>28</sup> which would imply little conjugation in the central  $N=C-C=N$ -part of the *c*-Hex-DAB molecule. The cyclohexyl ring is in a chair conformation with an average C-C distance of 1.517(6) Å and an average C-C-C angle of 111.4(4)°. The angle between the planar part  $C(3)C(4)C(6)C(7)$  of the cyclohexyl ring and the flat  $N=C-C=N$  part is 88°.

## Molecular geometry of *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](*t*-Bu-DAB)]

The crystal structure of this compound contains two independent, but very similar molecules, A and B. Some bond lengths and -angles are listed in Table 2.†

The Pd-coordination plane in *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](*t*-Bu-DAB)] is approximately square planar; deviations from the least-squares plane through Pd, Cl(1), Cl(2), N(1) and P are less than 0.091(1) and 0.109(2) for molecules A and B re-

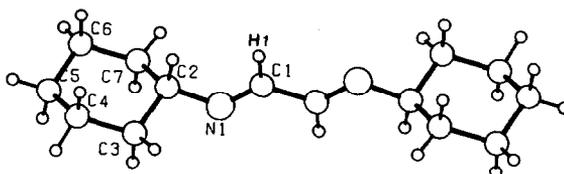


Fig. 3. Molecular geometry of *c*-Hex-DAB with atomic numbering.

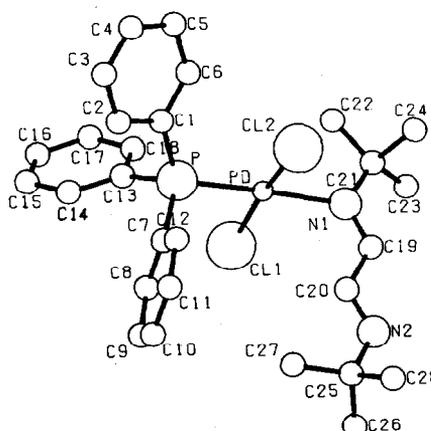


Fig. 4. Molecular geometry of *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](*t*-Bu-DAB)] with atomic numbering.

Table 1. Bond lengths (Å) and bond angles (°) with ESD's in parentheses in *c*-Hex-DAB

Table 1 : Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses in <i>c</i> -Hex-DAB.			
C(1)-C(1')	1.457(3)	N(1)-C(1)-C(1')	120.8(2)
C(1)-N(1)	1.258(3)	C(1)-N(1)-C(2)	117.7(2)
N(1)-C(2)	1.456(3)	N(1)-C(2)-C(3)	109.2(2)
C(2)-C(3)	1.518(3)	N(1)-C(2)-C(7)	108.9(2)
C(2)-C(7)	1.521(3)	C(3)-C(2)-C(7)	110.7(2)
C(3)-C(4)	1.524(3)	C(2)-C(3)-C(4)	111.3(2)
C(4)-C(5)	1.513(4)	C(3)-C(4)-C(5)	111.6(2)
C(5)-C(6)	1.509(4)	C(4)-C(5)-C(6)	111.6(2)
C(6)-C(7)	1.519(3)	C(5)-C(6)-C(7)	111.2(2)
		C(2)-C(2)-C(6)	112.0(2)

Table 2. Some bond lengths (Å) and bond angles (°) with ESD's in parentheses in *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)(*t*-Bu-DAB)]

	Molec. A		Molec. B		Molec. A		Molec. B	
Pd - Cl(1)	2.303(3)	2.309(3)	Cl(1)-Pd-Cl(2)	171.13(8)	170.15(8)			
Pd - Cl(2)	2.300(2)	2.292(3)	Cl(1)-Pd-P	90.51(8)	80.88(8)			
Pd - P	2.241(2)	2.244(2)	Cl(1)-Pd-N(1)	89.5 (1)	90.4 (2)			
Pd - N(1)	2.130(7)	2.126(5)	Cl(2)-Pd-P	90.75(8)	91.81(8)			
P - C(1)	1.831(8)	1.824(9)	Cl(2)-Pd-N(1)	88.8 (2)	88.7 (2)			
P - C(7)	1.821(7)	1.818(6)	P-Pd-N(1)	177.3 (2)	178.7 (2)			
P - C(13)	1.826(8)	1.822(7)	Pd-P-C(1)	118.6 (2)	115.9 (2)			
N(1)-C(19)	1.265(10)	1.265(12)	Pd-P-C(7)	105.9 (3)	107.9 (3)			
N(1)-C(21)	1.494(8)	1.494(9)	Pd-P-C(13)	116.5 (3)	116.2 (3)			
N(2)-C(20)	1.238(12)	1.275(12)	C(1)-P-C(7)	107.3 (3)	106.9 (3)			
N(2)-C(25)	1.484(9)	1.496(9)	C(1)-P-C(13)	100.6 (4)	100.6 (4)			
C(19)-C(20)	1.485(10)	1.472(10)	C(7)-P-C(13)	107.3 (4)	108.8 (4)			
			Pd-N(1)-C(19)	119.1 (5)	117.6 (5)			
			Pd-N(1)-C(21)	119.3 (5)	120.8 (5)			
			C(19)-N(1)-C(21)	121.5 (7)	121.6 (6)			
			N(1)-C(19)-C(20)	124.1 (8)	122.4 (8)			
			C(19)-C(20)-N(2)	118.6 (8)	118.6 (8)			
			C(20)-N(2)-C(25)	119.6 (7)	119.0 (7)			

spectively. This coordination plane makes an angle of 87.4° (mean) with the N=C-C=N plane. The conformation of the 2e;  $\sigma$ -N coordinated *t*-Bu-DAB molecule is the *E-s-trans-E* one, which is the same as in the free ligand.

The N=C-C=N skeleton is approximately planar; deviations from the least squares plane are less than 0.005(6) and 0.029(8) Å for molecules A and B, respectively.

The above mentioned coordination mode of the *t*-Bu-DAB-ligand brings the H(20) atom into the neighbourhood of the Pd-atom, above the coordination plane. The calculated distances are 2.60 and 2.58 Å for molecules A and B, respectively, which is less than the sum of Van der Waals radii for Pd and H, being 3.1 Å.<sup>29</sup> This geometry is similar to that found in [*trans*-{PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>}(*t*-Bu-DAB)] in which the *t*-Bu-DAB is bridged bonded<sup>4</sup> (see Fig. 2b). The extreme low field shift (9.91 ppm) of this H(20) atom

in <sup>1</sup>H NMR measurements indicates that the same conformation is present in solution.<sup>5</sup> The Pd...H interaction can be best described as a very weak one.<sup>4,5</sup>

The Pd-Cl bond distances are comparable with those found in other complexes with a *trans* Cl-Pd(II)-Cl configuration: they all fall in the range 2.29-2.31 Å,<sup>30</sup> being equal to the sum of the covalent radii for Pd and Cl.<sup>29</sup>

The Pd-P bond distances (2.241(2) and 2.244(2) for molecules A and B respectively) compare well with other Pd(II)-P distances in complexes in which there is a nitrogen donor ligand *trans* to the phosphine.<sup>31</sup> The Pd-N bond distances of 2.130(7) and 2.126(5) Å for molecules A and B respectively are exceptionally long. In other Pd(II) complexes with a P-atom in *trans* position, Pd(II)-N bond distances are normally 2.06 Å<sup>31a</sup> and in Pd(II)Cl<sub>2</sub>(imine)<sub>2</sub> complexes, Pd-N(imine) bond distances are found between 2.01

and 2.05 Å.<sup>30</sup> The longest previous Pd(II)-N(sp<sup>2</sup>) bond distance, to our knowledge, is 2.092(9) Å found in [PdBr(PPh<sub>3</sub>)(pyridine)]<sub>2</sub>.<sup>31b</sup>

Comparison of structural data of the N=C-C=N-skeleton in free and metal coordinated R-DAB ligands may provide an answer as to the extent of  $\sigma$ - and  $\pi$ -bonding operative in their complexes.

Figure 5 shows that  $\pi$ -backbonding in either the  $\sigma$ -N-monodentate or  $\sigma$ -N,  $\sigma$ -N'-chelate coordination fashion, comprises interaction of the ligands LUMO with a filled metal  $d$ -orbital. Any contribution of this backbonding would then lead to (i), shortening of the M-N- and C-C'- and (ii), lengthening of the C=N-bondlengths.† These trends have indeed been observed for the C=N- and C-C'- but not for the M-N-bond lengths‡ in a variety of complexes where  $\pi$ -backbonding can be expected to be operative.<sup>2b</sup> This expectation is justified by the presence in these complexes of a metal in a low formal oxidation state in combination with either a R-DAB ligand with enhanced  $\pi$ -accepting properties (e.g. if R = aryl)<sup>35</sup> or other ligands with poor  $\pi$ -accepting capacity. In *trans*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)(*t*-Bu-DAB)] none of the features favouring  $\pi$ -backbonding are present. This seems to be reflected by the similarity of the C=N- and C-C'-bond lengths in  $\sigma$ -N-bonded *t*-Bu-DAB, i.e. 1.265(10) and 1.478(10) Å, when compared with those found for free *c*-Hex-DAB, i.e. 1.258(3) and 1.457(3), respectively. Such data indicate that in the absence of  $\pi$ -backbonding, pure  $\sigma$ -N-coordination does not affect the C=N- and C-C'-bond lengths. This conclusion is supported by the C=N- and C-C'-distances found in e.g. [PtCl<sub>2</sub>(PBU<sub>3</sub>)<sub>2</sub>](*t*-Bu-DAB)<sup>4</sup> and [PtCl<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>C<sub>6</sub>H<sub>5</sub>)(*t*-Bu-DAB)]<sup>2b</sup> containing  $\sigma$ -N,  $\sigma$ -N' bridge and  $\sigma$ -N,  $\sigma$ -N'-chelate bonded *t*-Bu-DAB ligands, respectively.

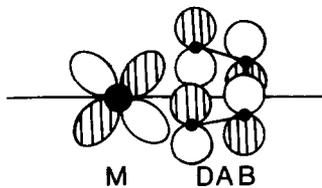


Fig. 5.  $\pi$ -Backbonding from a filled  $d$  orbital to the LUMO of the R-DAB ligand in a R-DAB-metal complex.

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†This bond length behaviour in the metal-heterobutadiene system is particularly found in metal-tetraaza-1,3-butadiene complexes. Tetraaza-1,3-butadiene, R-N=N-N-R, has a LUMO with the same character as that of R-DAB and an even stronger  $\pi$ -backbonding capacity,<sup>32</sup> which results in shorter M-N- and central N-N'- and long N=N-bond lengths in their complexes.<sup>1d</sup>

‡In [MnBr(CO)<sub>3</sub>](*c*-Hex-DAB) the C=N-, C-C'- and Mn-N-bond lengths are 1.28, 1.49 and 2.05 Å, respectively,<sup>33</sup> whereas in [Mn(*t*-Bu-DAB)<sub>2</sub>] these bond lengths are 1.32, 1.38 and 2.06 Å.<sup>34</sup>

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