Bonding analysis of transition metal NNR end-on complexes and comparison with isoelectronic NNR$_2$ species

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DFT calculations have been carried out on various NNR and NNR$_2$ transition metal complexes. The theoretical results have been analyzed together with a collection of structural data obtained through a Cambridge Data Base search covering ca. 140 compounds. When linearly coordinated in mono-substituted complexes and assuming the respective formal charges of -3 and -2, both hydrazide(-3) (NNR^{3-}) and hydrazide(-2) (NNR$_2{}^{2-}$) ligands act as 6-electron donors through their 3 occupied FMOs (one σ-type FMO and two non-equivalent π-type FMOs). Hydrazide(-3) is found to be a weaker π-donor ligand, in agreement with most of the reported X-ray structures. Calculations of the FMO occupations suggest that the ligand formal oxidation state of an NNR ligand is close to -1 and that of NNR$_2$ is intermediate between 0 and -1. In the case of the cis-di-substituted complexes, and still assuming the NNR^{3-} and NNR$_2{}^{2-}$ formal ligand charges, either the d^0 or the d^{-2} metal configuration is always found. In the former case, both cis ligands act together as a 10-electron system leading to the 18-electron count. In the latter case, the d^{-2} value is meaningless. Calculations show that the 2-electron oxidation of the d^0 species involves a ligand-based MO that is metal–ligand non-bonding, leaving the metal oxidation state unchanged, as well as the 18-electron count of the complex. Such an oxidation is associated with a 90° rotation of the cis ligands. A similar situation is computed for the 2-electron oxidation of d^2 18-MVE trans-dihydrazide(-2) models, in which the NNR$_2$ formal charge varies from -2 to -1, whereas the hydrazide system acts as an 8-electron donor in both the reduced and oxidized states. The trans-di(NNR^{3-}) compounds behave somewhat differently since their oxidized form is better described as a d^0 hydrazide(-3) 16-MVE system.

The importance of biological nitrogen fixation and the many questions still open concerning its mechanism have attracted considerable attention to model coordination compounds containing transition metal–nitrogen multiple bonds.[1] From this perspective many theoretical investigations of the bonding in these species have been carried out.[2] We recently published a semi-empirical analysis of the bonding between transition metals and NNR$_2$ ligands.[3] We now investigate the bonding between terminal NNR ligands, often called diazenide ligands in the literature, with transition metals and compare it to the bonding in complexes of NNR$_2$ ligands, generally called hydrazide(-2) ligands. In a first step the differences between the frontier orbitals of the NNR and NNR$_2$ ligands will be stressed, then the X-ray crystal structures of end-on NNR complexes available in the literature will be surveyed. Finally, results of density functional theory (DFT) calculations carried out on model compounds will be analyzed.

Results and discussion

Orbital description of the bonding ability of the NNR$_n$ ($n = 1$, 2) non-conical ligands

In our previous study on NNR$_2$ transition metal complexes we have shown that this planar (C_{2v}) ligand uses principally three frontier molecular orbitals (FMOs) to interact with the metal. One of them is a σ-type orbital while two are of π type
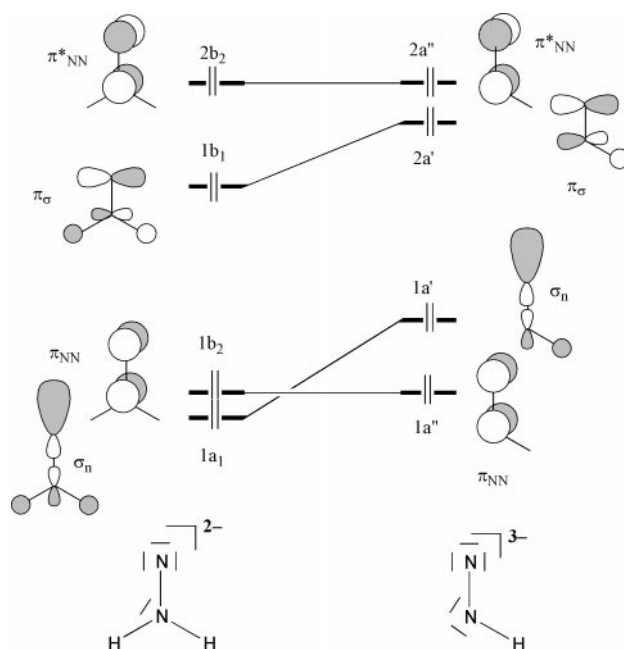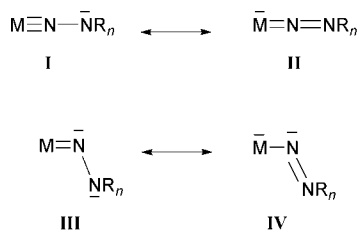

Fig. 1 The frontier orbitals of the C_{2v} NNH$_2{}^{-2}$ (left) and C_s NNH^{3-} (right) planar ligands. The anionic charges are purely arbitrary (see text).

[see Fig. 1, where the considered -2 charge, *i.e.* hydrazide(-2), is purely arbitrary]. The hybridized σ-type FMO can be associated with the σ lone pair on N_α (σ_n). The π-type FMOs lie in perpendicular planes. Since the NNH_2 unit is neither linear nor conical, these two FMOs are not degenerate. The π-in-plane (π_σ) FMO is largely localized on the N_α atom with some rather weak N–N antibonding character. The other π-type FMO lies higher in energy and can be identified as being the π^*_{NN} orbital. It is noteworthy that the π_{NN} bonding orbital of the NNR_2 ligand was found to be fully occupied in all the calculated complexes and very weakly involved in the $M-N_\alpha$ bonding, contributing to maintain significant N–N π-type bonding in the coordinated ligand. On the other hand, the participation of the π^*_{NN} FMO in the $M-N_\alpha$ bonding tends to weaken the N–N π-type bonding. Assuming arbitrarily the convention of the -2 formal charge for the NNR_2 ligand, that is hydrazide($2-$), its three FMOs are occupied (see Fig. 1), making it a potential 6-electron donor.

The orbitals of a NNR ligand of C_s symmetry can be easily derived from those of NNR_2 by the simple removal of one R substituent. This has no effect on the π^*_{NN} FMO, which by symmetry has no localization on the molecular plane, and only a moderate effect on σ_n and π_σ since they are mainly localized on N_α and only weakly concerned by what happens at N_β. The effect of the perturbation is sketched in Fig. 1 in the case of R = H, where the arbitrary -3 charge, that is hydrazide(-3), is considered. Because they have some N–R bonding character, the σ_n and π_σ FMOs of the NNR_2 ligand are somewhat destabilized upon removal of one R substituent. Therefore, π_σ comes closer in energy to π^*_{NN}. At the same time, it tends to relocalize on N_β, rendering it more similar to π^*_{NN}. In other words, the inequivalency of the π_σ and π^*_{NN} FMOs is less pronounced in the case of a NNR ligand, as compared to an NNR_2 ligand. The non-conical (non-axial) nature of a NNR fragment is less important than that of a NNR_2 unit. The removal of the R substituent from the NNR fragment would generate an N_2 conical (axial) unit in which both π-type FMOs would be degenerate and equivalent.[2a,b]

To summarize, both linearly coordinated NNR_2^{2-} [hydrazide(-2)] and NNR^{3-} [hydrazide(-3)] ligands are isolobal[4] 6-electron donors (the anionic formal charges should be considered as purely arbitrary). Like any conical ligand, they use 3 FMOs for bonding, one of σ type and two of π type. However, because of the inequivalency of their π_σ and π^*_{NN} FMOs, their bonding abilities do not exhibit the full axial symmetry of conical ligands such as N, NR or NR_3, for example. They can be considered as only approximate conical units, NNR^{3-} being closer to the conical (axial) symmetry than NNR_2^{2-}, especially when the $N_\alpha-N_\beta$–R angle is large. Because π^*_{NN} is involved in significant N–N multiple bonding in both ligands it will participate to a lesser extend than π_σ in the $M-N$ multiple bonding. In the case of NNR ligands π_σ is also somewhat involved in N–N multiple bonding (Fig. 1). Therefore, the weight of the canonical formula **II** in Scheme 1 is expected to be larger in the case of NNR ligands than for NNR_2 ligands.

Finally, it should be noted that bent $M-N_\alpha-N_\beta$ coordination modes are sometimes observed, for which the canonical formulae **III** and **IV** can be proposed and in which the

$$M\equiv N-\bar{N}R_n \longleftrightarrow \bar{\bar{M}}=N=NR_n$$

$$\text{I} \qquad\qquad\qquad \text{II}$$

$$M=\bar{N} \longleftrightarrow \bar{\bar{M}}-\bar{N}$$
$$\quad\ \ \backslash \qquad\qquad\qquad \backslash\backslash$$
$$\quad\ \ \underline{N}R_n \qquad\qquad\quad \underline{N}R_n$$

$$\text{III} \qquad\qquad\qquad \text{IV}$$

Scheme 1

NNR_2^{2-} and NNR^{3-} ligands retain a non-bonding lone pair on N_α and behave as 4-electron donors.

Structural survey and electron counting of NNR complexes

In the following and excepting cases clearly specified in the text, we will use the arbitrary convention of assuming the -3 and -2 charges for the NNR and NNR_2 ligands, respectively, that is hydrazide(-3) and hydrazide(-2). Assuming this convention the title ligands are always potential 6-electron donors. The considered metal oxidation states are calculated assuming these conventional ligand charges.

Mono-NNR complexes. The available X-ray molecular structures of NNR transition metal complexes were collected by exploiting the Cambridge Data Base system.[5] Table 1 lists most of the structurally characterized mono-NNR mononuclear (and related polynuclear) complexes, with some important structural data.[6–80] Only compounds with terminal NNR ligands (η^1-coordinated) are considered. Compounds in which the metal and NNR ligand form a heterocycle are not listed. A similar set of experimental structural data was collected for NNR_2 complexes in our previous paper.[3] Most of the listed compounds contain molybdenum, rhenium or tungsten in a high oxidation state and having an octahedral environment.

The $N_\alpha-N_\beta$ separation varies between 1.38 (**14**) and 1.11 Å (**13**). The corresponding range for NNR_2 complexes was found to lie between 1.47 and 1.25 Å.[3] Clearly, as mentioned above, NNR complexes exhibit a greater degree of N–N multiple bonding character than NNR_2 species. In most of the listed compounds, the $M-N_\alpha-N_\beta$ angle is close to 180°. However, there are several compounds in which this angle is $\approx$160°. Most of them bear π-donor ligands in addition to the NNR ligand. This moderate deviation from linearity will be discussed later. Assuming linear coordination for all these complexes and attributing the arbitrary -3 charge to the NNR ligand, this ligand is assumed to provide the metal center with 6 hydrazide(-3) valence electrons (HVE). The resulting metal valence electron (MVE) number is found to be 18 (or 16 in the case of a square-planar coordination mode) in most of the listed compounds (Table 1). Compounds **25**, **72**, **92** and **101** exhibits a significantly bent $M-N_\alpha-N_\beta$ angle ($\approx$115–125°), indicative of an sp^2 hybridization of N_α. Counting NNR^{3-} as a 4-HVE donor in these complexes results again in the expected 18-MVE, or 16-MVE count in the case of square-planar or square-pyramidal complexes.

In most of the listed compounds the $N_\alpha-N_\beta$–R angle is close to 120°, indicative of an sp^2 hybridization of N_β. There are, however, some compounds, namely **8**, **9**, **25**, **39**, **40**, **46** and **64**, for which this angle ($\approx$113–115°) is indicative of a hybridization mode closer to sp^3 than to sp^2. On the other hand, compounds **32**, **83**, **91** and **104** exhibit a particularly large $N_\alpha-N_\beta$–R angle (151–168°) which corresponds to an hybridization mode closer to sp than to sp^2 and renders the NNR ligand more conical. Such flexibility at the $N_\alpha-N_\beta$–R angle is not observed in the NNR_2 series in which N_β is always sp^2-hybridized.[3]

Di-NNR complexes. Table 2 lists the structurally characterized bis-NNR mononuclear (and related polynuclear) complexes,[9,44,54,60,81–98] with some important structural data collected from the Cambridge Data Base system.[5] In most of the reported complexes the metal lies in an octahedral environment. As for the mono-substituted series, the $N_\alpha-N_\beta$ distances are on average shorter than those observed for their NNR_2 relatives and the $N_\alpha-N_\beta$–R angle indicates a larger flexibility of the N_β hybridization mode. As already noted for the bis-NNR_2 complexes,[3] significant deviation from $M-N_\alpha-N_\beta$ linearity is present in many of the complexes.

Table 1 The structurally characterized mono-NNR mononuclear and related polynuclear complexes

Compound[a]	Distances/Å		Angles/°		Coord. number	FMC[b]	DFOS[c]	MVE[d] (HVE[e])	Ref.
	$M-N_\alpha$	$N_\alpha-N_\beta$	$M-N_\alpha-N_\beta$	$N_\alpha-N_\beta-R$					
1 $[Mo(m-NNC_6H_4NO_2)(S_2CNMe_2)_3]$	1.770(6)	1.262(9)	170.6(6)	117.9(7)	7	d⁰	−3	18(6)	6
2 $[Mo(NNPh)(S_2CNMe_2)_3]$	1.781(4)	1.233(6)	171.5(4)	120.5(5)	7	d⁰	−3	18(6)	6
3 $[Mo(NNCO_2Et)(S_2CNMe_2)_3]$	1.732(5)	1.274(7)	178.9(5)	117.0(6)	7	d⁰	−3	18(6)	7
4 $[Mo(m-NNC_6H_4NO_2)(S_2CNMe_2)_3]$	1.765(9)	1.268(13)	170.0(9)	118.0(1)	7	d⁰	−3	18(6)	8
5 $[Mo_2(NNPh)(NNHPh)(SCH_2CH_2S)_3(SCH_2CH_2SH)]^{2-}$	1.740(7)	1.35(2)	162.2(6)	NA[f]	7	d⁰	−3	18(6)	9
6 $[Mo(NNCO_2Me)(NH_2NCO_2Me)(S_2CNMe_2)_2]$	1.71(1)	1.33(2)	NA[f]	NA[f]	7	d⁰	−3	18(6)	10
7 $[Mo\{NNC(O)SMe\}\{NH_2NC(O)SMe\}(S_2CNEt_2)_2]$	1.764(6)	1.269(8)	176.1(5)	116.6(6)	7	d⁰	−3	18(6)	11
8 $[Mo\{NNC(O)SMe\}\{NH_2NC(O)SMe\}(ONEt_2)(\mu\text{-}OMe)]_2$	1.749(25)	1.24(3)	169(2)	113(3)	7	d⁰	−3	18(6)	11
9 $[Mo(NNCO_2Me)(NHNHCO_2Me)(S_2CNMe_2)_2]$	1.74(1)	1.30(2)	179.6(15)	114.5(16)	7	d⁰	−3	18(6)	12
10 $[Mo(NNCS_2Et)(NH_2NCS_2Et)(S_2CNMe_2)_2]$	1.776(9)	1.214(13)	178.3(8)	120.0(1)	7	d⁰	−3	18(6)	13
11 $[Mo\{NNCS_2Me\}\{NH_2NCS_2Me\}_2(ONMe_2)]$	1.763(8)	1.278(3)	177.8(2)	119.4	7	d⁰	−3	18(6)	13
12 $[Mo(NNC(S)OMe)(NH_2NC(S)OMe)(S_2CNEt_2)_2]$	1.72(3)	1.28(4)	174.0(2)	118.4	7	d⁰	−3	18(6)	14
13 $[Re(NNCO_2Me)Cl_2(PPh_3)_2(O_2)]$	1.798(40)	1.108(56)	170.2(22)	123.3	7	d⁰	−3	18(6)	15
14 $[Mo_2(NNPh)(NNHPh)(SCH_2CH_2S)_3(SCH_2CH_2SH)]^{2-}$	1.715(13)	1.382(19)	159.4(8)	119.0	7	d⁰	−3	18(6)	16
	1.751(14)	1.319(20)	159.2(11)	123.2					
	1.786(11)	1.286(19)	159.3(10)	120.5					
15 $[Re_2(NNPh)_2(SPh)_7]^-$	1.81(2)	1.23(3)	171.4(19)	NA[f]	7	d⁰	−3	18(6)	16
	1.81(2)	1.24(3)	170.0(18)						
16 $[Mo\{NNC(O)SMe\}(\mu\text{-}OMe)_2\{H_2NNC(O)SMe\}(ONEt_2)]_2$	1.747(2)	1.271(3)	171.0(1)	115.5(2)	7	d⁰	−3	18(6)	17
17 $[Mo(NNPh)(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$	1.814(3)	1.216(5)	171.7(3)	119.5	7	d⁰	−3	18(6)	18
18 $[Mo(NNC_5H_4N)(C_4H_3N_2S)_3]$	1.797(3)	1.234(4)	174.5(4)	118.4(3)	7	d⁰	−3	18(6)	19
19 $[Re(NNPh)Cl_2(PMe_2Ph)_3]$	1.80(1)	1.23(1)	172	118	6	d²	−3	18(6)	20
20 $[Mo(NNPh)(HB(pz)_3)(CO)_2]$	1.825(4)	1.211(6)	174.2(1)	121.2(2)	6	d²	−3	18(6)	21
21 $[Ru(p-NNC_6H_4Me)Cl_3(PPh_3)_2]$	1.796(9)	1.144(10)	171.2(9)	135.9(11)	6	d²	−3	18(6)	22
22 $[Re(NNPh)Cl_2(PPhMe_2)_3]$	1.77(2)	1.23(2)	173(2)	119(2)	6	d²	−3	18(6)	23
23 $[Re(NNCOPh)Cl_2(PPhMe_2)_3]$	1.74(2)	1.22(3)	170(2)	124(2)	6	d²	−3	18(6)	23
24 $[Ru(p-NNC_6H_4Me)Cl_3(PPh_3)_2]$	1.784(5)	1.158(6)	171.9(5)	137.1(5)	6	d²	−3	18(6)	24
25 $[Ir(o-NNC_6H_4NO_2)Cl_2(CO)(PPh_3)_2]$	2.05(4)	1.19(4)	115(3)	115(3)	6	d⁴	−3	18(4)	25
26 $[Mo(NNCOPh)Cl(dppe)_2]$	1.813(7)	1.255(10)	172.1(6)	116.7(7)	6	d²	−3	18(6)	26
27 $[W(NNMe)Cp(CO)_2]$	1.856(3)	1.215(5)	173.3(3)	116.5(4)	6	d²	−3	18(6)	27
28 $[Mn(o-NNC_6H_4CF_3)Cp'(CO)_2]^+$	1.693(7)	1.211(8)	171.8(8)	125.6(9)	6	d²	−3	18(6)	28
29 $[W\{NNC(Cl)C(CN)_2\}Br(dppe)_2]$	1.783(5)	1.289(8)	171.5(5)	124.9(6)	6	d²	−3	18(6)	29
30 $[W(NNCCl_2)Br(dppe)_2]^+$	1.75(2)	1.35(3)	169(2)	122(2)	6	d²	−3	18(6)	29
31 $[Mo(NNC_6H_4F)HB(pz)_3(SC_6H_4Me)_2]$	1.807(8)	1.229(9)	170.8(8)	121.4(9)	6	d⁰	−3	16ᵍ(6)	30
32 $[W(NNSiMe_3)I(PMe_2Ph)_4]$	1.815(17)	1.241(34)	167.9(19)	151.6(24)	6	d²	−3	18(6)	31
33 $[Mo\{NNCOPh\}\{NHNHCOPh\}\{PhC(S)N(Me)O\}_2]$	1.758(5)	1.292(7)	168.8(4)	117.5(4)	6	d²	−3	18(6)	32
34 $[Re(NNC_6H_4OMe)Cp(CO)(AuPPh_3)]$	1.777	1.286	170.8	118.6	6	d²	−3	18(6)	33
35 $[Re(NNPh)(NNHPh)Br_2(PPh_3)_2]$	1.793(11)	1.212(16)	172.4(10)	120.2(11)	6	d²	−3	18(6)	34
36 $[Mo_6(NNPh)O_{18}]^{3-}$	1.76(2)	1.31(3)	178.7(19)	116.3	6	d⁰	−3	—ʰ(6)	35
37 $[Mo\{NNpz'\}(CO)_2\{HC(pz)_3\}]^+$	1.842(10)	1.215(12)	164.5(8)	124.4(10)	6	d²	−3	18(6)	36
38 $[Re(NNCOC_6H_4\text{-}p\text{-}Cl)(SCH_2CH_2NMeCH_2CH_2NMeCH_2CH_2S)(PPh_3)]$	1.76(2)	1.31(2)	165.1(12)	115.6	6	d²	−3	18(6)	37
39 $[Re(NNCOPh)(SCH_2CH_2S(CH_2)_3SCH_2CH_2S)(PPh_3)]$	1.776(12)	1.27(2)	167.5(12)	113.9	6	d²	−3	18(6)	37
40 $[Re(NNCO_2Me)(SCH_2CH_2S(CH_2)_3SCH_2CH_2S)(PPh_3)]$	1.770(11)	1.30(2)	167.0(10)	114.9	6	d²	−3	18(6)	37
41 $[Re(o-NNC_6H_4Cl)(O_2SCH_2CH_2NMeCH_2CH_2NMeCH_2SO_2)(PPh_3)]$	1.75(2)	1.30(2)	158.8(17)	118.6	6	d²	−3	18(6)	37
42 $[Re(p-NNC_6H_4Me)Cl(\mu\text{-}dppm)_2(\mu\text{-}CO)PtCl]$	1.786(14)	1.270(18)	164.3(11)	119.2(14)	6	d²	−3	18(6)	38
43 $[Re(o-NNC_6H_4Br)Cl_2(PPh_3)_2(NH_3)]$	1.755(7)	1.25(1)	167.1(4)	119.9(6)	6	d²	−3	18(6)	39
44 $[Re(NNCOPh)Cl_2(PPh_3)_2(NCMe)]$	1.756(7)	1.25(1)	172.1(6)	120.5(7)	6	d²	−3	18(6)	39
45 $[Re(NNCO_2Me)Cl_2(PPh_3)_2(C_5H_5N)]$	1.72(2)	1.28(2)	166.9(12)	116.2	6	d²	−3	18(6)	39
46 $[Re(NNCO_2Me)Cl_2(PPh_3)_2(Me_2NCHO)]$	1.75(2)	1.28(2)	172.7(10)	114.1(13)	6	d²	−3	18(6)	39
47 $[Mo_6O_{18}(NNC_6F_5)]^{3-}$	1.75(2)	1.30(3)	170.6(21)	118.5	6	d⁰	−3	—ʰ(6)	40
48 $[Mo(p-NNC_6H_4CO_2Me)I\{Me_8[16]aneS_4\}]$	1.775(11)	1.257(15)	168.6(10)	117.6(11)	6	d²	−3	18(6)	41
49 $[Mo(p-NNC_6H_4F)Cl(NO)(HB(pz)_3)]$	1.857(3)	1.206(5)	170.7(4)	119.5(4)	6	d²	−3	18(6)	42
	1.877(3)	1.196(5)	163.4(3)	119.3(3)					
50 $[Mo(p-NNC_6H_4F)Cp(NO)(PPh_3)]^+$	1.876(3)	1.198(4)	178.3(3)	122.9(3)	6	d²	−3	18(6)	42
51 $[Mo(p-NNC_6H_4Me)Cp(CO)(PPh_3)]$	1.820(3)	1.244(4)	174.1(3)	118.2(5)	6	d²	−3	18(6)	43
52 $[Re(NNCOPh)Cl(maltol)(PPh_3)_2]$	1.708	1.309	165.5	117.0	6	d²	−3	18(6)	44
53 $[Tc(NNC_6H_4Cl)(PPh_3)(S_2CNMe_2)_2]$	1.763(3)	1.236(4)	178.6(4)	122.5(5)	6	d²	−3	18(6)	45
54 $[Mo_6O_{18}\{NNC_6H_3(NO_2)_2\}]^{3-}$	1.762	1.292	176.0	115.9	6	d²	−3	18(6)	46
55 $[Mo_6O_{18}\{NNC_6H_3(NO_2)_2\}]^{3-}$	1.733	1320	176.1	116.1	6	d²	−3	18(6)	47
56 $[WCl(CO)_2(PMe_2Ph)_2]_2(\mu\text{-}NNCMeCMeNN)$	1.78(1)	1.27(1)	168(1)	120(1)	6	d²	−3	18(6)	48
57 $[Re(NNCOPh)Cl_2(PPh_3)_2(H_2NNHC(S)Ph)]$	1.712(17)	1.267(24)	170.5(16)	117.4(20)	6	d²	−3	18(6)	49
58 $[Re(NNCOPh)Cl_2(PPh_3)_2\{H_2NNHC(O)SMe\}]$	1.732(3)	1.248(5)	172.0(3)	119.6(4)	6	d²	−3	18(6)	49
59 $[W(NNCH=CMe_2)F(dppe)_2]$	1.79(1)	1.29(1)	171.0(10)	119.6(16)	6	d²	−3	18(6)	50
60 $[W\{NN=CMeCH(CONHPh)_2\}F(dppe)_2]^+$	1.77(1)	1.33(2)	170.4(12)	122.2(16)	6	d²	−3	18(6)	50
61 $[\{W(\mu\text{-}NN=CHCHMeCHMeCH=NN)(dppe)_2\}_2F]^{2+}$	1.772(8)	1.34(2)	168.2(14)	120.5(22)	6	d²	−3	18(6)	50
62 $[Re(NNPh)Br_3(PPh_3)_2]$	1.793	1.201	170.0	126.5	6	d¹	−3	17(6)	51
63 $[Mo(NNPh)(Ph_2C(pz'))(CO)_2]^+$	1.844(9)	1.202(13)	171.4(9)	122.8(11)	6	d²	−3	18(6)	52
	1.856(9)	1.214(13)	169.8(8)	118.8(10)					

Table 1   Continued

Compound[a]	Distances/Å		Angles/°		Coord. number	FMC[b]	DFOS[c]	MVE[d] (HVE[e])	Ref.
	M–N_α	N_α–N_β	M–N_α–N_β	N_α–N_β–R					
64 $[Re(NNCOPh)Cl_2(NH_3)(PPh_3)_2]$	1.77(2)	1.24(2)	177.0(1)	114.5	6	d^2	−3	18(6)	53
65 $[Tc(NNPh)Cl(dppe)_2]^+$	1.917(19)	1.25(4)	163(2)	130(3)	6	d^2	−3	18(6)	54
66 $[Mo_6(NNC_6H_4NO_2)O_{18}]^{3-}$	1.747	1.292	179.1	116.6	6	d^0	−3	—[h](6)	55
67 $[Tc(p-NNC_6H_4Cl)(salen)(PPh_3)]$	1.764(8)	1.241(14)	173.6(7)	119.4(7)	6	d^2	−3	18(6)	56
68 $[W\{NN[(\eta^6-Ph)RuCp]\}(NCS)(dppe)_2]^+$	1.75(1)	1.28(1)	166(1)	122(1)	6	d^2	−3	18(6)	57
69 $[W\{NN[(\eta^6-p-C_6H_4CO_2Me)Cr(CO)_3]\}(NCS)(dppe)_2]$	1.784(4)	1.314(4)	164.9(3)	120.0(4)	6	d^2	−3	18(6)	57, 58
70 $[W\{NN[(\eta^6-p-C_6H_4CO_2Me)Cr(CO)_3]\}F(dppe)_2]$	1.80(1)	1.33(1)	161(1)	117(1)	6	d^2	−3	18(6)	57
71 $[W\{NN[(\eta^6-p-C_6H_4Me)FeCP]\}F(dppe)_2]^+$	1.778(8)	1.32(1)	164.0(7)	120.6(8)	6	d^2	−3	18(6)	57
72 $[Ir(NNC_6H_4OMe)Cp^*(PMe_3)_2]^+$	2.028(7)	1.210(10)	123.9(6)	117.1(8)	6	d^4	−3	18(4)	59
73 $[Re(p-NNC_6H_4Me)Cl(dmpe)_2]^+$	1.784(5)	1.233(7)	165.4(4)	122.4(5)	6	d^4	−3	18(6)	60
74 $[Tc(NNPh)(PMe_2Ph)_3Br_2]$	1.770(11)	1.208(16)	171.9(11)	122.1(11)	6	d^4	−3	18(6)	61
75 $[Mo(NNC_6H_3Me_2-2,6)Tp^*(CO)_2]$	1.824(2)	1.226(3)	172.6(2)	118.6(2)	6	d^4	−3	18(6)	62
76 $[Mo\{NN(ap)\}Tp^*(CO)_2]$	1.849(6)	1.221(9)	168.9(6)	126.1(7)	6	d^4	−3	18(6)	62
77 $[W(NNCHOCH_2CH_2CH_2)(CN)(dppe)_2]$	1.846(12)	1.281(17)	168.5(11)	119.2(12)	6	d^4	−3	18(6)	63
78 $[Re(NNPh)(NNHPh)\{2-SC_5H_3N-3-SiMe_3\}(PPh_3)_2]^+$	1.801(4)	1.228(4)	172.4(3)	122.3(4)	6	d^0	−3	18(6)	64
79 $[Re(NNCOPh)(C_5H_4NS)Cl(PPh_3)_2]$	1.751(8)	1.270(11)	174.8(8)	116.8(8)	6	d^2	−3	18(6)	65
80 $[Re(NNC_5H_4N)(HNNC_5H_4N)Cl_2(PPh_3)]$	1.78(1)	1.21(2)	172.8	120.9	6	d^2	−3	18(6)	66
81 $[Re(NNC_5H_4NH)(NNHC_5H_4N)Cl_3]$	1.741	1.255	168.1	115.8	6	d^2	−3	18(6)	66
82 $[W\{NNB(CHMe_2)_2\}(NCS)(dppe)_2]$	1.804(4)	1.262(7)	176.1(5)	133.6(6)	6	d^2	−3	18(6)	67
83 $[W(NNBC_8H_{14})(OSO_2CF_3)(dppe)_2]$	1.777(5)	1.235(6)	176.1(5)	168.3(7)	6	d^2	−3	18(6)	67
84 $[Re(NNC_5H_4NH)(HNNC_5H_4N)Cl_3]$	1.741(7)	1.254(12)	168.1(8)	115.9	6	d^2	−3	18(6)	19
85 $[Re(NNC_5H_4N)(HNNC_5H_4N)Cl_3]^-$	1.749(7)	1.267(10)	175.3(7)	118.7(8)	6	d^2	−3	18(6)	19
86 $[Re(NNC_3H_4N_2H)(HNNHC_3H_4N_2H)Cl_3]$	1.755(14)	1.28(2)	174.8(12)	116.0	6	d^2	−3	18(6)	19
87 $[Mo(NNC_5H_4NH)(HNNHC_5H_4N)Cl_3]$	1.761(3)	1.271(5)	170.6(3)	115.9(3)	6	d^2	−3	18(6)	19
88 $[Re(NNC_5H_4N)(HNNC_5H_4N)(C_5H_4NS)_2]$	1.766(5)	1.237(7)	176.2(4)	121.1(5)	6	d^2	−3	18(6)	19
89 $[Re(NNC_5H_4N)(HNNC_5H_4N)(C_4H_3N_2S)_2]$	1.704(27)	1.279(39)	176(2)	118(2)	6	d^2	−3	18(6)	19
90 $[Tc(NNC_5H_4N)(HNNC_5H_4N)(C_5H_4NS)_2]$	1.767(9)	1.237(13)	175.1(8)	123.5(9)	6	d^2	−3	18(6)	19
91 $[Ru(NNC_6H_4OMe)Cp(PPh_3)_2]^{2+}$	1.8561(23)	1.146(3)	175.4(3)	158.9(4)	6	d^2	−3	18(6)	68
92 $[Rh(NNPh)(dppp)_2Cl]^+$	1.961(7)	1.172(9)	125.1(6)	118.9(8)	5	d^4	−3	18(4)	69
93 $[Fe(NNPh)(CO)_2(PPh_3)_2]^+$	1.702(6)	1.201(7)	179.2(5)	124.2(6)	5	d^4	−3	18(6)	70
94 $[Os(NNPh)H(CO)(PPh_3)_2]$	1.867(6)	1.211(8)	171.1(6)	118.5(7)	5	d^4	−3	18(6)	71
95 $[Ir(NNPh)Cl(PMePh_2)_3]^+$	1.835(8)	1.241(11)	155.2(7)	118.8(8)	5	d^4	−3	18(6)	72
96 $[Mo(NNPh)(NCMe)\{SC_6H_2Pr^i_3-2,4,6\}_3]$	1.782(12)	1.211(17)	171.2(11)	124.7(13)	5	d^0	−3	14[g](6)	73
97 $[Fe(p-NNC_6H_4Me)\{P(OEt)_3\}_4]^+$	1.672(9)	1.224(13)	166.6(9)	120.3(10)	5	d^4	−3	18(6)	74
98 $[Ir(NNC_6H_4OMe)Cp^*(C_2H_4)]^+$	1.811(7)	1.205(9)	176.2(6)	120.4(6)	5	d^4	−3	18(6)	75
99 $[Ir(p-NNC_6H_4OMe)Cp^*\{P(p-Tol)_3\}]^+$	1.811(6)	1.205(8)	177.7(6)	120.2(7)	5	d^4	−3	18(6)	59
100 $[Ir(NNPh)Cl(PPh_3)_2]^+$	1.800(10)	1.163(11)	175.8(8)	126.9(10)	4	d^4	−3	16(6)	76
101 $[Pt(NNC_6H_4F)Cl(PEt_3)_2]$	1.975(28)	1.17(3)	118.3(20)	117.8(23)	4	d^6	−3	16(4)	77
102 $[Ir(NNC_6Cl_4)(PPh_3)_2Cl]$	1.824(6)	1.163(7)	174.7(2)	141.2(7)	4	d^6	−2[i]	16(6)	78
103 $[Rh(p-NNC_6H_4OMe)Cl(PPh_3)_2]^+$	1.793(8)	1.157(11)	179.4(7)	141.3(9)	4	d^4	−3	16(6)	79
104 $[Mo(NNSiMe_3)\{N[C(CD_3)_2Me](3,5-Me_2C_6H_3)\}]$	1.753(2)	1.221(3)	173.7(2)	157.0(3)	4	d^0	−3	18(6)	80

[a] Ligand abbreviations: dppe = 1,2-bis(diphenylphosphino)ethane; dppm = 1,2-bis(diphenylphosphino)methane; dmpe = 1,2-bis(dimethylphosphino)ethane; dppp = (3-diphenylphosphinopropyl)phenylphosphine; Cp = cyclopentadienyl; Cp* = η^5-C_5Me_5; Cp′ = η^5-C_5H_4Me; salen = dianion of N,N'-bis(salicylidene)ethane-1,2-diamine; ap = antipyrine = 2,3-dimethyl-5-oxo-1-phenyl-3-pyrazoline; Py = pyridine; pz = pyrazoly; pz′ = 3,5-dimethylpyrazolyl; HB(pz)_3 = hydridotris(pyrazolyl)borate; Tp* = hydridotris(3,5-dimethylpyrazolyl)borate; HC(pz)_3 = tris(pyrazolyl)methane. [b] Formal metallic electron configuration. [c] NNR formal oxidation state. [d] Number of metal valence electrons (MVE). [e] Number of hydrazido valence electrons (HVE) donated to the metal. [f] NA = not available. [g] Assuming no π donation from S atoms. [h] Polyoxometallate delocalized bonding. [i] R is formally −1 in this conjugated NNR^{2-} diazenide ligand.

Symmetry arguments have shown that two 6-electron terminal ligands situated in a *cis* position can donate only 10 electrons as a whole to the metal atom. When they are in the *trans* position they can donate no more than 8 electrons.[2u,3] Applying these rules to the compounds in Table 2 and assuming the same formal −3 charge for both NNR ligands would lead to a 16-MVE count for all of them, as well as a negative (d^{-n}) formal metallic configuration (FMC). In fact, the calculations described below show that in the case of the *cis* derivatives, the NNR ligands can be considered with the −2 formal charge and still behave as a 10-electron donor. This leads to an 18-MVE count for all the *cis* compounds listed in Table 2.

DFT investigation of the metal–NNR and metal–NNR$_2$ bonding

Hexacoordinate mono-substituted derivatives. We start the analysis by comparing the optimized geometries of the 18-MVE models $[Mo(PH_3)_4(NNH)X]$ and $[Mo(PH_3)_4(NNH_2)X]^+$ (X = H, Cl) shown on the left side of Fig. 2. The

NNH_2 models were found to adopt a C_{2v} symmetry, whereas the NNH species have C_s symmetry. The main DFT results are given in Table 3. They are in rather good agreement with recent DFT calculations on the isoelectronic models $[Mo(PH_3)_4(NNH)F]$ and $[Mo(PH_3)_4(NNH_2)F]^+$.[2a]

In agreement with the observation of the experimental structures (see above), the N_α–N_β distance is shorter in the NNH species (by ≈ 0.07 Å) than in the NNH_2 derivatives. Consistently, the Mo–N_α distance is longer for the NNH models (by ≈ 0.04 Å). This result confirms that the canonical formula **II** in Scheme 1 has a larger weight in the NNR case as compared to the NNR_2 one. The stronger Mo–N_α π-type interaction in the case of the NNH model is also supported by the larger pyramidalization of Mo in $[Mo(PH_3)_4(NNH_2)H]^+$ as compared to $[Mo(PH_3)_4(NNH)H]$. This pyramidalization disapears in the case of the chloro derivative because of the π-type effect of the halogen ligand.

As observed for several compounds of Table 1, the N_α–N_β–H angle is significantly smaller than 120° in the NNR derivatives. In both series of compounds, the substitution of hydrogen by a chlorine atom shortens the Mo–N_α bond

Table 2 The structurally characterized di-NMR mononuclear and related polynuclear complexes

Compound[a]	Distances/Å		Angles/°		Coord. number	FMC[b]	DFOS[c]	MVE[d] (HVE[e])	Ref.
	$M-N_\alpha$	$N_\alpha-N_\beta$	$M-N_\alpha-N_\beta$	$N_\alpha-N_\beta-R$					
105 *trans*-[Mo(NNPh)$_2$(TTP)]	2.060(5)	1.133(9)	149.1(9)	128.6(9)	6	d^0	−3	16(8)	81
106 *trans*-[Re(*p*-NNC$_6$H$_4$Me)$_2$(dppe)$_2$]$^+$	1.909(2)	1.223(3)	162.7(2)	121.5(3)	6	d^0	−3	16(8)	60
107 *trans*-[Re(*p*-NNC$_6$H$_4$Cl)$_2$(dmpe)$_2$]$^+$	1.928(4)	1.224(6)	147.3(5)	116.6(5)	6	d^0	−3	16(8)	60
	1.920(4)	1.204(6)	149.0(4)	118.2(5)					
108 *cis*-[Mo(NNC$_6$H$_4$F)$_2$Cp′Cl]	1.826(2)	1.229(4)	167.4(2)	117.4(3)	6	d^0	−2	18(10)	82
109 *cis*-[Mo(*p*-NNC$_6$H$_4$OMe)$_2$(S$_2$N$_2$C$_8$H$_{18}$)] (*C$_e$*)	1.81(1)	1.28(2)	170.4(17)	113.8(17)	6	d^0	−2	18(10)	83
	1.81(2)	1.20(3)	168.3(19)	119.6(17)					
110 *cis*-[Mo(*p*-NNC$_6$H$_4$OMe)$_2$(S$_2$N$_2$C$_8$H$_{18}$)] (*C$_{2/c}$*)	1.825(6)	1.228(8)	174.24	117.9	6	d^0	−2	18(10)	84
111 *cis*-[Mo(*p*-NNC$_6$H$_4$Me)$_2$F{HB(pz)$_3$}]	1.832(3)	1.217(4)	176.1(2)	118.2(3)	6	d^0	−2	18(10)	85
	1.832(3)	1.226(3)	175.2(2)	118.2(2)					
112 *cis*-[Mo$_2$(NNPh)$_4$(acac)$_2$(μ-OMe)$_2$] Isomer I	1.810(9)	1.240(13)	177.7(11)	117.1(12)	6	d^0	−2	18(10)	86
	1.802(14)	1.259(19)	175.9(11)	118.9(13)					
113 *cis*-[Mo$_2$(NNPh)$_4$(acac)$_2$(μ-OMe)$_2$] Isomer II	1.832(9)	1.216(14)	176.5(9)	119.7(10)	6	d^0	−2	18(10)	86
	1.859(11)	1.194(15)	173.3(9)	117.6(10)					
114 *cis*-[Mo$_4$O$_8$(NNPh)$_4$(μ-OMe)$_2$]$^{2-}$	1.826	1.207	168.2	119.6	6	d^0	−2	18(10)	87
	1.811	1.267	172.2	116.7					
	1.789	1.256	167.6	119.8					
	1.806	1.262	169.7	118.6					
115 *cis*-[Mo$_4$O$_8$(NNPh)$_4$(μ-OEt)$_2$]$^{2-}$	1.841	1.215	168.7	116.3	6	d^0	−2	18(10)	87a
	1.826	1.230	172.3	116.9					
	1.819	1.221	167.8	120.5					
	1.839	1.243	172.0	119.5					
116 *cis*-[Mo$_8$O$_{20}$(NNPh)$_6$]$^{4-}$	1.800(3)	1.27(1)	177.7	119.6	6	d^0	−2	18(10)	88
	1.805(3)	1.24(1)	174.2	116.1					
	1.808(3)	1.25(1)	170.2	116.3					
	1.777(4)	1.26(1)	165.3	117.4					
	1.820(3)	1.26(1)	174.8	122.5					
	1.803(3)	1.26(1)	175.8	116.1					
117 *cis*-[Mo$_4$O$_8$(NNC$_6$H$_4$NO$_2$)$_4$(μ-OMe)$_2$]$^{2-}$	1.823(8)	1.235(11)	174.9(7)	117.0(7)	6	d^0	−2	18(10)	88
	1.809(7)	1.240(11)	172.1(7)	118.0(8)					
118 *cis*-[Mo$_4$O$_{10}$(NNPh)$_2$(μ-OMe)$_2$]$^{2-}$	1.776(2)	1.304(7)	171.7(3)	116.9(3)	6	d^0	−2	18(10)	88
119 *cis*-[Mo$_2$(NNPh)$_4$(SPh)$_5$]$^-$	1.838(10)	1.221(15)	169.8(7)	119.7	6	d^0	−2	18(10)	9
	1.819(8)	1.219(11)	178.4(8)	122.0					
	1.813(7)	1.230(10)	170.7(8)	119.5					
	1.837(8)	1.213(12)	166.9(8)	118.9					
120 *cis*-[Mo$_4$O$_6$(NNPh)$_4$(μ-OMe)$_2$(C$_{10}$H$_6$O$_2$)$_2$]$^{2-}$	1.849(14)	1.293(16)	174.9(11)	109.2	6	d^0	−2	18(10)	89
	1.800(15)	1.235(15)	174.9(11)	118.1					
121 *cis*-[Mo$_4$O$_6$(OC$_6$H$_4$NH)$_2$(NNPh)$_4$(μ-OMe)$_2$]$^{2-}$	1.764(15)	1.263	167.2	122.7	6	d^0	−2	18(10)	89
	1.829(17)	1.229	163.4	123.8					
122 *cis*-[Mo$_2$(NNPh)$_4$(μ-OMe)$_2$(OC$_6$H$_4$NH$_2$)$_2$]	1.815(5)	1.242(8)	173.1(5)	117.3	6	d^0	−2	18(10)	89
	1.823(6)	1.227(9)	166.9(4)	119.6					
123 *cis*-[{Mo(NNPh)$_2$(μ-OEt)(PhCONHO)}$_2$]	1.817(8)	1.24(1)	171.6(7)	118.3(8)	6	d^0	−2	18(10)	90
	1.841(8)	1.26(1)	175.7(7)	118.2(9)					
124 *cis*-[{Mo(NNPh)$_2$(μ-OMe)(OMe)(PhNHNH$_2$)}$_2$]	1.830(3)	1.227(4)	170.3(3)	117.3(3)	6	d^0	−2	18(10)	90
	1.832(3)	1.231(4)	161.2(3)	121.4(3)					
125 *cis*-[{Mo(NNPh)$_2$Cl(μ-OMe)(PhNHNH$_2$)}$_2$]	1.822(6)	1.225(8)	171.0(5)	119.0(6)	6	d^0	−2	18(10)	90
	1.817(7)	1.227(8)	163.2(6)	121.8(6)					
126 *cis*-[{Mo(NNPh)$_2$Cl(μ-O-*n*-C$_3$H$_7$)(PhNHNH$_2$)}$_2$]	1.79(1)	1.23(1)	166.0(1)	119.0(1)	6	d^0	−2	18(10)	90
	1.84(2)	1.24(2)	170.0(1)	118.0(2)					
127 *cis*-[{Mo(NNPh)$_2$Cl(μ-OEt)(EtOH)}$_2$]	1.830(6)	1.235(9)	173.8(5)	119.1(6)	6	d^0	−2	18(10)	90
128 *cis*-[Mo(*p*-NNC$_6$H$_4$Me)Cp(*p*-NNC$_6$H$_4$F)(PPh$_3$)]$^+$	1.840(4)	1.196(6)	175.9(4)	123.0(4)	6	d^0	−2	18(10)	44, 91
	1.838(4)	1.211(6)	173.2(4)	122.9(4)					
129 *cis*-[Mo$_4$O$_8$(NNC$_6$H$_4$OMe)$_4$(μ-OMe)$_2$]$^{2-}$	1.811(8)	1.25(1)	175.2(7)	118.9(8)	6	d^0	−2	18(10)	92
	1.821(8)	1.22(1)	174.5(8)	116.0(8)					
130 *cis*-[Mo(NNPh)$_2${SC$_6$H$_3$Bu$^t_2$S(CH$_2$)$_2$C$_6$H$_3$Bu$^t_2$S}]	1.847(6)	1.222(8)	175.0(5)	118.1(6)	6	d^0	−2	18(10)	93
131 *cis*-[Mo(*p*-NNC$_6$H$_4$Me)$_2$(SCH$_2$CH$_2$NH$_2$)$_2$]	1.826(2)	1.229(3)	171.7(2)	118.4(2)	6	d^0	−2	18(10)	94
132 *cis*-[Mo(*p*-NNC$_6$H$_4$Me)$_2$(acac)$_2$]	1.75(3)	1.31(3)	177.8(25)	120.5(28)	6	d^0	−2	18(10)	95
	1.80(3)	1.27(3)	176.0(28)	118.0(32)					
133 *cis*-[Mo(*p*-NNC$_6$H$_4$OMe)$_2$(acac)$_2$]	1.80(2)	1.24(2)	176.8(14)	120.3(14)	6	d^0	−2	18(10)	95
	1.75(2)	1.23(2)	174.9(13)	118.8(15)					
134 *cis*-[Re(NNPh)$_2$(cat)$_2$]$^-$	1.83(1)	1.21(2)	163.9(9)	117.7	6	d^0	−2	18(10)	96
	1.81(1)	1.20(1)	170.0(9)	120.1					
135 *cis*-[Re(NNPh)$_2$(cat)$_2$]$^-$	1.82(1)	1.21(1)	172.3(4)	118.3	6	d^0	−2	18(10)	96
136 *cis*-[Re(NNC$_6$H$_4$Br)$_2$Cl(PPh$_3$)$_2$]	1.80(2)	1.24(3)	172.0(27)	120.0(26)	5	d^2	−2	18(10)	97
	1.73(2)	1.32(3)	164.7(18)	116.2(23)					
137 *cis*-[Re(NNC$_6$H$_4$Br)$_2$(PPh$_3$)$_2$(SC$_6$H$_3$-2,5-Me$_2$)]	1.73(1)	1.32(2)	160.9(2)	119.8(13)	5	d^2	−2	18(10)	97
	1.80(2)	1.25(2)	178.1(12)	117.6(14)					
138 *cis*-[Tc(NNC$_6$H$_4$Br)$_2$Cl(PPh$_3$)$_2$]	1.796(6)	1.229(9)	170.7(7)	119.7(7)	5	d^2	−2	18(10)	98
	1.783(7)	1.224(8)	166.2(6)	117.0(7)					
139 *cis*-[Tc(*p*-NNC$_6$H$_4$Cl)$_2$(PPh$_3$)$_2$]	1.792	1.225	172.1	119.5	5	d^2	−2	18(10)	54
	1.776	1.246	166.0	116.3					

[a] Ligand abbreviations: TTP = dianion of *meso*-tetratolylporphyrin; dppe = 1,2-bis(diphenylphosphino)ethane; dmpe = 1,2-bis(dimethylphosphino)ethane; acac = acetylacetonate; cat = catecholate; HB(pz)$_3$ = hydridotris(pyrazoly)borate; Cp = C$_5$H$_5$; Cp′ = C$_5$H$_4$Me. [b] Formal metallic electron configuration: [c] Diazenido formal oxidation state. [d] Number of metal valence electrons (MVE). [e] Number of hydrazido valence electrons (HVE) donated to the metal. [f] Polyoxometallate delocalized bonding.
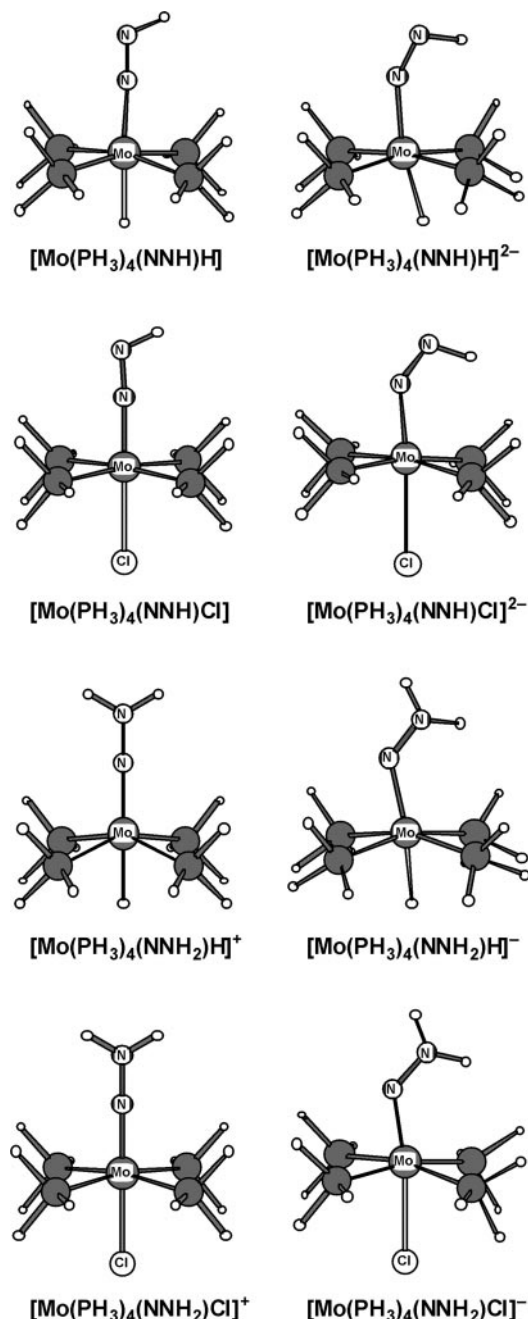
Fig. 2 Optimized geometries of the models $[Mo(PH_3)_4(NNH)X]^{0/2-}$ and $[Mo(PH_3)_4(NNH_2)X]^{1+/1-}$ (X = H, Cl).

whereas the N_α–N_β distance is not significantly changed, suggesting a σ-type *trans* effect.

The ligand FMO population analysis based on the $[Mo(PH_3)_4X]$ + NNH and $[Mo(PH_3)_4X]^+$ + NNH$_2$ fragment decompositions leads to the occupancies given in Table 3. These values confirm that, remaining almost fully occupied after interaction, the π_{NN} FMO is never significantly involved in the M–N_α bonding. The σ_n FMOs of NNH and NNH$_2$ interact similarly. This is not the case for π^*_{NN} and π_σ which are less occupied in the case of NNH, indicating a weaker involvement in the the M–N_α bonding, again supporting a larger weight for structure **II** in Scheme 1 in the case of NNR as compared to NNR$_2$ ligands.

Oxidation states of the NNH and NNH$_2$ ligands can be approximated by rounding their FMO occupancies to their nearest integer value. This would correspond to $(\sigma_n)^2(\pi_{NN})^2(\pi_\sigma)^1(\pi^*_{NN})^1$ for both NNH and NNH$_2$, that is hydrazide(-1) and hydrazyl(0), respectively. This approximation is more crude in the latter case, owing to the values of

the π_σ occupancies which are significantly larger than 1. Taking this fact into account, one is led to suggest that NNH$_2$ can be described as intermediate between hydrazyl(0) and hydrazide(-1).

Adding two electrons to the studied models is expected to induce a Jahn–Teller distortion that would help to maintain the favorable 18-MVE count of the complex. This is achieved by Mo–N_α–N_β bending (see Fig. 2) in such a way that the NNR^{3-} and NNR^{2-} ligands now act as 4-electron donors, as shown by the optimized geometries of the $[Mo(PH_3)_4(NNH)X]^{2-}$ and $[Mo(PH_3)_4(NNH_2)X]^-$ (X = H, Cl) models shown on the right side of Fig. 2, the main DFT results are given in Table 3. It is interesting to note that in the NNH cases the Mo–N_α–N_β angle is much larger than 120°, although the N_α–N_β separations do not differ that much from those found for the $[Mo(PH_3)_4(NNH)X]$ and $[Mo(PH_3)_4(NNH_2)X]^+$ (X = H, Cl) series. As expected, the Mo–N_α distances are longer in the reduced compounds. This is primarily the consequence of larger π_σ FMO occupations in the reduced states (Table 3).

Going back to the $[Mo(PH_3)_4(NNH)X]$ and $[Mo(PH_3)_4(NNH_2)X]^+$ (X = H, Cl) series, one can note that the formal oxidation state of Mo is 4 +, the metal configuration is d^2. Our previous extended Hückel study of NNR$_2$ complexes suggested that in principle diamagnetic octahedral complexes could also be stable in a d^0 configuration, that is for MVE = 16.[3] DFT calculations on the $[Mo(PH_3)_4(NNH)X]^{2+}$ and $[Mo(PH_3)_4(NNH_2)X]^{3+}$ (X = H, Cl) models do not confirm this suggestion. No significant HOMO–LUMO gap could be obtained for any of these models, suggesting that if such electron-deficient octahedral L$_5$M(NNR$_n$) (n = 1, 2) species could be generated they would likely be very reactive. This is due to the fact that the orbital containing the two metal electrons of the stable 18-MVE species is not the HOMO, but lies lower in energy. As a matter of fact, most of the complexes listed in Table 1 are 18-MVE species. The situation is similar within the series of NNR$_2$ complexes.[3]

Hexacoordinate *trans* di-substituted derivatives. In a symmetrical *trans*-L$_4$Mo(NNR$_n$)$_2$ (n = 1, 2) species, the two NNR^{3-} or NNR^{2-} terminal ligands act together as an 8-electron ligand system, whatever their rotational conformation (staggered, eclipsed or intermediate).[2u,3] This means that by symmetry, only 4 of the 8 π-type electrons of the NNR^{3-} or NNR^{2-} ligands can be donated to the metal.

We start the analysis with the NNH$_2$ species, which are more symmetrical and which we previously investigated in detail with extended Hückel calculations.[3] The optimized geometry of the 18-electron model *trans*-$[Mo(PH_3)_4(NNH_2)_2]$ has C_{2v} symmetry and is very close to D_{2d}, the lowering of symmetry being due to the preference for some peculiar rotational orientation of the PH$_3$ ligands (see Fig. 3 and Table 4). In this species, the rotational barrier of the NNH$_2$ ligand is ≈0.6 eV, a value larger than that suggested by extended Hückel calculations[3] and indicative of the non-axial (non-conical) nature of this ligand. A simplified DFT MO interaction diagram of the *trans*-$[Mo(PH_3)_4(NNH_2)_2]$ model in the D_{2d} idealized symmetry is sketched on the right side of Fig. 4. Levels derived from the σ_n NNH$_2$ FMOs are not shown. It is interesting to note that the HOMO is a NNH$_2$ level of *e* symmetry and can be identified as containing the 4 π-type non-bonding electrons of the NNR$_2$$^{2-}$ ligands. The b_1 level containing the 2 Mo^{IV} electrons lies lower in energy. A similar situation occurs in the unstable D_{2h} conformation where the non-bonding π-type hydrazide b_{2u} HOMO lies even higher in energy (see left side of Fig. 4).

It follows that the 2-electron oxidation of *trans*-$[Mo(PH_3)_4(NNH_2)_2]$ will involve the hydrazide(-2) ligands, leaving the metal center in its Mo^{IV} (d^2) formal oxidation

Table 3 Main DFT results for MO(PH$_3$)$_4$(NNH)X]$^{0/2-}$ and [Mo(PH$_3$)$_4$(NNH$_2$)X]$^{1+/1-}$ (X = H, Cl)

	[Mo(PH$_3$)$_4$(NNH)X]^n				[Mo(PH$_3$)$_4$(NNH$_2$)X]^n			
	$n = 0$ (C_s)		$n = -2$ (C_s)		$n = 1$ (C_{2v})		$n = -1$ (C_s)	
	X = Cl	X = H	X = Cl	X = H	X = Cl	X = H	X = Cl	X = H
HOMO–LUMO gap/eV	2.38	2.49	0.70	0.50	2.03	2.13	1.31	1.55
Geometrical parameters								
Mo–N$_\alpha$/Å	1.842	1.884	2.003	1.997	1.806	1.835	1.966	2.009
N$_\alpha$–N$_\beta$/Å	1.222	1.217	1.239	1.224	1.287	1.288	1.297	1.287
N$_\alpha$–H/Å	1.036	1.037	1.097	1.111	1.021	1.022	1.026	1.047
							1.044	1.029
Mo–N$_\alpha$–N$_\beta$/°	175.9	177.3	139.2	149.0	180.0	180.0	127.6	129.6
N$_\alpha$–N$_\beta$–H/°	114.1	114.8	109.4	110.7	120.2	120.4	120.3	121.0
							120.9	121.6
H–N$_\beta$–H/°					119.6	119.2	118.8	117.4
Mulliken atomic net charges								
Mo	0.38	0.56	0.45	0.20	0.42	0.62	0.44	0.67
N$_\alpha$	−0.27	−0.25	−0.28	−0.22	−0.40	−0.42	−0.39	−0.38
N$_\beta$	−0.22	−0.20	−0.34	−0.30	0.12	0.12	0.08	0.09
H	0.05	0.05	−0.13	−0.15	0.04	0.03	−0.12	−0.04
							0.06	−0.12
NNH and NNH$_2$ FMO occupancies								
π^*_{NN}	0.61	0.56	0.36	0.38	0.92	0.90	0.74	0.70
π_σ	1.00	0.98	1.44	1.32	1.41	1.41	1.71	1.77
π_{NN}	2.01	2.00	1.99	1.99	2.00	2.00		
σ_n	1.77	1.79	1.86	1.84	1.81	1.84	1.89	1.87

state. This is shown by the DFT results on the oxidized model *trans*-[Mo(PH$_3$)$_4$(NNH$_2$)$_2$]$^{2+}$. As expected from the higher energy of the HOMO of the reduced forms in this conformation, the oxidized species is of D_{2h} symmetry (see Fig. 3 and Table 4). With a partially occupied *e* HOMO, the D_{2d} conformation is Jahn–Teller unstable with respect to the D_{2h} one. It follows from these results that the oxidized form of the Mo^{IV} 18-electron *trans*-[Mo(PH$_3$)$_4$(NNH$_2$)$_2$] complex is still a Mo^{IV} 18-electron species. Indeed, if the ligands are considered as formally NNH$_2^{2-}$ in *trans*-[Mo(PH$_3$)$_4$(NNH$_2$)$_2$], then they should be described (on average) as NNH$_2^-$ in *trans*-[Mo(PH$_3$)$_4$(NNH$_2$)$_2$]$^{2+}$, the only change upon oxidation being the removal of an electron pair that is delocalized on both hydrazide ligands and has no metal participation. This is exemplified by the variation upon oxidation of the π^*_{NN} FMO population of the considered model (Table 4). Since this level is somewhat N$_\alpha$–N$_\beta$ antibonding, significant shortening of this bond arises (Table 4). Unfortunately, to our knowledge, there is only one example of a *trans*-di-NNR$_2$ complex, which is isoelectronic to [Mo(PH$_3$)$_4$(NNH$_2$)$_2$]$^{2+}$.[99] As in this model, both NNR$_2$ ligands lie in the same plane. However, they exhibit some bending at N$_\alpha$ ($\approx$166°), presumably caused by the strong π-donor effect of the other ligands.[3]

The optimized geometry of the 18-electron model *trans*-[Mo(PH$_3$)$_4$(NNH$_2$)$_2$]$^{2-}$ (isoelectronic to *trans*-[Mo(PH$_3$)$_4$(NNH$_2$)$_2$]) has C_{2h} symmetry (see Fig. 3 and Table 4). Contrary to its NNH$_2$ relative, the Mo–N$_\alpha$–N$_\beta$ angle is significantly bent. This is also the case for most of the di-NNR compounds reported in Table 2. This bending is the result of a tendency for the localization of lone pairs on the N$_\alpha$ atoms. As stated above, in the linear Mo–N$_\alpha$–N$_\beta$ arrangement, there are two combinations of π-type ligand FMOs, which cannot interact with the metal by symmetry and are equally distributed on both ligands.[3] In the case of the less symmetrical NNR ligands, the bending at N$_\alpha$ tends to localize them in somewhat more stable hybrids. Nevertheless, the stabilization afforded by bending is small (0.12 eV), as is the rotational barrier of the NNR ligands ($\approx$0.12 eV).

The computed HOMO–LUMO gap of *trans*-[Mo(PH$_3$)$_4$(NNH$_2$)$_2$]$^{2-}$ is not very large (0.67 eV). As a matter of fact, all the *trans* di-NNR complexes reported in Table 2 have 2 electrons less than this model compound. The HOMO–LUMO gap computed for the oxidized model *trans*-[Mo(PH$_3$)$_4$(NNH)$_2$] is much larger (1.52 eV) (see Fig. 3 and Table 4). Although being of C_1 symmetry, its geometry is not very different from C_s with both NNR ligands lying approximately in the same plane. Because of the lower symmetries of the reduced and oxidized forms of the di-NNH models as compared to their di-NNH$_2$ relatives, it is more difficult to assign a change of formal oxidation state to a single atom or
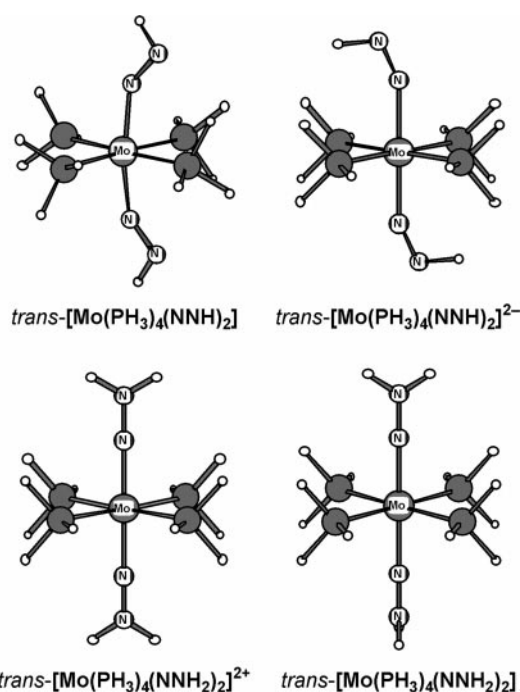

trans-[Mo(PH$_3$)$_4$(NNH)$_2$]   *trans*-[Mo(PH$_3$)$_4$(NNH)$_2$]$^{2-}$

trans-[Mo(PH$_3$)$_4$(NNH$_2$)$_2$]$^{2+}$ *trans*-[Mo(PH$_3$)$_4$(NNH$_2$)$_2$]

Fig. 3 Optimized geometries of the models *trans*-[Mo(PH$_3$)$_4$(NNH)$_2$]$^{0/2-}$ and *trans*-[Mo(PH$_3$)$_4$(NNH$_2$)$_2$]$^{2+/0}$

Table 4 Main DFT results for *trans*-[Mo(PH₃)₄(NNH)₂]$^{0/2-}$ and *trans*-[Mo(PH₃)₄(NNH₂)₂]$^{2+/0}$

	trans-[Mo(PH₃)₄(NNH)₂]^n		*trans*-[Mo(PH₃)₄(NNH₂)₂]^n	
	$n = 0$ (C₁)	$n = -2$ (C₂ₕ)	$n = +2$ (D₂ₕ)	$n = 0$ (C₂ᵥ "D₂d")
HOMO–LUMO gap/eV	1.52	0.67	0.88	1.99
Mo–N$_\alpha$/Å	1.975	2.041	1.919	1.943
	1.967			1.933
N$_\alpha$–N$_\beta$/Å	1.226	1.216	1.240	1.291
N$_\alpha$–H/Å	1.049	1.130	1.036	1.027
Mo–N$_\alpha$–N$_\beta$/°	146.4	154.8	180.0	180.0
	147.3			
N$_\alpha$–N$_\beta$–H/°	111.0	111.0	121.6	122.0
	111.0			
H–N$_\beta$–H/°			116.8	116.1
Mulliken atomic net charges				
Mo	0.31	0.07	0.36	0.60
N$_\alpha$	−0.24	−0.22	−0.28	−0.44
	−0.24			−0.44
N$_\beta$	−0.19	−0.28	0.21	0.03
	−0.20			0.03
H	0.04	−0.20	0.06	−0.02
	0.05			−0.02
NNH and NNH₂ FMO occupancies				
π^*_{NN}	0.32	0.26	0.49	0.96
π_σ	1.28	1.52	1.60	1.67
π_{NN}	1.99	1.99	2.00	2.00
σ_n	1.75	1.84	1.81	1.74

ligand upon oxidation. It should be noted, however, that the computed atom Mulliken charges vary differently upon oxidation from those of the di-NNH₂. The ligand is less depopulated and the metal charge varies in the opposite way. There is no shortening of the N$_\alpha$–N$_\beta$ bond. From these results we suggest that the oxidized form be considered as a 16-electron rather than 18-electron species, keeping in mind that we are dealing with the limits of the meaning of such formalisms. The
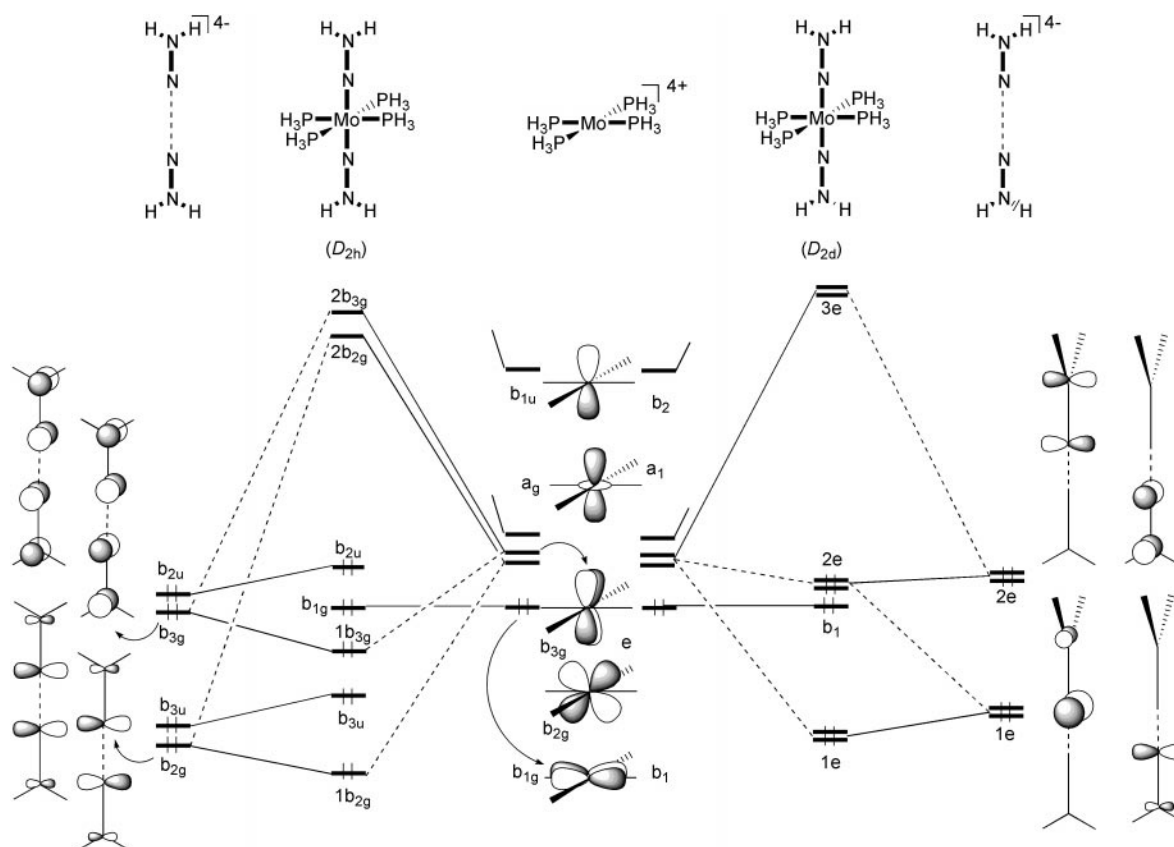
Fig. 4 Qualitative interaction MO diagram of the model *trans*-[Mo(PH₃)₄(NNH₂)₂] in the idealized D₂ₕ and D₂d conformations. Only the metal-hydrazido π-type interactions are shown.

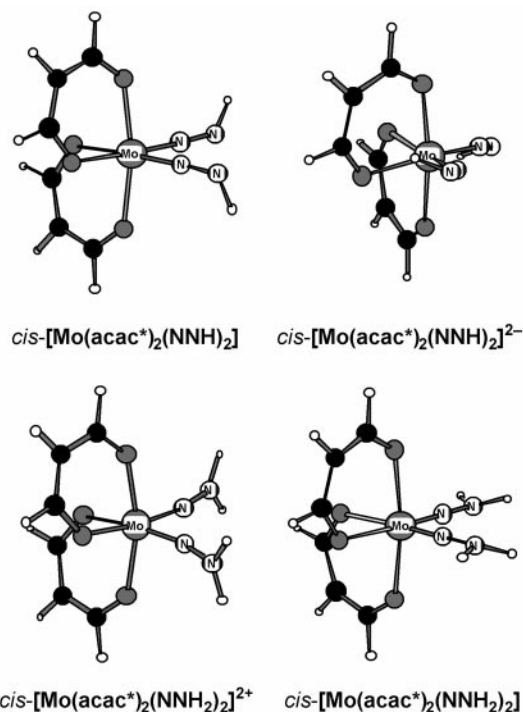**Fig. 5** Optimized geometries of the models *cis*-[Mo(acac*)$_2$(NNH)$_2$]$^{0/2-}$ and *cis*-[Mo(acac*)$_2$(NNH$_2$)$_2$]$^{2+/0}$. acac* = [HC(=O)CHC(=O)H]$^-$.

rotational barrier of the NNH ligands is computed to be ≈0.23 eV.

Hexacoordinate *cis* di-substituted derivatives. When linearly coordinated in *cis*-L$_4$Mo(NNR$_n$)$_2$ species, the NNR^{3-} or NNR$_2$$^{2-}$ ligands act as a whole as a 10-electron ligand system, whatever their rotational conformation (staggered, eclipsed or intermediate).[2u,3] This means that the metal uses 5 valence AOs for bonding with the nitrogen ligands and 4 for bonding with the other ligands. There is no non-bonding metal AO left, consequently the only possible MVE count for

this d^0 complex is 18, at least if one assumes that the NNR^{3-} or NNR$_2$$^{2-}$ couples *always* behave as 10-electron donors.

The optimized geometries of the 18-MVE models *cis*-[Mo(acac*)$_2$(NNH)$_2$]$^{2-}$ and *cis*-[Mo(acac*)$_2$(NNH$_2$)$_2$] {acac* = [HC(=O)CHC(=O)H]$^-$} are shown in Fig. 5 and the main DFT results are given in Table 5. The optimized conformation of the NNH$_2$ derivative has C_2 (approximately C_{2v}) symmetry and corresponds to that predicted by extended Hückel theory and to the known experimental molecular structures.[3] The optimized geometry of the NNH model derives from that of the NNH$_2$ one by single deprotonation of each NNH$_2$ ligand, associated with some Mo–N$_\alpha$–N$_\beta$ bending. The energy gained upon bending is ≈0.53 eV. Obviously, the presence of several π-donor ligands on the metal favors such bending (see the structural survey discussion above).

All the *cis*-L$_4$M(NNR)$_2$ octahedral complexes reported in Table 2 have 2 electrons less than *cis*-[Mo(acac*)$_2$(NNH)$_2$]$^{2-}$ and apparently appear to be 16-MVE complexes. In order to understand this contradiction, calculations were also carried out on the oxidized models *cis*-[Mo(acac*)$_2$(NNH)$_2$] and *cis*-[Mo(acac*)$_2$(NNH$_2$)$_2$]$^{2+}$. Their optimized geometries, of C_2 symmetry, are shown in Fig. 4. They exhibit rotational conformations of the NNR$_n$ ligands that are different from those of their reduced relatives. In the reduced forms, the NNR$_n$ ligand lies in the "horizontal" plane. In the oxidized forms, they are perpendicular to this plane. As a matter of fact, all of the iso-electronic *cis* derivatives listed in Table 2 have their NNR planes lying in (or close to) the "vertical" plane.

To understand the reason for this ligand rotation upon oxidation, it should be remembered that one of the 6 combinations of the NNR$_n$ FMOs does not interact with the metal.[3] This occupied MO is a combination of π-type ligand FMOs,[3] as illustrated in Fig. 6, which shows the simplified DFT MO interaction diagram of the *cis*-[Mo(PH$_3$)$_4$(NNH$_2$)$_2$] model in the C_{2v} idealized symmetry of both considered rotational conformations. When the ligands are "horizontal", this level of b_1 symmetry is made up of π$_\sigma$ FMOs. When the ligands are "vertical", it is made of π$^*_{NN}$ FMOs, and consequently lies at higher energy, becoming, in this less stable rotational conformation, the HOMO of the reduced form and favoring its 2-electron oxidation. The b_1 π$^*_{NN}$ combination becomes the LUMO of the oxidized form and affords supple-

Table 5 Main DFT results for *cis*-[Mo(acac*)$_2$(NNH)$_2$]$^{0/2-}$ and *cis*-[Mo(acac*)$_2$(NNH$_2$)$_2$]$^{2+/0}$. acac* = [HC(=O)CHC(=O)H]$^-$

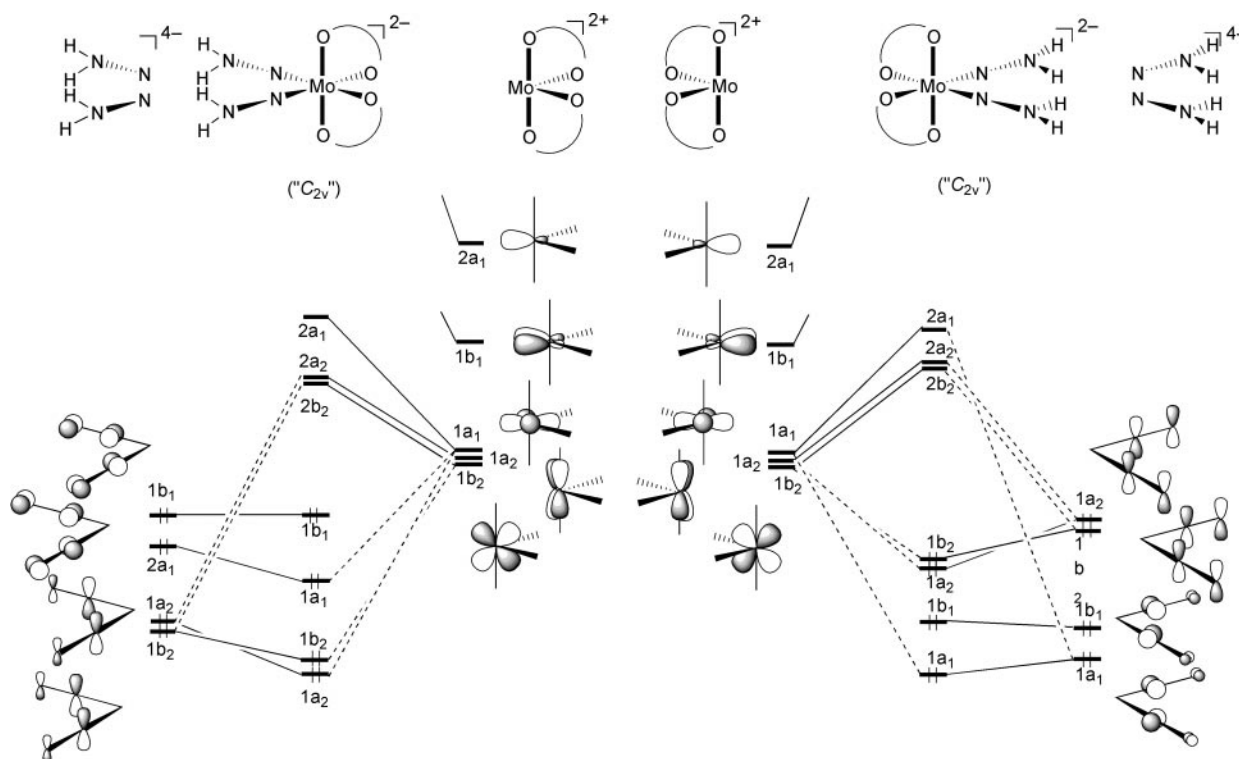|	*cis*-[Mo(acac*)$_2$(NNH)$_2$]^n		*cis*-[Mo(acac*)$_2$(NNH$_2$)$_2$]^n	
	$n = 0$ (C_2)	$n = -2$ (C_2)	$n = +2$ (C_2)	$n = 0$ (C_2)
HOMO–LUMO gap/eV	2.398	0.99	1.777	2.27
Mo–N$_\alpha$/Å	1.857	1.92	1.882	1.814
N$_\alpha$–N$_\beta$/Å	1.203	1.244	1.232	1.283
N$_\alpha$–H/Å	1.043	1.071	1.038	1.026
			1.038	1.025
Mo–N$_\alpha$–N$_\beta$/°	174.5	147.9	169.7	176.9
N$_\alpha$–N$_\beta$–H/°	114.1	109.2	121.5	119.6
			120.6	119.5
H–N$_\beta$–H/°			117.9	116.9
Mulliken atomic net charges				
Mo	1.77	1.58	2.25	1.89
N$_\alpha$	−0.22	−0.31	−0.28	−0.42
N$_\beta$	−0.16	−0.36	0.24	0.04
H	0.07	0.01	0.09	0.03
			0.07	
NNH and NNH$_2$ FMO occupancies				
π$^*_{NN}$	0.40	0.49	0.46	0.90
π$_\sigma$	1.03	1.28	1.52	1.60
π$_{NN}$	2.01	2.00	2.01	2.01
σ$_n$	1.79	1.84	1.81	1.76

Fig. 6 Qualitative interaction MO diagram of the model *cis*-[Mo(PH$_3$)$_4$(NNH$_2$)$_2$] in the two idealized C_{2v} rotational conformations. Only the metal-hydrazido π-type interactions are shown.

mentary destabilization through shortening of the N–N bond (Table 5). Therefore, as shown for the *trans*-[Mo(PH$_3$)$_4$(NNH$_2$)$_2$]$^{2+}$ model, the apparently 16-MVE *cis*-L$_4$Mo(NNR$_n$)$_2$ (n = 1, 2) complexes are in fact true 18-MVE species in which the ligands have to be considered formally as NNR^{2-} or NNR$_2^-$, still acting as a whole as a 10-electron ligand system. Contrary to the *trans* derivatives, both NNR and NNR$_2$ models are found to behave quite similarly in their oxidized and reduced states (see Table 5 and Fig. 5).

Conclusion

When linearly coordinated, both NNR^{3-} and NNR$_2^{2-}$ isolobal ligands (anionic charges are arbitrary) are potential 6-electron donors through their 3 occupied FMOs (one of σ type and two of π type). The non-equivalency of their π-type orbitals induces non-conical (non-axial) bonding abilities, NNR^{3-} being in principle closer than NNR$_2^{2-}$ to axial symmetry, although it can avoid this somewhat through some Mo–N$_\alpha$–N$_\beta$ bending. NNR^{3-} is also a weaker π-donor ligand. As far as oxidation states are meaningful, calculations on mono-substituted derivatives suggest that the formal oxidation state of a NNR ligand is −1 and that of NNR$_2$ is intermediate between 0 and −1.

Attributing arbitrarily the formal ligand charges −3 and −2 to the NNR and NNR$_2$ ligands, respectively, the d^0 metal configuration should arise in the case of *cis*-L$_4$Mo(NNR$_n$)$_2$ (n = 1, 2) species. Since in this case both *cis* ligands act as a whole as a 10-electron system, an 18-MVE species is expected for these d^0 complexes. Their 2-electron oxidation would lead to the d^{-2} configuration. Such a negative value is meaningless and indicates that the oxidation takes place at the ligands, which should be considered in this case as formally NNR^{2-} and NNR$_2^-$. A 90° rotation of the *cis* ligands accompanies this 2-electron oxidation.

A similar situation is found for the 2-electron oxidation of d^2 18-MVE *trans*-L$_4$Mo(NNR$_2$)$_2$ models, in which the NNR$_2$ formal charge varies from −2 to −1, whereas the hydrazide

system acts as an 8-electron donor in both the reduced and oxidized states. The *trans*-L$_4$Mo(NNR)$_2$ compounds behave somewhat differently since their oxidized form is better described as a d^0 NNR^{3-} 16-MVE system.

Computational details

DFT calculations were carried out using the Amsterdam Density Functional (ADF) program[100] developed by Baerends and coworkers[101] using the local density approximation (LDA) in the Vosko–Wilk–Nusair parametrization.[102] Test calculations at a higher level of non-local density (NLDA) approximation on [Mo(PH$_3$)$_4$(NNH)X]$^{0/2-}$ and [Mo(PH$_3$)$_4$(NNH$_2$)X]$^{+/-}$ (X = H, Cl) and on *trans*-[Mo(PH$_3$)$_4$(NNH$_2$)$_2$]$^{0/2+}$ lead to similar molecular structures and Mulliken charges, the major difference lying in the Mo–N distances, which were found to be 2 to 6% longer at the NLDA level. These results gave us confidence in carrying out the whole study at the less computer-time consuming LDA level.

The atom electronic configurations were described by a triple-ζ Slater-type orbital (STO) basis set for H 1s, C 2s and 2p, N 2s and 2p, O 2s and 2p and P 3s and 3p, augmented with a 3d single-ζ polarization STO for C, N, O and P, and with a 2p single-ζ polarization STO for H. A triple-ζ STO basis set was used for Mo 4d and 5s augmented with a single-ζ STO for Mo 5p. A frozen-core approximation was used to treat the core shells up to 1s for C, N and O, up to 2p for P and up to 4p for Mo.[101a] The geometries were fully optimized using the analytical gradient method implemented by Verluis and Ziegler.[103]

The auxiliary ligands of the calculated models were chosen in such a way that they could be representative of the largest number of compounds reported in the literature. For the mono-substituted derivatives, phosphine auxiliary ligands were used in addition to hydride and chloride (see Table 1). In the case of the *trans* di-substituted derivatives, phosphine ligands were used (see compounds **105**, **106** and **107** in Table 2). For the *cis* di-substituted derivatives, which generally bear

π-donor auxiliary ligands, the acetylacetonate (acac) ligand, modelled by $[HC(=O)CHC(=O)H]^-$ (acac*) was chosen (see for example compounds **132** and **133** in Table 2). It is interesting to note that the use of acac* auxiliary ligands for *trans* di-substituted models leads to small HOMO–LUMO gaps or to triplet ground states. This is due to the presence of four π-donor oxygen atoms lying in the same plane, which destabilize the highest occupied levels of the models. Therefore, it is likely that *trans* di-substituted complexes containing π-donor ligands are unstable. As a matter of fact, no complex of this type has been isolated so far (see Table 2).

Acknowledgements

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