Structure and bonding in late transition metal dinuclear complexes with local trigonal planar geometries

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A study of the structures preferred by the M_2X_2 rings in the dinuclear complexes of late transition metals of types $[M_2(\mu\text{-}XR_2)_2L_2]$ and $[M_2(\mu\text{-}XR_3)_2L_2]$ is presented, based on qualitative orbital arguments supported by DFT calculations on model compounds. The main conclusions agree well with the results of a structural database analysis. With the simplified electron counting scheme applied, complexes with six or four electrons available for bonding of the M_2X_2 framework are predicted to have two possible minimum energy structures, with either a short M–M or X–X distance, whereas compounds with eight framework electrons are expected to present no short through-ring distance. Such behavior is consistent with the framework electron counting rules reported earlier for compounds with different coordination spheres and provides a general description of the structure and bonding in a variety of compounds with M_2X_2 diamonds.

Introduction

A systematic study of electronic structure and through-ring bonding in M_2X_2 skeletons of dinuclear complexes with the general formula $[M_2(\mu\text{-}XR_y)_2L_{2z}]$ (where M is any transition metal, X is a main group element and L is any monodentate ligand) has been carried out by our research group in the last years.[1] So far we have focused on systems with $z = 4$ ($y = 2, 3$),[2] $z = 2$ ($y = 0$–3, with either square planar[3] or tetrahedral[4] geometry around the metal atoms), or $z = 3$ ($y = 0$).[5] In a broad sense, we can say that all the families studied may present three alternative structures: a regular *square* with no short through-ring distance (**1a**), or a compressed rhombus with either a short M–M (**1b**) or X–X distance (**1c**). There is a large variety of these complexes, given the choice of metal, bridge, bridge substituents, terminal ligand, metal coordination number and oxidation state. Nevertheless, all of them seem to follow the same electron counting rules derived from a delocalized bonding description that stems from semiempirical (extended Hückel) or density functional calculations. We have also verified that the electron counting scheme developed agrees well with the large number of available structural experimental data.

1a   **1b**   **1c**
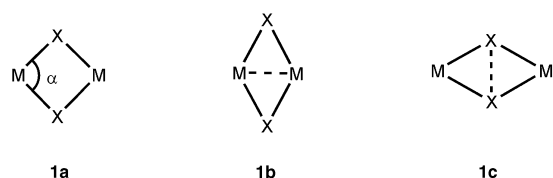
In a simplified delocalized molecular orbital (MO) description of the bonding in these M_2X_2 rings all σ bonds between the four framework atoms are associated with the four framework bonding MOs schematically depicted in **2a** (we assume that their four antibonding counterparts are empty and will be disregarded throughout this paper). Full occupation of these orbitals, identified by us as a *framework electron count* (FEC) of eight, accounts for the four skeletal bonds in **1a**. If two electrons are taken out from these orbitals (thus giving a FEC of 6), a short metal–metal distance across the ring **1b** may be favored,

as indicated by the orbital occupation in **2b**, where the MO with σ* metal–metal character is emptied. Alternatively, a short bridge–bridge distance **1c** can also be stabilized for FEC = 6, corresponding to the electron configuration **2c**. The reader can easily verify that in a system with two less electrons (FEC = 4), in which the b_{2g} orbital (with both metal–metal and bridge–bridge π* character) is emptied, the compressed rings **1b** and **1c** are expected to be further stabilised with respect to the regular ring **1a**.

2a   **2b**   **2c**
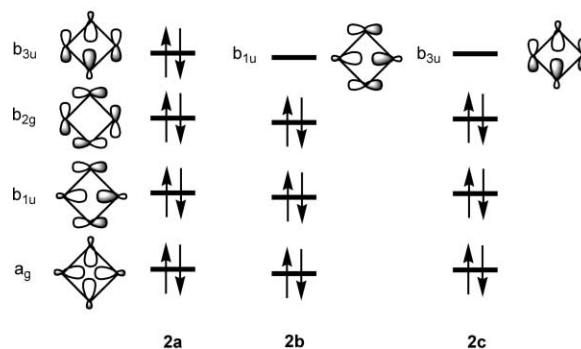
Although such electron counting rules are at first sight astonishingly simple, one needs first to learn how many of the valence electrons in the complex can be assigned to the M_2X_2 framework. The possible ambiguities arise because one needs to guess how many electrons occupy the non-bonding d orbitals of the metal atoms. Our theoretical studies combined with structural database analyses have shown that the metal d electrons can either be involved in framework bonding or remain localized at the metal atoms, depending on the molecular composition and geometry.[1] For example, we have shown that the equilibrium between oxo-bridged Cu(III) and peroxo-bridged Cu(II) species is associated with the conversion of delocalized framework bonding orbitals into localized d and σ*(O–O) orbitals, and how such electron drift is affected by the stereochemistry of the terminal ligands.[5,6] Interestingly, the opposite process seems to provide a good rationale for the oxygen evolving step in model complexes of Photosystem II.[7] Hence, for our

study of the bonding within the M_2X_2 rings we found it useful to consider the total *number of ring electrons* provided by the bridging ligands and the metal d electrons (abbreviated NRE). We therefore assume the terminal ligands to be two-electron donors and do not count such electrons as belonging to the ring. This way of counting electrons makes no *a priori* supposition on the bonding or electron distribution within the M_2X_2 framework. It is also independent of whether one chooses to count the bridging ligands as neutral or anionic (*e.g.*, four electron donor R_2P^-, or three electron donor R_2P) and therefore does not depend on the formal oxidation state assigned to the metal atom. Consider for example the compound [Cr$_2$-(μ-PMe$_2$)$_2$(CO)$_8$]. If we count the bridging ligands as phosphido anions, the oxidation state of the metal atoms is Cr(I), with a d^5 electron configuration. If we add the ten d electrons and the two lone pairs from each phosphido bridge, we end up with a NRE of 18. Counting the bridging ligands as neutral (thus three electrons available for bonding from each PMe$_2$ group), and the chromium atoms as zerovalent (d^6), the same NRE results.

The number of ring electrons (NRE), the number of d electrons per metal atom (n) and the framework electron count (FEC) in a compound with the general formula [M$_2$(μ-XR$_y$)$_2$-L$_{2z}$] must obey the following relationship:

$$NRE = 2n + FEC \qquad (1)$$

In some instances one might be interested in considering the total number of valence electrons (NVE) associated with the metal atoms to establish a connection with other electron counting schemes, notably the 18- and 16-electron rules or the Wade–Mingos rules for clusters. For a [M$_2$(μ-XR$_y$)$_2$L$_{2z}$] complex, we need to add the electron pairs donated by the terminal ligands to the number of ring electrons (NRE), and the following relationship between NVE and FEC results:

$$NVE = 4z + 2n + FEC \qquad (2)$$

In this paper we present a theoretical study of the bonding in the M_2X_2 rings that appear in compounds of the type [LM-(μ-XR$_2$)$_2$ML], in which the metal atoms present an approximate trigonal planar coordination sphere (**3**). In particular, we wish to (i) present a general MO diagram, (ii) search for possible trends in the bonding associated with the electron count, (iii) address the possible structural isomerism that may arise from the formation of X–X or M–M bonds across the ring, (iv) analyze the existence of π bonding in some of those complexes, and (v) provide a general description of the bonding that applies also to those complexes that cannot be accounted for by simple Lewis structures. We hope that the present work will provide a new useful piece of information in our quest for a general description of the bonding features in any ABCD ring in which A, B, C and D may be any ML$_z$ fragment or XR$_y$ group (M being any transition metal and X any main group element).

R$_2$
X
L—M - - - - M—L
X
R$_2$
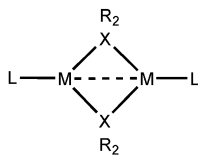
3

Results and discussion

Electron count and through-ring bonding in compounds with XR$_2$ bridges

Density functional calculations have been carried out for several model compounds of the [M$_2$(μ-XR$_2$)$_2$L$_2$] family with different electron counts, M being a late transition metal. In all cases studied the d orbitals are fully occupied, and the different electron counts affect only the occupation of the framework orbitals schematically depicted in **2**. Therefore, it seems reasonable to assume that for a late transition metal the framework electron count is directly related to the NRE

$$NRE = 20 + FEC \qquad (3)$$

The most relevant bonding parameters of the optimized structures are presented in Table 1. Since we wish to rationalize that the structures analyzed present different metal and bridging atoms, it is better to decide whether a through-ring M $\cdots$ M distance is short or long by comparing it with the atomic radii sum, $\Delta_{MM} = d(M–M) - 2r_M$. For phosphido-bridged complexes with 28 ring electrons, such as [Zn$_2$(μ-PH$_2$)$_2$-(PH$_2$)$_2$] and [Zn$_2$(μ-PH$_2$)$_2$(PH$_3$)$_2$]$^{2+}$ with approximately trigonal planar metal atoms, the 16-electron rule implies a d^{10} electron configuration, thus leaving 8 electrons for framework bonding (*i.e.*, FEC = 8). For these compounds, the optimized geometry of the Zn$_2$P$_2$ core corresponds to a regular square **1a**, with ring bond angles close to 90° and large positive Δ_{MM} values. Although minima were also found for structures of type **1c** with a short P–P distance (2.22 and 2.25 Å, respectively), these have a very high energy relative to **1a** and long Zn–P$_{bridge}$ distances.

A surprising result is that the isoelectronic complexes [Zn$_2$-(μ-NH$_2$)$_2$(NH$_2$)$_2$] and [Zn$_2$(μ-NH$_2$)$_2$(NH$_3$)$_2$]$^{2+}$ give minima with Zn–Zn distances close to the sum of the atomic radii, consistent with that experimentally found in [Zn$_2$(μ-NPh$_2$)$_2$(NPh$_2$)$_2$] (Δ_{MM} = −0.01 Å), even if those compounds have a FEC of eight. The N–Zn–N bond angles, though, are close to 90° as corresponds to a regular square with no through-ring interaction and as found also for the phosphido-bridged analogues. We conclude that the short Zn–Zn distance across the ring cannot be attributed in this case to a bonding interaction, but is imposed by the short Zn–N$_{bridge}$ distances. This conclusion is also supported by a careful analysis of the nature and occupation of the Zn centered molecular orbitals and by the quite small Zn–Zn overlap population (less than 0.01 electrons in a Mulliken population analysis).

Our theoretical results for [Pd$_2$(μ-PH$_2$)$_2$(PH$_3$)$_2$] indicate that reduction of the FEC to 6 favors a short metal–metal distance across the ring, as expected from the general rules outlined in the introductory section. The experimental Δ_{MM} values for some of the compounds considered in this paper can be compared to the theoretical values of the closest model compounds, as shown in Fig. 1. An excellent qualitative agreement is found
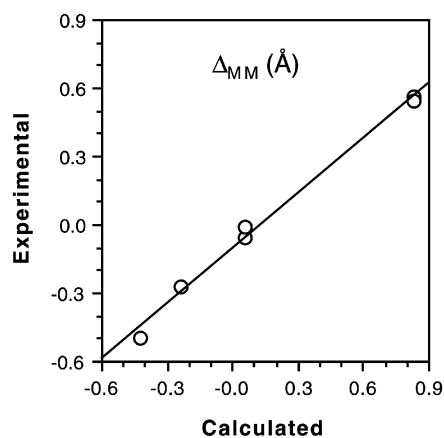
Fig. 1 Comparison of the difference between the metal–metal distance and the sum of the atomic radii sum (Δ_{MM}) in some model compounds and in the related experimental structures (Tables 1 and 2, compounds marked with an asterisk).

between the results of the model calculations and the experimental data. The dependence of the metal–metal distance on the NRE is clearly seen in Fig. 2: the compounds with NRE of 26 or less present metal–metal distances shorter than the atomic

Table 1 Theoretical (B3LYP) structural data [a] for $[M_2(\mu\text{-}XH_2)_2(EH_z)_2]$ complexes (M = Group 10 or 11 metal; E = N, P, Cl)

NRE[b]	Compound	Energy[c]/kcal mol⁻¹	M–M	Δ_{MM}	X–X	X–M–X
28*	$[Zn_2(\mu\text{-}NH_2)_2(NH_2)_2]$		2.896	0.06	2.840	88.9
28	$[Zn_2(\mu\text{-}NH_2)_2(NH_3)_2]^{2+}$		2.841	0.00	2.843	90.0
26	$[Zn_2(\mu\text{-}NH_2)_2(NH_3)_2]^{4+}$	0.0	∞		1.423	
		217.0	3.902	1.06	2.972	74.6
28*	$[Zn_2(\mu\text{-}PH_2)_2(PH_2)]$	0.0	3.670	0.83	3.437	86.2
		138.4	6.072	3.23	2.223	40.7
28*	$[Zn_2(\mu\text{-}PH_2)_2(PH_3)_2]^{2+}$	0.0	3.494	0.65	3.493	90.0
		98.6	5.600	2.71	2.254	43.8
28	$[Pd_2(\mu\text{-}PH_2)_2(PH_3)_2]^{2-}$		3.873	0.99	3.480	83.9
26*	$[Pd_2(\mu\text{-}PH_2)_2(PH_3)]$	0.0	2.599	−0.24	4.139	115.7
		36.4	4.087	1.20	3.022	73.0
24*	$[Ni_2(\mu\text{-}CH_2)_2Cl_2]^{2+}$	71.8	2.357	−0.42	3.202	107.3
		0.0	3.792	1.01	1.503	44.7
24	$[Ni_2(\mu\text{-}CMe_2)_2Cl_2]^{2+}$	26.3	2.296	−0.48	2.986	104.9
		0.0	3.727	0.95	1.486	43.5

[a] All distances in Å, angles in °. [b] Compounds marked with an asterisk are those compared with experimental data in Fig. 1. [c] Relative to the lowest energy geometry for each compound.

Table 2 Experimental structural data for late transition metal complexes of type $[M_2(\mu\text{-}XR_2)_2L_2]^{y-}$ (M = Group 10 or 11 metal)

NRE[c]	Compound	M–M	Δ_{MM}	X–X	X–M–X	Refcode	Ref.
28	$[Zn_2(\mu\text{-}NPh_2)_2Me_2]$	2.913	0.07	2.947	90.7	cadcep	8
28	$[Zn_2(\mu\text{-}NPhSiMe_3)_2(NPhSiMe_3)_2]$	2.870	0.03	2.934	91.3	kiqpij	9
28	$[Zn_2(\mu\text{-}NHR)(CH_2SiMe_3)_2]^{b}$	2.919	0.08	2.861	88.8		10
		2.932	0.09	2.845	88.3	robfuj	
28*	$[Zn_2(\mu\text{-}NPh_2)_2(NPh_2)_2]$	2.828	−0.01	2.921	91.9	nekseb	11
28*	$[Zn_2(\mu\text{-}N^iPr_2)_2(N^iPr_2)_2]$	2.782	−0.06	2.951	93.4	napmog	12
28	$[Cd_2(\mu\text{-}N\{SiMe_3\}_2)_2(\eta^1\text{-}Cp^*)_2]$	3.228	0.35	3.255	90.4	volsiy	13
28*	$[Zn_2(\mu\text{-}P\{SiMe_3\}_2)_2(^iPr)_2]$	3.379	0.54	3.434	90.9	yirbac	14
28	$[Zn_2(\mu\text{-}P\{SiMe_3\}_2)_2(CH_2SiMe_3)_2]$	3.391	0.55	3.438	90.8	yirbik	14
28*	$[Zn_2(\mu\text{-}P\{SiMe_3\}_2)_2(P\{SiMe_3\}_2)_2]$	3.402	0.56	3.444	90.7	jesheu10	15
28	$[Cd_2(\mu\text{-}P\{SiMe_3\}_2)_2(P\{SiMe_3\}_2)_2]$	3.710	0.83	3.627	88.7	jutjud	15
28	$[Zn_2(\mu\text{-}As^tBu_2)_2{}^tBu_2]$	3.622	0.78	3.467	87.5	pihpol	16
28*	$[Zn_2(\mu\text{-}As\{SiMe_3\}_2)_2(As\{SiMe_3\}_2)_2]$	3.509	0.67	3.543	90.6	zarxev	17
28*	$[Zn_2(\mu\text{-}CHPPh_3)_2(N\{SiMe_3\}_2)_2]$	2.782	−0.06	3.060	95.4	paxvep	18
26	$[Ni_2(\mu\text{-}PPh_2)_2(PPh_3)_2]$	2.604	−0.18			dptppt	19
26	$[Pt_2(\mu\text{-}SiMe_2)_2(PCy_3)_2H_2]$	2.708	−0.07	3.896	110.4	hmsppt	20
26	$[Ni_2(\mu\text{-}PR_2)_2(C_2H_4)_2]$	2.386	−0.39	3.566	112.4	chxpen	21
26	$[Ni_2(\mu\text{-}P^tBu_2)_2(PMe_3)_2]$	2.375	−0.40	3.640	113.7	bumseh	22
26	$[Ni_2(\mu\text{-}P\{SiMe_3\}_2)_2(PMe_3)_2]$	2.382	−0.40	3.667	114.0	bitfit	23
26*	$[Pd_2(\mu\text{-}P^tBu_2)_2(PMe_3)_2]$	2.571	−0.27	3.886	113.0	fuvmak	24
26	$[Pd_2(\mu\text{-}PCy_2)_2(PCy_2OPh)_2]$	2.620	−0.22	3.821	111.1	hempeu	25
26	$[Pd_2(\mu\text{-}P^tBu_2)_2(PH^tBu_2)H]^+$	2.611	−0.23	3.915	111.7	kostiv10	26
26	$[Pd_2(\mu\text{-}P^tBu_2)_2(PH^tBu_2)]$	2.594	−0.25	3.884	112.5	vontib	27
26	$[Pt_2(\mu\text{-}P^tBu_2)_2(PH^tBu_2)(CO)]$	2.613	−0.17	3.816	111.2	feqcej	28
26	$[Ni_2(\mu\text{-}As^tBu_2)_2(PMe_3)_2]$	2.429	−0.35	3.823	115.1	doxfol	29
24	$[Zn_2(\mu\text{-}Ph_2)_2Ph_2]$	2.685	−0.16	3.425	101.4	tagfow	30
24	$[Ni_2(\mu\text{-}N\{PPh_2\}_2)_2(NPh_2)_2]$	2.327	−0.45	3.033	105.0	dagkur	31
24*	$[Ni_2(\mu\text{-}C\{SiMe_3\}PMe_3)_2Cl_2]$	2.281	−0.50	3.053	106.5	vetlel	32

[a] All distances in Å, angles in °. [b] Disordered structure. [c] Compounds marked with an asterisk are those compared with theoretical data in Fig. 1.
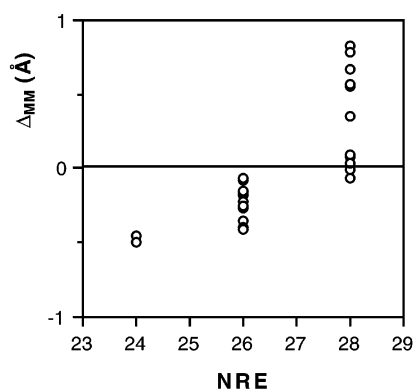
Fig. 2 Difference between the metal–metal distance and the atomic radii sum (Δ_{MM}) in the experimental structures of late transition metals (Table 2) classified according to their number of ring electrons (NRE).

radii sum.† Among compounds with NRE of 28 we can distinguish two cases: (a) those with Zn_2N_2 or Zn_2C_2 cores and (b) those with Cd_2N_2 or M_2X_2 (M = Zn, Cd; X = P, As) cores. In the former case, the Zn–Zn distance is approximately equal to the atomic radii sum, but the N–Zn–N bond angles are close to 90°, indicating that the short Zn–Zn distance is imposed by the short Zn–N bonds, as found in our calculations and discussed above. In the second case, Δ_{MM} is clearly positive (larger than 0.35 Å), as predicted by our calculations and by the framework electron counting rules.

A case that is worth discussing is that of the model compound with 24 ring electrons (*i.e.*, FEC = 4) bearing carbido

† *Note added at proof*: The recently reported structure of $[Pd_2$-$(\mu\text{-}SiN_2C_2H_2tBu_2)_2(PPh_3)_2]$ (A. Fürstner, H. Krause and C. W. Lehman, *Chem. Commun.*, 2001, 2372) presents a short Pd–Pd distance of 2.650 Å, consistent with an NRE of 24.

Table 3 Theoretical (B3LYP) structural data[a] for $[Zn_2(\mu\text{-}XH_2)_2(EH_2)_2]$ complexes (X = N, P) and experimental structural data for related $[Zn_2(\mu\text{-}XR_2)_2(ER_2)_2]$ complexes[b] with 28 ring electrons

| Compd.	Geometry	Energy[c]	M–M	Δ_{MM}	M–E	Σ_E[d]
$[Zn_2(\mu\text{-}NH_2)_2(NH_2)_2]$	coplanar (**4**)	0.0	2.896	0.06	1.839	360
	pyramidal (**5**)	8.5	2.901	0.11	1.872	333
	rotated (**6**)	14.1	2.932	0.41	1.885	334
$[Zn_2(\mu\text{-}NPh_2)_2(NPh_2)_2]$	coplanar (**4**)		2.828	−0.01	1.859	360
$[Zn_2(\mu\text{-}N^iPR_2)_2(N^iPR_2)_2]$	coplanar (**4**)		2.782	−0.06	1.844	360
$[Zn_2(\mu\text{-}NPhSiMe_3)_2(NPhSiMe_3)_2]$	rotated (**6**)		2.870	0.03	1.902	360
$[Zn_2(\mu\text{-}CHPPh_3)_2(N\{SiMe_3\}_2)_2]$	rotated (**6**)		2.782	−0.06	1.930	360
$[Zn_2(\mu\text{-}Ph_2)_2(Ph_2)_2]$	coplanar (**4**)	16.0	3.557	0.83	2.246	360
	pyramidal (**5**)	0.0	3.652	0.88	2.318	330
	rotated (**6**)	4.8	3.694	1.30	2.343	328
$[Zn_2(\mu\text{-}P\{SiMe_3\}_2)_2(P\{SiMe_3\}_2)_2]$	pyramidal (**5**)		3.402	0.56	2.294	317

[a] All distances in Å, angles in °. [b] See Table 2 for references to experimental data. [c] In kcal mol^{-1}. [d] Σ_E is the sum of the bond angles around atom E.

bridges, $[Ni_2(\mu\text{-}CH_2)_2Cl_2]^{2-}$. Calculations (Table 1) predict it to be more stable with a short C–C distance (**1c**). Should we trust this prediction? The related experimental structure, that of $[Ni_2(\mu\text{-}C\{SiMe_3\}PMe_3)_2Cl_2]$ presents a short Ni–Ni distance ($\Delta_{MM} = -0.50$ Å), in agreement with the electron counting rule, but in contradiction to the calculations that predict a short C–C distance instead. We believe that such a discrepancy is due to the steric hindrance produced by the methyl groups in the experimental compound that prevent the two carbon atoms from getting close enough. If the calculations are repeated with CMe_2 bridges, the energy difference between the C–C and the Ni–Ni bonded isomers decreases from 72 to 26 kcal mol^{-1}, and a further increase of the bulkiness in the $C\{SiMe_3\}PMe_3$ bridges should be enough to invert the relative energies of the two structures. In fact, when the experimental structure is modified to bring the two carbon atoms to the calculated distance, there are four H ··· H contacts of 2.06 Å, indicative of the high steric repulsion that destabilizes such a structure.

Complexes with amido or phosphido terminal ligands

Among the family of compounds studied here, a particular group is formed by complexes having NR_2 or PR_2 terminal ligands. The former present planar NR_2 groups that may be oriented parallel or perpendicular to the M_2X_2 framework, whereas in the latter the phosphorus atom is strongly pyramidalized (as indicated by bond angle sums Σ_P much smaller than 360°, see Table 2). We have therefore theoretically explored the possible existence of π-bonding between the metal and terminal ligand. To that end we have optimized the structures of $[Zn_2(\mu\text{-}XH_2)_2(EH_2)_2]$ by freezing the terminal ligands in three different orientations (**4**–**6**). The relative energies of the three conformations (Table 3) are clearly different for the amido than for the phosphido ligands. In the former case, the most stable conformation is the coplanar one (**4**), while pyramidalization (**5**) and rotation (**6**) of the amido groups progressively destabilize the molecule. For the phosphido ligands, in contrast, the coplanar conformation is the most unstable one and pyramidalization stabilizes the molecule. These results are in agreement with the conformations found in the experimental structures (Table 3): two amido complexes appear in the coplanar conformation, while two other amido complexes with $SiMe_2$ substituents are rotated probably due to steric congestion. What is interesting is that the coplanar complexes present Zn–N distances to the terminal ligand significantly shorter than the rotated ones. Also the experimentally characterized phosphido complex appears in a pyramidal conformation, as predicted by calculations.

The existence of Zn=E double bond character for the case of unsaturated terminal ligands in the coplanar conformation is confirmed by the analysis of the Kohn–Sham orbitals, for which the π-type orbitals schematically depicted in **7** are found.
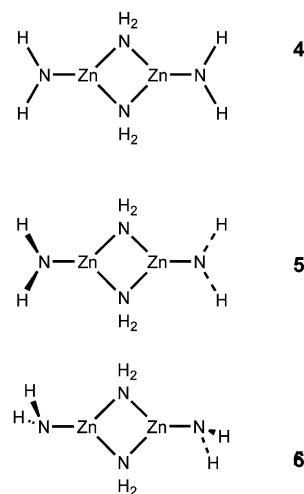
Those orbitals reflect the π donation from the terminal ligand π-type lone pairs to the empty Zn p_z orbitals, as verified by the existence of net electron populations of 0.12 and 0.16 (for E = N and P, respectively) in the latter atomic orbital. This orbital explanation is consistent with the effect of rotation and pyramidalization on the Zn–E bond distances, which are shorter in the coplanar conformation and increase upon bending and rotation (Table 3). Comparison with the analogous complexes having saturated terminal ligands, $[Zn_2(\mu\text{-}XH_2)_2(EH_3)_2]^{2+}$, shows shorter distances (by more than 0.1 Å) to the unsaturated ligands. Although an analysis of the molecular orbitals has not allowed us to detect the existence of formal Zn–Zn bonding in these compounds with FEC = 8, small variations in the calculated Zn–Zn distance with the orientation of the terminal ligands suggests that the π bonding is somewhat delocalized through the Zn_2X_2 ring.
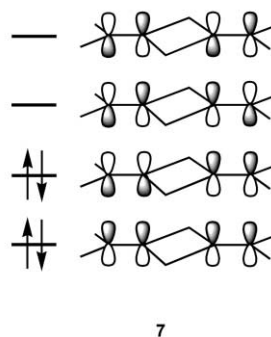
Compounds with two-electron donor bridges

The electronic structure of analogous systems with two-electron donor bridging ligands such as methyl, phenyl, hydride or acetylide differs from that discussed above in a significative

Table 4 Experimental structural data and number of ring electrons (NRE) for transition metal complexes of type $[M_2(\mu\text{-}X)_2L_2]$, where X is a two-electron donor[a]

Compound	Refcode	NRE	M $\cdots$ M	Δ_{MM}	Ref.
$[Ph_2Zn_2(\mu\text{-}Ph)_2]$	tagfow	24	2.685	−0.16	30
$[(\eta^2\text{-}C_2R_2)_2Cu_2(\mu\text{-}C{\equiv}CR)_2]$	lexdoh	24	2.385	−0.38	33
$[Mes_2Co_2(\mu\text{-}Mes)_2]$	karcub	18	2.519	−0.25	34
			2.511	−0.26	
$[(^iPr_3C_6H_2)_2Fe_2(\mu\text{-}^iPr_3C_6H_2)_2]$	pomzia	16	2.666	−0.36	35
$[Mes_2Fe_2(\mu\text{-}Mes)_2]$	laftuh	16	2.617	−0.41	36
			2.610	−0.42	
$[(^tBu_2MeC_6H_2\text{–}O)_2Fe_2(\mu\text{-}Mes)_2]$	tugsix	16	2.567	−0.46	37
$[(^tBu_2MeC_6H_2\text{–}O)MesFe_2(\mu\text{-}Mes)_2]$	tugsod	16	2.589	−0.44	37

[a] All distances in Å.

aspect.[3] In essence, the b_{2g} and b_{1u} framework orbitals (**2**) do not have the bridging ligand contribution and are therefore high energy empty orbitals centered at the metal atoms. The outcome is that the framework orbitals with metal–metal σ and π character (a_g and b_{3u}) are occupied for any NRE of four or higher, whereas their σ* and π* counterparts (b_{2g} and b_{1u}) are empty and short metal–metal distances should be expected, consistent with a FEC of four.

Structural data for dinuclear compounds with two bridging ligands of this type and one terminal ligand at each metal atom are collected in Table 4. It can be seen that in all cases the through-ring metal–metal distance is clearly shorter than the sum of the atomic radii and the MXM angles are smaller than 77°, in good agreement with their classification as rings with a FEC of four.

A special case is that of the compounds of formula [RM-(μ-SiHPh₂)₂MR] with M = Pt and R = cyclohexyl,[20] or M = Pd and R = Et,[38] that present structures of type **8b**, with agostic interactions between the silyl bridges and the metal atoms. We can describe such a structure as intermediate between that of a dimer of ML groups with two silyl-bridges and no agostic interaction (**8a**) and that of a dimer of MHL fragments with two silylene bridges (**8c**), in which a square planar coordination of the metal atoms is completed by a terminal hydride. The former (**8a**) corresponds to the case of two-electron donor bridges with FEC = 4 just discussed, for which a short through-ring metal–metal distance should be expected. In the latter case (**8c**) the total number of ring electrons (NRE = 22) in a system with disubstituted bridges and two square planar metal fragments corresponds[3] to FEC = 6 (eqn. (1)) and also a short metal–metal distance is to be expected. Of course, these two descriptions differ in the details of the electronic structure and bonding, but both agree with the expectation of a short metal–metal distance.

8a   **8b**   **8c**
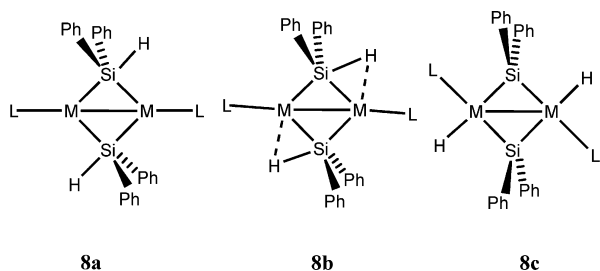
Complexes with XR bridges

Although we have not performed calculations for complexes with monosubstituted bridges, [LM(μ-XR)₂ML], one should expect these to behave in a similar way as the disubstituted bridges discussed above. We need only assume that the bridging atom X obeys the octet rule and both the substituent and one lone pair are pointing away from the center of the M_2X_2 ring, whereas the remaining two lone pairs are devoted to framework bonding (**9**). For these compounds, the same relationship

between NRE and FEC established above (eqn. (3)) holds. Hence, we find that all complexes with NRE = 28 (i.e., FEC = 8) have metal–metal distances at least 0.10 Å longer than the sum of the atomic radii[39–58] with the exception of two Zn compounds[9,59] with N or O bridging atoms, that have $\Delta_{MM} \approx 0$. The X–M–X bond angles of around 90° or less in these two compounds indicate that their short M–M distances are geometrically imposed by the short metal-bridge distances. All compounds with fewer ring electrons and a clearly established low or intermediate spin configuration[60–63] have $\Delta_{MM} \leqslant 0.10$ Å. Finally, there are several compounds with NRE smaller than 26, but for which the magnetic behavior has not been very well studied and their electron configurations are therefore not well established. In one case[64] the bulky *t*Bu substituents at the bridging atoms and at the terminal ligands probably prevent the two metal atoms from getting in close contact. The magnetic behavior and the low temperature structure of other compounds[60,65–69] have not been investigated, and these are worthwhile to study both experimentally and theoretically.


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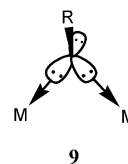
Open shell complexes

Analogous systems with XR₂ bridges and electron counts of less than 24 have not been studied in this work, but several such compounds have been well characterized in the past (16 ≤ NRE ≤ 22, Table 5). As happens for similar complexes with hexacoordinated metal atoms and less than six d electrons per metal,[2] in the presently studied compounds all electrons short of NRE = 24 do not affect the occupation of the framework orbitals, but mostly the non-bonding d orbitals (or metal–terminal ligand π-antibonding orbitals) that may result in paramagnetism but retain (or even shorten) the short metal–metal distance across the M_2X_2 ring, as shown in Fig. 3, where only three exceptions are observed that will be discussed below. Therefore, one can formally assign a framework electron count of 6 to all $[M_2(\mu\text{-}XR_2)_2L_2]$ systems with 24 or less ring electrons, and therefore short metal–metal distances should be expected. This has been verified for the Hoppe anion $[Co_2O_4]^{4-}$ with NRE = 22 in a theoretical study that clearly showed the existence of two double bonds between the Co atoms and the two terminal oxo groups, while retaining four framework electrons and a short Co–Co distance.[70]

The exceptions to this rule are three phosphido- or arsenido-bridged Mn complexes that show large positive values of Δ_{MM} (Fig. 3), and correspondingly X–M–X bond angles close to 90°. This behavior is undoubtedly associated with the high spin configuration presented by those complexes that must result in the partial occupation of the orbital bearing σ*(MM) character, analogous to b_{1u} (**2b**) in the homonuclear complexes

Table 5 Number of ring electrons (NRE), and experimental structural and magnetic data for $[M_2(\mu\text{-}XR_2)_2L_2]^{y-}$ complexes (M = Group 3 to 9 metal) with less than 24 ring electrons[a]

NRE	Compound	M–M	Δ_{MM}	X–M–X	μ_{eff}[b]$/\mu_B$	Refcode	Ref.
22	$[Co_2(N(SiMe_3)_2)_4]$	2.583	−0.19	102.4	4.83	cuwnaj	71
22	$[Co_2(NPh_2)_4]$	2.565	−0.20	100.1	4.83	daglay	31
20	$[Fe(tBuNSi(Me)_2OSi(Me)_2N^tBu)_4]$	2.700	−0.33	99.1	–	sufxum	72
20	$[Fe_2(N(SiMe_3)_2)_4]$	2.663	−0.37	100.6	–	jirwuc	73
20	$[Fe_2(NPh_2)_4]$	2.715	−0.31	96.4	–	jirxaj	73
20	$[Fe(\mu\text{-}PMes_2)(N(SiMe_3)_2)_2]$	2.882	−0.15	103.9	4.9	kivvug	74
		2.906	−0.12	102.7	4.9		
18	$[Mn_2(\mu\text{-}P^tBu_2)_4(CH_2^tBu)_2]$	3.292	0.15	97.7	3.1	kacpot	62
18	$[Mn(\mu\text{-}PMes_2)(N(SiMe_3)_2)_2]$	3.364	0.23	94.5	5.9	kivvoa	74
18	$[Mn(\mu\text{-}AsMes_2)(N(SiMe_3)_2)_2]$	3.677	0.54	88.7	6.7	kivwan	74
18	$[Mn_2(N^iPR_2)_4]$	2.843	−0.30	96.7	2.6	koclod	75
18	$[Mn_2(N(SiMe_3)_2)_4]$	2.811	−0.33	99.4	3.34	msiamn01	71
18	$[Mn(^tBuNSi(Me)_2OSi(Me)_2N^tBu)_4]$	2.857	−0.28	97.4	–	sufyat	72
18	$[Fe(azasilaborolyl)_4]$	2.688	0.01	97.6	–	focgej	76
16	$[Cr_2(N^iPr_2)_4]$	2.866	0.03	92.4	2.3	vahnun	77
16	$[Cr_2(NCy_2)_4]$	2.838	0.00	93.2	2.6	wafbag	78
16	$[Cr(AdNXyl)_4]$	2.854	0.02	88.6	2.5	gabqab	79

[a] Distances in Å, angles in °. [b] Per metal atom, in μ_B.
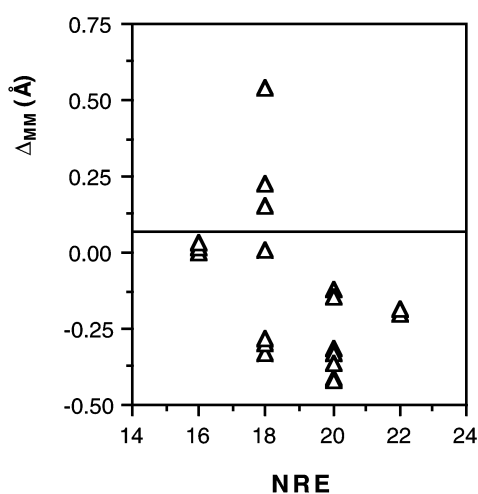
Fig. 3 Difference between the metal–metal distance and the atomic radii sum (Δ_{MM}) in the experimental structures of transition metals with a number of ring electrons (NRE) of less than 24 (Table 4).
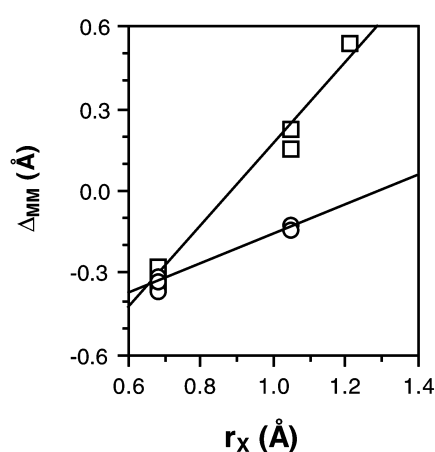

Fig. 4 Difference between the metal–metal distance and the atomic radii sum (Δ_{MM}) in the experimental structures of transition metals with a number of ring electrons (NRE) of 18 (□) and 20 (○) as a function of the atomic radius of the bridging atom r_X.

studied here. As found above for the Zn complexes, the short Mn–Mn distance in the nitrido-bridged complexes may be geometrically imposed by the short Mn–N bond distances, as seen in Fig. 4, where a clear correlation is found between the Mn–Mn distances and the atomic radii of the bridging atoms. In contrast, for other electron counts a short M–M distance is found even with large bridging atoms (Fig. 4). It is worth noting also that the short Mn–Mn distance in nitrido-bridged complexes favors intermediate- or low-spin configurations that leave the b_{1u}-type orbital empty and allow us to describe such short Mn–Mn distances as bonding. Hence, the short Mn–Mn distance should be attributed to a synergetic combination of steric and electronic effects.

It has been noted by Poli[80] that the exchange energy which favors the high spin configuration reaches a maximum for a d^5 electron configuration, thus explaining the tendency of Mn(II) complexes, including manganocene, to adopt a high spin configuration. This explanation should also apply to the Mn(II) and Fe(III) complexes studied here. Since the FEC rules are based on the assumption of spin-paired electron configurations, one should be cautious not to apply them to high spin complexes, particularly those of d^5 ions of the first transition series.

Extension to complexes with two different coordination spheres

A powerful feature of the framework electron counting scheme is that it can be applied to a wide variety of four-membered

rings, since only the electrons actually involved in framework bonding are considered. Hence, the electron counting scheme devised so far for symmetric systems with two identical ML_z fragments and two XR_y bridges can be extended to complexes constituted by two different metal fragments, ML_z and $M'L_w$. To illustrate this principle, we show in Table 6 the number of ring electrons (NRE) that corresponds to eight framework electrons for several combinations of ML_z and $M'L_w$ fragments with XR_2 bridges. These are the cases for which the bridging ligands act as two-electron donors toward each metal atom and the number of valence electrons corresponds to the two metal atoms complying with the 18-electron (for ML_4X_2 fragments) or the 16-electron rule (for square planar ML_2X_2 or trigonal planar MLX_2 fragments), or with one ML_4X_2 group obeying the 18-electron rule and one square planar ML_2X_2 group obeying the 16-electron rule. From Table 6 it can be seen that valence electron counts from 32 to 36 give rise to the same number of framework electrons, depending on the number and arrangement of ligands around the two metal atoms, stressing how the FEC rules allow us to apply a uniform criterion to complexes with different numbers of valence electrons.

Several examples of heterodinuclear complexes $[LM(\mu\text{-}XR_2)_2\text{-}M'L_w]$ (w = 2 or 4) closely related to the homodinuclear complexes theoretically studied here have been structurally characterized and are shown in Table 7, together with structural data and the corresponding FEC. For complexes of type $[LM(\mu\text{-}XR_2)_2M'L_2]$ with M' in a tetrahedral environment

Table 6 Number of ring electrons (NRE) that correspond to a framework electron count of 8 for different combinations of ML_z groups with XR_2 bridging ligands (coordination sphere of the ML_zX_2 core given in parenthesis). Numbers of metal valence electrons given in square brackets for each case

	ML_4 (oct.)	ML_2 (sq. planar)	ML_2 (tetrahedral)	ML (trigonal)[a]
ML_4 (octahedral)	20 [36]	22 [34]	24 [36]	**24** [34]
ML_2 (square planar)		24 [32]	26 [34]	**26** [32]
ML_2 (tetrahedral)			28 [36]	**28** [34]
ML (trigonal)				28 [32]

[a] In boldface cases for which structural data are given in Table 7.

Table 7 Experimental structures of hetero-coordinated $[LM(\mu-XR_2)_2M'L_2]$ and $[LM(\mu-XR_2)_2M'L_4]$ dinuclear complexes

| NRE	Compound	M–M/Å	Δ_{MM}	X–M–X/°	X–M'–X/°	τ^{a}/°	μ_{eff}^{b}	Refcode	Ref.
$[LM(\mu-XR_2)_2M'L_2]$									
26	$[(OC)Ni(\mu-P^tBu_2)_2Ni(CO)_2]$	2.413	−0.37	116.4	110.5	89.3	0[c]	cafgar	81
26	$[(Me_3P)Ni(\mu-P^tBu_2)_2Ni(CO)_2]$	2.446	−0.33	116.3	108.8	88.9	0[c]	gepliw	81
26	$[(Ph_3P)Ni(\mu-P^tBu^tBu^tBu_2)_2Ni]$	2.490	−0.29	110.7	109.8	55.6	0[c]	topxur	82
24	$[(Ph_3P)Pd(\mu-PPh_2)_2Pt(C_6F_5)_2]$	2.658	−0.15	112.8	105.1	0.5	0[c]	yexxuu	83
23	$[(Me_3P)Co(\mu-P^tBu_2)_2Co(PMe_3)Cl]$	2.507	−0.26	117.4	106.7	89.6	0.85	bumsad	22
18	$[(\{Me_3Si\}_2P)Mn(\mu-P\{SiMe_3\}_2)_2$-$Mn(thf)(P\{SiMe_3\}_2)]$	3.397	0.26	96.8	94.1	82.6	3.33	jutkoy	15
$[LM(\mu-XR_2)_2M'L_4]$									
22	$[(Ph_3P)Pd(\mu-PCy_2)_2Mo(CO)_4]$	2.760	−0.25	118.7	101.2		0[c]	ducpas	84
22	$[(\eta^2-C_2R_2)Pt(\mu-PPh_2)_2W(CO)_4]$	2.794	−0.22	112.5	102.3		0[c]	cocsoc	85
22	$[(Ph_3P)Pt(\mu-PPh_2)_2W(CO)_4]$	2.765	−0.25	117.8	100.8		0[c]	cocsiw	85
22	$[(^iPr_3P)Rh(\mu-PPh_2)_2Rh(acac)_2]$	2.632	−0.24	103.7	92.6		0[c]	goyhad	86
22	$[(Et_3P)Pt(\mu-PPh_2)_2Mo(CO)_4]$	2.766	−0.26	117.7	100.6		0[c]	kawbuf	87
22	$[(Ph_3P)Pd(\mu-PPh_2)_2Mo(CO)_4]$	2.748	−0.31	117.6	101.8		0[c]	vothan	88

[a] τ is the angle between the $M'X_2$ and the $M'L_2$ planes. [b] Per metal atom, in μ_B. [c] No magnetism reported, diamagnetism assumed from NMR spectra.

(indicated by values of τ, the torsion angle between the MX_2 and $M'L_2$ planes, close to 90°), an electron count of NRE = 28 (see Table 6) corresponds to eight framework electrons. Therefore, all compounds of this family shown in Table 7 have six or less framework electrons and we would predict negative or small positive values of Δ_{MM} as found in all cases with just one exception. The exception corresponds to a Mn(II) compound which shows a magnetic moment of 3.33 μ_B per metal atom at room temperature. We suspect that in such a case there is an admixture of spin states at room temperature and the long Mn–Mn distance is an average of a short distance corresponding to the low spin state (for which the σ^*_{MM} framework orbital would be empty) and a long distance corresponding to the high spin state with the same orbital partially occupied. A re-examination of the magnetic properties and of the structure of such a compound at low temperature would therefore be very helpful for a better understanding of the chemical bonding in diamonds of open shell metal atoms. If the tetracoordinated metal atom is in a square planar environment ($\tau \approx 0°$), a NRE of 26 corresponds to eight framework electrons, and thus the FEC of the only such compound characterized, $[(Ph_3P)Pd(\mu-PPh_2)_2Pt(C_6F_5)_2]$ with NRE = 24, is six, in excellent agreement with the short metal–metal distance found.

All structurally characterized compounds of type $[LM-(\mu-XR_2)_2M'L_4]$ (Table 6) have NRE = 22, which corresponds to FEC = 6 (Table 6), and present short through-ring metal–metal distances, as indicated by the negative values of Δ_{MM}.

Let us stress that these complexes provide specific examples in which the FEC rules are of practical use because there is no need to decide on the particular oxidation state of each metal atom. Consider, for instance, the compound sketched in **10**.[83] There is no unique choice of oxidation states for the Pd and Pt atoms. One could choose to consider the phosphido and pentafluorophenyl ligands as monoanionic, whereupon one could assign (a) oxidation state +2 to both Pd and Pt, (b) oxidation states +1 to Pd and +3 to Pt, or (c) oxidation state 0 to Pd and +4 to Pt. Alternatively, we could consider the phosphido

bridges as neutral three-electron donors and the pentafluorophenyl ligands as one electron donors, resulting in (d) zerovalent Pd and Pt atoms. The reader can verify that the NRE is 24 in all cases (a–d) regardless of the electron counting scheme applied.

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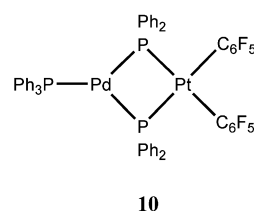
Conclusions and outlook

Density functional calculations and experimental data consistently show that dinuclear complexes with trigonal coordination around the metal atoms obey the framework electron counting rules previously deduced for M_2X_2 rings with different numbers of terminal ligands: molecules with eight framework electrons present regular undistorted rings, whereas those with six or less framework electrons present distorted rings with short M–M distances. The number of ring electrons (NRE) is counted as the total occupation of the metal d orbitals plus the electrons donated by the bridging ligands to the metals. Given the d^{10} electron configuration favored for trigonal coordination of a late transition metal, the number of ring electrons and that of framework electrons are related by NRE = 20 + FEC.

Complexes with 28 ring electrons and terminal amido ligands show unequivocal Zn=N double bond character, as evidenced by the molecular orbital description, and consistent with the experimental bond distances.

These rules can probably be extended to complexes with fewer ring electrons, assuming that the framework orbital with $\sigma^*(MM)$ character is empty for an NRE of 26 or less, and accepting a formal FEC of six that would predict a short

through-ring metal–metal distance. The Mn(II) compounds with a high spin configuration are an exception and the FEC rules can therefore not be applied to them. Further experimental and theoretical investigation of the electronic structure and bonding in these open shell systems is highly desirable.

With the present contribution we have increased the number of systems with M_2X_2 rings that have been evaluated with regard to the framework electron counting rules both by calculations and by structural database analyses. The results obtained so far can be summarized in Chart 1, which indicates

Chart 1

the presence of through-ring bonding in complexes with six or four framework electrons having different coordination spheres. It is seen that one can reduce the number of framework electrons (and therefore favor a short M–M distance) in different ways: (a) by oxidation or reduction by two to four electrons while keeping the molecular topology unchanged (as in **11**), represented in Chart 1 by diagonal displacements which modify both the NRE and the FEC but not the number of d electrons; (b) by switching the coordination environment of one metal atom from square planar to tetrahedral, or from octahedral to square planar without changing the NRE (as in **12**), corresponding to horizontal displacements in Chart 1 that convert framework electrons into d electrons or *vice versa*; (c) by association or dissociation of a ligand the NRE is not modified, but both the FEC and the number of d electrons are affected (as in **13**), corresponding to a different kind of horizontal displacement in Chart 1.

Appendix

The search for experimental structural data was carried out with the help of the Cambridge Structural Database.[89] Searches were performed for all transition metal with XR_2 bridges, X being any Group 14, 15 or 16 element. The terminal
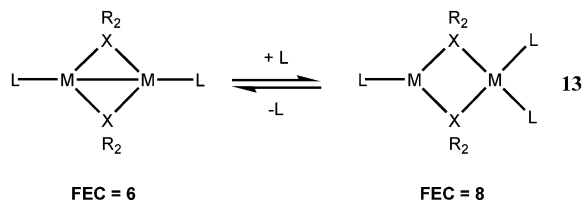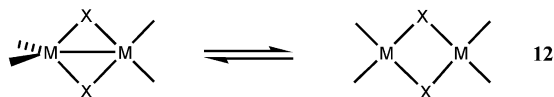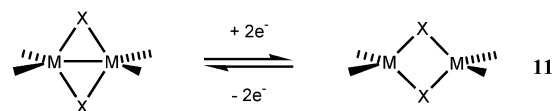
ligands were allowed to be any group linked to the transition metal through a donor atom of Groups 14–17. The atomic radii used for transition metal atoms to calculate Δ_{MM} were obtained in a systematic way and have been reported previously.[2]

Density functional calculations were carried out using the GAUSSIAN94 package.[90] We applied the hybrid B3LYP-DFT method, in which the Becke three parameters exchange functional[91] and the Lee–Yang–Parr correlation functional[92] were used. The double-ζ basis set for the valence and outermost core orbitals combined with pseudopotentials known as LANL2DZ were used for all the atoms.[93,94] The geometries were fully optimized using gradient techniques.

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