Through-ring bonding in edge-sharing dimers of square planar complexes

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Abstract

A qualitative molecular orbital study on the title compounds has allowed us to establish the factors which determine the possibility of through-ring bonding. Orbital interaction diagrams and the resulting relationship between framework electron count (FEC) and through-ring bonding are analyzed for XR_2 bridging groups, as well as for XR_3 and other isolobal bridges. The influence of the electronegativity of the bridging atom X, and of the bulk of the terminal ligands has also been studied. The predictions made from the qualitative bonding model developed are consistent with existing structural data.

Key words: Extended Hückel calculations; Molecular orbital calculations; Platinum; Bridging ligand; Rhodium; Square planar

1. Introduction

In a recent study of through-ring metal–metal interactions in binuclear complexes of d^{10} metal ions with a tetrahedral coordination sphere (1), we found [1] that metal–metal bonding across the M_2X_2 ring can be accounted for by a simple electron-counting rule deduced from a molecular orbital analysis of such systems. In essence, to a first approximation the orbital topological explanation considers only the orbitals in the plane of the ring. In the general case, each fragment occupying a corner of the diamond, be it an ML_n or an XR_m group (where X is a Main Group element) has two orbitals in the plane of the molecule capable of interacting with those in the other corners, and therefore contributing to the bonding of the M_2X_2 framework. The lobes of the correct topology are either symmetric (S) or antisymmetric (A), schematically represented in 2, and they may be sp hybrids, p orbitals or d orbitals. Therefore, the four corners of the diamond can form eight framework molecular orbitals (FO), four of which are M–X bonding and four antibonding. Consequently, when eight electrons occupy the four

framework bonding orbitals, the net bond order is four for the M–X bonds, zero for the M $\cdots$ M and X $\cdots$ X interactions, and a regular geometry would be expected for the ring. However, when only six or four electrons are available, the FO's with M $\cdots$ M (or X $\cdots$ X) antibonding character are empty, and a short through-ring M $\cdots$ M (or X $\cdots$ X) distance might be expected. We have coined the expression Framework Electron Count (FEC) for the number of electrons occupying the FO's, and have shown that the structures of a large number of diamonds of type 1 behave as predicted by this simple electron-counting rule [1].

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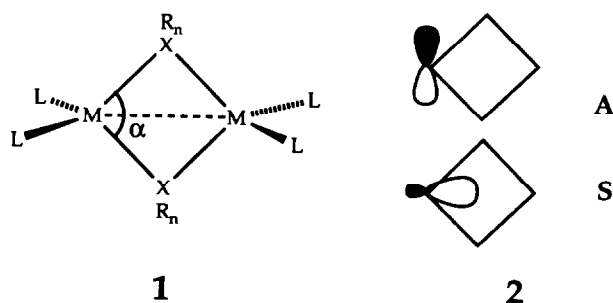
Closely related to the diamonds of type 1 are the edge-sharing dimers of square-planar complexes, **3**, where X is a main group element and $n = 0, 1, 2,$ or 3. An obvious extension of our previous work is a study of

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the through-ring interactions in this family of compounds, to determine how their electronic structure could be controlled to produce compounds with or without M · · · M or X · · · X "bonds".

3
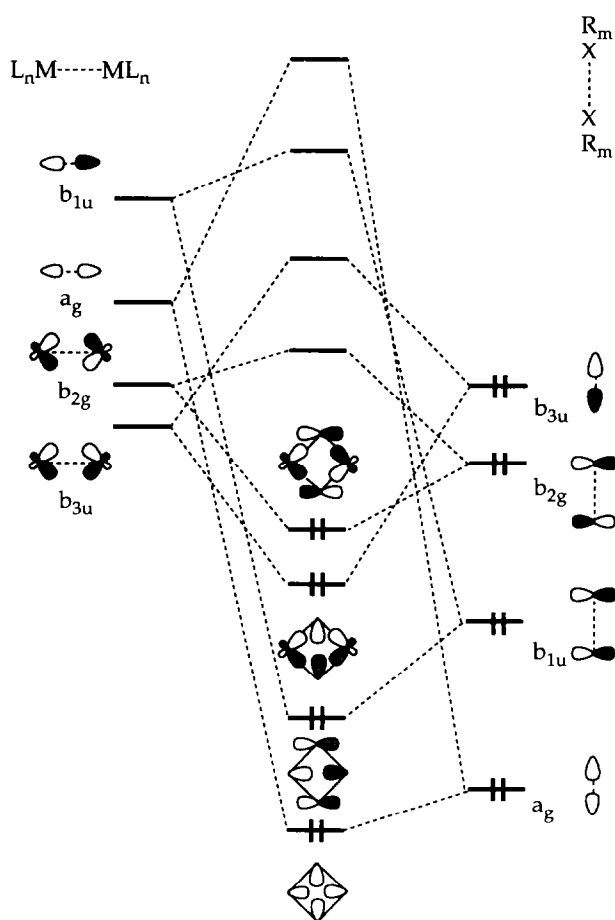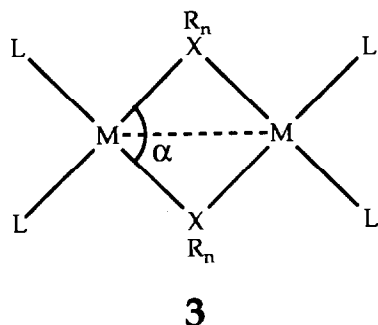

Fig. 1. Generalized orbital interaction diagram between two ML_n fragments (left) and two XR_m bridges (right) to form an $[M_2L_{2n}(\mu\text{-}XR_m)_2]$ diamond. The orbitals are labelled according to their representations in the D_{2h} point group. Only in-plane orbitals are considered, and the non-bonding d orbitals are omitted for simplicity.

2. Generalized orbital interaction diagram

Let us start by introducing a qualitative description of the framework orbital interactions for a general M_2X_2 planar ring, more or less distorted from the regular ring, which is a perfect square ($\alpha = 90°$) only when the M and X atoms have identical atomic radii. In general, the regular ring is the one in which the two pairs of antipodal atoms are at the largest interatomic separation compatible with the existence of M–X bonds [1].

For the subsequent discussion it will be useful to visualize the M_2X_2 ring as formed by two separate fragments, each having a set of antipodal atoms, i.e., M_2L_4 and X_2R_{2m}. The framework molecular orbitals of a regular $[M_2(\mu\text{-}XR_m)_2L_4]$ diamond with $\alpha \sim 90°$ are obtained as combinations of the σ, σ^*, π (in-plane) and π^* (in-plane) orbitals of each fragment, as represented in Fig. 1, where the non-bonding d orbitals are omitted for simplicity. Of course, the order of energies of the four bonding FOs is strongly dependent on the angle α, but for symmetry and topological considerations it is enough in most cases to consider the composition of the molecular orbitals at a fixed geometry ($\alpha = 90°$), and this will be used throughout except when otherwise specified. For regular diamonds through-ring overlap is weak, M–X interactions predominate, and the optimum electronic structure is that with the non-bonding d orbitals and the four bonding FO's occupied (i.e., FEC = 8). However, for small (or large) α, the b_{3u} and b_{2g} (or b_{1u} and b_{2g}) FO's, strongly X · · · X (or M · · · M) antibonding, are pushed above the d-block. Consequently, upon removal of two or four electrons (i.e., FEC = 6 or 4) elongated diamonds are more stable than the regular rings. Since electrons are removed preferentially from framework orbitals of the regular ring, the block of non-bonding d orbitals is considered to be fully occupied for electron-counting purposes.

3. Compounds with XR$_2$ bridges

In the case of $[\{ML_2(XR_2)\}_2]$ diamonds with square-planar coordination spheres at the metal atoms, the generalized orbital picture of Fig. 1 applies. The frontier orbitals of an ML_2 fragment [2] are shown in **4**. The sp hybrid and the d_{xz} orbitals are in this case suitable for framework bonding, with the rest of the d orbitals being non-bonding. Hence, for electron-counting purposes, one must consider the metal atom as d^8, and any additional electrons must be counted as framework electrons. In order to check the predictions which stem from the general scheme discussed above, we carried out geometry optimization for several model

TABLE 1. Calculated through-ring Pt $\cdots$ Pt distances and X $\cdots$ X distances (in parentheses) for dimers of square-planar complexes (3) with XR$_2$ bridges. For compounds with X = P or S and FEC = 6 and 4 the data for two minima are given. FEC given correspond to d^8 electron configuration for the metal atom.

Compound	Pt $\cdots$ Pt (Å)		
	FEC: 8 ($n = 0$)	6 ($n = 2$)	4 ($n = 4$)
[Pt$_2$Cl$_4$(μ-SH$_2$)$_2$]$^{n+}$	3.53 (3.10)	3.28	3.39
[Pt$_2$(CO)$_4$(μ-SH$_2$)$_2$]$^{(n+4)+}$	3.52 (3.11)	2.90	2.80
		(1.78)	(1.77)
[Pt$_2$Cl$_4$(μ-PH$_2$)$_2$]$^{(n-2)+}$	3.75 (2.83)	3.45	3.53
[Pt$_2$(CO)$_4$(μ-PH$_2$)$_2$]$^{(n+2)+}$	3.56 (3.07)	2.91	2.88
		(2.14)	(2.14)
[Pt$_2$Cl$_4$(μ-SiH$_2$)$_2$]$^{(n-4)+}$	4.02 (2.44)	3.19	2.48
[Pt$_2$(CO)$_4$(μ-SiH$_2$)$_2$]$^{n+}$	4.03 (2.42)	2.90	2.02

TABLE 2. Structural data for diamonds of square-planar ML$_2$ fragments and XR$_2$ bridging groups (3)

Compound	M	M$\cdots$M (Å)	α (°)	Ref.
[Rh$_2$(μ-P{Me$_3$C}$_2$)$_2$(CO)$_4$]	Rh	3.717	79.5	[3]
[Rh$_2$(μ-As{Me$_3$C}$_2$)$_2$(CO)$_4$]	Rh	3.884	77.8	[4]
[Ir$_2$(μ-As{Me$_3$C}$_2$)$_2$(CO)$_4$]	Ir	3.895	77.9	[5]
[Pt$_2$(μ-SiPhCl)$_2$(PEt$_3$)$_4$]	Pt	3.974	66.4	[6]
[Pt$_2$(μ-SiCyH)(μ-CySiCl)(PEt$_3$)$_4$]	Pt	4.046	64.5	[7]
[Pt$_2$Cl$_2$(Cy$_2$P{CH$_2$}$_3$PPh)$_2$]	Pt	3.545	76.3	[8,9]
[Pt$_2$Cl$_2$(μ-P[NMe]$_2$CO}$_2$PNEt$_2$)$_2$]	Pt	3.557	77.3	[10]
[Pt$_2$(μ-PPh$_2$)$_2$(C$_6$F$_5$)$_2$(phen)]	Pt	3.569	75.1	[11]
[Pt$_2$Cl$_2$(μ-Cy$_2$P{CH$_2$}$_3$PPh)$_2$]	Pt	3.577	76.6	[9]
[Pt$_2$(μ-PPh$_2$)$_2$Cl$_2$(HPPh$_2$)$_2$]	Pt	3.586	77.2	[12]
[Pt$_2$(μ-PHPh)$_2$(MePPh$_2$)$_4$]$^{2+}$	Pt	3.686	75.1	[13]
[Pt$_2$(μ-PPh$_2$)$_2$(dppe)$_2$]$^{2+}$	Pt	3.699	76.1	[12]
[Pt$_2$(μ-PHPh)$_2$(MePPh$_2$)$_4$]$^{2+}$	Pt	3.706	74.6	[13]
[Pt$_2$(μ-PPh$_2$)$_2$(C$_6$F$_5$)$_4$]	Pt	2.722		[14]
[Pt$_2$(μ-SEt$_2$)$_2$Br$_4$]	Pt	3.368	81.9	[15]
[Pt$_2$(μ-SEt$_2$)$_2$Me$_4$]	Pt	3.610	79.9	[16]
[Au$_2$(μ-NMe$_2$)$_2$Me$_4$]	Au	3.231	82.0	[17]

compounds. Keeping the M–X distances constant and varying α, we optimized the through-ring distances M $\cdots$ M and X $\cdots$ X. The results are presented in Table 1. For an FEC of 8, the general rules predict a regular ring with no short through-ring distances. This is what is found for the compounds with X = S and P (for X = Si, see below).

For FEC's of 6 or 4, distorted diamonds with a short through-ring distance are predicted by the general rules. However, the data in Table 1 for the models having chloride as a terminal ligand indicate that the energy is minimum for long through-ring distances. This violation of the general rules can be rationalised from a careful analysis of the corresponding Walsh diagrams and ascribed to strong X $\cdots$ L repulsions. If a less bulky terminal ligand such as CO is used the results (Table 1) conform to the general rules, and short through-ring distances are predicted. That some

sp

d$_{xz}$

d block

4

calculated distances are too short compared to the covalent radii is a well known artefact of the neglect of internuclear repulsions in the EH methodology, but it must be interpreted qualitatively as a clear indication of a strong bonding interaction. Notice that for FEC = 6 or 4, two minima are found, corresponding to short M $\cdots$ M (first line for each compound in Table 1) and short X $\cdots$ X (second line for each compound in Table 1) distances, a result expected from our previous study on related compounds [1]. All the structural data for square planar dimers with PR$_2$ and SR$_2$ bridges and an FEC of 8 (Table 2) are indeed in qualitative agreement with the calculated results. We could find no examples of similar compounds with FEC's of 4 or 6 in the literature, but Forniés et al. have recently synthesized the anionic complex [Pt$_2$(μ-PPh$_2$)$_2$(C$_6$F$_5$)$_4$]$^{2-}$ which, upon oxidation, yields the neutral diamagnetic analogue with an FEC of 6 and a rather short Pt $\cdots$ Pt distance [14].

Two exceptions to the general rule that compounds with FEC = 8 must have no short through-ring distances are provided by [Pt$_2$(CySiH)(CySiCl)(PPh$_3$)$_4$] and [Pt$_2$Cl$_2$(Cy$_2$P{CH$_2$}$_3$PPh)$_2$], with relatively short Si $\cdots$ Si distances ($\sim$ 2.6 Å). This apparent violation of the FEC rules deserves closer analysis. In Fig. 2 we show the interaction diagram for the framework orbitals of model compounds with PH$_2$ and SiH$_2$ bridges for comparison. Both follow the same trends as the general scheme (Fig. 1), although with differences due to the electronegativities of the P and Si atoms. The main difference resides in the b$_{3u}$ and b$_{2g}$ FO's. When the bridging atom is P, the interactions between the fragment orbitals of B$_{3u}$ and B$_{2g}$ symmetries are highly
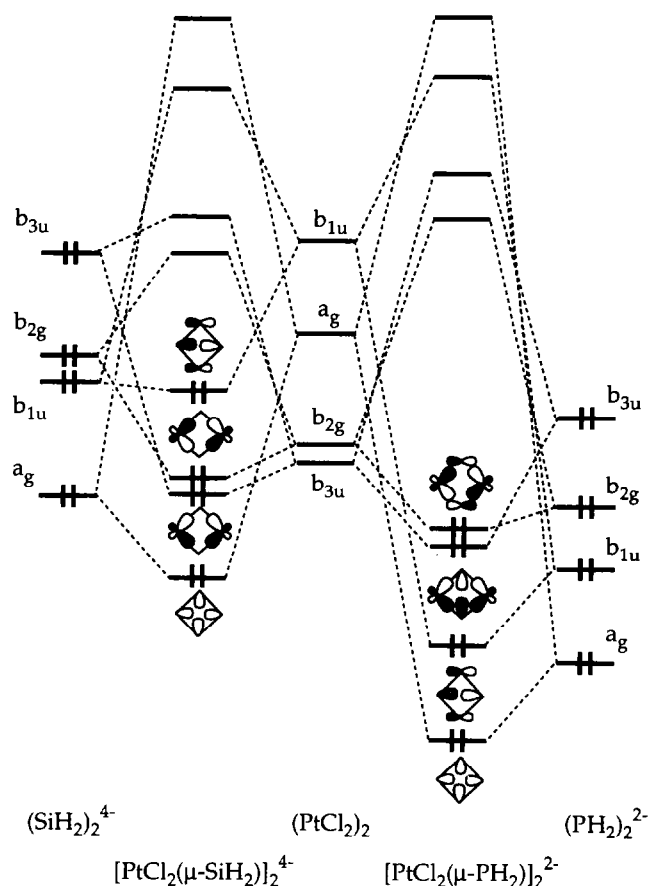
$(SiH_2)_2^{4-}$ $(PtCl_2)_2$ $(PH_2)_2^{2-}$

$[PtCl_2(\mu\text{-}SiH_2)]_2^{4-}$ $[PtCl_2(\mu\text{-}PH_2)]_2^{2-}$
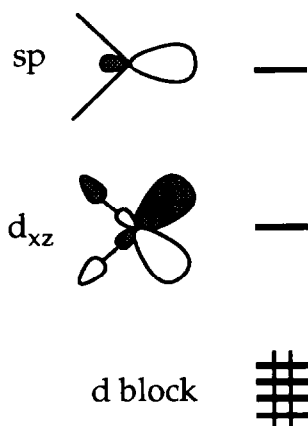
Fig. 2. Orbital diagram for the interaction of a $(PtCl_2)_2$ fragment with two $(SiH_2)^{2-}$ (left) or two $(PH_2)^-$ (right) bridges, to form a ring with $\alpha = 90°$.

covalent, and the resulting molecular orbitals are strongly delocalized throughout the ring (Table 3). When the bridging atom is Si, the higher energy of its atomic orbitals results in the localization of the M–X bonding molecular orbitals on the metal atoms and of the antibonding orbitals on the Si atoms (Table 3), as illustrated in **5** for the case of σ_{XX}^*. A similar situation

TABLE 3. Electron density (%) localization of the occupied framework orbitals b_{3u} and b_{2g} in the atoms of the M_2X_2 rings of model compounds with $(PH_2)^-$ or $(SiH_2)^{2-}$ bridges at different geometries.

Atom	b_{3u}			b_{2g}		
	$\alpha = 70°$	$90°$	$100°$	$70°$	$90°$	$110°$
$[Pt_2Cl_4(\mu\text{-}SiH_2)_2]^{4-}$						
Pt	76	64	56	70	70	78
Si	6	18	24	20	18	12
$[Pt_2Cl_4(\mu\text{-}PH_2)_2]^{2-}$						
Pt	68	38	32	36	38	58
P	14	38	42	30	28	22

results for π_{XX}^*. The outcome is that two occupied MO's are now non-bonding (essentially metal d orbitals), and the empty ones are formally σ_{SiSi}^* and π_{SiSi}^*.

5

FEC = 8

4 M-X bonds

a

FEC = 4

2 X-X bonds
4 d electrons

b

6
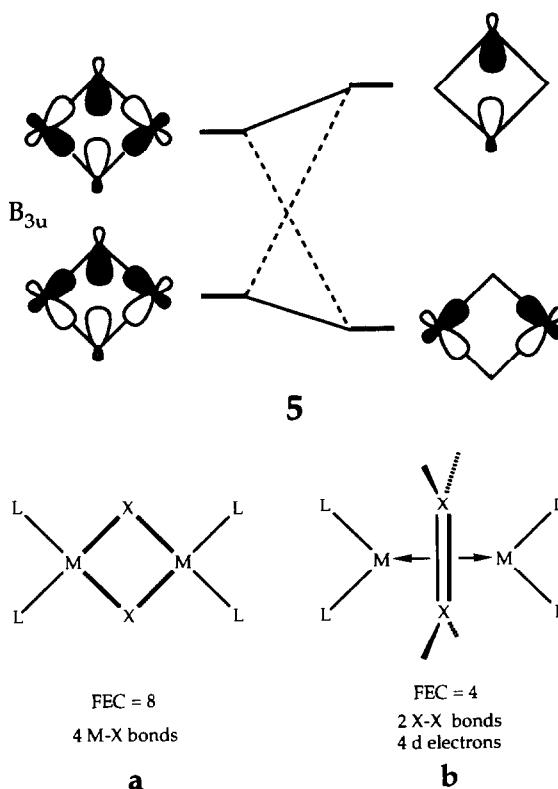
According to the molecular orbital analysis, the non-applicability of the FEC rules to the silicon compounds results because the assumption of a d^8 electron configuration is not justified. In other words, one should describe them as Pt^0 compounds with ten non-bonding d electrons. The correct FEC is then 4, for which a short through-ring interaction would be expected. Since the bonding FO's are centred largely at the Si atoms, the bonding in this compound is best described in terms of a binuclear complex with a bridging silylene, a situation which is not common, although there are some examples with bridging olefins [18]. In essence, the differences in the orbital interactions found between the PH_2 and SiH_2 bridges translate into the different Lewis structures shown in **6**: in the former case eight electrons are used for framework bonding (**6a**), whereas in the latter case four electrons are kept in the d orbitals of the metal atoms, and the remaining four framework electrons are dedicated to an X–X double bond which can act as a weak donor to the metal atoms (**6b**). The influence of the electronegativity on the adoption of the alternative structures **6a** or **6b** is nicely exemplified by the decrease in the optimized $X \cdots X$ distances for the series of $[Pt_2L_4(\mu$-

TABLE 4. Calculated geometries for planar rings of ML_2 groups bridged by one lobe ligands.

Compound	M	FEC	M···M (Å)	α (°)
$[Rh_2Cl_4(\mu\text{-H})_2]^{4-}$	Rh^I, d^8	4	2.57	88.2
$[Rh_2Cl_4(\mu\text{-H})_2]^{6-}$	Rh^0, d^9	6	2.87	73.5
$[Pd_2Cl_4(\mu\text{-CO})_2]$	Pd^{II}, d^8	4	2.76	92.4
$[Pd_2Cl_4(\mu\text{-CO})_2]^{2-}$	Pd^I, d^9	6	2.80	90.8
$[Pt_2Cl_4(\mu\text{-C}_6\text{H}_5)_2]^{2-}$	Pt^{II}, d^8	4	3.12	89.5
$[Pt_2Cl_4(\mu\text{-C}_6\text{H}_5)_2]^{4-}$	Pt^I, d^9	6	3.09	90.7
$[Pt_2(CO)_4(\mu\text{-C}_6\text{H}_5)_2]^{2+}$	Pt^{II}, d^8	4	3.03	93.1
$[Pt_2(CO)_4(\mu\text{-C}_6\text{H}_5)_2]$	Pt^I, d^9	6	3.06	91.7

$XH_2)_2]$ compounds (Table 1, $n = 0$) on going from S to P to Si.

4. Complexes bridged by XR_3 or isolobal groups

Since it was previously found [1] that bridging groups with only one lobe available for framework bonding, such as CH_3, CO, H^-, py, and C_6H_5, behave differently from those fragments with two or more lobes, we must consider the former case separately. In this section we discuss the results of extended Hückel (EH) calculations on model compounds with carbonyl, hydrido or phenyl bridges.

The resulting interaction diagram (Fig. 3) has a significant difference from the generalized diagram shown in Fig. 1. Since the bridging groups have no A lobes (2), the π^*_{MM} and σ^*_{MM} fragment orbitals (b_{2g} and b_{1u}) cannot mix with those of the bridging groups and are M–X non-bonding. In summary, there are two M–X bonding (a_g and b_{3u}), two non-bonding (b_{2g} and b_{1u}) and two antibonding ($2a_g$ and $2b_{3u}$) FO's. With four framework electrons, the most stable situation corresponds to a short M···M distance, leaving b_{1u} (σ^*_{MM}) and b_{2g} (π^*_{MM}) empty, and hence a formal M–M double bond. If the FEC is augmented to six,
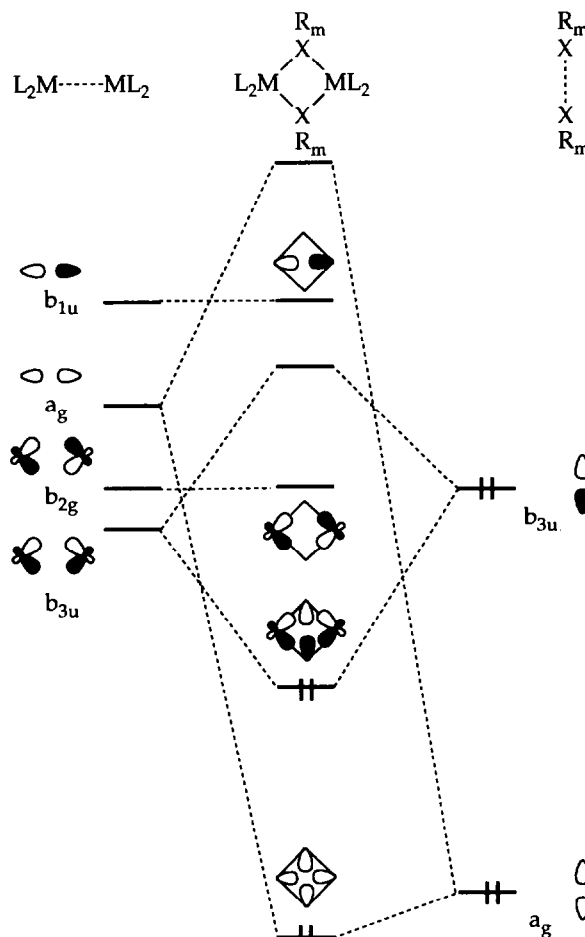

Fig. 3. Orbital diagram for the interaction between two (ML_2) fragments (left) and two XR_m bridges with only one lobe (right).

two things may happen: either (i) the $\pi^*_{MM}(b_{1u})$ is occupied, the formal M–M bond order is reduced from two to one, and the M···M distance is increased, or (ii) one of the ML_2 fragments may be rotated to a

TABLE 5. XR_3-bridged binuclear complexes of square-planar metals with essentially planar M_2X_2 diamonds. θ is the angle between the two MX_2 planes.

Compound	M	M···M (Å)	α (°)	θ (°)	FEC	Ref.
$[Rh_2(\mu\text{-H})_2(dippe)_4]$	Rh	2.627	80.5	160	4	[19]
		2.629	83.2	180	4	
$[Rh_2(\mu\text{-H})_2(P\{OCHMe_2\}_3)_4]$	Rh	2.647	85.8	180	4	[20]
$[Pt_2(\mu\text{-H})_2(PCy_3)_2(Et_3Si)_2]$	Pt	2.692	(81.7) [a]	–	4	[21]
$[Pt_2(\mu\text{-C}_6F_5)_2(C_6F_5)_4]^{2-}$	Pt	2.714	101.3	152	4	[22]
$[Rh_2(\mu\text{-H})(\mu\text{-CO})(dppe)_2]^+$	Rh	2.716	76.5	180	4	[23]
$[Pt_2(\mu\text{-H})(\mu\text{-CO})(dppf)_2]^+$	Pt	2.790	81.0	163	6	[24]
$[Pd_2(\mu\text{-CO})_2Cl_4]^{2-}$	Pd	2.685	95.4	180	6	[25]
		2.709	94.3	180	6	
$[Ni_2(\mu\text{-H})_2(Cy_2P\{CH_2\}_3PCy_2)_2]$	Ni	2.441	78.8	176	6	[26]

dippe = 1,2-bis(diisopropylphosphino)ethane; dppe = 1,2-bis(diphenylphosphino)ethane; dppf = 1,2-bis(diphenylphosphino)ferrocene.
[a] Estimated from the experimental Pt–Pt distance and Pt–H = 1.78 Å [27].

tetrahedral geometry, converting a d^8 metal ion into a d^{10}, and effectively reducing the FEC to four. Further increase of the FEC to eight results in the occupation of the b_{1u} (σ_{MM}^*) orbital, ultimately breaking the M $\cdots$ M bond or converting the coordination sphere of the two metal atoms to tetrahedral (see below).
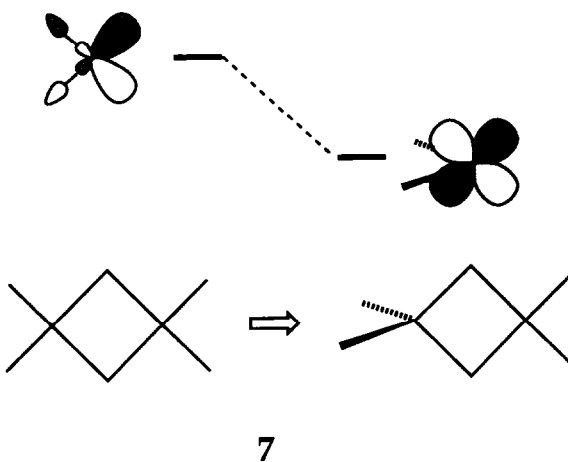
Consistent with this qualitative picture, the EH calculations predict energy minima at short M $\cdots$ M distances for the dimers of d^8 metal ions with H$^-$ and CO bridges and an FEC of 4 or 6 (Table 4). These inferences are fully consistent with the short M $\cdots$ M distances found in binuclear derivatives of d^8 metal ions with one$^-$ lobe bridges (Table 5). Notice that compounds with FEC = 6 also have short M $\cdots$ M distances, though a little longer than in a similar compound with FEC = 4, consistent with $\sigma^2\pi^2\pi^{*2}$ (FEC = 6) and $\sigma^2\pi^2$ (FEC = 4) configurations relative to the M $\cdots$ M bond. When PH_3 is bridging, strong steric repulsion between the bridging and terminal ligands destabilize the geometry with large α. Calculations on a model compound with a C_6H_5 bridge also yield a Pt $\cdots$ Pt distance shorter than the van der Waals sum but larger than the experimental value, which may be attributed to the steric repulsions in our idealized planar model. Steric hindrance in the $[Pt_2(\mu$-$C_6F_5)_2(C_6F_5)_4]^{2-}$ ion is evident in its structure from a bending of the M_2X_2 ring and a displacement of the pentafluorophenyl groups away from the diamond. Bending the optimized structure to the same degree found experimentally would give Pt $\cdots$ Pt = 2.94 Å, in qualitative agreement with the experimental value of 2.71 Å.

5. Comparison of square-planar and tetrahedral derivatives

Now that we have shown how the FEC scheme accounts accurately for the structural data of bridged dimers of ML_2 groups with tetrahedral [1] or square-planar geometries, it is interesting to analyze the similarities and differences between both cases. For this purpose we consider a model compound, $[Rh_2Cl_4(\mu$-$PH_2)_2]^{4-}$ (3), with an FEC of 8, and computationally rotate one of its ML_2 groups, resulting in an isomer with one square-planar and one tetrahedral metal atom (7). We focus on the qualitative aspects related to the general picture presented above only, since a detailed theoretical study of these compounds has been reported earlier by Albright *et al.* [28].

The main effect is that the antisymmetric orbital in the plane of the ring, d_{xz}, which is M–L antibonding and hybridized toward the XR_m bridges in the square

planar case, becomes M–L non-bonding (7) and mostly a d orbital. In other words, the tetrahedral metal atom employs sp^3 hybrids for framework bonding, and the five d orbitals, formally non-bonding, are expected to be occupied. This change in the bonding characteristics of d_{xz} on going from the square planar to the tetrahedral geometry is detected in the calculations on the model compound as a change in its electron occupation from 0.94 to 1.99 electrons. In terms of framework-electron-counting, all this means is that one must assign eight d electrons to the metal in a square-planar environment, but ten d electrons to that with a tetrahedral geometry. Therefore, in the rotation sketched in 7 two framework electrons become non-bonding d electrons, and the FEC is consequently reduced from eight to six. According to the previously discussed rules, such a compound must be expected to have the two metal atoms within bonding distance. It is clear that the conversion of the second metal atom to a tetrahedral geometry, as in 1, has a similar result, further reducing the FEC to four and a shorter M $\cdots$ M distance would result.

7

This qualitative model finds its experimental counterpart in the series of Rh diamonds **8** [3,29]. The FEC of compound **8a** is eight, and the Rh $\cdots$ Rh distance is clearly non-bonding. Consistent with the above discussion, the change in the coordination sphere of one Rh atom from square-planar to tetrahedral (**8a** → **8b**) reduces the FEC in two electrons, and this is accompanied by a dramatic shortening of the through-ring Rh $\cdots$ Rh distance (from 3.72 to 2.76 Å). A similar change in the coordination sphere of the second Rh atom (**8b** → **8c**) reduces the FEC to 4, and produces a further shortening of the Rh–Rh distance. Alternatively, the FEC can be modified through redox reactions, as can be seen by comparing **8c** and **8d**. The two extra electrons in **8d** increase the FEC from four to six, with a consequent increase in the Rh–Rh bond length.

FEC = 8

3.72 Å

8a

FEC = 6

2.76 Å

8b

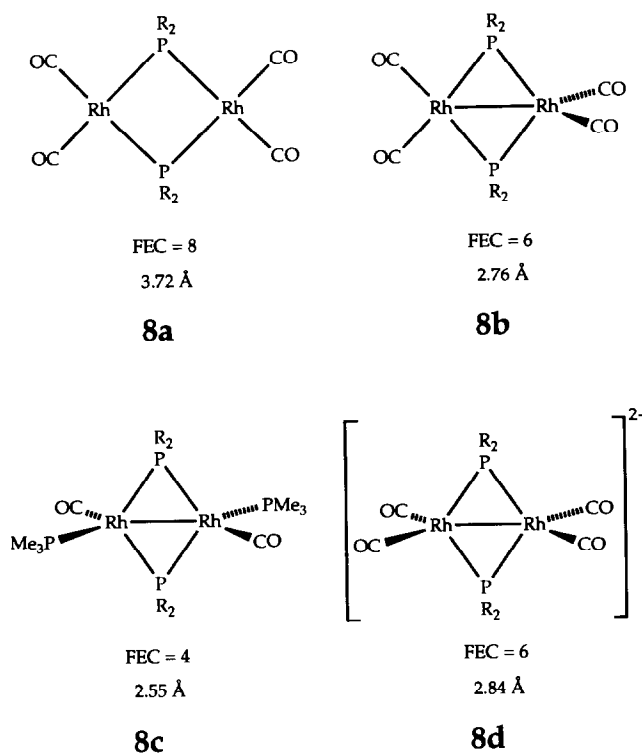FEC = 4

2.55 Å

8c

FEC = 6

2.84 Å

8d

TABLE 6. Atomic parameters used for the extended Hückel calculations: $H_{\mu\mu}$'s are the orbital ionization potentials, $\zeta_{i\mu}$ the exponents of the Slater orbitals, and c_i the coefficients in the double-ζ expansion of the d orbitals.

Atom	Orbital	$H_{\mu\mu}$	$\zeta_{1\mu}$	(c_1)	$\zeta_{2\mu}$	(c_2)	Ref.
Rh	5s	−8.09	2.135				[34]
	5p	−4.57	2.100				
	4d	−12.50	5.542	(0.5563)	2.398	(0.6119)	
Pd	5s	−7.32	2.190				[35]
	5p	−3.75	2.152				
	4d	−12.02	5.983	(0.5535)	2.613	(0.6701)	
Pt	6s	−9.08	2.554				[36]
	6p	−5.47	2.554				
	5d	−12.59	6.013	(0.6334)	2.696	(0.5513)	
Si	3s	−17.30	1.383				[37]
	3p	−9.20	1.383				
P	3s	−18.60	1.750				[36]
	3p	−14.00	1.300				
S	3s	−20.00	1.817				[38]
	3p	−13.30	1.817				
Cl	3s	−30.00	2.033				[39]
	3p	−15.00	2.033				
C	2s	−21.40	1.625				[31]
	2p	−11.40	1.625				
O	2s	−32.30	2.275				[31]
	2p	−14.80	2.275				
H	1s	−13.60	1.300				[31]

6. Concluding remarks

The number of framework electrons determines the possibility of through-ring bonding in the diamonds of square-planar dimers, in much the same way as in those of tetrahedral metal ions. For electron-counting purposes, 10 non-bonding d electrons must be counted for each tetrahedral metal atom, but only 8 for square-planar. The rest of the metal and bridge electrons available for bonding are included in the Framework Electron Count (FEC). With this simple electron accounting scheme, a short through-ring distance is predicted for compounds with FEC = 4 or 6, but no short distance is expected for those with FEC = 8. However, steric repulsions between bridging and terminal ligands are stronger than in the tetrahedral analogues and may result in violations of the FEC rules. For more electropositive bridging atoms such as Si, the FEC rules apply if the square-planar metal atoms are considered as d^{10}. A large number of compounds with XR_2 and XR_3 bridges can be classified according to their FEC, and their structures are entirely consistent with the simple FEC rules discussed in this paper. Changes in the stereochemistry of the metal atoms, as well as redox reactions, are efficient ways of modifying the FEC and the bonding in these compounds. The final goal of our work in this field is the extension of the qualitative approach presented here to diamonds of transition metal atoms with other d^n electron configu-

rations. A preliminary survey suggests that such a simplified bonding model can be of wide applicability [30] to other metal fragments.

Appendix: methodological aspects

Molecular orbital calculations of the extended Hückel type [31] were carried out using the modified Wolfsberg–Helmholz formula [32] on the following model compounds with different net charges corresponding to FEC's of 8, 6 and 4: [Pt$_2$L$_4$(μ-XH$_2$)$_2$] (for L = Cl, or CO; X = Si, P, or S), [Pd$_2$Cl$_4$(μ-CO)$_2$], [Rh$_2$Cl$_4$(μ-H)$_2$], [Rh$_2$Cl$_4$(μ-PH$_3$)$_2$], and [Pt$_2$(CO)$_4$(μ-C$_6$H$_5$)$_2$]. The atomic parameters used are shown in Table 6. The following bond distances were used: M–X = 2.35 Å (M = Pt, Rh, X = Si, P, S), Rh–Cl = Pt–Cl = 2.40, Pd–Cl = 2.33, Rh–H = 1.79, Pd–CO (bridge) = 1.99, Pt–Ph (bridge) = 2.20, Pt–CO (terminal) = 1.85,

S–H = 1.35, P–H = 1.42, Si–H = 1.48, C–C = 1.40, C–H = 1.08, and C–O = 1.15 Å. The search for structural data was carried out using the Cambridge Structural Database [33].

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