Edge-Sharing Binuclear d^8 Complexes with XR Bridges: Theoretical and Structural Database Study of their Molecular Conformation

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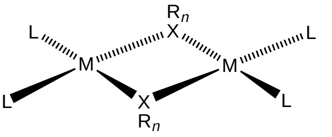
Abstract: The binuclear complexes of d^8 transition metal ions of the types $[M_2(\mu\text{-}Y)(\mu\text{-}XR)L_4]$ and $[M_2(\mu\text{-}XR)_2L_4]$ (where $M = Rh^I$, Ir^I, Ni^{II}, Pd^{II}, Pt^{II}, or Au^{III}; X = O, S, Se, or Te; Y = Cl or S) appear in a variety of molecular conformations in which the coordination planes around the two metal atoms are sometimes coplanar and sometimes bent, and the substituents at the bridging atoms adopt different orientations relative to the metal framework and to each other. Ab initio theoretical studies on a number of representative complexes, complemented with a structural database analysis, provides a rationale for the experimentally observed structures. The choice of molecular geometry is seen to result from the interplay of several factors including the conformational preference of the bridging atoms, the existence of weak metal ⋯ metal bonding in the bent structures, and different steric or hydrogen-bonding interactions implicating the terminal ligands and the substituents at the bridging atoms.

Keywords: ab initio calculations · ligand effects · metal–metal interactions · square-planar complexes · structural database analysis

Introduction

The doubly bridged binuclear complexes of type $[M_2(\mu\text{-}XR_n)_2L_4]$ ($n = 0$ to 2; **1**) with square-planar coordination geometries around the metal atoms form a large family, with XR being most commonly alkoxo or thiolato[1] groups. Some of these compounds have proved useful for the synthesis of mixed-ligand mononuclear complexes.[2, 3] Other interesting properties of these compounds include their catalytic activity,[2, 4–6] luminescent behavior,[7] or their potential use as therapeutic agents for cisplatin nephrotoxicity.[8] Despite the large amount of available structural data, a full understanding of the factors that determine the molecular structure of a particular compound has not been achieved. For the simplest compounds in this family, those with unsubstituted bridges ($n = 0$), the structural choice is restricted to planar or bent structures, the degree of bending being defined by the angle θ (see structure **2**). For those cases with monosubstituted



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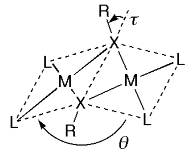

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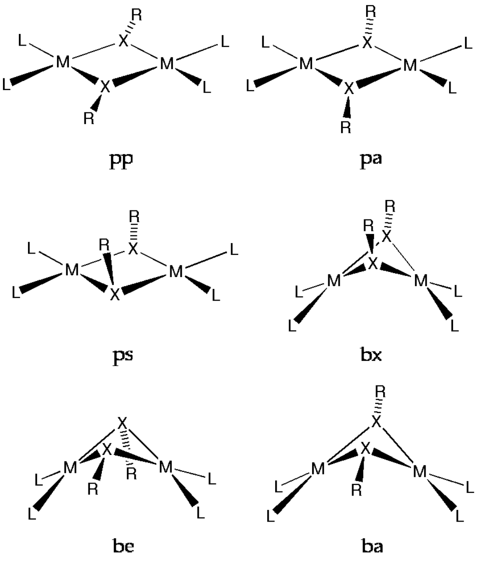

pp pa

ps bx

be ba

3

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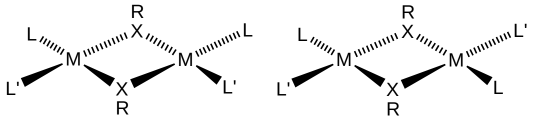
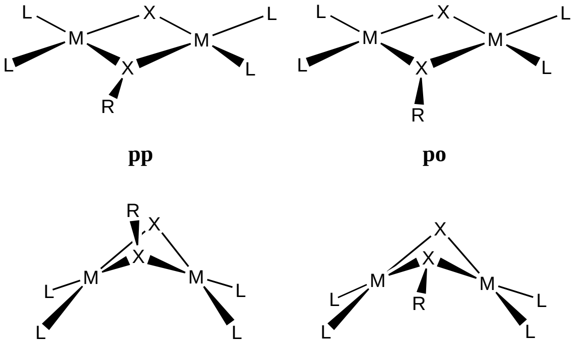
bridges ($n = 1$), a larger number of molecular conformations exist; these are depicted as **3**. From here on we will refer to the different structures with two letters, the first one to indicate whether there is a planar (**p**) or bent (**b**) M_2X_2 skeleton, and the second letter will refer to the relative orientation of the substituents at the bridging atoms: coplanar (**p**), *syn* (**s**), *anti* (**a**), *exo* (**x**), or *endo* (**e**). For a planar $[M_2(\mu\text{-XR})_2L_4]$ molecule there are three different conformations, considering the bending of the two substituents R away from the X–X hinge (defined by the angle τ; see **2**): coplanar (**pp**), *syn* (**ps**) or *anti* (**pa**). If the molecule is bent, there are two *syn* conformations, *endo* (**be**) or *exo* (**bx**), and an *anti* conformation (**ba**). Finally, one can expect geometrical isomerism when the two terminal ligands at each metal center are different (*cis* or *trans*, **4**) with two nonequivalent bent *anti* forms in the *cis* case. For the case of a compound with mixed bridges, $[M_2(\mu\text{-Y})(\mu\text{-XR})L_4]$, a smaller number of conformations exist (**5**): with a planar framework the substituent may be in the plane (**pp** conformation), or out of the plane (**po** conformation), whereas for a bent molecule, the substituent may be in an *endo* or *exo* orientation (**be** and **bx** conformations, respectively).



cis *trans*

4



pp **po**

bx **be**

5

Abstract in Catalan: *Els complexos binuclears d'ions de metalls de transició d^8 dels tipus $[M_2(\mu\text{-Y})(\mu\text{-XR})L_4]$ i $[M_2(\mu\text{-XR})_2L_4]$ (amb $M = Rh^I, Ir^I, Ni^{II}, Pd^{II}, Pt^{II}$ o Au^{III}; $X = O, S, Se$, o Te; $Y = Cl$ o S) es troben en diverses conformacions moleculars en què els plans de coordinació al voltant dels dos àtoms metàl·lics poden apareixer formant un angle o bé en forma coplanar, mentre que els substituents dels àtoms pont adopten diferents orientacions en relació amb l'esquelet M_2X_2 i l'un respecte l'altre. Estudis teòrics ab initio per a complexos representatius, complementats amb una anàlisi de base de dades estructurals, permeten organitzar de forma racional les estructures observades. L'elecció de la geometria molecular resulta d'un joc de diversos factors com ara la preferència conformacional dels àtoms pont, l'existència d'interaccions metall···metall a les estructures plegades, o les diferents interaccions estèriques o d'enllaç d'hidrogen en què participen els lligands terminals i els substituents dels àtoms pont.*

Despite the variety of structures available, we are not aware of the existence of structurally characterized isomers or conformers, thus suggesting that electronic, steric, or packing effects make one of the possible conformers more stable than the other ones. In the only example known to us in which two isomers have been structurally characterized, these correspond to two conformations of the chelate ring formed by a bidentate terminal ligand with one of the nickel atoms.[9] Nevertheless, the fact that compounds with similar composition present different conformations suggest that energy differences are small. Furthermore, studies in solution suggest that interconversion between conformers may have a low activation barrier in some cases.[10–12] For instance, interconversion of *syn* and *anti* isomers in solution has been proposed for rhodium, palladium, and platinum complexes based on their ^{19}F- or ^{1}H-NMR spectra[13–16] even if only one conformer can be isolated in the solid state in each case. Similarly, the *syn-endo* forms found for rhodium and iridium complexes in the solid state present ^{13}C and ^{1}H NMR spectra in solution that are consistent with an inversion of the M_2S_2 rings.[17–20] *Cis* and *trans* isomers (**4**) have also been shown to coexist in solution,[2, 21, 22] although the isomerization process presents a higher activation energy.[15]

The distribution of the different structural types for compounds with XR bridges, as obtained through a Cambridge Structural Database search,[23] is summarized in Figure 1. There, it is seen that most of the possible geometries are frequently found. Only the planar *syn* conformation is rare, in contrast with the bent structures which are most common in the *syn* (either *endo* or *exo*) rather than in the *anti* conformation. Such behavior is markedly different to that previously found for the analogous complexes with unsubstituted bridges,[24] for which the planar structure was found to be much more common than the bent one. It is worth stressing that the bending angle θ for a particular metal shows a bimodal distribution with one maximum at $\theta = 180°$ and another one at a small angle (e.g., at $\theta \approx 120°$ for Ni and Rh) separated by a clear gap at intermediate angles, as previously found for the X bridges.[24] Finally, it appears that different

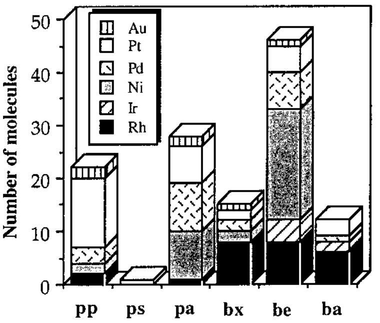


Figure 1. Distribution of the different conformers (**3**) for the binuclear complexes of d^8 metal ions of the type $[M_2(\mu\text{-XR})_2L_4]$, as found in a structural database search.

metals have different structural preferences: whereas rhodium and iridium are most frequently found in bent structures, other metals (Ni, Pd, Pt, Au) appear with similar frequencies in planar and bent forms.

In our previous analysis of the bent and planar structures for complexes with unsubstituted bridges we discussed the factors that affect the structural choice.[24] Since these effects should be expected to operate also in the presently studied compounds, we briefly summarize here our previous conclusions. The two main factors are the existence of weak metal$\cdots$metal bonding in the bent form and the increased steric repulsion between terminal ligands upon bending. The analysis of these two factors allowed us to establish the following general trends, which are consistent with the structural data for 139 independent molecules: i) The tendency to form bent structures increases when descending along a group of the periodic table and from right to left along a period, tht is, Ir > Rh > Pt > Pd > Ni. ii) Complexes with two good σ-donor (and preferably good π-acid) terminal ligands (e.g., CO, bipyridine, cyclooctadiene or other diolefins) favor metal$\cdots$metal interactions, except for those ligands with important steric hindrance (e.g., PEt_3, $PRPh_2$, PPh_3, dppe, $SiCl_3$), in agreement with the experimental findings of Connick et al.[25] for face-to-face dimers or stacks. In contrast, complexes with two or more π-basic or poor σ-donor terminal ligands (halides, amides, thioethers, C_6F_5) tend to adapt a planar structure.

When going from the unsubstituted bridges to the monosubstituted ones, three new factors may be expected to influence the choice between the various available structures: i) the conformational preference of the bridging atom, ii) the steric repulsion between the substituents R, and iii) the repulsion between the bridge substituents and the terminal ligands.

In this paper we present a systematic theoretical study of a variety of compounds of the types $[M_2(\mu\text{-}Y)(\mu\text{-}XR)L_4]$ and $[M_2(\mu\text{-}XR)_2L_4]$ in a quest to establish the relative importance of the factors that may in principle affect the relative stabilities of the available molecular conformations. To that end, ab initio calculations including the correlation energy at the MP2 level were carried out (see Appendix for computational details) guided by the results of our previous qualitative extended Hückel studies.[26] We will start by briefly discussing the conformational preference of the RXZ_2 groups based on the results of semiempirical calculations on a single model compound and of ab initio computations for the model XH_3^+ groups (X = O, S, Se, Te). Then we will present the results of ab initio calculations for a variety of binuclear complexes. Finally, we will attempt a systematization of the available structural data by using the guidelines obtained from the theoretical results.

Results and Discussion

Conformational preference of RXZ_2 groups (X = O, S, Se, Te)

Let us start by looking at the conformational preferences in a model compound $[Rh_2(\mu\text{-}XH)_2Cl_4]^{4-}$, where X = O or S, assuming a planar M_2X_2 core (i.e., $\theta = 180°$), according to calculations at the EH level. The corresponding potential energy surfaces are presented in Figure 2, where the energy contours are shown as a function of the XMX angle (α) and the out of plane displacement of the R groups (τ). There, it can be seen that for the hydroxo bridge the minimum appears with the H atom in the molecular plane, whereas for a thiolato bridge the hydrogen atom is clearly out of the plane. It is worthy of notice also that the potential-energy surface is shallower for the hydroxo than for the thiolato bridge. In essence, these results suggest that there is not a strong preference for an sp^2 or sp^3 hybridization around the oxygen atom, whereas an sp^3 hybridization is strongly preferred for the sulphur bridging atom. If one considers the sum of the three bond angles around the X atom (Σ), the deviation of this parameter from 360° indicates the degree of pyramidalization around X. These results can be summarized by saying that the angle sum Σ for tri-substituted oxygen atoms should be close to 360°, whereas smaller values are to be expected at sulfur atoms. Let us recall that for the binuclear complexes under study there are three alternative structures with pyramidal

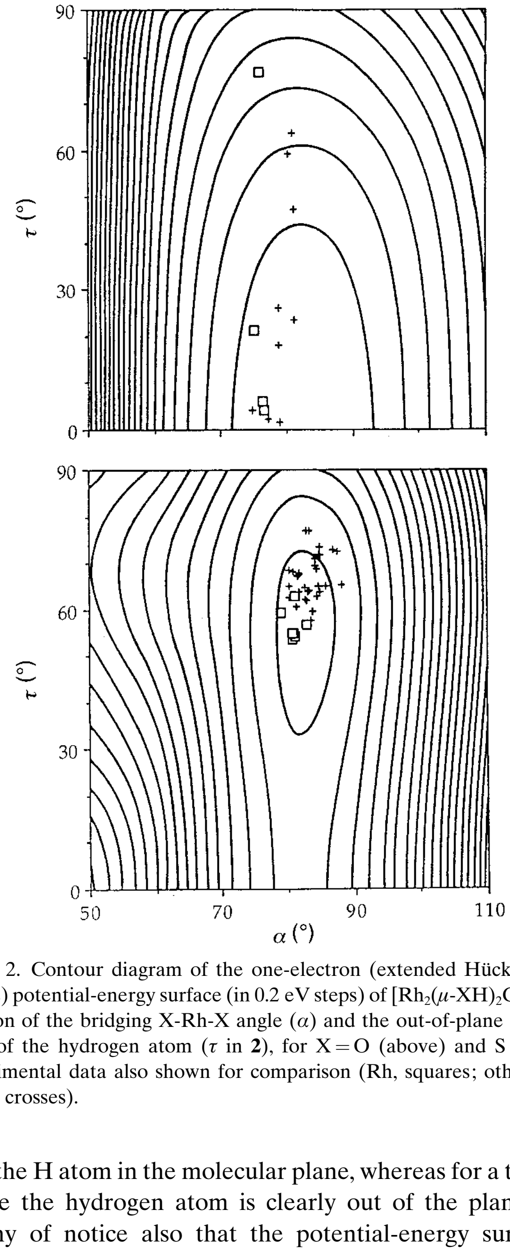


Figure 2. Contour diagram of the one-electron (extended Hückel calculations) potential-energy surface (in 0.2 eV steps) of $[Rh_2(\mu\text{-}XH)_2Cl_4]^{4-}$ as a function of the bridging X-Rh-X angle (α) and the out-of-plane displacement of the hydrogen atom (τ in **2**), for X = O (above) and S (below). Experimental data also shown for comparison (Rh, squares; other metal atoms, crosses).

RXM_2 groups when the molecule is bent ($\theta < 180°$): **be**, **bx**, or **ba** (**3**). These structures should be expected to have similar energies as far as the conformational preference of the bridging atom is concerned. Similarly, for a planar framework, the **ps** and **pa** structures should have comparable energies, whereas the **pp** structure, for which $\Sigma = 360°$, is expected to be less stable.

It can be shown that the different degree of pyramidalization around the oxygen and sulfur atoms is attached to the very nature of those atoms and is affected by the substituents to a lesser degree. Thus, we have taken the simplest models for RXZ_2 groups, the XH_3^+ ions (X = O, S, Se, Te), and optimized their geometries at the MP2 level used throughout in this paper (see Appendix for computational details). The results (Table 1) are in good qualitative agreement with the above description. For X = O, the most stable geometry is little pyramidalized and is only 4.4 kcal mol^{-1} more stable than the planar form. In contrast, the XH_3^+ ions of the other chalcogenides are strongly pyramidalized and the energy required for the planar conformation is quite high (from 31 to 47 kcal mol^{-1}), in excellent agreement with experimental values for R_3S^+ ions (24–36 kcal mol^{-1} [1, 27]). Results of density functional calculations on SH_3^+ consistently predicts its planar form to be 32.8 kcal mol^{-1} higher than the pyramidal one.[28] The effect of substituents, tested through calculations for the $MeXH_2^+$ ions (Table 1), is seen to be small for X = S, Se, and Te, and almost negligible for X = O.

Table 1. Calculated sum of the bond angles (Σ) in the XH_3^+ and $MeXH_2^+$ ions, and relative energies [kcal mol^{-1}] of their planar form. Mean values of Σ in tricoordinate RXZ_2 groups (X = O, S, Se, Te; Z = C, Si, Ge; R = H, Z) from a structural database analysis also shown for comparison (standard deviation in brackets).

	O	S	Se	Te
E (planar XH_3^+)	4.4	31.0	39.8	47.0
E (planar $MeXH_2^+$)	5.3	28.1	36.1	43.1
Σ calcd (XH_3^+)	327	286	279	274
Σ calcd ($MeXH_2^+$)	328	295	287	281
Σ exp. (mean)	352 [8]	308 [7]	303 [5]	286 [4]
structures	20	145	15	47
data sets	26	173	16	110

The tendency of first-row main-group elements to present larger bond angles and a smaller barrier to inversion than heavier elements of the same group was discussed by Kutzelnigg.[29] Those differences were attributed to a smaller mixing of the X(p) orbitals in the bonding MOs for the lighter elements. In particular, the barriers of inversion for NH_3 and PH_3 were reported to be of 6 and 38 kcal mol^{-1}, respectively, amazingly close to the values found by us for OH_3^+ and SH_3^+.

The calculated energy required for a planar conformation around the chalcogen atom in XH_3^+ should not be taken as a quantitative estimate of the corresponding value in the complexes under study, since it is well known that the coordination of a sulfur lone pair to a transition metal significantly lowers the barrier to pyramidal inversion.[1, 27, 30, 31] Similarly, the experimental values obtained from variable temperature NMR spectra of selenium coordinated to transition metal complexes are sensibly smaller (15–18 kcal mol^{-1} [27]) than calculated for the model SeH_3^+ ion, and comparable to those of sulfur derivatives. What the calculated values clearly tell us is that the energy gained upon pyramidalization of a sulfur, selenium, or tellurium atom is much larger than that gained in the case of oxygen. A structural database search confirms the trend predicted for the values of Σ (Table 1) in RXZ_2 groups (X = O, S, Se, Te; Z = C, Si, Ge; R = H, Z). In Table 1, it is seen that Σ varies only between 290 and 320° for X = S, without ever approaching the value of 360° that would correspond to a planar geometry for the central atom. That this is a general behavior can be seen in Figure 3, where the distribution of the Σ values for RXZ_2 groups (X = O, S) in the Cambridge Structural Database is presented. There it is seen that the values for oxygen-bridged compounds concentrate at $\Sigma = 360°$, whereas the distribution of Σ for sulfur-bridged compounds is centered at around 310°. A result of the angular preference of the bridging atom is that only for the small, highly electronegative oxygen bridging atom can the **pp** structure be expected. In general, if only the conformational preference around the bridging atoms is considered, the rest of the structures (**ps**, **pa**, **bx**, **be**, and **ba**) are expected to have similar energies.

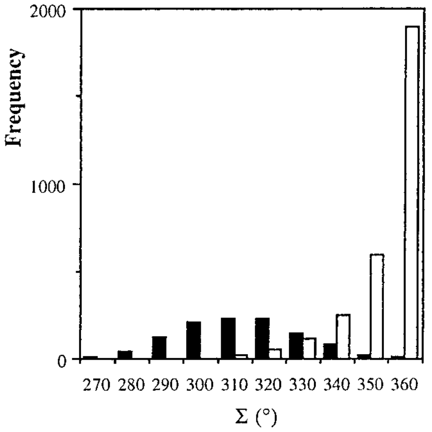


Figure 3. Distribution of the sum of the bond angles (Σ) around the central X atom in M_2XY groups, for X = O (white bars) and S (black bars), in structures retrieved from the Cambridge Structural Database.

A corollary of the quasi invariance of the Σ value for a particular bridging atom (~330° and ~290° at the O or S atom, respectively) is that the orientation of the substituent R (τ angle) must change upon bending the M_2X_2 core. Semiempirical extended Hückel calculations on the model compound $[Rh_2(\mu\text{-}SH)_2Cl_4]^{4-}$ indicate an optimum value of τ of approximately 54° for the planar case (a slightly larger value is predicted by ab initio calculations), and τ is predicted to vary with θ as seen in Figure 4 (solid lines). Such trend is confirmed by the ab initio calculations (Figure 4, triangles) and by the experimental data for binuclear thiolato-bridged rhodium complexes (Figure 4, squares). The large out-of-plane motion of the substituents upon bending reflected in the τ values should be mostly attributed to the attempt to maintain the degree of pyramidalization around the bridging atom practically constant. It is interesting to realize that the correlation between τ and θ provides a tool for molecular design in this

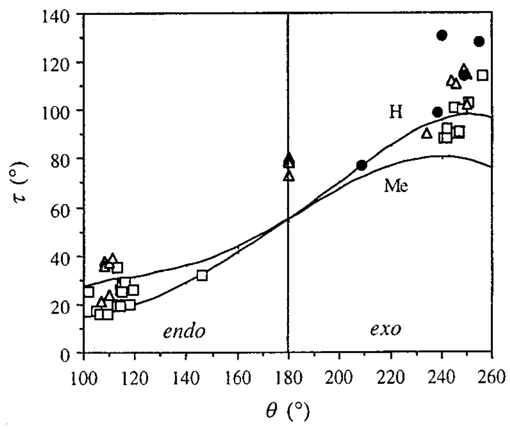


Figure 4. Orientation of the substituent at the bridging atom (angle τ defined in **2**) as a function of the bending angle θ calculated at the EH level for $[Rh_2(\mu\text{-}SR)_2Cl_4]^{4-}$ (R = H, Me; solid lines), and at the MP2 level (triangles) for $[Rh_2(\mu\text{-}SR)_2(PH_3)_4]$ (R = H, Me; Table S2). Experimental values for the *endo* and *exo* substituents in bent structures of thiolato-bridged rhodium compounds are represented by empty squares, and black circles correspond to structures **E.33**–**35** (see text). Bending angles θ are taken between 100° and 180° for *endo* and between 180° and 260° for *exo* groups.

family of compounds. Indeed, the value of τ can be easily modulated by the use of bidentate bridging ligands as in **7e** (for structure of **7e**, see section on nickel compounds). The use of a single linker between the two bridging atoms (e.g., Li^+ or Cu^+ ions,[32, 33] compounds **E.31** and **E.32**, Table 8) in platinum complexes, induces a large value of τ, hence a large degree of bending. If the number of linkers is increased, as in the series of mixed-metal complexes[34] of formula $[(PPh_3)_2Pt(\mu\text{-}S\{CH_2\}_n)Rh(cod)]^+$, the value of τ is made progressively smaller and the molecules approach planarity, as seen by the structural data (Figure 4, black circles; Table 8, compounds **E.33**–**35**).

Ab initio results

Ab initio MP2 calculations (see Appendix for computational details) were performed on model complexes $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PH_3)_4]^+$, $[M_2(\mu\text{-}XR)_2(PH_3)_4]^{n+}$, $[Rh_2(\mu\text{-}SH)_2(CO)_4]$, and $[Au_2(\mu\text{-}SR)_2L_4]$ (M = Ni, Pd, Pt, Rh, Ir; X = O, S; L = Me, Cl; and R = H, Me). The results of such calculations should provide us with information on how the metal atom, the nature of the bridging atom, and the nature of its substituent affect the structural choice.

Relative energies: For the compounds with mixed bridges, $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PH_3)_4]^+$ (R = H, Me), the calculated MP2 energies for the different conformations relative to that of the **po** conformer are those presented in Table 2. It is clear that the bent conformations are more stable than the planar ones, with the *exo* form being slightly more stable than the *endo* one, in excellent agreement with the experimental data (see below) and with the qualitative conclusions of the preceding section. Substitution of the thiolato bridge by a methylthiolato introduces enhanced substituent ⋯ ligand repulsions in the **be** conformer, which are in part relieved by changes in the Pt-S-Pt and τ angles, resulting in a net destabilization of only 2 kcal mol^{-1} relative to the **bx** form. Notice that the sulfur atom in the methylthiolato-bridged compound is less pyramidalized than in the hydrogensulfido-bridged complex (see values of Σ in Tables S1–S4 in Supporting Information), thus showing the same trend found for the simpler RXH_2^+ ions (R = H, Me; see Table 1).

For the complexes with two substituted bridges, $[M_2(\mu\text{-}XR)_2L_4]$, the calculated MP2 energies for the six conformers of each model compound (**3**) are presented in Table 2, relative to that of the **pa** form. The most relevant optimized structural parameters are deposited as Supporting Information (Tables S1–S5). As a visual guide for the present discussion, we present in Figure 5 the relative energies of

Table 2. Calculated energies (kcal mol^{-1}) for the different conformers[a] of $[M_2(\mu\text{-}Y)(\mu\text{-}XR)L_4]$ and $[M_2(\mu\text{-}XR)_2L_4]$ complexes relative to that of the **po** or **pa** forms (see **3** and **5**).

M	Y	XR	L	**pp**	**po**	**bx**	**be**		
Pt	S	SH	PH_3	19.7[b]	0.0[b]	– 6.4	– 4.4		
Pt	S	SMe	PH_3	19.9[b]	0.0[b]	– 6.3	– 2.3		
				pp	**ps**	**pa**	**bx**	**be**	**ba**
Rh		OH	PH_3	5.9[b]	0.0[b]	0.0[b]	– 3.6	– 2.1	– 4.2
Rh		OMe	PH_3	3.8 (e)[b]	0.1 (e)[b]	0.0 (s)[b]	– 0.5 (e)	– 1.5 (e)	– 6.1 (s)
Rh		SH	PH_3	23.1[b]	0.2[b]	0.0[b]	– 9.3	– 8.7	– 9.8
Rh		SMe	PH_3	25.5 (s)[b]	0.6 (e)[b]	0.0 (s)[b]	– 1.4 (s)	– 3.9 (e)	– 6.2 (s)
Rh		SH	CO	19.8[b]	0.2[b]	0.0[b]	– 6.6	– 12.1	– 10.2
Ir		SH	PH_3	27.3[b]	0.0[b]	0.0[b]	– 10.4	– 9.6	– 10.6
Ni		OH	PH_3	1.1[b]	0.8[b]	0.0	2.7[b]	2.1[b]	1.7[b]
Ni		SH	PH_3	26.7[b]	0.5[b]	0.0[b]	– 1.4	– 0.1	– 2.0
Ni		SMe	PH_3	32.4 (s)[b]	1.5 (e)	0.0 (s)[b]	11.5 (e)[b]	9.8 (e)	3.8 (s)
Pd		SH	PH_3	32.1[b]	0.3[b]	0.0[b]	– 3.3	– 1.3	– 3.0
Pt		OH	PH_3	3.8[b]	0.3[b]	0.0	– 0.8	1.4[b]	0.1[b]
Pt		OMe	PH_3	4.1 (s)[b]	0.1 (e)[b]	0.0 (s)[b]	– 5.5 (e)	5.3 (e)[b]	0.4 (s)[b]
Pt		SH	PH_3	33.6[b]	0.3[b]	0.0[b]	– 2.8	– 0.3	– 2.3
Pt		SMe	PH_3	33.0 (e)[b]	0.9 (e)[b]	0.0 (s)[b]	7.3 (e)[b]	3.6 (e)	– 0.8 (s)
Au		SH	Me	25.1[b]	0.1[b]	0.0[b]	– 1.1	– 2.5	– 2.3
Au		SH	Cl	41.7[b]	0.2[b]	0.0[b]	5.1[b]	– 4.1	– 0.7
Au		SMe	Cl	40.9[b]	0.5[b]	0.0	19.3[b]	– 3.0	1.8[b]

[a] The relative orientation of the methyl groups is indicated in parentheses: e = eclipsed, s = staggered. [b] Not a minimum; θ or τ (or both) have been frozen for this calculation.

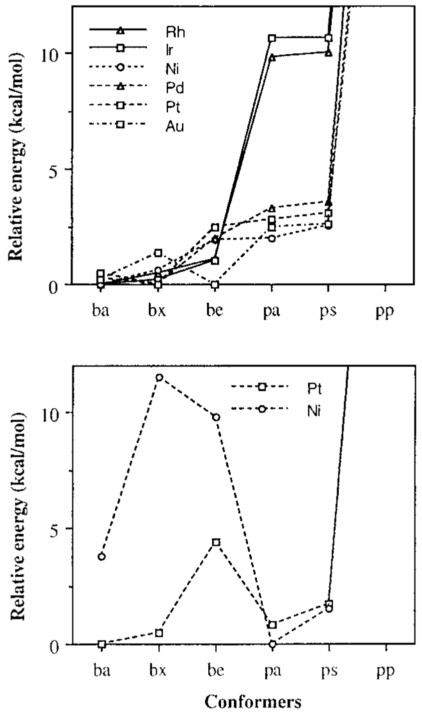


Figure 5. Calculated MP2 relative energies (kcal mol^{-1}) for the six conformers (**3**) of the $[M_2(\mu\text{-SR})_2L_4]$ compounds ($L = PH_3$ except for M = Au, for which L = Me) relative to the most stable one for each metal, with R = H (above) or Me (below).

the different conformers for the thiolato-bridged complexes. From the analysis of the calculated energies some general conclusions can be drawn. First, the oxygen and sulfur bridges show quite different behavior. For the hydroxo-bridged compounds, the energy differences between the six conformers are small for nickel and platinum, and larger for rhodium. Substitution of the hydrogen atom by a methyl group in the platinum compound enhances the differences between conformers.

In contrast, for X = S (Figure 5) the completely planar structure (**pp**) is highly unstable relative to the other five conformers in most cases. Such a difference is undoubtedly related to the much stronger tendency to pyramidalization of the sulfur atom compared with oxygen, as discussed above. In fact, the **pp** conformer is the most unstable one for all the studied compounds except for $[Ni_2(\mu\text{-OH})_2(PH_3)_4]^{2+}$. The remaining planar structures (**ps** and **pa**) are similar in energy to the bent forms for M = Ni, Pd, Pt, or Au. For M = Rh and Ir, though, all the planar structures are clearly less stable than the bent ones (Figure 5). The presence of the bulkier methyl group at the bridging atom destabilize the **be** conformer of nickel and platinum. Only for nickel is the **bx** conformer destabilized by introducing a methyl group, a fact that can be attributed to the shorter Ni–X distances that force a closer contact between the two R groups. These results suggest that interligand interactions play an important role in determining the preferred conformation.

It is worth noting that for X = O and M = Ni or Pt, only one energy minimum was found, whereas for M = Rh or Ir the three bent conformers appear to be minima in the potential-energy surface. A minimum was also found for every bent conformer of the compounds with X = S. These results suggest that there is a chance for some of the studied compounds to exist in more than one geometry and are probably associated to the relatively high barrier for inversion around the sulfur atom (let us recall that we have calculated 31 kcal mol^{-1} for an SH_3^+ group).

Another finding that is relevant for the subsequent discussion of the experimental data is related to the partial optimization of structures in which a planar environment was imposed on the bridging atom (i.e., $\Sigma = 360°$). Even if such a constraint is compatible with a structure of type **bx**, a planar structure was obtained unless the molecule was forced to bend by freezing the θ angle. These results suggest that sp^2 bridging atoms (as in $R_2C=S$) should favor the **pp** structure.

Molecular structures: We have shown in a previous study on analogous systems with unsubstituted bridges that there is a general good agreement between the optimized structural parameters and the experimental data. For the interested reader, structural parameters from 17 experimental data sets of 15 compounds are presented as Supporting Information (Table S5) together with those calculated for the corresponding conformers of eleven closely related model complexes. Despite the differences in substituents and terminal ligands, the agreement between calculated and experimental data is good except for $[Au_2(\mu\text{-SH})_2Me_4]$. The average error for the M–L distances is 0.03 Å, and 0.05 Å for the M–X distances. The largest differences appear in the angular parameters associated with the bridge substituents (τ and Σ). In the case of the OH bridge this may be due to the uncertainty associated with the determination of the position of the hydrogen atom in the X-ray diffraction experiment. In other cases, the differences between calculated and experimental values of τ and Σ can be attributed to the different substituent at the bridging atoms in the model and experimental molecules.

In this section we will try to summarize the most salient structural features of the calculated molecules (Tables S1–S4). 1) Among the complexes with the same metal atom, the bent forms show a larger degree of bending (smaller θ) for X = S than for X = O. This is a direct result of the longer M–X distance in the former case, thus requiring a larger bending to achieve a sufficiently short $M\cdots M$ contact. 2) Accordingly, the τ values are significantly smaller (and those of Σ larger) for the alkoxo than for the thiolato bridges, as expected from the above discussion on the pyramidalization of the X atom. Also, the M-X-M angles are significantly smaller for X = S than for X = O. 3) The **ps** and **pa** conformers of the same compound present the same value of τ ($\pm 1°$) for the XH and XMe bridges, indicating that such a structural parameter in the planar structures is little affected by steric problems, at least for the substituents explored. 4) The *exo* group in the **ba** conformers presents larger values of τ than in the corresponding **bx** structure, by 3–24° (comparing only structures found to be a minimum in the **ba** and **bx** forms), but no correlation can be found between these changes and the values of Σ. 5) The *endo* groups in bent structures give values in the range $17° < |\tau| < 28°$ for the OR and in the range $16° < |\tau| < 60°$ for the SR bridges, whereas the values for the *exo* groups appear in the ranges $62^\circ < \tau < 106^\circ$ and $80^\circ < \tau < 117^\circ$ for OR and SR bridges, respectively. 6) In those compounds with the **ba** conformation, the *exo* group is always more pyramidalized (smaller Σ value) than the *endo* one. 7) For every conformer, the substitution of the hydrogen by a methyl group results in a decrease of $|\tau|$ by at least 5° and, consistently, an increase in Σ of at least 10°. This result, combined with the previous observation suggests that the change in this parameter is due to an electronic rather than a steric substituent effect, as confirmed by the fact that $MeXH_2^+$ shows a larger Σ value than XH_3^+ (for X = S, Se, Te, Table 1).

Since the effect of the terminal ligands has been previously discussed[24, 25, 35] for the stacking $d^8\cdots d^8$ interactions and for the bent binuclear complexes with unsubstituted bridges, we have not varied the terminal ligands in a systematic way in the present study. Nevertheless, the results for the gold complexes with methyl and chloro terminal ligands are consistent with the general rule that a combined poor σ-donor and good π-donor character induces a poorer metal$\cdots$metal interaction, whereas the good σ-donor and π-acceptor ligands favor the bonding nature of such interaction. This is reflected in bending angles of 136° and 120° for the **ba** form with Cl or Me as terminal ligands, respectively.

Interaction terms: From the energy differences between the different conformers (**3** and **5**), one can obtain a rough estimate of the different contributions to their relative stability, neglecting ligand–substituent interactions in the **pp** conformer. For the compounds with mixed bridges those interaction terms can be estimated through Equations (1)–(3), in which the subindices for the calculated energies indicate the conformer (**5**).

$$V_X = E_{po} - E_{pp} \tag{1}$$

$$I_{MM} = E_{bx} - E_{po} \tag{2}$$

$$I_{LR} = E_{be} - E_{bx} \tag{3}$$

The symbol I is used for the estimated interaction energies between the two metal atoms and their terminal ligands in the bent forms (I_{MM}), or between the substituent and terminal ligand in the *endo* form (I_{LR}). V_X represents the energy difference between planar and pyramidal conformations of the substituted bridging X atom. The estimated contributions will be discussed below together with the data obtained for compounds with two substituted bridges.

For the compounds with two substituted bridges, an estimate of the different contributions to the total energy of the various conformers can also be obtained, assuming that ligand–substituent interactions are only siginificant for the *endo* substituents, and substituent–substituent interactions only in the **bx** form. Also, we assume that the structural parameters are similar for the different conformers, except for the interplanar angle θ when comparing planar and bent structures, and for the orientation of the substituent (τ angle) when comparing *endo*, *exo* or coplanar orientations. The expressions employed for the estimation of such interaction terms are given in Equations (4)–(7).

$$V_X = (E_{pa} - E_{pp})/2 \tag{4}$$

$$I_{LR} = E_{be} - E_{ba} \tag{5}$$

$$I_{MM} = E_{ba} - E_{pa} - I_{LR} \tag{6}$$

$$I_{RR} = E_{bx} - E_{ba} + I_{LR} \tag{7}$$

In Equations (4)–(7), the subindices for the calculated MP2 energies correspond to the conformations defined in **3**. In addition to the interaction terms described before, we introduce here the interaction between the substituents in the *exo* form (I_{RR}). For $[Pt_2(\mu\text{-}SMe)_2(PH_3)_4]^{2+}$, the optimization of the **bx** conformer resulted in a relatively large interplanar angle ($\theta = 160)^\circ$, compared with 113–124° in **be** and **ba** structures. In order to make the contributions calculated from Equations (4)–(7) sensible, we used the **bx** calculated energy with a similar degree of bending ($\theta = 119^\circ$), instead of that of the minimum.

It must be kept in mind that not only the conformation changes from one structure to another, but also structural parameters such as the bending angle θ, the M$\cdots$M distance, the position of the R group measured by τ, or other bond distances and angles. Hence, one should expect the calculated energy contributions to provide only a rough estimate of the relative importance of different terms and of the way in which they change upon substitution of one of the constituents of the complex (metal atom, bridging atom, or substituent).

Pyramidalization of the bridging atom: The stabilization obtained on going from a planar to a pyramidal conformation of the M_2XR group, measured by the V_X term (Table 3), is small for X = O (1–3 kcal mol^{-1}) and larger for X = S (12–20 kcal mol^{-1}). Notice that it depends mainly on the nature of the X atom, while the substituent and the metal atom are responsible for smaller variations in V_X. The differences in the V_X values for the different compounds with X = O are associated to the different degrees of pyramidalization of X (Σ values) found in the optimized **pa** structures used to estimate V_X [Eqs. (1) and (4)]. For X = S, in contrast, no clear correlation is found between V_X and Σ. The relative values of V_X for oxygen and sulfur are smaller than those calculated for the corresponding XH_3^+ ions; this is in agreement with the finding that the coordination of a sulfur lone pair to a transition metal significantly lowers the barrier to pyramidal inversion, and with barriers of approximately 15–18 kcal mol^{-1} reported for the MSR_2 groups in mononuclear complexes of Pd^{II}, Ir^{I} or Au^{III},[27, 30, 31] compared with 24–36 kcal mol^{-1} for R_3S^+ groups.[1, 27] Since the tendency of selenium towards pyramidalization is similar to that of sulfur, the V_X values presented for thiolato bridges in Table 3 can be taken as reasonable estimates for analogue selenolato-bridged compounds.

Table 3. Estimated contributions [kcal mol^{-1}] to the energies of the different conformations of binuclear compounds with monosubstituted bridges [Eqs. (1)–(7)]. V_X values calculated for the XH_3^+ ions (X = O, S, Se, Te) included for comparison. For the definition of E_{a1}, E_{a2}, and E_{a3} see **8** and Equations (8)–(10) later.

Compd.	V_X	I_{MM}	I_{LR}	I_{RR}	E_{a1}	E_{a2}	E_{a3}
OH_3^+	−4.4						
SH_3^+	−31.0						
SeH_3^+	−39.8						
TeH_3^+	−47.0						
$[Rh_2(\mu\text{-}OH)_2(PH_3)_4]$	−3.0	−6.3	2.1	2.7	4.2	3.8	2.1
$[Rh_2(\mu\text{-}OMe)_2(PH_3)_4]$	−1.9	−7.6	1.5	2.0	6.1	2.3	4.6
$[Rh_2(\mu\text{-}SH)_2(PH_3)_4]$	−11.6	−10.9	1.1	1.6	9.8	22.0	8.7
$[Rh_2(\mu\text{-}SMe)_2(PH_3)_4]$	−12.8	−8.5	2.3	7.1	6.2	23.2	3.9
$[Rh_2(\mu\text{-}SH)_2(CO)_4]$	−9.9	−8.3	−1.9	1.8	10.2	21.7	12.1
$[Ir_2(\mu\text{-}SH)_2(PH_3)_4]$	−13.7	−11.6	1.0	1.2	10.6	26.4	9.6
$[Ni_2(\mu\text{-}OH)_2(PH_3)_4]^{2+}$	−0.6	1.3	0.4	0.6	–	0.8	–
$[Ni_2(\mu\text{-}SH)_2(PH_3)_4]^{2+}$	−13.3	−3.9	1.9	2.5	2.0	24.8	0.1
$[Ni_2(\mu\text{-}SMe)_2(PH_3)_4]^{2+}$	−16.2	−2.1	5.9	13.6	–	26.5	–
$[Pd_2(\mu\text{-}SH)_2(PH_3)_4]^{2+}$	−16.0	−4.8	1.7	1.4	3.0	35.1	1.4
$[Pt_2(\mu\text{-}OH)_2(PH_3)_4]^{2+}$	−1.9	−1.2	1.3	0.4	0	2.5	–
$[Pt_2(\mu\text{-}OMe)_2(PH_3)_4]^{2+}$	−2.0	−4.4	4.9	−1.0	0	–	–
$[Pt_2(\mu\text{-}SH)_2(PH_3)_4]^{2+}$	−16.8	−4.2	1.9	1.4	2.3	31.6	0.4
$[Pt_2(\mu\text{-}SMe)_2(PH_3)_4]^{2+}$	−16.0	−5.2	4.4	4.9	0.8	27.7	–
$[Pt_2(\mu\text{-}S)(\mu\text{-}SH)(PH_3)_4]^+$	−19.7	−6.4	2.0	–	4.4	17.7	4.4
$[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PH_3)_4]^+$	−19.9	−6.3	4.0	–	2.3	15.9	2.3
$[Au_2(\mu\text{-}SH)_2Me_4]$	−12.5	−2.2	−0.2	1.1	2.4	25.2	2.6
$[Au_2(\mu\text{-}SH)_2Cl_4]$	−20.9	2.7	−3.4	2.4	0.7	45.1	4.1
$[Au_2(\mu\text{-}SMe)_2Cl_4]$	−20.4	6.7	−4.8	12.7	–	45.6	2.9

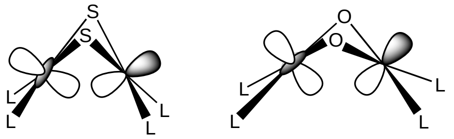
Ligand$\cdots$Substituent interaction: The term representing the ligand$\cdots$substituent interaction, I_{LR}, is positive in most cases, thus representing a steric repulsion. Such repulsion appears to be small for L = PH_3 or Me and R = H (0 – 2 kcal mol^{-1}) when X = O or S. Substitution of the hydrogen atom by a methyl group results in an increased repulsion by about 3 kcal mol^{-1} per each R group. These results reflect the destabilization of the **be** form by the increased steric bulk of the terminal ligands or of the substituents at the bridging atom. The **ba** conformation, in turn, is less affected by these steric factors, since only one L$\cdots$R interaction is present in this conformer. It must be stressed, however, that the L$\cdots$R repulsions are minimized in the case of the SMe bridge by readjusting the orientation of the substituent. Thus, the τ angle is reduced by up to 30° upon methyl substitution in the *endo* conformer (Tables S1–S4). Notice that the L$\cdots$R interactions are expected to be much weaker for those complexes with a bidentate ligand spanning a terminal and a bridging position (**7c**; for structure see section on nickel compounds).

An interesting situation appears for the cases of $[Au_2(\mu\text{-}SH)_2Cl_4]$, $[Au_2(\mu\text{-}SMe)_2Cl_4]$, and $[Rh_2(\mu\text{-}SH)_2(CO)_4]$, for which I_{LR} seems to be attractive (Table 3). In the former case this might be due to incipient hydrogen bonds of the type S–H$\cdots$Cl (Cl$\cdots$H = 3.1 Å) in the *endo* forms, well within the range found for other X–H$\cdots$Cl hydrogen bonds[36] involving coordinated chlorides. The possible existence of weak attractive Cl$\cdots$H–C interactions in the second case is consistent with experimental evidence found in the structures of two polymorphic forms[37] of *cis*-$[PtCl_2(PMePh_2)_2]$, in which the shortest Cl$\cdots$H (phosphine) distance (2.71 Å) is associated with the smallest Cl-Pt-P bond angle (83.3°). As for the third case, interactions between hydrogen atoms and carbonyl groups have not been systematically studied from a theoretical point of view, but experimental data supporting the existence of such interactions can be found in the literature. A nice example in a compound related to those studied here has been given by Terreros et al.,[38] who showed that the coordinated carbonyl group in *trans*-$[Rh(SC_6F_5)(CO)(PPh_3)_2]$ presents contacts to hydrogen atoms of the phenyl groups at 2.5–2.7 Å, and the CO stretching mode is shifted by 50 cm^{-1} to lower wavenumbers compared with a polymorph of the same compound showing no such contacts. A similar differential behavior was reported for the interaction between the methyl group of a methylcyclopentadienide and a carbonyl ligand in the two polymorphic forms of a manganese complex.[39] A detailed account of the existence of weak hydrogen bonds to carbonyl groups coordinated to transition metal atoms has been recently reported by Braga, Desiraju, and co-workers.[40] We will show below that the existence of such weak attractions between the carbonyl groups and alkyl or aryl substituents at the bridging atoms may explain the experimental conformations found for a handful of carbonyl complexes.

Substituent$\cdots$substituent interaction: The repulsion between the hydrogen atoms in the **bx** form of the hydroxo-bridged compounds (I_{RR} term) is small (less than 1 kcal mol^{-1}), except for the rhodium derivative, for which the hydrogen atoms are closer (compare $\tau = 95°$ for Rh with $\tau = 66$ and 71° for Ni and Pt, respectively). Such repulsion is slightly larger in the case of the thiolato bridge (1–3 kcal mol^{-1}), and is also associated with the larger τ values in the thiolato than in the alkoxo bridges. Substitution of the hydrogen atoms by the bulkier methyl group results in an increase of I_{RR} by up to 11 kcal mol^{-1}. These results clearly reflect the strong destabilization of the *exo* forms by the steric bulk of the substituents. For the methoxo-bridged platinum complex, the small degree of pyramidalization required by the bridging oxygen atom results in a relatively small angle τ (69° compared with 105° for SH and 80° for SMe) that makes the I_{RR} term negligible. Obviously, the repulsion between the two substituents, I_{RR}, should be expected to be negligible whenever a bidentate ligand occupies the two bridging positions (**7e**). Although this case is not considered by our model calculations, it is easy to discount the I_{RR} contributions to obtain a sensible estimate of the relative energies of the different conformers when bidentate bridges are present.

Metal$\cdots$metal and ligand$\cdots$ligand interactions: The effect of the M$\cdots$M and L$\cdots$L interactions that appear combined in the I_{MM} term is small and negative in most cases (Table 3). Comparison of the series of compounds $[M_2(\mu\text{-}SH)_2(PH_3)_4]^{n+}$ (M = Ni, Pd, Pt, Rh, Ir) and $[Au_2(\mu\text{-}SH)_2Me_4]$ shows that $|I_{MM}|$ increases in the following order: Au < Ni ≈ Pd ≈ Pt < Rh ≈ Ir. For instance, for all platinum complexes the I_{MM} values lie between −1 and −6 kcal mol^{-1}; this is consistent with the stabilization energy obtained by bending the unsubstituted analogues $[Pt_2(\mu\text{-}X)_2(PH_3)_4]$ of −4.0 and −4.8 kcal mol^{-1} for X = O and S, respectively.[24] For systems with the same metal and terminal ligands, the stabilization is larger for the thiolato- than for the hydroxo-bridged complex;

a result that can be attributed to the softer nature of the sulfur atom and to the longer M–X distance that allows for a better orbital overlap (**6**). The fact that the I_{MM} term for the OMe-bridged platinum compound is significantly more stabilizing than the corresponding value for the OH-bridged analogue should be attributed to a shorter Pt$\cdots$Pt contact achieved by the **bx** conformer in the former case (3.071 vs. 3.135 Å). Notice that for the compounds of gold with L = Me$^-$ and Cl$^-$ the terminal ligand has a strong influence on the I_{MM} value. This can be attributed to the combination of two effects: a) the enhancement of the M$\cdots$M attraction by the soft terminal ligands (Me$^-$) compared with a harder π-donor[35] and b) the stronger L$\cdots$L repulsion for the bulkier ligands (Cl$^-$).



6

Analysis of the structural data for compounds with mixed bridges

Having learnt about the factors that influence the structural choice from a theoretical point of view, it is appropriate to analyze the available structural data for several families of compounds (Tables 4–9) and verify how the theoretical predictions can be of help in rationalizing the experimental structures. We note that in this family only the structures of thiolato-bridged compounds have been reported. In this case, even for a weak M$\cdots$M interaction the bent structure **bx** is expected to be the most stable one (Table 2), favored by the attractive I_{MM} term and by the absence of an I_{LR} repulsion term. Hence it is no surprise that most of the compounds of this type reported so far have a **bx** structure with a fairly large angle τ for the *exo* substituent ($78° < \tau < 116°$, in excellent agreement with the calculated values, $\tau = 116$ and 100° for R = H and Me, respectively), compared with those found for compounds with two substituted bridges in an *anti* conformation ($54° < \tau < 84°$, Tables 5–9, consistent with the values calculated for $[\mathrm{Pt_2}(\mu\text{-SR})_2(\mathrm{PH_3})_4]$, 80 and 73° for R = H and Me, respectively). Nevertheless, the **be** structure can be adopted for those combinations of terminal ligand and substituent that give a small or negative I_{LR} term. Computationally, we have found such an effect with CO as terminal ligand in $[\mathrm{Rh_2}(\mu\text{-SH})_2(\mathrm{CO})_4]$; this is consistent with the experimental structure of the *cis*-dicarbonyl complexes **A.15** and **A.16** in which the *endo* substituent occupies the position close to the CO ligands. Notice that in the *cis*-$[\mathrm{M_2}(\mu\text{-Y})(\mu\text{-XR})(\mathrm{CO})_2\mathrm{L_2}]$ compounds (**A.11–16**), the terminal ligands that are vicinal to the substituted bridge are the carbonyls, whereas for *cis*-$[\mathrm{M_2}(\mu\text{-Y})(\mu\text{-XR})\mathrm{Cl_2}(\mathrm{PR_3})_2]$ (**A.2–5** and **A.10**), the vicinal positions are occupied by the phosphines. It is not clear in the light of the present theoretical study why compounds **A.6** and **A.7** appear in the **po** structure.

Analysis of the structural data for $[\mathrm{M_2}(\mu\text{-XR})_2\mathrm{L_4}]$ compounds

Let us stress that the presence of a double bond between the bridging atom and its substituent imposes a planar coordination around X (i.e., $\Sigma \approx 360°$), in contrast with bridges such as RO$^-$ or RS$^-$ for which their bridging atom can adopt an sp^3 hybridization. In this paper we will not consider the former type of complexes, since for them a **pp** structure is favored by the sp^2 bridging atom. Let us just mention some compounds of **pp** structure that will not be considered in the subsequent discussion, such as a nickel complex with a macrocyclic ligand,[54] or nickel and platinum compounds with SNSN^{2-} or SeNSeN^{2-} ligands,[55–58] in which the bridging sulfur or selenium atoms have double bonds to nitrogen atoms. A similar situation appears[59] for the bridging azido groups in $[\mathrm{Pd_2}(\mu_1\text{-N_3})_2(\mathrm{N_3})_4]^{2-}$. Still, in these compounds, small deviations of the substituents from the molecular plane can be observed (e.g., $\tau = 2$ and 15° for the two nickel compounds). The largest deviation appears in a rhodium compound with an iminic bridging nitrogen atom,[60] in which bending of the metal coordination spheres ($\theta = 123°$, Rh$\cdots$Rh = 2.83 Å) is made compatible with a trigonal planar geometry around the nitrogen atom ($\Sigma = 360°$).

Table 4. Structural data (**2**, distances in Å, angles in degrees) for dimers of d^8 metal ions with mixed bridges, $[\mathrm{M_2}(\mu\text{-Y})(\mu\text{-XR})\mathrm{L_4}]$.

	Compound	M$\cdots$M	θ	τ	Σ	struct.	ref.	refcode
A.1	*cis*-$[\{\mathrm{Pd}(\mu\text{-Cl})(\mu\text{-SMe})\}_2(\mu\text{-SMe})_2(\mathrm{dppm})_2]$	3.027	118	99	294	**bx**	[41]	ziscej
		3.053	121	99	292	**bx**		
A.2	*cis*-$[\mathrm{Pd_2}(\mu\text{-Cl})(\mu\text{-S}t\mathrm{Bu})\mathrm{Cl_2}(\mathrm{PMe_3})_2]$	3.209	140	85	307	**bx**	[42]	junxiz
A.3	*cis*-$[\mathrm{Pd_2}(\mu\text{-Cl})(\mu\text{-SEt})\mathrm{Cl_2}(\mathrm{PMe_2Ph})_2]$	3.234	136	96	295	**bx**	[43]	kifdae
A.4	*cis*-$[\mathrm{Pd_2}(\mu\text{-Cl})(\mu\text{-SMe})\mathrm{Cl_2}(\mathrm{PMe_3})_2]$	3.296	146	92	297	**bx**	[42]	junxev
A.5	*cis*-$[\mathrm{Pd_2}(\mu\text{-Cl})(\mu\text{-SC_3H_6Cl})\mathrm{Cl_2}(\mathrm{PMe_3})_2]$	3.305	150	79	310	**bx**	[44]	jityiu
		3.353	157	78	307	**bx**		
A.6	*cis*-$[\mathrm{Pd_2}(\mu\text{-Cl})(\mu\text{-SPh})\mathrm{Cl_2}(\mathrm{PMe_3})_2]$	3.407	176	– 69	301	**po**	[42]	junxof
A.7	*cis*-$[\mathrm{Pt_2}(\mu\text{-Cl})(\mu\text{-TePh})\mathrm{Cl_2}(\mathrm{P}n\mathrm{Bu_3})_2]$	3.670	176	– 72	295	**po**	[45]	jozjaj
A.8	$[\mathrm{Pt_2}(\mu\text{-S})(\mu\text{-SAuPPh_3})(\mathrm{PPh_3})_4]^+$	3.279	136	116	263	**bx**	[46]	factuy
A.9	$[\mathrm{Pt_2}(\mu\text{-S})(\mu\text{-SMe})(\mathrm{PPh_3})_4]^+$	3.306	138	95	293	**bx**	[47]	daxtif
A.10	*cis*-$[\mathrm{Pt_2}(\mu\text{-Cl})(\mu\text{-SEt})\mathrm{Cl_2}(\mathrm{PMe_2Ph})_2]$	3.299	138	95	299	**bx**	[48]	junxar
A.11	*cis*-$[\mathrm{Rh_2}(\mu\text{-Cl})(\mu\text{-SC_6H_9Me}i\mathrm{Pr})(\mathrm{CO})_2(\mathrm{As}t\mathrm{Bu_3})_2]$	3.233	126	99	295	**bx**	[49]	sopkud
A.12	*cis*-$[\mathrm{Rh_2}(\mu\text{-Cl})(\mu\text{-SC_6H_9Me}i\mathrm{Pr})(\mathrm{CO})_2(\mathrm{P}t\mathrm{Bu_3})_2]$	3.286	127	99	296	**bx**	[50]	jongoi
A.13	*cis*-$[\mathrm{Rh_2}(\mu\text{-Cl})(\mu\text{-S}t\mathrm{Bu})(\mathrm{CO})_2(\mathrm{As}t\mathrm{Bu_3})_2]$	3.411	144	83	309	**bx**	[51]	deldih
A.14	*cis*-$[\mathrm{Rh_2}(\mu\text{-Cl})(\mu\text{-S}t\mathrm{Bu})(\mathrm{CO})_2(\mathrm{P}t\mathrm{Bu_3})_2]$	3.456	145	82	311	**bx**	[52, 53]	cbtpri10
A.15	*cis*-$[\mathrm{Rh_2}(\mu\text{-Cl})(\mu\text{-SCH_2C_6H_9CMe_2})(\mathrm{CO})_2(\mathrm{P}t\mathrm{Bu_3})_2]$	3.316	122	– 18	321	**be**	[50]	jongic
A.16	*cis*-$[\mathrm{Rh_2}(\mu\text{-Cl})(\mu\text{-SC_6H_4Cl})(\mathrm{CO})_2(\mathrm{P}t\mathrm{Bu_3})_2]$	3.440	128	– 24	319	**be**	[52]	coltus

0947-6539/99/0505-1399 $ 17.50+.50/0

The experimental absolute values of the τ angles for the compounds with X = S, Se, or Te, and a variety of metal atoms and terminal ligands (Tables 4–9) follow the same trend as the theoretical prediction: $|\tau|$ appears in the range 13–59° for the *endo* groups in **ba** and **be** structures (calculated values: 16–60°, Tables S1–S4), 47–96° in the **pa** and **po** compounds (73–83° computationally), and 83–128° for the *exo* groups in the **ba** and **bx** structures (80–124° in our calculations, Tables S1–S4). As found in our calculations, the *exo* group is always more pyramidalized (smaller Σ value) than the *endo* one in compounds with an *anti* geometry.

Rhodium and iridium compounds: Given the tendency of the rhodium and iridium complexes to form M···M contacts (see I_{MM} values in Table 3), owing to the diffuse nature of their atomic orbitals, it is not strange that all their complexes are bent with only four exceptions (Table 5). Most complexes with hydroxo or alkoxo bridges appear in a **bx** conformation (**B.1**–**7**), which is expected from our model calculations to be practically isoenergetic with the **be** one (Table 2). In one case (**B.2**), the *exo* orientation is forced by chemically binding the two bridging atoms. The few rhodium and iridium compounds that appear in a planar conformation (**B.8**–**11**) all have oxygen as the bridging atom, the case for which our calculations (Table 2) predict its energy to be closest to that of the bent forms. Furthermore, the fact that these compounds do not behave as expected from our calculations can be easily understood by looking at the differences in L and R groups between the model and the real compounds. For instance, compounds **B.10** and **B.11** have bulky phosphines as terminal ligands, making the I_{MM} term less negative than in our analogous model, $[Rh_2(\mu\text{-}OH)_2(PH_3)_4]$, thus destabilizing the bent conformations relative to the **ps** and **pa** ones. The same behavior is found for analogous rhodium complexes with unsubstituted bridges[24] such as Cl^-, for which the only planar complexes are those having bulky PPh_3 or $PiPr_3$ as terminal ligands. In another case (compound **B.9**), the bent structure is clearly prevented by the two *ortho*-phenyl substituents of the phenoxo bridging group. Finally, the **pp** structure of compound **B.8**, is not easy to rationalize, since that structure is

Table 5. Structural data (**2**, distances in Å, angles in degrees) for binuclear complexes of d^8 metal ions of formula $[M_2(\mu\text{-}XR)_2L_4]$ (M = Rh, Ir). For the **ba** structures, the parameters τ and Σ corresponding to the *endo* XR group are given first, those for the *exo* groups in the second place.

	Compound	M···M	θ	τ	Σ	struct.	ref.	refcode
B.1	$[Rh_2(\mu\text{-}OSiPh_3)_2(CO)_4]$	2.926	130	37	357	**bx**	[61]	lihwuu
B.2	$[(cod)_2Rh_2(\mu,\eta^2\text{-}OTi\{OtBu\}_2O)_2Rh_2(cod)_2]$	2.791	125	54	347	**bx**	[62]	hehdaz
B.3	$[Rh_2(\mu\text{-}OEt)_2(cod)_2]$	2.853	121	1	342	**bx**	[63]	telbuh
B.4	$[Rh_2(\mu\text{-}OH)_2(cod)_2]$	2.878	124			**b**	[64]	yivwop
B.5	$[Rh_2(\mu\text{-}OSiMe_3)_2(cod)_2]$	2.810	123	54	350	**bx**	[65]	zijxev
B.6	$[Rh_2(\mu\text{-}OSiMe_3)_2(nbd)_2]$	2.983	135	25	359	**bx**	[66]	tukpoe
B.7	$[Rh_2(\mu\text{-}OSiPh_3)_2(cod)_2]$	2.785	117	46	354	**bx**	[61]	lihwoo
B.8	$[Rh_2(\mu\text{-}OMe)_2(cod)_2]$	3.231	180	4	360	**pp**	[67]	buhton
B.9	$[Rh_2(\mu\text{-}OC_6H_3Ph_2)_2(CO)_4]$	3.270	177	6	360	**pp**	[68]	kihlui
B.10	$[Rh_2(\mu\text{-}OH)_2(PPh_3)_4]$	3.278	180	21	354	**pa**	[69]	sacdij
B.11	$[Rh_2(\mu\text{-}OH)_2(PiPr_3)_4]$	3.330	173	77		**pa**	[70]	tesmuz
B.12	$[Rh_2(\mu\text{-}SPh)_2(CO)_4]$	3.097	116	– 29	304	**be**	[71]	pefler
		3.087	115	– 27	306	**be**		
B.13	$[Rh_2(\mu\text{-}SC_6H_4F)_2(CO)_4]$	3.076	115	– 28	304	**be**	[72]	vihwue
		3.070	114	– 26	307	**be**		
B.14	$[Rh_2(\mu\text{-}SEt)_2(CO)_4]$	2.820	102	– 25	298	**be**	[71]	pefliv
B.15	$[(cod)Rh(\mu\text{-}SPh)_2Rh(CO)_2]$	3.119	114	– 20	315	**be**	[12]	tpchrh
B.16	$[Rh_2(\mu\text{-}S\{CH_2\}_3NMe_2)_2(cod)_2]$	2.960	106	– 16	313	**be**	[73]	yajmeb
B.17	$[Rh_2(\mu\text{-}S\{CPh{=}NR\})_2(cod)_2]$	3.517	142	– 26	329	**be**	[20]	rijgia
		3.527	143	– 26	330	**be**		
B.18	$[Rh_2(\mu\text{-}SMe)_2(cod)_2]$	2.947	105	– 17	312	**be**	[74]	jesteg
B.19	$[Rh_2(\mu\text{-}SC_6H_4\text{-}o\text{-}NHMe)_2(cod)_2]$	3.481	146	– 32	325	**be**	[75]	
B.20	$[Rh_2(\mu\text{-}SC_6F_5)_2(cod)_2]$	2.955	118	92	296	**bx**	[76]	dodtar
B.21	$[Rh_2(\mu\text{-}SC_6F_4H)_2(cod)_2]$	2.956	118	91	298	**bx**	[77]	jissot
B.22	$[Rh_2(\mu,\eta^2\text{-}S\{CH_2\}_3S)(cod)_2]$	2.896	112	100	289	**bx**	[78]	wayjub
B.23	$[Rh_2(\mu,\eta^2\text{-}S\{CH_2\}_2S)(cod)_2]$	2.876	104	114	275	**bx**	[78]	wayjov
B.24	$[Rh_2(\mu\text{-}S_2CNMePh)(cod)_2]^+$	2.895				**bx**	[79]	
B.25	*trans*-$[Rh_2(\mu\text{-}SC_6H_4PPh_2)_2(CO)_2]$	2.979	113	– 35	292	**be**	[80]	zapgus
B.26	$[Rh_2(\mu\text{-}SC_{12}H_6\text{-}C_{12}H_6S)(P\{OC_6H_4tBu\}_3)(CO)_3]$	2.973	109	– 16, 103	317, 290	**ba**	[81]	zunciu
B.27	*cis*-$[Rh_2(\mu\text{-}StBu)_2(CO)_2(dppf)]$	3.089	119	– 26, 88	312, 308	**ba**	[82]	sacjov
B.28	*cis*-$[Rh_2(\mu\text{-}StBu)_2(CO)_2(PPh_3)_2]$	3.103	118	– 20, 88	319, 310	**ba**	[83]	jiftex
B.29	*cis*-$[Rh_2(\mu\text{-}SPh)_2(CO)_2(PMe_3)_2]$	3.061	115	– 25, 101	309, 291	**ba**	[84]	cpmprh
B.30	*cis*-$[Rh_2(\mu\text{-}StBu)_2(CO)_2(\{tBuC_5H_4\}_2Zr\{CH_2PPh_2\}_2)]$	3.044	114	– 19, 90	317, 307	**ba**	[85]	jesbeo
B.31	*cis*-$[Rh_2(\mu\text{-}StBu)_2(CO)_2(PPh_2\{C_2H_4NMe_2\})_2]$	3.038	113	– 20, 90	318, 307	**ba**	[86]	yipxea
B.32	*cis*-$[Rh_2(\mu\text{-}StBu)_2(CO)_2(dppb)]$	3.038	113	– 19, 91	315, 306	**ba**	[82]	sacjip
B.33	$[Ir_2(\mu\text{-}SPh)_2(CO)_4]$	3.104	115	– 29	303	**be**	[87]	bztirc10
		3.106	115	– 31	300	**be**		
B.34	$[Ir_2(\mu\text{-}S\{CH_2\}_3NMe_2)_2(cod)_2]$	2.960	106	– 15	314	**be**	[19]	zazzef
B.35	$[Ir_2(\mu\text{-}SPh)_2(cod)_2]$	3.181	117	– 13	325	**be**	[18]	gempap
B.36	$[Ir_2(\mu\text{-}SC_6F_5)_2(CO)_4]$	3.066	114	– 25, 100	307, 294	**ba**	[88]	wethuy
B.37	*cis*-$[Ir_2(\mu\text{-}StBu)_2(CO)_2(P\{OMe\}_3)_2]$	3.216	123	– 23, 85	318, 313	**ba**	[89]	sbupir

expected to be the less stable one for rhodium and iridium under any circumstances.

To illustrate the predictive ability of the model calculations it is worth discussing with some detail the family of thiolato-bridged rhodium and iridium complexes with cyclooctadiene (COD) as bidentate terminal ligand, **B.16**–**24** and **B.34**–**35**. From the model calculations with phosphine or carbonyl terminal ligands (Table 2), bent structures should be expected in any case, as experimentally found in this family. However, the conformation of the bridging ligands is not so easy to predict, since the three conformers of the model compounds with hydrogensulfide bridge are calculated to be practically isoenergetic (Table 2). Even if the calculations with methylthiolato-bridges and phosphine terminal ligands predict the **ba** conformation to be more stable, none of the structurally characterized COD complexes present such structure. Several compounds (**B.16**–**19** and **B.34**–**35**) crystallize with the **be** conformation, which is predicted to be the most stable one with carbonyl terminal ligands. For compounds **B.22**–**24**, which are found in the **bx** conformation, other structures are precluded by the bidentate nature of the bridging ligands (**7e**). Rhodium compounds with polyfluorophenyl substituents (**B.20**–**21**) probably constitute a special case, with **bx** structures and the two aromatic substituents arranged in a face-to-face stacking with distances between the centroids of 3.45 and 3.48 Å, respectively. Two possible explanations can be sought for this fact: either the I_{LR} term disfavors the *endo* orientation of the polyfluorophenyl substituents, or an attractive stacking interaction substitutes the I_{RR} repulsion. From the structural data for $[Zn(C_6F_5)_2]$, which presents an intermolecular stacking arrangement of the C_6F_5 groups at practically the same distance (3.5 Å),[90] the second hypothesis is favored.

Practically all the thiolato-bridged complexes with four terminal carbonyl ligands (**B.12**–**14** and **B.33**) behave as predicted by our calculations on $[Rh_2(\mu\text{-}SH)_2(CO)_4]$, for which **be** is the most stable conformation. The only exception is an iridium compound with $R = C_6F_5$ and a **ba** conformation (**B.36**). The fact that the iridium carbonyl complex prefers the **ba** conformation, whereas the rhodium-COD compound with the same bridges prefer the **bx** structure, should be taken as an indication of the delicate balance between the I_{LR} and I_{RR} terms: the bulkier cyclooctadiene ligand may produce larger I_{LR} repulsion than the carbonyls thus disfavoring the *endo* position of a pentafluorophenyl group in the **ba** structure. A clear corollary is that an evaluation of such terms for a variety of L and R groups should be needed before one is able to predict beforehand the conformations of real compounds.

There are no structurally characterized rhodium or iridium compounds with thiolato bridges and phosphines as terminal ligands. Our calculations predict $[Rh_2(\mu\text{-}SH)_2(PH_3)_4]$ to be more stable in the **bx** conformation, indicating that the *endo* position of the R group is disfavored; this in contrast with the terminal carbonyls for which the *endo* position is preferred. Consistently, compounds of the type *cis*-$[M_2(\mu\text{-}SR)_2(CO)_2(PR_3)_2]$ (**B.27**–**32**, **B.37**) and $[Rh_2(\mu\text{-}SR)_2(CO)_3(PR_3)]$ (**B.26**) appear in the **ba** conformation, with the *endo* substituents at the side of the molecule with two carbonyl ligands. In agreement with the weak attractive interaction found between a terminal carbonyl ligand and alkyl substituents, all the structures of the *cis*-biscarbonyl complexes of rhodium (**B.27**–**32**) and iridium (**B.37**) present a **ba** conformation with relatively short OC···H (2.5–2.6 Å) or OC···C (3.2–3.5 Å) contacts to organic groups attached to the bridging atom; this is well in the range accepted by Braga, Desiraju, and co-workers[40] as weak C–H···O hydrogen bonds in organometallic carbonyl complexes. A different case is that of a compound with two *trans* carbonyls, in which the bidentate ligands spanning one terminal and one bridging position (**B.25**) impose the **be** conformation, as will be also found below for other metals.

Nickel compounds: Given the weak Ni···Ni attraction found in our calculations (see I_{MM} term in Table 3), the most favorable conformation for the nickel compounds is expected to be **pa**, except for the specific case of the SH^- bridges, for which the bent structures can be slightly more stable. Accordingly, a number of structures are found for that conformation with alkoxo and thiolato bridges (**C.3**–**11**; Table 6). The planar structure can be thought to be imposed by a rigid pentadentate ligand in one case (**C.4**), and the out of plane shift of the hydrogen atom of the bridging hydroxo group is favored by hydrogen bonding with a neighboring perchlorate anion (2.21 Å). In other cases, though, the choice can probably be attributed to the combined electronic and steric factors summarized in Table 3. Even for the little sterically demanding hydroxo bridges (i.e., with a very small I_{RR} term, see Table 3), the ligand···ligand repulsion introduced by bulky terminal ligands such as C_6F_5 or diphenyl substituted phosphine (**C.1** and **C.2**), probably overweighs the weak Ni···Ni attraction, yielding a positive I_{MM} interaction term that favors the planar structure. Although the position of the hydrogen atoms of the hydroxo bridges are not well determined from the crystal structure in those cases, our model calculations clearly point to an out of plane position of those atoms.

According to the general trends discussed above, the **bx** structure is energetically favorable only for the case of the hydrogensulfide bridge, is slightly more unstable than the **pa** form for a hydroxo bridge, and clearly unstable for bulkier thiolato bridges. Such conformation is actually found in three compounds with alkoxo bridges (**C.12**–**C.14**). In these cases, even if the bridging groups are in an *exo* conformation, their positions ($\tau = 8$, 29, and 3°, respectively) do not correspond to that usually found for *exo* groups ($\tau \approx 90°$), or predicted by our calculations on the hydroxo-bridged nickel complex ($\tau = 66°$). In one of them, a *syn* conformation is imposed by a bidentate bridging ligand (**C.12**), whereas in the other two cases a planar structure is prevented by strong L···R repulsions, with *anti* or *syn* conformations being destabilized by strong R···R repulsions (**C.13**) or by the tridentate nature of the ligands (**C.14**, case **7a**). Notice that in all three cases the bridging atom has a practically planar coordination ($\Sigma = 355$, 359, and 351°, respectively), which we have shown above that is affordable only when the bridging atom is oxygen, but not when it is S, Se or Te.

Surprisingly, there is a large number of nickel compounds with the **be** structure, which our model calculations predict to

Table 6. Structural data (**2**, distances in Å, angles in degrees) for binuclear compounds of d^8 metal ions of the type $[Ni_2(\mu\text{-}XR)_2L_4]$.

	Compound	Ni···Ni	θ	τ	Σ	struct.	ref.	refcode
C.1	$[Ni_2(\mu\text{-}OH)_2(C_6F_5)_4]^{2-}$	2.884	180			**p**	[91]	jowbom
C.2	$[Ni_2(\mu\text{-}OH)_2(\{Ph_2PCH_2\}_2CMeR)_2]^{2+}$	2.880	180			**p**	[92]	gakdol
C.3	$[Ni_2(\mu\text{-}OC_6F_5)_2(C_6F_5)_4]^{2-}$	2.988	180	18	355	**pa**	[93]	rafjox
C.4	$[Ni_2(\mu\text{-}OH)(\mu\text{-}OC_6H_3\{CH=NCH_2C_4H_7NBz\}_2)]^{2+}$	2.849	178	8	349	**pa**	[94]	zulbox
C.5	$[Ni_2(\mu\text{-}SC_6H_4OH)_2(SC_6H_4O)_2]^{2-}$	3.255	180	64	310	**pa**	[95, 96]	gihhag10
C.6	$[Ni_2(\mu\text{-}SC_6H_4Cl)_2(SC_6H_4Cl)_4]^{2-}$	3.273	180	73	297	**pa**	[97]	kigxut
C.7	*trans*-$[Ni_2(S,C,S\text{-}C_3H_2N_2\{C_6H_4S\}_2)_2]$	3.281	180	63	312	**pa**	[98]	judkuo
C.8	$[Ni_2(\mu\text{-}SPh)_2(dppe)_2]^{2+}$	3.254	180	72	297	**pa**	[99]	lazxoz
C.9	$[Ni_2(Me_2N\{CH_2\}_3S)_2(dppe)_2]^{2+}$	3.310	180	65	309	**pa**	[100]	kekcim
C.10	$[Ni_2(\mu\text{-}SEt)_2(SEt)_4]^{2-}$	3.355	180	64	312	**pa**	[101]	detjan
		3.356	180	68	307	**pa**		
C.11	$[Ni_2(\mu\text{-}SeC_6H_2Me_3)_2(SeC_6H_2Me_3)_4]^{2-}$	3.511	180	58	318	**pa**	[102]	tatwug
C.12	*trans*-$[Ni_2(S\{Me_2N\}C=NN=C\{Me\}MeC_6H_3O)_2]$	2.728	136	8	355	**bx**	[103]	lahbeb10
C.13	$[Ni_2(\mu\text{-}OSi\{OtBu\}_3)_2(allyl)_2]$	2.666	135	29	359	**bx**	[104]	kesyem
C.14	$[Ni_2(\mu\text{-}OC_6H_4CMe=N\text{-}N=C\{NMe_2\}S)_2]$	2.720	135	3	351	**bx**	[105]	zebred
C.15	$[Ni_2(SCH\{CH_2CH_2NH_2\}_2)_2]^{2+}$	3.136	144	–48	303	**be**	[106]	fezkea
C.16	*trans*-$[Ni_2(SCH_2CH_2S)_2(PEt_3)_2]$	2.988	125	–38	300	**be**	[107]	yeypex
C.17	$[Ni_2(SCH_2CH_2S)_3]^{2-}$	2.941	122	–37	300	**be**	[108, 109]	durxod01
C.18	*trans*-$[Ni_2(\mu\text{-}SCH_2CH_2S)_2(PPh_3)_2]$	2.893	116	–28	308	**be**	[110]	pezdut
C.19	*trans*-$[Ni_2(Ph_2P\{CH_2\}_2S)_2Cl_2]$	2.679	104	–28	295	**be**	[111]	bomrea
C.20	*trans*-$[Ni_2(S\{MeC_6H_3\}S)_2(PBu_3)_2]$	2.678	101	–25	300	**be**	[112]	vusdiw
C.21	*trans*-$[Ni_2(SCH_2CH\{Me\}S)_2(PPh_3)_2]$	2.867	113	–30	301	**be**	[113]	vubwuk
C.22	$[Ni_2(\mu\text{-}Se\{CH_2\}_3Se)_2(Se\{CH_2\}_3Se)]^{2-}$	3.094	119	–28	308	**be**	[102]	tatwiu
C.23	$[Ni_2(nsn)]^{2+}$	3.163	151	–59	294	**be**	[114]	websax
C.24	$[Ni_2(eia)_2]$	2.691	141	–31	324	**be**	[115]	nietac
C.25	$[Ni_2(py\{CH_2\}_2NH\{CH_2\}_3S)_2]^{2+}$	3.048	134	–44	299	**be**	[116]	kerbeo
C.26	$[Ni_2(\mu\text{-}SCH_2CH_2N(Me)CH_2CH_2SO_2)_2]^{2+}$	2.721	110	–38	288	**be**	[9]	zurzer
C.27	$[Ni_2(\mu\text{-}SC_6H_4N=C(Me)CH=C(Me)O)_2]$	2.764	112	–41	283	**be**	[117]	topyig
C.28	$[Ni_2(nsn)]^{2+}$	3.141	150	–57	295	**be**	[118]	tofsuc
		3.149	150	–56	297	**be**		
C.29	*trans*-$[Ni_2(pyC_2H_4\{C_2H_4SMe\}NC_2H_4S)_2]$	2.850	113	–35	294	**be**	[119]	pidjuh
C.30	*trans*-$[Ni_2(S\{CH_2CH_2S\}_2)_2]$	2.738	112	–35	293	**be**	[107, 120, 121]	mrcsni11
C.31	$[Ni_2(pyCH_2CH_2NHCH_2CH_2S)_2]^{2+}$	2.739	110	–37	287	**be**	[122]	peaeni
C.32	*trans*-$[Ni_2(MeN\{C_2H_4S\}_2)_2]$	2.679	108	–39	283	**be**	[123]	yelsox
C.33	$[Ni_2(MeSCH_2CH_2N\{CH_2CH_2S\}_2)_2]$	2.635	105	–38	283	**be**	[97]	kigyaa
C.34	*trans*-$[Ni_2(MeN\{CH_2CH_2Se\}_2)_2]$	2.721	104	–43	275	**be**	[123]	yelsud
C.35	$[Ni_2(\mu\text{-}SBz)_2(S_2CSBz)_2]$	2.794	115	–33	298	**be**	[124]	bztcdn
C.36	$[Ni_2(\mu\text{-}SPh)_2(S_2CS)_2]^{2-}$	2.831	116	–28	306	**be**	[125]	vusfeu
C.37	$[Ni_2(\mu\text{-}SMe)_2(S_2CNHMe)_2]$	2.829	117	–31	301	**be**	[126]	yegsos
		2.761	112	–31	297	**be**		
C.38	$[Ni_2(\mu\text{-}SEt)_2(S_2CS)_2]^{2-}$	2.762	112	–28	301	**be**	[127]	pafgei

be feasible only with $R=H$, but strongly destabilized by bulkier R groups. The explanation is that all those structures can be classified in two groups:

1) Those in which the bridging and terminal donor atoms are chemically connected, corresponding to cases **7a** (**C.24**, **C.25**, **C.29–34**), **7b** (**C.15**), **7c** (**C.16–22**), and **7d** (**C.23**, **C.26–28**). In these cases, the L···R repulsion is replaced by chemical bonds, favoring the *endo* conformation Also, the chelate rings involving the bridging ligand would be highly strained in the *exo* position, as evidenced by the optimized values of τ ($62^\circ < \tau < 117^\circ$), with the X–R bond pointing in a direction opposite to that of the terminal donors (see **3bx**). Consequently, the **be** structure is per force the preferred one for systems of types **7a–d**.
2) Those in which the terminal donor atoms have no substituents pointing to the outside of the molecule, as happens in compounds **C.35–38**, in which the terminal positions are occupied by bidentate dithiocarbamato or trithiocarbonato ligands. In such cases, the lone pair at the donor atom pointing toward the bridging region can form a weak L···H–C hydrogen bond with the substituents.

Finally, we note that those nickel compounds with terminal N-donor ligands are less bent ($134 < \theta < 151^\circ$) than those with S or P donors. The only exception to this rule corresponds to a complex with N-donor atoms incorporated into a macrocyclic ligand, in which larger bending ($\theta \approx 110^\circ$ for **C.26** and **C.27**) may result from ring strain.

Palladium compounds: For the palladium compounds one should expect the **pp** structure to be highly unstable compared with any other conformer, according to our theoretical results (Table 2). In fact, in the only case for which a **pp** structure has been reported (**D.1**, Table 7),[128] such geometry is imposed by the planar portion of the macrocyclic ligand spanning the L-X-L positions (**7b**). Notice that the **pa** conformer in our theoretical study is not too high in energy relative to the **bx** and **ba** forms with PH_3 as terminal ligand. Obviously, the presence of bulkier ligands such as triphenylphosphine should destabilize the **ba** conformation through L···R repulsions, whereas bulky substituents R would destabilize the **bx** and **ba** conformations through the R···R and L···R repulsions, respectively. Given the weak M···M attraction to be expected

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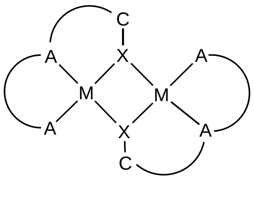
Table 7. Structural data (**2**, distances in Å, angles in degrees) for Pd^{II} binuclear complexes of the type $[Pd_2(\mu\text{-}XR)_2L_4]$. For the **ba** structures, the parameters τ and Σ corresponding to the *endo* XR group are given first, those for the *exo* groups in the second place.

	Compound	Pd···Pd	θ	τ	Σ	struct.	ref.	refcode
D.1	$[Pd_2(tacteneO_2)]^{2+}$	3.151	180	2	360	**pp**	[128]	ladmim
D.2	$[Pd_2(\mu\text{-}OH)_2(PMe_3)_4]^{2+}$	3.179	180	59	319	**pa**	[129]	yunboy
D.3	$[Pd_2(\mu\text{-}OH)_2(C_6F_5)_4]^{2-}$	3.147	180			**p**	[130]	soghol
D.4	*trans*-$[Pd_2(\mu\text{-}SPh)_2Cl_2(PEt_3)_2]$	3.463	180	69	304	**pa**	[42]	junxul
D.5	$[Pd_2(SC_5H_9NMe)_2(dppe)_2]^{2+}$	3.495	180	73	297	**pa**	[131]	kurmoz
D.6	*trans*-$[Pd_2(\mu\text{-}SPh)_2(PPh_3)_2(SPh)_2]$	3.506	180	69	303	**pa**	[99]	lazxuf
D.7	*trans*-$[Pd_2(\mu\text{-}S\{CH_2\}_3NMe_2)_2Cl_2]$	3.442	180	65	306	**pa**	[132]	cegmac
D.8	$[Pd_2(\mu\text{-}SPh)_2(SPh)_4]^{2-}$	3.505	180	64	311	**pa**	[133]	sokfon
D.9	$[Pd_2(\mu\text{-}SC_6H_4OH)_2(OC_6H_4S)_2]^{2-}$	3.404	180	65	308	**pa**	[134, 135]	zahlid10
D.10	*trans*-$[Pd_2(\mu\text{-}SC_6H_4OH)_2Cl_2(PPh_3)_2]$	3.495	180	60	316	**pa**	[136]	texbih
D.11	*trans*-$[Pd_2(\mu\text{-}SC_6F_5)_2(SC_6F_5)_2(PPh_3)_2]$	3.532	180	60	316	**pa**	[137]	pfsppd
		3.552	180	65	310	**pa**		
D.12	*trans*-$[Pd_2(\mu\text{-}SC_6F_5)_2(SC_6F_5)_2(PPh_3)_2]$	3.651	180	68	307	**pa**	[138]	fbtppd
D.13	$[PdPt(\mu\text{-}SC_5H_9NMe)_2(dppe)_2]^{2+}$	3.542	180	72	299	**pa**	[131]	kurnam
D.14	$[Pd_2(\mu\text{-}OH)_2(dppp)_2]^{2+}$	3.100	146			**b**	[139]	jihjit
		3.095	144			**b**		
D.15	*trans*-$[Pd_2(\mu\text{-}OH)_2Ph_2(PPh_3)_2]$	2.981	131	28	360	**bx**	[140]	lanbor
D.16	$[Pd_2(S_3N_2)Cl_4]^{2-}$	2.916	121	97	293	**bx**	[141]	kojgev
D.17	$[Pd_2(S_3N_2)Br_4]^{2-}$	2.857	117	96	294	**bx**	[142]	zojhel
D.18	$[Pd_2(\mu\text{-}SC_2H_4\{C_5H_9NMe\})_2Cl_2]$	3.374	143	−41	311	**be**	[143]	gihmoz
D.19	*trans*-$[Pd_2(\mu\text{-}SCH_2CH_2S)_2(PPh_3)_2]$	3.038	113	−30	302	**be**	[144]	yuxzog
D.20	*trans*-$[Pd_2(\mu\text{-}SC_6H_4PPh_2)_2I_2]$	2.965	110	−28	300	**be**	[145]	ibzdpd
		2.915	107	−30	295	**be**		
D.21	*trans*-$[Pd_2(\mu\text{-}SC_2H_4CpPPh_2\{FeCp\})_2Cl_2]$	3.363	141	−43	309	**be**	[146]	
D.22	*trans*-$[Pd_2(\mu\text{-}SC_2H_4CpPPh_2\{Fep\})_2(CNR)_2]^{2+}$	3.215	130	−26	316	**be**	[146]	
D.23	$[Pd_2(\mu\text{-}OMe)_2(hfacac)_2]$	2.984	154	−28	335	**be**	[147]	bijpal
D.24	$[Pd_2(\mu\text{-}StBu)_2(S_2CStBu)_2]$	3.162	132	−32, 83	313, 311	**ba**	[124]	butcpd



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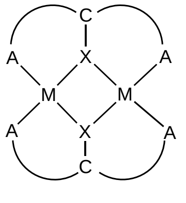

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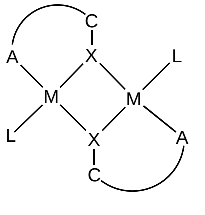

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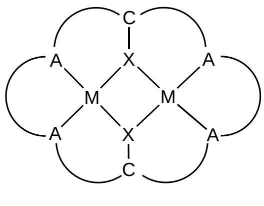

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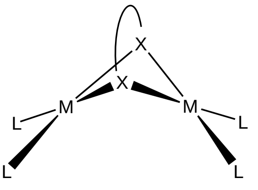

7e

for palladium and platinum compounds, it is understandable that the **pa** structure becomes the most stable one in a large number of cases, as found in the solid-state structures of compounds **D.2**–**D.13**.

The preferred **bx** structure for our model compound with a bridging hydrogensulfido group, is obtained when two bridging donors belong to the same bidentate ligand (**7e**), as in **D.16** and **D.17**, or when a bridging hydroxo group is present and the bulky triphenylphosphine ligands are in *trans* positions (**D.15**). That structure is predicted by our calculations for $[Pt_2(\mu\text{-}OH)_2(PH_3)_4]$ and it is presumably adopted by **D.14**, although the position of the hydrogen atoms are not well determined in that structure. Molecules in which the bridging atom is chemically connected to terminal atoms (**D.18**–**22**, case **7c**), appear in the **be** conformation, as discussed above for the nickel compounds. In the case of compound **D.23**, the **be** structure found should be attributed to a small I_{LR} repulsion or even a weak O···H–C hydrogen bond. Similarly, in compound **D.24**, a weak S···H–C hydrogen bond might be responsible for a nonrepulsive ligand···substituent interaction, although the steric bulk of the *t*Bu substituents disfavors a *syn* conformation (I_{RR} term), thus resulting in the **ba** structure experimentally found. Comparison of two analogous compounds, **D.21** and **D.22**, clearly show the influence of the terminal ligands. As previously discussed[24, 35] for the stacking $d^8 \cdots d^8$ interactions and for the bent complexes with unsubstituted bridges, the less favorable ligands for a bonding metal···metal interaction are those with poor σ-donor and good π-donor character, and the most favorable ones are the good σ donors and π acceptors. In the present case, the substitution of only one chloride by an isonitrile ligand at each metal center results in an increased bending (i.e., a decrease in the value of θ from 141° to 130°) around the X–X hinge, consequently reducing the Pd···Pd distance by 0.15 Å.

Platinum compounds: As found for palladium, one should expect both planar and bent structures among the platinum compounds, given the weakness of the Pt$\cdots$Pt interaction. Planar structures are more common with the small bridging oxygen atom, as seen in Table 8, although there are a few hydroxo-bridged compounds with bent structures. The structural differences between similar compounds in this family reflect the small energy differences found in our calculations. As an example, the $[Pt_2(\mu\text{-}OH)_2(Me_2SO)_4]^{2+}$ cation in **E.2**, **E.3**, and **E.9** has a planar structure, whereas substitution of two dimethylsulfoxide ligands by chloride ions in *cis*-$[Pt_2(\mu\text{-}OH)_2Cl_2(Me_2SO)_2]$ (**E.26**) gives a bent structure.

According to the theoretical predictions, the L$\cdots$R repulsions make the **be** form clearly unstable compared with other structures. This is reflected in the experimental data, since the only known **be** structures are those with bridging groups constrained to the *endo* orientation by the formation of chelate rings spanning a bridging and a terminal position (**7c**, structures **E.36–38**), as discussed above for nickel. According to our above discussion, compounds with carbonyl or chloro terminal ligands could also give rise to **be** conformers, but none of these has been structurally characterized so far.

If the two bridging atoms belong to a bidentate ligand (**7e**), an *anti* structure is unrealistic. Then, among the three *syn* conformers, **ps**, **be**, and **bx**, it is the latter which is predicted to be more stable, as actually found in a compound with such type of bridging ligands (**E.31**). A related case is that of compound **E.23**, in which the two carboxylato groups from the bridging substituents are connected by hydrogen bonding to a water molecule (O$\cdots$O distances 2.76 and 2.94 Å). Such hydrogen bonds clearly impose a *syn* conformation that can be realized in either of the **ps**, **bx**, or **be** cases. Among these, it is the **ps** conformer that provides the right orientation (the calculated value of $|\tau|$ for $[Pt_2(\mu\text{-}SH)_2(PH_3)_4]^{2+}$ is 81°, 105°, and 46° in the **ps**, **bx** and **be** conformations, respectively; Table S3) to allow for the hydrogen bonding between the two substituents, as found in the experimental structure of **E.23** ($\tau = 78°$) with the **ps** conformation.

The **ba** conformation is found in those complexes (**E.27–29**) in which one terminal ligand (nitrite, thiolate, or chloride) at each metal atom has a lone pair pointing to a bridging

Table 8. Structural data (**2**, distances in Å, angles in degrees) for binuclear Pt^{II} compounds of the type $[Pt_2(\mu\text{-}XR)_2L_4]$ and $[PtM(\mu\text{-}XR)_2L_4]$. For the **ba** structures, the parameters τ and Σ corresponding to the *endo* XR group are given first, those for the *exo* groups in the second place.

	Compound	Pt$\cdots$Pt	θ	τ[a]	Σ	struct.	ref.	refcode
E.1	$[Pt_2(\mu\text{-}OH)_2(NH_3)_4]^{2+}$	3.085	180			**p**	[148]	
E.2	$[Pt_2(\mu\text{-}OH)_2(Me_2SO)_4](BF_4)_2$	3.144	180			**p**	[149]	julwiw
E.3	$[Pt_2(\mu\text{-}OH)_2(Me_2SO)_4](CF_3SO_3)_2$	3.142	180			**p**	[149]	julwoc
E.4	$[Pt_2(\mu\text{-}OH)_2(C_6F_5)_4]^{2-}$	3.211	180	26	358	**pa**	[150]	komweo
E.5	$[Pt_2(\mu\text{-}OH)_2(Me_2en)_2]^{2+}$	3.138	180			**p**	[151]	kuywik
E.6	$[Pt_2(\mu\text{-}OLi\{thf\}_2)_2(CH\{PPh_2\}_2)_2]$	3.112	180	64	312	**pa**	[32, 152]	wekyam10
E.7	$[Pt_2(\mu\text{-}OAuPPh_3)_2(cod)_2]$	3.093	180	26	351	**pa**	[153]	
E.8	$[Pt_2(\mu\text{-}OH)_2(thtO)_4]^{2+}$	3.137	180			**p**	[154]	favkiw
E.9	$[Pt_2(\mu\text{-}OH)_2(Me_2SO)_4]^{2+}$	3.146	180			**p**	[155]	defluv
E.10	$[Pt_2(\mu\text{-}OH)_2(dppm)_2]^{2+}$	3.270	180	4	360	**p**	[32, 152]	wekxuf10
E.11	$[Pt_2(\mu\text{-}OH)_2(dppf)_2]^{2+}$	3.226	180			**p**	[156]	gaglab
E.12	$[Pt_2(\mu\text{-}OH)_2(dppb)_2]^{2+}$	3.215	180			**p**	[152]	zotlid
E.13	$[Pt_2(\mu\text{-}OH)_2(PMe_3)_4]^{2+}$	3.261	180			**p**	[157]	vidvuz
E.14	$[Pt_2(\mu\text{-}OH)_2(PPh_3)_4]^{2+}$	3.153	180			**pa**	[152]	zotlav
E.15	$[Pt_2(\mu\text{-}SC_5H_9NMe)_2(en)_2]^{2+}$	3.451	180	62	314	**pa**	[158]	komzuh
E.16	$[Pt_2(\mu\text{-}SC_5H_{10}NMe)_2(en)_2]^{4+}$	3.447	180	64	311	**pa**	[158]	konbeu
E.17	$[Pt_2(\mu\text{-}SC_5H_9NMe)_2(dppe)_2]^{2+}$	3.549	180	71	301	**pa**	[131]	kurmuf
E.18	*trans*-$[Pt_2(\mu\text{-}SPh)_2Ph_2(PMe_2Ph)_2]$	3.570	180	62	314	**pa**	[159]	lepcak
E.19	$[Pt_2(\mu\text{-}SAuCl)_2(PPh_3)_4]$	3.567	180	96	270	**pa**	[46]	factos
E.20	*trans*-$[Pt_2(\mu\text{-}SCH_2CH_2CMe{=}CH_2)_2I_2(PPh_3)_2]$	3.539	180	67	308	**pa**	[15]	jejsew
E.21	$[PdPt(\mu\text{-}SC_5H_9NMe)_2(dppe)_2]^{2+}$	3.542	180	72	299	**pa**	[131]	kurnam
E.22	*trans*-$[Pt_2(\mu\text{-}SeEt)_2Cl_2(PEt_3)_2]$	3.647	177	71	301	**pa**	[21]	zeljuv
E.23	*trans*-$[Pt_2(\mu\text{-}SCH_2CH\{CO_2\}NHAc)_2(bpy)_2]$	3.441	167	78	301	**ps**	[14, 160]	perlut10
E.24	$[Pt_2(\mu\text{-}OH)_2(PEt_3)_4]^{2+}$	3.115	144			**b**	[161]	hepptb
E.25	$[Pt_2(\mu\text{-}OH)_2(dppp)_2]^{2+}$	3.120	143			**b**	[162]	hejsiy
E.26	*cis*-$[Pt_2(\mu\text{-}OH)_2Cl_2(Me_2SO)_2]$	3.050	148			**b**	[163]	lespee
E.27	*cis*-$[Pt_2(\mu\text{-}SMe)_2(NO_2)_2(PPh_3)_2]$	3.341	144	−47, 89	303, 303	**ba**	[47]	daxtol
E.28	*cis*-$[Pt_2(\mu\text{-}SBz)_2(SBz)_2(PMePh_2)_2]$	3.348	137	−42, 95	305, 298	**ba**	[164]	birjan
E.29	*cis*-$[Pt_2(\mu\text{-}SEt)_2Cl_2(PPr_3)_2]$	3.206	129	−35, 95	307, 302	**ba**	[165]	ethpdp
E.30	$[Pt_2(\mu\text{-}OPt\{cod\}Cl)_2(cod)_2]$	3.039	151	27	358	**bx**	[153]	
E.31	$[Pt_2(\mu\text{-}O_2LiBF_4)(PPh_3)_4]$	2.969	140	128	255	**bx**	[32]	kibteu10
E.32	$[\{Pt_2(\mu_3\text{-}S)_2(dppe)_2\}_2Cu]^{2+}$	3.072	118	132	244	**bx**	[33]	nilder
		3.129	121	130	245	**bx**		
E.33	$[(PPh_3)_2Pt(\mu\text{-}S\{CH_2\}_2S)Rh(cod)]^+$	3.010	111	114	265	**bx**	[34]	
E.34	$[(PPh_3)_2Pt(\mu\text{-}S\{CH_2\}_3S)Rh(cod)]^+$	3.065	121	99	292	**bx**	[34]	
E.35	$[(PPh_3)_2Pt(\mu\text{-}S\{CH_2\}_4S)Rh(cod)]^+$	3.408	151	77	311	**bx**	[34]	
E.36	$[Pt_2(\mu\text{-}SC_5H_9NMe)_2Br_2]$	3.142	127	−37	303	**be**	[166]	sewnud
E.37	*trans*-$[Pt_2(\mu\text{-}SCH_2COCH_2)_2(PPh_3)_2]$	3.088	116	−38	293	**be**	[167]	piffit
E.38	*trans*-$[Pt_2(\mu\text{-}SC_2H_4C\{Me\}{=}CH_2)_2I_2]$	3.027	116	−36	294	**be**	[15]	jejsas

[a] Negative values correspond to the *endo* substituent.

ligand. In such cases, the bridging group closer to the lone-pair-carrying terminal ligands is invariably found in the *endo* position, probably favored by a negative I_{LR} term (i.e., a weak L ··· H–C hydrogen bond). In all these compounds, contacts between the α carbon atom of the bridging ligand and the donor atom of the terminal ligand can be found between 3.26 and 3.50 Å.

Gold compounds: The gold compound closer to one of our models, [$Au_2(\mu$-SEt$)_2Me_4$] (**F.1** in Table 9), has a **be** structure as predicted for [$Au_2(\mu$-SH$)_2Me_4$] (Table 2). However, it must be noticed that the degree of bending experimentally found ($\theta = 142°$) is much less than in our calculations ($\theta = 118°$). The degree of bending of the **bx** structure of **F.2** is also relatively small ($\theta = 151°$). The rest of the structurally characterized gold compounds appear in the **pa** conformation, which is expected to be some 2 – 4 kcal mol^{-1} less stable than one of the bent forms in our model calculations. The disagreement between the experimental structures and the results of our calculations is not surprising given the small energy differences, but we think that it is due to the existence of weak hydrogen bonding between the terminal ligands and the hydrogen atoms of the substituents in the model molecules that are absent in the experimental compounds. A special case is that of [$Au_2(\mu$-SPh$)_2Cl_4$], which shows the **bx** conformation (**F.2**), probably because the stacking interactions between the phenyl groups makes the I_{RR} term an attractive one (it is repulsive in the model compounds, Table 3). Such interaction between two benzene molecules has been estimated by ab initio calculations to be attractive (1.2 kcal mol^{-1}) at an optimum distance of 3.71 Å,[168] practically identical to that between the centroids of the two phenyl groups in **F.2** (3.64 Å). Compared with our model calculations for [$Au_2(\mu$-SH$)_2Cl_4$], the stabilization of the **bx** form as a result of the stacking interaction, combined with the enhanced I_{LR} repulsion between the phenyl groups and the chloro ligands that destabilize the **ba** and **be** conformers, can explain the **bx** conformation shown by **F.2**.

Contrary to the expectations from our calculated energies Table 2), most of the gold compounds appear in the planar **pa** conformation. This is not strange since the I_{MM} term is found to be positive for the gold complexes with chloro terminal ligands and thiolato groups as bridges. Hence, the planar structure should be expected to be stable, especially in the **pa** conformation in which both L ··· R and R ··· R repulsions are absent. The fact that our model calculations predict the **be** and **ba** conformations to be more stable than that experimentally found is probably owing to existence of weak hydrogen bonds between the HS$^-$ bridging groups and the terminal chlorides in the model compound, whereas such interactions are absent in the real compounds with non-hydrogen substituents at the bridging atoms. The different degree of bending experimentally found for the compounds with Me and Cl terminal ligands is in good agreement with the dependence of the M ··· M interaction on the nature of terminal ligands as established previously.[35]

Dynamic behavior: some hints

As summarized in the introductory section, there is spectroscopic evidence of the coexistence in solution of different conformers of the binuclear compounds under study. This is consistent with the similar stability of the different conformers found in our calculations. However, for such intramolecular reactions to occur thermally, a low activation energy is needed. Although we did not intend to carry out a mechanistic study, and no attempt has been made to locate transition states, the relative energies of the different conformers can provide some hints on three of the possible dynamic processes. We focus first on the **ba** conformer, for which the two R groups are nonequivalent, and exchange of the *endo* and *exo* positions can in principle proceed through two alternative pathways: a) by ring inversion through a transition state close to the **pa** conformer (**8**), or b) by bridge inversion through a *syn* conformation with the bridging atoms in a planar trigonal geometry (**st** in **8**). According to the energy partition scheme described above, we can estimate the barrier for the two pathways, neglecting the ligand ··· sub-

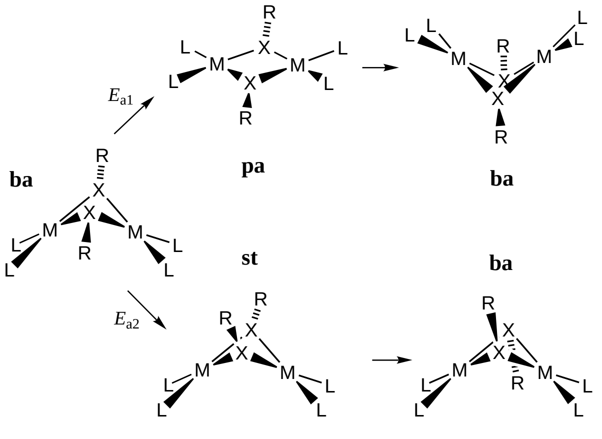

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Table 9. Structural data (**2**, distances in Å, angles in degrees) for Au^{III} binuclear complexes of the type [$Au_2(\mu$-XR$)_2L_4$].

	Compound	Au ··· Au	θ	τ	Σ	struct.	ref.	refcode
F.1	[$Au_2(\mu$-SEt$)_2Me_4$]	3.458	142	– 41	310	**be**	[169]	culyir
F.2	[$Au_2(\mu$-SPh$)_2Cl_4$]	3.357	151	87	297	**bx**	[170]	viflif
F.3	[$Au_2(\mu$-OH$)_2(C_4Ph_4)_2$]	3.425	180			**p**	[171]	hxpaup
		3.431	180			**p**		
F.4	[$Au_2(\mu$-OH$)_2(C_6H_4NO_2)_4$]	3.150	180	47	331	**pa**	[172]	zutjaz
F.5	[$Au_2(\mu$-TeC$_6$H$_2$Ph$_3)_2I_4$]	3.854	180	67	306	**pa**	[173]	yeknor
		3.957	180	69	306	**pa**		
F.6	[$Au_2(\mu$-SAuCl$)_2Cl_4]^{2-}$	3.440	180	77	294	**pa**	[174]	zodlin
F.7	[$Au_2(\mu$-SAuCl$)_2Cl_4]^{2-}$	3.463	180	77	294	**pa**	[174]	zodlot

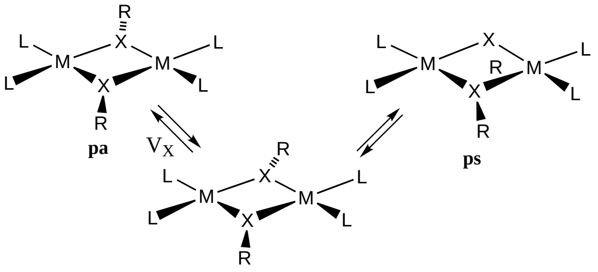
stituent and substituent ··· substituent repulsions in the **st** form [Eqs. (8) and (9)].

$$E_{a1} = E_{pa} - E_{ba} \approx - I_{MM} - I_{LR} \quad (8)$$

$$E_{a2} = E_{st} - E_{ba} \approx - 2\,V_X - I_{LR} \quad (9)$$

The estimated values of E_{a1} (Table 3) for those model complexes for which a bent structure was found to be more stable are much lower than the corresponding E_{a2} values, except for the hydroxo- and alkoxo-bridged compounds. In other words, the bridge inversion is expected to have a much higher activation energy than the ring inversion for thiolato-bridged complexes, in keeping with the low stabilization associated with their bent forms (I_{MM}) as compared with the energy of pyramidalization of the bridging atom (V_X). Since the pyramidalization is much less favored for oxygen than for the other studied bridges, it is no surprise that in the hydroxo- and alkoxo-bridged compounds the two pathways seem to be competitive. The estimated low activation energies, on the other hand, are in good agreement with the finding that the fluxional process is intramolecular in *cis*-[$Pt_2(\mu$-$SEt)_2Cl_2(PPr_3)_2$].[11] Furthermore, the theoretically estimated barrier of 9.8 kcal mol^{-1} for [$Rh_2(\mu$-$SH)_2(PH_3)_4$] (assuming that the entropy contribution is comparatively small) is in excellent agreement with the experimentally estimated free energy of activation in solution of about 10 kcal mol^{-1} for a rhodium complex[12] that presents the **ba** conformation in the solid state.

Another process for which we can obtain some insight from the computational results is the interconversion of the **pa** and **ps** conformers, conceivably proceeding through a transition state in which one of the bridging atoms is inverted (**9**). The activation energy can be roughly estimated as the corresponding V_X value with negative sign. Such process has been detected in the NMR spectra of the platinum compounds **E.23**, which crystallizes in the **ps** conformation, and **E.20**, with a solid state **pa** conformation. Their activation energies have been estimated[15, 175] in the range between 13 and 20 kcal mol^{-1} for thiolato bridges, with somewhat larger barriers for analogous selenolato bridges. Such results are in excellent agreement with the computational value of $-V_X$ for [$Pt_2(\mu$-$SMe)_2(PH_3)_4]^{2+}$ (16 kcal mol^{-1}).



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Finally, the solution isomerization at room temperature of rhodium and iridium complexes that appear in the solid state as a **be** conformer, may consist of a ring-inversion process through a **ps** transition state leading to the **bx** conformer.[12, 17–20] The activation energy for such process can therefore be estimated as in Equation (10); this is found (Table 3) to be of 2 kcal mol^{-1} for the hydroxo-bridged rhodium compound, and between 9 and 12 kcal mol^{-1} for the thiolato-bridged rhodium and iridium complexes.

$$E_{a3} = E_{ps} - E_{be} \approx - I_{MM} - 2\,I_{LR} \quad (10)$$

Conclusions

The combined use of theoretical studies and a structural database analysis has allowed us to establish some guidelines for understanding the structural choice between the possible conformers in binuclear compounds of d^8 transition metals with monosubstituted bridges of the types [$M_2(\mu$-$Y)(\mu$-$XR)L_4$] and [$M_2(\mu$-$XR)_2L_4$]. A systematic ab initio study was carried out for the different conformers of complexes with a variety of combinations of metal atom, bridging atom, bridge substituent, and terminal ligands. In general, the predicted conformation for a particular molecule is in good qualitative agreement with its experimentally determined structure. Simplifications introduced in the theoretical model (i.e., replacing a PPh_3 terminal ligand by PH_3) may alter the relative stabilities of the different conformers within a few kcal mol^{-1}.

Theoretical studies at the ab initio MP2 level for RXH_2^+ ions (X = O, S, Se, or Te; R = H or Me), show that the tendency towards pyramidalization increases in the order $O \ll S < Se < Te$. The same trend is found at the EH level for the model [$Rh_2(\mu$-$XR)_2Cl_4]^{4-}$ complexes and at the ab initio MP2 level for [$M_2(\mu$-$Y)(\mu$-$XR)L_4$] and [$M_2(\mu$-$XR)_2L_4$] compounds. The pyramidalization of the bridging atom is slightly favored for X = O (1–3 kcal mol^{-1}), but represents an important stabilization factor for X = S (12–20 kcal mol^{-1}). Such behavior is reflected in both the calculated and experimental structural data by the sum of the bond angles around the bridging atom, Σ, which is close to 360° for X = O, but significantly smaller for X = S, Se, or Te. The tendency towards a pyramidal geometry around the sulfur bridging atoms results in a correlation between the bending of the coordination planes (θ) and the out of plane displacement of the bridge substituent (τ). Consequently, imposing a given value of τ by means of bidentate ligands allows for a control of the degree of bending.

A driving force for bending the molecules is the weak $d^8 \cdots d^8$ interaction between the two ML_2 fragments; this is decreased in part by the steric repulsion between the terminal ligands. The strength of such interaction increases in the order $Au < Ni \approx Pd \approx Pt < Rh \approx Ir$. The nature of the terminal ligands is seen to affect the M ··· M interaction. Also larger, less electronegative bridging atoms seem to favor the weak M ··· M bonding.

Ligand ··· substituent interactions are destabilizing in most cases, as would be expected from steric arguments. Such repulsions are relieved in part by changes in the M-X-M and τ angles. Therefore, the bent conformers have all similar energies when X = H, but the **be** structure is clearly destabilized by stronger ligand ··· substituent interactions for X = Me. When chloro or carbonyl groups occupy the terminal coordination positions, the ligand ··· substituent term appears to be attractive, indicating weak hydrogen bonding that stabilizes the *endo* conformation of the bridging group *cis* to them.

Repulsions between the bridge substituents in the *exo* conformation are very small for the XH bridges, but increase by about 10 kcal mol^{-1} upon substitution by a methyl group. A special case, according to the experimental data, is provided by the C_6F_5 and C_6F_4H substituents, which apparently favor the *exo* conformation. For the model compound with mixed bridges, $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PH_3)_4]^+$ (R = H, Me), the bent conformations are more stable than the planar ones, and the methyl group introduces substituent ··· ligand repulsions in the **be** conformer.

An analysis of the experimental structural data confirms the general trends revealed by the theoretical study. Furthermore, other features not present in the model calculations can be detected that might be useful for the design of new compounds.

a) The presence of chelate rings involving the bridging atom and at least one terminal donor atom favor the **be** structure.
b) Linking the bridging atom with a terminal ligand through chemical bonds stabilize the **be** conformer, making it a very common structural motif among complexes of type **7a**–**7d**.
c) Bidentate ligands occupying the two bridging positions favor the **bx** conformation (**7e**).

Comparison of the energies of the different conformers can provide some hints on the possible mechanisms of dynamic processes.

1) Fluxionality of **ba** compounds can proceed easily through a ring inversion mechanism, and only for oxygen-bridged complexes does the bridge inversion provide a competitive mechanism.
2) Interconversion of **pa** and **ps** conformers of palladium and platinum is likely to proceed through a bridge inversion mechanism.
3) The dynamic behavior observed for rhodium and iridium **be** compounds may correspond to an isomerization to **bx** through ring inversion, which is estimated to have a low activation barrier.

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Appendix—Computational Details

Extended Hückel calculations[176, 177] were used to illustrate the qualitative discussion, taking $[Rh_2(\mu\text{-}XR)_2Cl_4]^{4-}$ as a model compound. Cl-Rh-Cl and S-C-H bond angles were taken as 90 and 110°, respectively. The following bond distances were used: Rh–Cl = 2.40, Rh–O = 2.07, Rh–S = 2.35, S–C = 1.82, S–H = 1.35, C–H = 1.09, and O–H = 0.96 Å. The calculations were carried out with the YAeHMOP[178] program using the modified Wolfsberg-Helmholz formula.[179] Standard atomic parameters were used for Rh,[180] Cl,[181] S,[182] H, C, and O.[177] All ab initio calculations were performed with the GAUSSIAN 94 suite of programs.[183] A molecular orbital ab initio method with introduction of correlation energy through the second-order Møller–Plesset (MP2) perturbation[184] approach was applied, excluding excitations concerning the lowest energy electrons (frozen-core approach). The MP2 level was used because it is well established that Hartree–Fock calculations do not adequately describe the M ··· M contacts. A basis set with double-ζ quality for the valence orbitals was used for all atoms, supplemented by polarization functions with effective core potentials for the innermost electrons, except for the H atoms of the PH_3 and Me groups, for which a minimal basis set was used.[185] More details on the basis set can be found in our previous paper.[24] The internal structures of the methyl and phosphine ligands were kept frozen in the optimizations (C–H = 1.094, P–H = 1.42 Å; H-C-H = 110.2, H-P-H = 93.2°). All other geometrical parameters were optimized to find the most stable structure for each compound. For those compounds in which R = Me, the relative orientation of the two methyl groups were optimized for the rhodium model compounds. Since the methyl groups in the optimized structures were always found either in an eclipsed (**e**) or a staggered (**s**) conformation, calculations for other metals were carried out only at these two orientations, and the energies and structural parameters given in Tables 2–3 and S1–S5 correspond to the most stable one. In order to evaluate the energy differences between the bent and planar geometries, optimizations were performed for the least stable structure of each compound, while keeping the value of the angle θ fixed at 180° or about 120°. With the energies for the different conformers calculated in this way, the different energy contributions (Table 3) were evaluated through Equations (1)–(7).[186] Symmetry restrictions were introduced in the optimizations when possible. The reported energies are quite similar to those calculated at the MP2 level for the Hartree–Fock optimized geometries of thiolato-bridged platinum compounds in a previous paper.[187]

The collection of structural data was obtained through a systematic search of the Cambridge Structural Database[23] (version 5.12) for compounds of general formula $[M_2(\mu\text{-}XR)_2L_4]$, in which M was imposed to be a metal at its oxidation state with a d^8 configuration: Co^I, Rh^I, Ir^I, Ni^{II}, Pd^{II}, Pt^{II}, Au^{III}, Ru^0, or Os^0, and X was allowed to be any element of Groups 13–17. The bending angle θ was obtained as that between the two MX_2 planes.

Abbreviations

bpy = 2,2′-bipyridine; cod = 1, 5-cyclooctadiene; dppb = 1,4-bis(diphenylphosphino)-butane; dppe = 1,2-bis(diphenylphosphino)etane; dppf = 1,1′-bis(diphenylphosphino)-ferrocene; dppm = bis(diphenylphosphino)methane; dppp = 1,3-bis(diphenylphosphino)-propane; eia = N-(2′-ethanolato)-acetylacetoniminate(2-); en = 1,2-ethylenediamine; hfacac = hexafluoro-acetylacetonate(1-); nbd = 2,5-norbornadiene; nsn = N,N′-bis-(4-methyl-2,6-dimethylene-phenylthiolate)-bis(1,3-diamino-propane) (2-); tacteneO$_2$ = 11,23-dimethyl-3,7,15,19-tetraazatricyclo-hexacosa-2,7,9,11,13-(26),14,19(25),22,24-decaene-25,25-diolate(2-); thf = tetrahydrofuran; thtO = tetrahydrothiophene oxide.

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[186] A referee has pointed out that the interaction energies in the bent structures may be exaggerated due to a basis set superposition error (BSSE). Although it is not clear how to deal with the BSSE for intramolecular interactions, a rough estimate of the BSSE has been calculated for a palladium and a rhodium compound that give small and large interaction energies, respectively. To that end, the energy of the mononuclear compound *cis*-$[Pd(SH)_2(PH_3)_2]$ has been calculated both with its basis set and with the basis set of the **pa** and **ba** binuclear compounds $[Pd_2(\mu\text{-}SH)_2(PH_3)_4]^{2+}$. The energy of the monomers decrease by 11.4 and 12.8 kcal mol^{-1}, respectively, indicating an additional stabilization of the **ba** conformer of about 1.4 kcal mol^{-1} due to the different BSSE in the two cases, whereas the calculated energy difference was of 3.0 kcal mol^{-1}. For the analogous Rh^{I} compound, the difference that could be attributed to the BSSE is of the order of 2.5 kcal mol^{-1}, compared with an interaction energy of 9.8 kcal mol^{-1}. These results suggest that the energies reported here should not be taken as accurate values, while the deduced trends are not expected to change if a proper evaluation of the BSSE could be assesed.

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