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# Structural Correlations and Conformational Preference in Edge-Sharing Binuclear $d^8$ Complexes with $XR_2$ Bridges. A Theoretical Study

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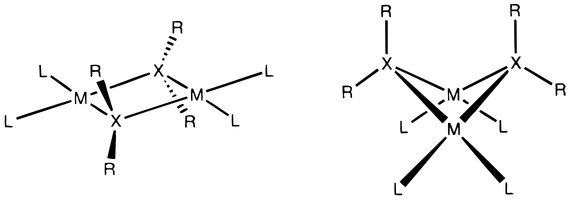
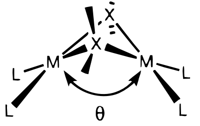
The binuclear complexes of $d^8$ transition metal ions of the type $[M_2(\mu\text{-}XR_2)_2L_4]$ (where M = $Rh^I$, $Ir^I$, $Ni^{II}$, $Pd^{II}$, $Pt^{II}$, or $Au^{III}$; X = S, N, P, or As) appear in a variety of molecular conformations in which the coordination planes around the two metal atoms are sometimes coplanar, sometimes bent. For the bent compounds with asymmetric bridges, $XR^1R^2$, the substituents adopt different orientations relative to the metal framework and to each other. Ab initio theoretical studies on the different conformers of 30 representative complexes, complemented with a structural database analysis, have allowed the establishment of structural correlations in this family of compounds. The conformational choice results from a delicate balance of different interactions which are qualitatively analyzed, such as the changes in bond angles around the bridging atoms, the existence of weak metal···metal bonding in the bent structures, and steric interactions involving the terminal ligands and the substituents at the bridging atoms.

Double bridged binuclear complexes of the type $[M_2(\mu\text{-}XR_n)_2L_4]$ ($n = 0-2$) with square planar coordination geometries around the metal atoms can be found in different molecular conformations, with either a planar or bent skeleton (**1**) and several possible orientations for the substituents at the bridging atoms.[1−4] These compounds have found a variety of applications, including catalytic activity,[3,5−7] luminiscence[8] or potential use as therapeutic agents for cisplatin nephrotoxicity.[9] 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 those compounds with disubstituted bridges ($n = 2$), we can distinguish two cases, depending on whether the two substituents are identical or different. In the former case, $[M_2(\mu\text{-}XR_2)_2L_4]$, there are two basic molecular shapes, with a planar (abbreviated **p** from here on) or a bent (**b**) skeleton, for which the degree of bending is defined by the angle $\theta$ (**2**). For these compounds we will worry also about the orientation of the substituents R, as defined by the parameters $\tau$ and $\omega$. In short, $\tau$ describes the uplift of the substituents **(3)** as the molecule bends down around the X- - -X hinge. In principle, one should expect $\tau$ to be close to zero for a planar molecule but increase upon bending in order to keep a pseudotetrahedral geometry around the bridging atom, i.e., with the two substituents arranged symmetrically with respect to the $XM_2$ plane. In practice, the two substituents are often asymmetrically disposed, especially in the bent molecules, and we measure such asymmetry by the angle $\omega$ (**4**) between the bisector of the RXR angle and the $XM_2$ plane.

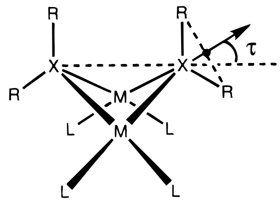


**p** **b**

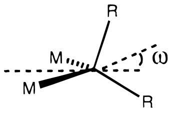
**1**



**2**



**3**



**4**

For compounds with two different substituents, $[M_2(\mu\text{-}XR^1R^2)_2L_4]$, a larger number of conformations can be expected, as schematically represented in **5**. We conventionally take $R^2$ to be the bulkier substituent, whenever the bulkiness of the two substituents can be clearly differentiated. In particular, for the calculations reported in this paper using asymmetric bridges, we take $R^1$ = H and $R^2$ = Me. With such a convention, the molecular conformations for a planar skeleton can be *syn* **(ps** structure) or *anti* (**pa**), whereas the bent skeleton gives rise to *anti* (**ba**) or *syn* conformations of the substituents. In the latter

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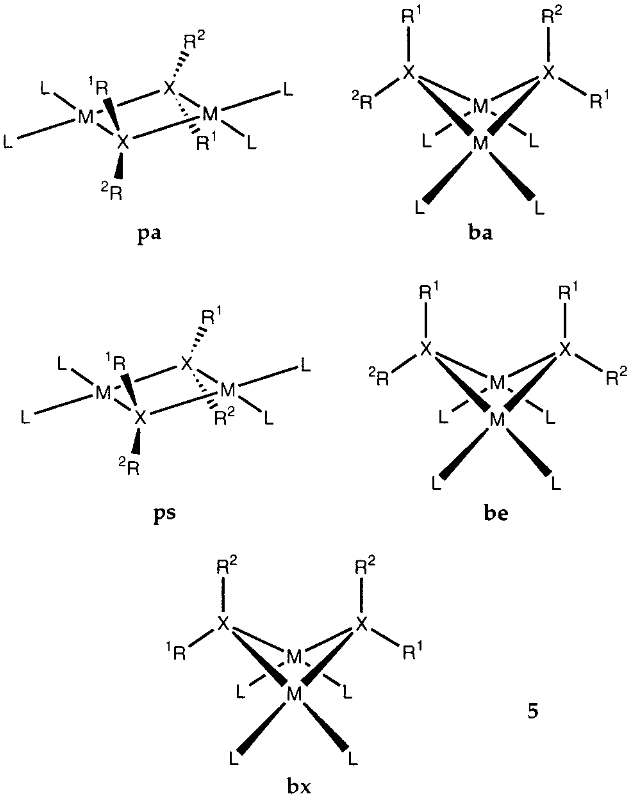
case we differentiate between the conformation with the bulkier substituents $R^2$ in *endo* (**be**) or *exo* (**bx**) situations relative to the roof-shaped skeleton.



**5**

Despite the variety of available conformations, only in one case have two of the isomers depicted in **5** been isolated and structurally characterized[10,11] (**ps** and **pa**). For a Pd compound, two isomeric crystals of different color were isolated, but no structural characterization was reported.[12] Evidence for the existence of more than one isomer in solution has been proposed in several cases,[13−19] based on the NMR spectra. An extra structural variability may appear when the two terminal ligands at the same metal atom are different, since the equivalent ligands attached to different metal atoms can appear either in a transoid or in a cisoid conformation.[13,20]

The structures of compounds with $XR_2$ bridges are distributed between the planar and bent forms without a clear pattern (Figure 1), except for the absence of **ba** structures, according to a Cambridge Structural Database search.[21] It is worth stressing that the bending angle $\theta$ for a particular metal shows a bimodal distribution with one maximum at $\theta = 180°$ and another one at a small angle separated by a clear gap at intermediate angles, as previously found for the X and XR bridges.[22,23] For example, no structure with $\theta$ between 170° and 140° appears for M = Rh.

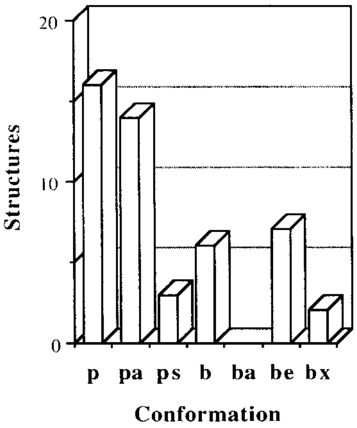


**Figure 1.** Distribution of the molecular conformations of complexes of the types $[M_2(\mu\text{-}XR_2)_2L_4]$ and $[M_2(\mu\text{-}XR^1R^2)_2L_4]$ (see **1** and **5**) as determined from X-ray diffraction data deposited in the Cambridge Structural Database.

The factors that affect the structural choice in complexes with unsubstituted or monosubstituted bridges have been previously discussed.[22,23] For the former, weak metal···metal bonding combined with steric repulsion between terminal ligands favors a bent structure. The tendency to bend increases with increasing size of the metal atom, that is, when descending along a group of the periodic table and from right to left along a period. In summary, the tendency to give bent structures decreases along the series Ir > Rh > Pt > Pd > Ni > Au. Also good $\sigma$-donor (and preferably good $\pi$-acid) terminal ligands (e.g., $PR_3$, CO, bipy, cyclooctadiene or other diolefins) favor bent structures. In the compounds with monosubstituted bridges, three new factors were found 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 in the *exo* conformation, and (iii) the repulsion between the bridge substituents and the terminal ligands in the *endo* conformation.

In this paper we present an ab initio theoretical study of a variety of compounds of types $[M_2(\mu\text{-}XR_2)_2L_4]$ and $[M_2(\mu\text{-}XR^1R^2)_2L_4]$, where M is a $d^8$ square planar transition metal ion and X = N, P, or S, in an attempt to advance toward the understanding of the factors that affect the relative stabilities of the available molecular conformations. Compounds with $SiR_2$ bridges and a different electron count present through-ring Si− Si[24,25] or Rh−Rh[26] bonds and will not be considered here. Similarly, complexes with aryl bridging groups[27] are disregarded because of the different hybridization at the bridging atom and

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the different electronic structure.[28] Before analyzing the results (geometry and relative energy) for the variety of model complexes studied, we briefly discuss in the next section the degree of agreement between calculated and experimental structures. After showing that the present calculations can provide structural data with chemical accuracy, we will analyze the structural preferences and some structural correlations between bonding parameters. Then we will discuss the relative energies of the various conformers. Finally, the structural choice in the experimentally characterized molecules will be discussed in light of the theoretical conclusions.

## Calibration of Theoretical Structures

Ab initio MP2 calculations (see Appendix for computational details) were performed for $d^8$ model complexes $[M_2(\mu\text{-}XR^1R^2)_2L_4]$ (M = Rh, Pt, Au; X = N, P, S; $R^1$, $R^2$ = H, Me; L = CO, $PH_3$, Me) in the different conformations represented in **1** and **5**. A total of 102 structures of 30 compounds were optimized with the only restrictions that the terminal ligands were kept frozen and that the bending angle was kept fixed in 55 structures. The atomic coordinates of the 47 minima are supplied as Supporting Information. To facilitate identification of the different model compounds whose formulas can be found in Tables 1 and 2, we label them with an **M** followed by a sequential number. Similarly, the experimentally determined structures will be identified by an **E**, and their structures and references can be found in Table 4. Before discussing the most relevant structural features of the calculated geometries, we wish to verify how reliable our computational results are compared to experimental data. Calculated structural data for some of the model compounds, together with the experimental information[29−40] for closely related molecules with the same molecular conformation, can be found as Supporting Information (Table S1). The following observations can be made on the agreement between calculated and experimental structures:

(a) Calculated M−X and M−L bond distances are in general good agreement with the corresponding experimental values, the average deviations being 0.03 and 0.04 Å, respectively. The worst result corresponds to the platinum-bridging sulfur distance in model compound **M.19**, that is 0.09 Å longer than in the experimental structure **E.23**.

(b) Calculated XMX, MXM, and LML bond angles differ from the experimental values by less than 7° (average deviations of 1°, 2°, and 3°, respectively). Not unexpectedly, larger deviations (of 9°) appear for the P−M−P angles when the chelating dppe ligand is present in an experimental structure, since monodentate phosphines were used in our calculations.

**Table 1.** Energy of the Bent Form of the $d^8$ $[M_2(\mu\text{-}XR_2)_2L_4]$ Complexes Relative to the Planar Geometry (R = H, Me), Together with Conformational Parameters Defined in **2**−**4** for the Bent Geometry[a]

| | | | | | planar | bent | | | |
|---|---|---|---|---|---|---|---|---|---|
| compd | M | X | R | L | $\theta$[b] | $E_b^R$ | $\theta$[b] | $\tau$ | $\omega$ |
| **M.1** | Rh | N | H | CO | 180* | −6.2 | 127 | 39 | 9 |
| **M.2** | Rh | P | H | CO | 180* | −8.8 | 118 | 42 | 8 |
| **M.3** | Rh | N | H | $PH_3$ | 180* | −7.7 | 124 | 41 | 10 |
| **M.4** | Rh | P | H | $PH_3$ | 180* | −8.3 | 119 | 41 | 7 |
| **M.5** | Pt | N | H | $PH_3$ | 180* | −1.4 | 141 | 29 | 6 |
| **M.6** | Pt | P | H | $PH_3$ | 180* | −1.5 | 141 | 30 | 7 |
| **M.7** | Pt | S | H | $PH_3$ | 180 | 4.1 | 142* | 27 | 3 |
| **M.8** | Pt | N | H | Me | 180 | 1.2 | 142* | 28 | 4 |
| **M.9** | Pt | P | H | Me | 179 | 1.9 | 141* | 30 | 6 |
| **M.10** | Pt | S | H | Me | 180 | 4.0 | 139* | 21 | −2 |
| **M.11** | Au | N | H | Me | 180* | −0.1 | 154 | 18 | 3 |
| **M.12** | Au | P | H | Me | 180* | −0.7 | 146 | 29 | 9 |
| **M.13** | Rh | N | Me | CO | 180* | −1.0 | 155 | 16 | 1 |
| **M.14** | Rh | P | Me | CO | 180* | −4.1 | 133 | 26 | −1 |
| **M.15** | Rh | N | Me | $PH_3$ | 178 | 12.8 | 122* | 24 | −7 |
| **M.16** | Rh | P | Me | $PH_3$ | 180* | 0.3 | 149 | 23 | 3 |
| **M.17** | Pt | N | Me | $PH_3$ | 179 | 8.7 | 141* | 20 | −3 |
| **M.18** | Pt | P | Me | $PH_3$ | 178 | 2.7 | 142* | 24 | 0 |
| **M.19** | Pt | S | Me | Me | 180 | 5.9 | 140* | 21 | −2 |
| **M.20** | Au | N | Me | Me | 179 | 3.2 | 154* | 15 | 0 |
| **M.21** | Au | P | Me | Me | 180* | −0.3 | 156 | 20 | 6 |

[a] Energies in kcal/mol, angles in degrees. [b] The $\theta$ parameter marked with an asterisk was frozen and the rest of the structure optimized. All other structural parameters were optimized for each structure, except for the internal structure of the terminal ligands.

(c) The angular parameters associated with bending around the X⋯X hinge, $\theta$ and $\tau$, are in good agreement with the experimental ones, provided that the terminal ligands in the model and experimental structures are identical and that the bridge substituents in the latter are not significantly bulkier.

(d) The non bonded M⋯M distance is fairly well reproduced, and large deviations from the experimental values should be attributed to the presence of terminal ligands bulkier than those used in the calculations, or to the long Pt−S distance of **M.19** mentioned above. Although the conformational preference will be discussed below, we note in passing that the preference for a bent or a planar structure computationally found is in agreement with the observed structures in most cases.

## Main Structural Trends

The large number of calculated structural data allows us to focus on the general trends in this family of compounds, rather than concentrating on every particular compound. The optimized conformational parameters to be discussed in this section ($\theta$, $\tau$, and $\omega$) are collected in Table 1 for $XR_2$-bridged (R = H, Me) and in Table 2 for XHMe-bridged complexes.

A wide range of bending angles appears in the optimized structures, although some regularities can be found. For all the bent minima, the extent of bending is larger (i.e., smaller values of $\theta$) for Rh than for Pt or Au with the same set of ligands, a result that can be associated with the stronger M⋯M interaction usually found for Rh.[22] Another trend observed for the bent conformations is a larger degree of bending for X = P than for X = N, other things being equal, with the only exception of compounds **M.5** and **M.6**, which show the same degree of bending. This trend was previously detected in analogous

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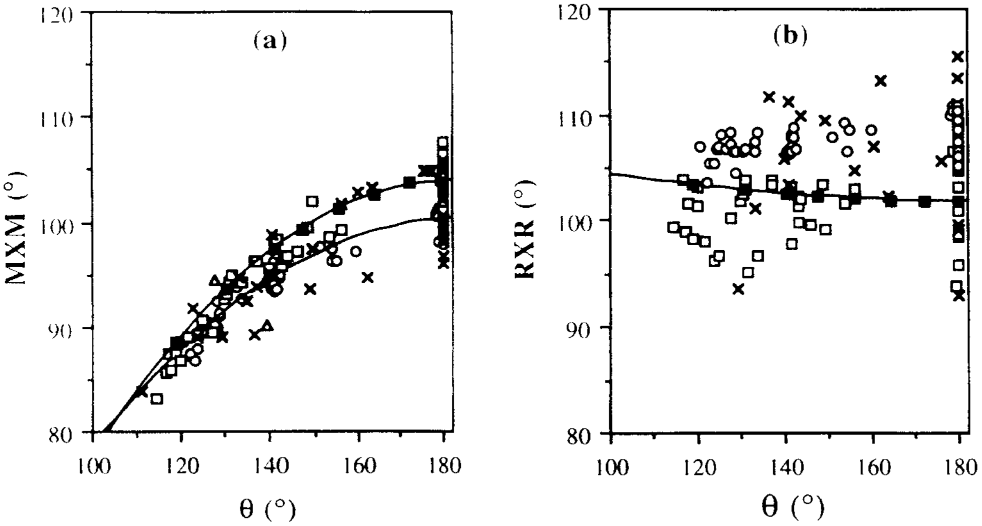


**Figure 2.** Variation of the MXM (a) and RXR (b) bond angles as a function of the bending around the X- - -X hinge (**2**) for the model compound $[Pt_2(\mu\text{-}PH_2)_2(PH_3)_4]^{2+}$ (solid squares and solid line). Data for other model complexes at their optimized conformations are also shown: open circles and lower line in panel (a) for $NR_2$ bridges, open squares for $PR_2$ bridges and open triangles for $SR_2$ bridges (see Appendix and data in Tables 1 and 2). Experimental data also shown for comparison (crosses, see Table 4 for references).

**Table 2.** Relative Energies for the Planar and Bent Forms of the Model $d^8$ Complexes $[M_2(\mu\text{-}XHMe)_2L_4]$,[a] Together with the Conformational Parameters Defined in **2**−**4**

| | M | X | L | | pa | ps | be | ba[b] | bx |
|---|---|---|---|---|---|---|---|---|---|
| **M.22** | Rh | N | CO | $E$ | 0.0 | 0.0 | −7.4 | −6.1 | −2.9 |
| | | | | $\theta$ | 180* | 180* | 125 | 128 | 141 |
| | | | | $\tau$ | 9 | 8 | 45 | 44/26 | 17 |
| | | | | $\omega$ | 9 | 8 | 14 | 14/−3 | −6 |
| **M.23** | Rh | P | CO | $E$ | 0.0 | 0.0 | −10.8 | −8.7 | −4.8 |
| | | | | $\theta$ | 180* | 180* | 116 | 120 | 128 |
| | | | | $\tau$ | 4 | 4 | 44 | 41/34 | 26 |
| | | | | $\omega$ | 4 | 4 | 10 | 8/0 | −3 |
| **M.24** | Rh | N | $PH_3$ | $E$ | 0.0 | 0.2 | −7.1 | −6.8 | −5.8 |
| | | | | $\theta$ | 180* | 180* | 121 | 125 | 141 |
| | | | | $\tau$ | 4 | 4 | 50 | 50/26 | 16 |
| | | | | $\omega$ | 4 | 4 | 16 | 18/−5 | −4 |
| **M.25** | Rh | P | $PH_3$ | $E$ | 0.0 | 0.0 | −6.9 | −6.5 | −4.7 |
| | | | | $\theta$ | 180* | 180* | 117 | 122 | 134 |
| | | | | $\tau$ | 2 | 2 | 45 | 42/34 | 26 |
| | | | | $\omega$ | 2 | 2 | 10 | 9/0 | −1 |
| **M.26** | Pt | N | $PH_3$ | $E$ | 0.0 | 0.1 | −0.2 | −2.0 | −4.1 |
| | | | | $\theta$ | 180* | 180* | 128 | 133 | 151 |
| | | | | $\tau$ | 4 | 4 | 45 | 44/24 | 13 |
| | | | | $\omega$ | 4 | 4 | 15 | 16/−4 | −4 |
| **M.27** | Pt | P | $PH_3$ | $E$ | 0.0 | 0.1 | −0.8 | −1.6 | −2.1 |
| | | | | $\theta$ | 180* | 180* | 131 | 137 | 148 |
| | | | | $\tau$ | 2 | 2 | 42 | 38/26 | 19 |
| | | | | $\omega$ | 2 | 2 | 12 | 12/0 | −1 |
| **M.28** | Pt | S | Me | $E$ | 0.0 | 0.0 | 4.4 | 4.7 | 5.3 |
| | | | | $\theta$ | 180 | 178 | 139* | 139* | 139* |
| | | | | $\tau$ | 0 | −1 | 24 | 23/22 | 20 |
| | | | | $\omega$ | 0 | 0 | 0 | −1/−2 | −4 |
| **M.29** | Au | N | Me | $E$ | 0.0 | −0.1 | 1.3 | 0.4 | −1.3 |
| | | | | $\theta$ | 180* | 180* | 134 | 142 | 160 |
| | | | | $\tau$ | 4 | 4 | 39 | 34/19 | 8 |
| | | | | $\omega$ | 4 | 4 | 13 | 13/−3 | −3 |
| **M.30** | Au | P | Me | $E$ | 0.0 | 0.0 | −1.6 | −1.1 | −0.3 |
| | | | | $\theta$ | 180* | 180* | 140 | 144 | 154 |
| | | | | $\tau$ | 2 | 2 | 35 | 33/27 | 20 |
| | | | | $\omega$ | 2 | 2 | 12 | 12/6 | 4 |

[a] An asterisk indicates a $\theta$ parameter that has been frozen in the calculation. [b] For the **ba** conformer the first value given for $\tau$ and $\omega$ corresponds to the *endo* group, the second value to the *exo* group.

complexes with unsubstituted or monosubstituted bridges,[22,23] and was attributed to the longer M−X distances in the former case, that facilitates a better overlap between the $z^2$ and $p_z$ metal orbitals while keeping the terminal ligands of the two metals farther apart. It can also be noted that, for each compound with XHMe bridges, $\theta$ decreases in the order **be** < **ba** < **bx**. Finally, the extent of bending is significantly smaller (10−30° less) in the $XMe_2$- than in the analogous $XH_2$-bridged complex (compare, e.g., data for rhodium compounds in Table 1).

Two clear trends can be observed for the orientation of the bridging ligands in the complexes with symmetric bridges. The uplift of the $XMe_2$ groups (measured by $\tau$) is significantly reduced compared to that of the $XH_2$ analogues, in an attempt to keep the bulkier substituents as far apart from each other as possible. On the other hand, bending favors a closer approach of the *endo* than the *exo* groups to the $XM_2$ planes for the $XH_2$-bridged complexes, as reflected by positive values of $\omega$. The reverse occurs with the $XMe_2$-bridged compounds that present negative or small positive values of $\omega$ in their bent minima.

The M−X bond distances are little affected by bending of the coordination planes. As an example, the bridging Pt−N distances in model complexes with $PH_3$ as terminal ligands and $NR^1R^2$ bridges vary only between 2.076 and 2.106 Å. The trans influence associated with substitution of the terminal phosphines by methyl ligands has a much more significant effect on the same bond distance, producing a lengthening from 2.076 to 2.155−2.162 Å. Obviously, if the M−X distances and the XMX angles are practically unaffected by bending (as found both in our calculations and in the experimental structural data), the MXM bond angle must decrease upon bending. This geometrical constraint can be illustrated by the behavior of $[Pt_2(\mu\text{-}PH_2)_2(PH_3)_4]^{2+}$, represented in Figure 2 (closed squares). For the whole set of model compounds studied, different MXM bond angles can be found for a given hinge angle $\theta$. It is interesting to note that such variability is much wider for the planar than for the strongly bent structures, resulting in a wedge-like region of allowed angles XMX and $\theta$, that defines a general trend for all calculated compounds, regardless of the nature of the metal atom, bridging ligands, or terminal ligands. The same qualitative behavior can be found for the experimental structures (Figure 2a, crosses). In contrast, the RXR angles in the model compound $[Pt_2(\mu\text{-}PH_2)_2(PH_3)_4]^{2+}$ are little affected by bending (Figure 2b, solid line), but the values for different complexes show a wide dispersion. Such dispersion can be associated in part with the

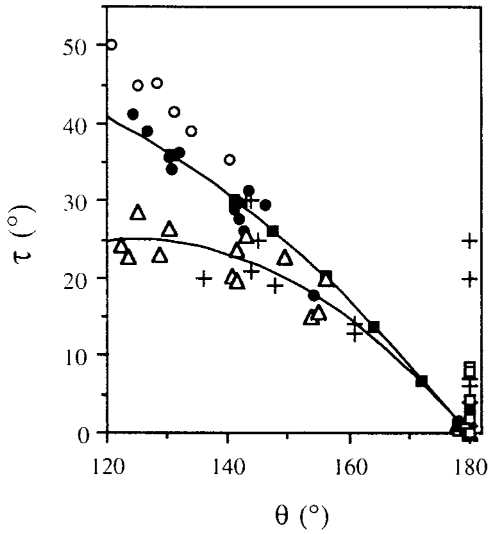


**Figure 3.** Extent of the flapping motion of the bridging $XR_2$ groups ($\tau$) as a function of the degree of bending around the X- - -X hinge ($\theta$) in the model binuclear compounds with X = N, P. The solid squares (and the associated solid line) correspond to the stepwise bending of $[Pt_2(\mu\text{-}PH_2)_2(PH_3)_4]^{2+}$, open circles to the optimized or frozen bent structures of all $[M_2(\mu\text{-}XHMe)_2L_4]$ compounds with the **be** conformation, solid circles to all $[M_2(\mu\text{-}XH_2)_2L_4]$ model compounds, open triangles (and associated solid line) to $[M_2(\mu\text{-}XMe_2)_2L_4]$ compounds, and open squares to all planar structures. Experimental data for Pt compounds are represented by crosses.

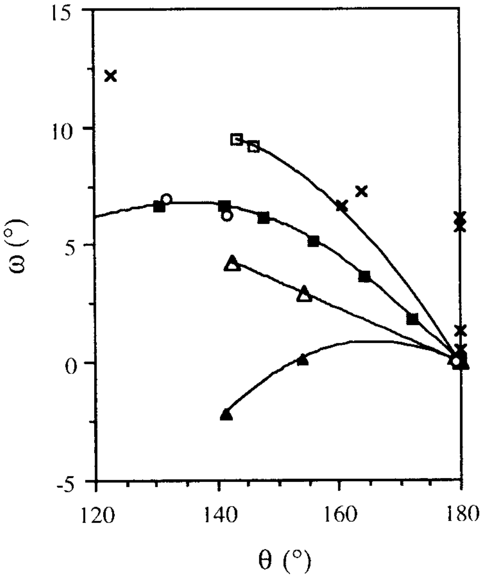
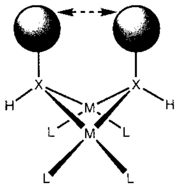


**Figure 4.** Distortion from the local pseudotetrahedral geometry of the $M_2XR_2$ groups ($\omega$, see **4**) as a function of the degree of bending around the X- - -X hinge ($\theta$), for the model complex $[Pt_2(\mu\text{-}PH_2)_2(PH_3)_4]^{2+}$ at fixed values of $\theta$ (closed squares). Also shown are the data corresponding to Au complexes with $NH_2$ (open triangles), $PH_2$ (open squares), or $NMe_2$ bridges (closed triangles), and Pt compound with $PH_2$ bridges (open circles), all having Me as terminal ligands. Experimental data for bent complexes with symmetric bridges (crosses) also shown for comparison.

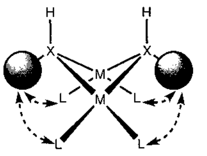
nature of the bridging atom, since $NR_2$ bridges (Figure 2b, open circles) clearly show larger angles than $PR_2$ bridges (Figure 2b, open squares).

It is interesting to notice that the orientation of the substituents at the bridging atoms is correlated with the degree of bending. When the molecule is planar, the two substituents are symmetrically arranged relative to the MXM plane, as indicated by the calculated values of $\tau$ (**3**) between 0° and 4° for all planar compounds, corresponding to a pseudotetrahedral coordination around X. The experimental data for planar complexes (Figure 3) also show small deviations from $\tau = 0°$, with only two exceptions ($\tau \geq 20°$, compounds **E.35** and **E.36**), corresponding to complexes in which one of the R groups is a Pt atom. Bending the binuclear molecule results in a tilting of the $XR_2$ group, and $\tau$ is per force increased. That the raising of the bridge substituents is correlated with the degree of bending can be seen in a number of ways. The most simple example is given by the optimized values of $\tau$ at different bending angles in the model compound $[Pt_2(\mu\text{-}PH_2)_2(PH_3)_4]^{2+}$ (Figure 3, solid squares), for which a decrease in $\theta$ results in positive values of $\tau$. Practically the same behavior can be found for all the model complexes with $NH_2$, $PH_2$ (Figure 3, closed circles), or $SH_2$ bridges (not shown in Figure 3 for clarity).

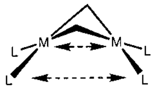
The presence of a Me substituent at the bridging atom, though, strongly affects the orientation of the bridging groups in the bent conformers. As a result of bending, the two *exo* substituents become closer (represented by spheres in **6a**), and the *endo* substituents approach the terminal ligands (**6b**). Hence, the steric repulsion between the *exo* Me groups is minimized by adjusting the bending angle $\theta$ (as discussed above) and the orientation of the substituents (angles $\tau$ and $\omega$). Such an effect can be seen in values of $\tau$ smaller than 28° (Figure 3, triangles) for the **bx** structure of complexes with XHMe bridges and for the bent structure with $XMe_2$ bridges, to be compared with values of up to 42° for $XH_2$ bridged compounds. The orientation of the XHMe bridges with an *endo* Me group (in the optimized **be** and **ba** conformers) is clearly different from that in the analogous molecule with $XMe_2$ bridges at a comparable degree of bending. Thus, the values of $\tau$ are found in the range between 22° and 38° for the **ba** structure, between 33° and 50° for the **be** form (Figure 3, open circles), and between 15° and 28° for $XMe_2$ bridges. These results can be rationalized considering that L···R repulsions decrease and the R···R ones increase with increasing $\tau$, and taking into account the number of L···R contacts per molecule in the **be** and **ba** structures. The experimental data for the bent structures of Pt compounds (Figure 3, crosses) are well within the range defined by the theoretical values.



**6a**



**6b**



**6c**

Another aspect of the orientation of the bridging ligand that can be observed in the calculated structures is the loss of the local pseudotetrahedral geometry around the bridging atom, as indicated by the angle $\omega$ (see **4**). In all planar forms with two identical substituents, these are symmetrically arranged with respect to the MXM plane, as indicated by $\omega = 0$. Again, the two exceptions correspond to compounds **E.35** and **E.36** with highly asymmetric bridges. Things are somewhat different for the bent molecules. Consider first the model complex $[Pt_2(\mu\text{-}PH_2)_2(PH_3)_4]^{2+}$, for which we have optimized the structure at different bending angles. The results (Figure 4, black squares) show that the two substituents become asymmetrically distributed above and below the $XM_2$ plane, with $\omega$ increasing upon bending (i.e., for $\theta$ smaller). For a large degree of bending, though, the trend is reversed, possibly because the two *exo* groups start to repel each other and the *endo* groups get too

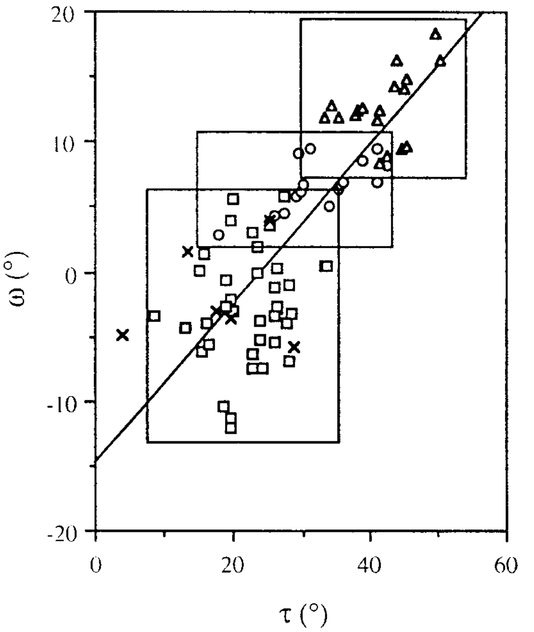


**Figure 5.** Asymmetry of the two bridge substituents relative to the $XM_2$ plane (ω) as a function of the flapping motion of the $XR_2$ group (τ) in the calculated model structures. The rectangles indicate the ranges of values found for compounds with XHMe bridges (triangles) having the methyl group in the *endo* position (**ba** and **be** conformers), for compounds with $XH_2$ bridging groups (circles), and for compounds with $XMe_2$ or XHMe bridges (squares) having the Me group in the *exo* position (**ba** and **bx** conformers). Experimental data represented by crosses.

close to the terminal ligands. The nature of the bridges dramatically affects the relationship between θ and ω, as illustrated by the data sets for the Au compounds with $NH_2$ or $PH_2$ bridges (Figure 4, open triangles and squares, respectively). Similarly, substituting the H atoms in the $NH_2$ bridges (open triangles) by Me groups (closed triangles) has a strong influence on the correlation between ω and θ. However, such structural correlation is not significantly influenced by changes in the terminal ligands, as can be seen by comparing the $PH_2$-bridged Pt complexes with $PH_3$ or Me terminal ligands (Figure 4, closed squares and open circles, respectively). Similarly, compounds with different metal atoms but identical ligand sets show practically the same dependence of ω on θ. The experimental data for nonplanar complexes with symmetric bridges (Figure 4, crosses), even if scarce, seem to be consistent with the calculated data (only structures with non-hydrogen substituents shown: compounds **E.5**, **E.18**, and **E.46**, Table 4). In particular we notice that only positive values of ω are found for symmetric bridges, indicating that the distortion from $C_{2v}$ symmetry around the bridging atoms tends to put the substituents away from the region of space occupied by the terminal ligands.

For XHMe bridges we find that the methyl group is farther from the $M_2X_2$ plane than the hydrogen atom (positive values of ω). Furthermore, the values of τ and ω are identical for the **ps** and **pa** conformations of the same compound (Table 2), suggesting that such deviation might be due to electronic and not to steric factors. In such compounds, the asymmetric position of the bridges (for X = N or P) relative to the $XM_2$ plane seems to be correlated with the degree of substituent raising, τ (Figure 5). The data points shown there can be roughly classified in three groups that are enclosed in boxes. The XHMe groups with the hydrogen atom in the *exo* and the methyl group in the *endo* position present larger values of τ and ω. The $XH_2$ groups, with hydrogen atoms in both the *exo* and *endo* positions, have intermediate values of τ and ω. Finally, the $XMe_2$ and XHMe bridges with an *exo* methyl group present smaller values of τ and ω, and even negative values for the latter parameter. The trends just discussed can be ascribed to the enhanced steric repulsion between the bulkier *exo* substituents at larger values of τ and ω, together with increased steric repulsion between the bulkier *endo* substituents and the terminal ligands. The experimental data (Figure 5, crosses) are consistent with the theoretical behavior. The wide dispersion around the general trend just discussed can be attributed to the variety of metal atoms, bridges, and terminal ligands that have been considered.

## Conformational Preferences

In this section we discuss the relative energies of the different conformers studied. Although energy differences between conformers are not high and can be affected in practice by several factors, including packing forces, some general trends can be found that will be useful for explaining the experimental structures. An attempt to rationalize the conformational differences by obtaining estimates of several energy contributions will be presented in the next section. For the Rh compounds, the bent forms with symmetric bridges are clearly more stable than the planar ones (Table 1), in keeping with the stronger ability of Rh to form metal−metal bonding interactions,[22,23] whereas for the Pt and Au complexes the energy difference is generally small.

Comparison of the relative energies of the bent conformers for similar compounds with $XH_2$ and $XMe_2$ bridges ($E_b^R$, Table 1) indicates that the Me substituent destabilizes the bent form in all cases. The bridging N atom has a stronger destabilizing effect upon methyl substitution than P or S. The reason is that the shorter M−N distances (compare, e.g., Pt−P ≈ 2.34 Å vs Pt−N ≈ 2.10 Å) induce a shorter Me···Me contact that is responsible for the destabilization of the bent form relative to the planar one.

A look at the energies of the planar geometries with XHMe bridges (Table 2) shows that the **pa** and **ps** forms have practically the same energy in all cases, suggesting that the Me···Me repulsion in the planar *syn* form is negligible. Among the bent forms, **bx** is slightly more unstable than the other two structures, as a result of the larger R···R repulsion.

## Energy Contributions

In general, we can consider four different contributions to the relative energies of each conformer: (i) the interaction between the two $ML_2$ fragments, $I_{MM}$ (conceivably including both M···M attractive and L···L repulsive contributions); (ii) the energy $V_\beta$ associated with the decrease in the MXM bond angles from the planar form to the bent geometry; (iii) the increased interaction $I_{RR}$ between the *exo* substituents of the two bridges in the bent form; and (iv) the increased interaction between the *endo* substituents and the terminal ligands in the bent forms, represented from here on by $I_{LR}$.

The effect of the terminal ligands on the M···M interaction has been previously discussed[22,41,42] for the stacked dimers of $d^8$ complexes[41] and for the bent binuclear complexes with unsubstituted bridges.[22] We simply recall here that two factors appear combined in the energetics of the interaction between the two $ML_2$ groups (**6c**): the weakly bonding M···M interaction that stabilizes the bent forms is favored by good σ donor ligands,

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whereas the bulky substituents (as in $PPh_3$ or dppe) introduce steric L···L repulsions that destabilize the bent conformers.

Since bending around the X- - -X hinge implies a decrease in the MXM bond angles of up to 20° (Figure 2), it is worth evaluating the energy involved in such a structural change, represented here by $V_\beta$. As a crude approximation, we have calculated the energy of the $XH_4^{n+}$ species ($X = N, P, n = 1$; $X = S, n = 2$) at the same computational level used throughout this paper, varying one of the HXH bond angles ($\beta$) and reoptimizing the rest of the geometry in each case. As an example, a change in $\beta$ from 100° to 90° requires 6.2 kcal/mol for X = N, and 4.4 kcal/mol for X = P or S. Although one should be aware that such values must vary when the H atoms are substituted by two metal atoms and two organic groups as in the presently studied complexes, they point to the importance of the changes in MXM bond angles upon bending, taking into account that two bridging atoms are present in these compounds.

An estimate of the $I_{MM}$ and $V_\beta$ terms in the complexes under study can be obtained by comparing the relative energies of the different conformers. Hence, for compounds with $XH_2$ bridges, assuming[23] $I_{RR} \approx I_{LR} \approx 0$, the energy of the bent conformer relative to the planar one can be approximately expressed as

$$E_b{}^H \approx I_{MM} + 2V_\beta \qquad (1)$$

Notice that the values of $2V_\beta$ calculated above for the $XH_4^{n+}$ species and those of $I_{MM}$ calculated for face-to-face stacked complexes[43] or for edge-sharing binuclear complexes with monosubstituted bridges[23] are of the same order of magnitude but opposite in sign in most cases. Hence, it is not surprising that the energy differences between the two conformers (Table 1, compounds **M.1−12**) are in most cases less than 10 kcal/mol, with either the planar or the bent conformation being more stable depending on the case. For those compounds with $PH_3$ or CO terminal ligands the bending energies are comparable to those reported previously[23] for analogous compounds with XR bridges (between −6 and −11 kcal/mol for Rh, between +4 and −2 kcal/mol for Pt), suggesting that the decrease in the MXM angle requires similar energies for the $RXM_2$ and $R_2XM_2$ groups. The fact that the bent form is more favorable for Rh than for Pt or Au can be attributed to the stronger M···M bonding interaction for the former that is well established.[22,23] The fact that compounds with Me terminal ligands present positive values of $I_{MM} + 2V_\beta$ might be attributed to the stronger L···L repulsions (hence more positive $I_{MM}$ terms) for the Me than for the $PH_3$ terminal ligands, due to the shorter Pt−C bond distances (2.10 Å) compared to the Pt−P ones (2.34 Å).

For complexes with substituted $XR_2$ bridges, one can similarly express the energy of a bent conformer relative to the planar one as

$$E_b{}^R \approx I_{MM} + 2V_\beta + I_{RR} + 2I_{LR} \qquad (2)$$

An estimate of the combined repulsion terms $I_{RR} + 2I_{LR}$ (R = Me) can be obtained by approximating $I_{MM} + 2V_\beta$ to the value obtained for the analogous compound with $XH_2$ bridges. Since the geometries of the optimized structures for the analogous complexes with $XH_2$ and $XMe_2$ bridges are different in many cases, we have estimated the interaction term by calculating the energy of the methyl-substituted compound with the bending angle frozen at the value obtained for the unsubstituted bridge (Table 3). From the large positive values of $I_{RR} + 2I_{LR}$ obtained for R = Me we can conclude that the main effect of the introduction of Me substituents is a net destabilization of the bent form relative to the planar one. Such an effect is so important that in several cases no bent minimum was found at all for the methyl-substituted compound. The interaction term $I_{RR} + 2I_{LR}$ for R = Me increases along the series Au < Pt < Rh, as a result of the increased degree of bending (see values of $\theta$ in Table 1). The increased repulsion is however compensated by the enhanced M···M bonding interactions, as noted above. The fact that the interaction term significantly increases when terminal CO ligands are substituted by the bulkier $PH_3$ ones might be interpreted as resulting from the non-negligible $I_{LR}$ contribution.

**Table 3.** Energy Interaction Terms[a] ($I_{MM} + 2V_\beta$) Estimated from Calculated Energies of the $[M_2(\mu\text{-}XH_2)_2L_4]$ Complexes (Eq 1), ($I_{RR} + 2I_{LR}$) from calculations on $[M_2(\mu\text{-}XMe_2)_2L_4]$ Compounds, and $I_{RR}$ from the $[M_2(\mu\text{-}XHMe)_2L_4]$ Analogues at a Comparable Degree of Bending (Eqs 2 and 3)

| M | X | L | ($I_{MM} + 2V_\beta$) | ($I_{RR} + 2I_{LR}$) | ($I_{RR}$) |
|---|---|---|---|---|---|
| Rh | N | CO | −6.2 | 12.1 | 3.4 |
| Rh | P | CO | −8.8 | 6.2 | 5.4 |
| Rh | N | $PH_3$ | −7.7 | 20.5 | 4.9 |
| Rh | P | $PH_3$ | −8.3 | 10.1 | 4.0 |
| Pt | N | $PH_3$ | −1.4 | 10.2 | 0.7 |
| Pt | P | $PH_3$ | −1.5 | 4.2 | 0.8 |
| Pt | S | Me | 4.0 | 1.9 | 1.3 |
| Au | N | Me | −0.1 | 3.4 | 0.1 |
| Au | P | Me | −0.7 | 1.1 | 0.4 |

[a] All values in kcal/mol.

In summary, for those molecules with R = Me, the repulsion term $I_{RR} + 2I_{LR}$ that destabilizes the bent form relative to the planar one increases with decreasing Me···Me distances (Figure 6). In addition, the repulsion term increases with decreasing L···Me distance for compounds with the same terminal ligand. Such dependence is more pronounced at the degree of bending considered for $PH_3$ than for the smaller CO or Me ligands.

Through arguments similar to those presented above for symmetric bridges, the following relationships between the energies of the different conformers and the interaction terms can be written for complexes with XHR bridges:

$$E_{\mathbf{bx}} - E_{\mathbf{ps}} \approx I_{MM} + 2V_\beta + I_{RR} \qquad (3)$$

$$E_{\mathbf{ba}} - E_{\mathbf{pa}} \approx I_{MM} + 2V_\beta + I_{LR} \qquad (4)$$

where we have assumed that the degree of bending of the **b**, **bx**, and **ba** forms of a given molecule is practically the same, and the repulsion terms involving hydrogen atoms are neglected. Approximating $I_{MM} + 2V_\beta$ as the value for the analogous complex with $XH_2$ bridges at a similar degree of bending, one can obtain estimates for $I_{RR}$ and $I_{LR}$. Given the approximations adopted, one should expect an uncertainty of at least 1−2 kcal/mol for the estimated energy terms. Therefore, we focus more on the large effects and on qualitative trends, rather than on the resulting numerical values.

The values of $I_{RR}$ (R = Me) estimated from the energies of the **bx** conformers with asymmetric bridges are significantly smaller than the $I_{RR} + 2I_{LR}$ terms estimated from the calculated energies of the compounds with $XMe_2$ bridges (Table 3). These results indicate that the $I_{LR}$ term is important in the latter case, due to the presence of *endo* methyl groups. Another clear result is the very large difference between the two estimates when the bridging atom is N, a fact that we associate with the shorter M−X bond distance and the enhanced L···R repulsions. We

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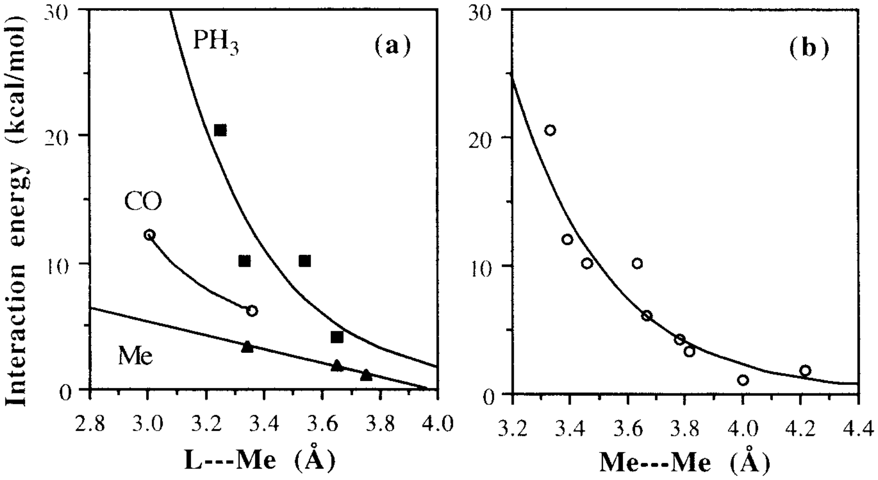

**Figure 6.** (a) Estimated interaction energy term ($I_{LR}$ for R = Me, kcal/mol) as a function of the distance between the *endo* methyl substituents at the bridging atom and the terminal ligands L = CO (circles, C···C distance), PH$_3$ (squares, C···P distance), or Me (triangles, C···C distance). (b) Estimated interaction energy term ($I_{RR}$ for R = Me, kcal/mol) as a function of the distance between the carbon atoms of the methyl substituents at the two bridging atoms in compounds with XMe$_2$ bridges.

have seen above that, as a result of Me···Me repulsion, the **bx** conformer presents larger values of $\theta$ than the **be** or **ba** conformers, the uplift of the substituents is restricted to $\tau < 28°$, and negative values of $\omega$ result. The $I_{RR}$ terms for R = Me (Table 3) reflect such geometrical reorganization, since the larger repulsions (around 5 kcal/mol) correspond to the strongly bent structures of the rhodium compounds.

The $I_{LR}$ (R = Me) terms estimated from the energies of the **ba** and **pa** forms (eq 4) are small in all cases (<2 kcal/mol). In a couple of cases small negative values are obtained, that are most likely due to the uncertainty of these energy contributions due to the approximations employed.

## Analysis of the Experimental Conformations

The molecular conformation of most of the structurally characterized complexes (Table 4) can be rationalized by applying the qualitative ideas that stem from our theoretical study. Let us consider first those compounds with symmetrically substituted bridges. In the Pt compounds with NH$_2$ bridges (**E.24**−**26**), the bent conformation is the one experimentally found, as predicted for most Pt complexes having NH$_2$ or PH$_2$ bridges (Table 1). The presence of Me substituents at the bridging ligands was shown above to destabilize the bent form relative to the planar one, due to the increased R···R and L···R repulsions. In agreement with such prediction, practically all complexes with symmetric bridges in which R is not hydrogen (**E.1**−**3**, **E.8**−**10**, **E.18**−**23**, **E.42**, and **E.46**) present planar structures, certainly favored by the bulky nature of the substituents ($^t$Bu or Ph in most cases). The exception is **E.5**, whose bent structure is probably favored by the stacking interaction between the two *exo* phenyl substituents of the bridging ligands (at a distance between centroids of 4.10 Å) together with the tendency of Rh to form Rh···Rh contacts. The change of only the rhodium atoms for Pt (compound **E.20**) with less tendency to form metal···metal contacts is enough to give a planar structure.

Among the compounds with asymmetric bridges, all those with NHR or PHR as bridging ligands are planar (**E.4**, **E.11**−**14**, **E.29**−**34**, and **E.45**) or **be** (**E.7**, **E.16**, **E.38**, and **E.43**). Our calculations for [M$_2$($\mu$-XHMe)$_2$(PH$_3$)$_4$] complexes (X = N or P), though, predict the bent structures to be somewhat more stable than the planar ones. But one must recall that the repulsion between terminal ligands bulkier than the simple ones used in our calculations (PH$_3$, CO, and CH$_3$) should be expected to destabilize the bent conformers. Unconstrained molecules are found in a bent conformation in compounds **E.7** and **E.43**, in which the terminal ligands are the small CO or Me groups (small $I_{LR}$ term) and the *exo* substituents in the **be** conformation are hydrogen atoms ($I_{RR} \approx 0$). From our calculations, the two planar structures, **ps** and **pa**, are practically isoenergetic. Although most of the experimental planar structures present the **pa** conforma-

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**Table 4.** Experimental Structural Data[a] for Dimers of $d^8$ Metal Ions of Type $[L_2M(\mu\text{-}XR_2)_2ML_2]$

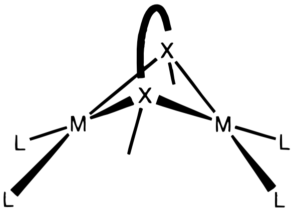
| compound[b] | M···M | $\theta$ | $\tau$ | struct | ref | refcode[c] |
|---|---|---|---|---|---|---|
| **E.1** $[Rh_2(\mu\text{-}P^tBu_2)_2(CO)_4]$ | 3.717 | 180 | 1 | **p** | 37 | cabfam |
| **E.2** $[Rh_2(\mu\text{-}As^tBu_2)_2(CO)_4]$ | 3.884 | 180 | 1 | **p** | 44, 45 | daslak10 |
| **E.3** $[Ir_2(\mu\text{-}As^tBu_2)_2(CO)_4]$ | 3.895 | 180 | 1 | **p** | 46 | fuphed |
| **E.4** $[Rh_2(\mu\text{-}NHPh)_2(PPh_3)_4]$ | 3.376 | 180 | 1 | **pa** | 18 | nonhaz |
| **E.5** $[Rh_2(\mu\text{-}PPh_2)_2(dppe)_2]$ | 3.471 | 136 | 30 | **b** | 29 | buckal |
| **E.6** $[Rh_2(\mu\text{-diaminonaphthalene})(CO)_4]$ | 2.810 | 116 | 26 | **bx** (**7a**) | 38 | jajlub |
| **E.7** $[Ir_2(\mu\text{-}NH\{p\text{-tol}\})_2(CO)_4]$ | 2.968 | 125 |  | **be** | 39 | vupbud01 |
| **E.8** $[Ni_2(\mu\text{-}PPh_2)_2(PPh_2\{NPh\}_2)_2]$ | 3.430 | 180 | 3 | **p** | 47 | rehcuc |
| **E.9** $[Pd_2(\mu\text{-}PPh_2)_2Cl_2(HPPh_2)_2]$ | 3.612 | 180 | 0 | **p** | 48 | kuxsol01 |
| **E.10** $[Pd_2(\mu\text{-}PPh_2)_2(hfacac)_2]$ | 3.565 | 180 | 2 | **p** | 49 | yalpik |
| **E.11** *trans*-$[Pd_2(\mu\text{-}NHPh)Ph_2(PMe_3)_2]$ | 3.181 | 180 | 9 | **pa** | 13 | pommin |
|  | 3.190 | 180 | 10 | **pa** |  | pommin |
| **E.12** *trans*-$[Pd_2(\mu\text{-}NH\{2,6\text{-}^iPr_2C_6H_3\})Cl_2py_2]$ | 2.958 | 180 | 13 | **pa** | 16 | niqxiu |
| **E.13** *trans*-$[Pd_2(\mu\text{-}NHCH_2\{C_4H_3S\})_2(acac)_2]$ | 3.063 | 180 |  | **pa** | 50 | wegzen |
| **E.14** *trans*-$[Pd_2(\mu\text{-}NHPh)_2(C_6H_4\{CH{=}NPh\})_2(PMe_3)_2]$ | 3.141 | 164 | 4 | **ps** | 13 | pommot |
| **E.15** $[Pd_2(\mu\text{-}N\{p\text{-tol}\}CH_2py)_2Cl_2]$ | 2.875 | 141 | 18 | **be** (**7b**) | 51 | runlob |
| **E.16** *trans*-$[Pd_2(\mu\text{-}NHPh)_2(C_6F_5)_2(^tBuNC)_2]$ | 3.046 | 147 |  | **be** | 20 | hasneu |
| **E.17** *trans*-$[Pt_2\{\mu\text{-}P(NMeCONMe)_2PNEt_2\}_2Cl_2]$ | 3.557 | 180 | 4 | **p** (**7b**) | 52 | gewyai |
| **E.18** $[Pt_2(\mu\text{-}PPh_2)_2(C_6F_5)_2(phen)]$ | 3.569 | 161 | 14 | **p** | 53 | sidzou |
| **E.19** *trans*-$[Pt_2(\mu\text{-}PPh_2)_2Cl_2(Ph_2PH)_2]$ | 3.586 | 180 | 1 | **p** | 34 | bexyae |
| **E.20** $[Pt_2(\mu\text{-}PPh_2)_2(dppe)_2]^{2+}$ | 3.699 | 180 | 6 | **p** | 34 | bexyei |
| **E.21** *trans*-$[Pt_2(\mu\text{-}PPh_2)_2(PHPh_2)_2(C{\equiv}C^tBu)_2]$ | 3.649 | 180 | 8 | **p** | 54 |  |
| **E.22** $[Pt_2(\mu\text{-}SEt_2)_2Br_4]$ | 3.368 | 180 | 4 | **p** | 55 | desdpt |
| **E.23** $[Pt_2(\mu\text{-}SEt_2)_2Me_4]$ | 3.610 | 180 | 1 | **p** | 30 | dovdoh |
| **E.24** *trans*-$[Pt_2(\mu\text{-}NH_2)_2Cl_2(PPh_3)_2]$ | 3.106 | 143 | 30 | **b** | 56, 57 | fultah10 |
|  | 3.117 | 144 | 30 | **b** |  |  |
| **E.25** $[Pt_2(\mu\text{-}NH_2)_2(MePPh_2)_2(Ph_2PO)_2]$ | 3.087 | 136 |  | **b** | 31, 32 | fekfoq10 |
| **E.26** $[Pt_2(\mu\text{-}NH_2)_2(MePPh_2)_4]^{2+}$ | 3.135 | 148 | 19 | **b** | 33 | kidzom |
| **E.27** *trans*-$[Pt_2(\mu\text{-}PPh\{CH_2\}_3PCy_2)_2Cl_2]$ | 3.577 | 180 | 7 | **pa** (**7b**) | 10, 11 | cibdas10 |
| **E.28** *trans*-$[Pt_2(\mu\text{-}PPh\{CH_2\}_3PCy_2)_2Cl_2]$ | 3.545 | 161 | 13 | **ps (7b)** | 10, 11 | boppeb20 |
| **E.29** $[Pt_2(\mu\text{-}NHPh)_2(dppm\text{-}H)_2]$ | 3.210 | 176 | 16 | **ps** | 19 |  |
| **E.30** $[Pt_2(\mu\text{-}NHPh)_2(POPh_2)_2(PMePh_2)_2]$ | 3.307 | 180 | 1 | **pa** | 19 |  |
| **E.31** *trans*-$[Pt_2(\mu\text{-}PHMes)_2Cl_2(PPh_3)_2]$ | 3.597 | 180 |  | **pa** | 17 | zuqwud |
| **E.32** *trans*-$[Pt_2(\mu\text{-}PHMes)_2Cl_2(PEt_3)_2]$ | 3.605 | 180 | 7 | **pa** | 17 | zuqwox |
| **E.33** $[Pt_2(\mu\text{-}PHPh)_2(Ph_2PMe)_4]^{2+}$ | 3.686 | 180 |  | **pa** | 40 | jesnie |
| **E.34** $[Pt_2(\mu\text{-}PHPh)_2(Ph_2PMe)_4]^{2+}$ | 3.706 | 180 |  | **pa** | 40 | jesnok |
| **E.35** $[Pt_2(\mu\text{-}\{SNC_5H_4\}Pt\{C_6F_5\}_2)_2(C_6F_5)_4]^{2-}$ | 3.575 | 180 | 20 | **pa** | 58 | pucfau |
| **E.36** $[Pt_2\{\mu\text{-}(S_2COEt)Pt(C_6F_5)_2\}_2(C_6F_5)_4]^{2-}$ | 3.603 | 180 | 25 | **pa** | 59 | zuhbal |
| **E.37** $[Pt_2\{(\mu\text{-}NHNH_2)_2Li(thf)_2\}(dppm\text{-}H)_2]^+$ | 3.072 | 141 | 44 | **bx** (**7a**) | 19 |  |
| **E.38** *trans*-$[Pt_2(\mu\text{-}NHCH\{C_2H_4SOMe\}CO_2)_2]$ | 2.861 | 136 | 20 | **be** (**7d**) | 60 | amsbpt10 |
| **E.39** *trans*-$[Pt_2(\mu\text{-}NMeC_6H_4CH_2{=}CMe)Cl_2]$ | 2.980 | 144 | 21 | **be** (**7b**) | 61 | borboz |
| **E.40** *trans*-$[Pt_2(\mu\text{-}PPh\{CH_2\}_3PPh_2)_2Me_2]$ | 3.521 | 145 | 25 | **be** (**7b**) | 11, 62, 63 | mpprpt20 |
| **E.41** *trans*-$[Pt_2(\mu\text{-}PPh_2)(\mu\text{-}NHC_6H_2Me_2N{=}S)Ph(PPh_3)_2]$ | 3.151 | 127 |  | **b** | 64 | ptnpap |
| **E.42** $[Au_2(\mu\text{-}NMe_2)_2Me_4]$ | 3.231 | 180 | 3 | **p** | 35 | caspiv |
| **E.43** $[Au_2(\mu\text{-}NHMe)_2Me_4]$ | 3.090 | 136 |  | **be** | 36 | devlul |
| **E.44** $[Rh_2(\mu\text{-}S\{PPh_2OCH_2CHR\}_2)_2]$ | 3.641 | 180 |  | **p** (**7c**) | 65 | hefrep |
| **E.45** $[Pt_2(\mu\text{-}PHMes)_2(dppe)_2]^{2+}$ | 3.702 | 180 |  | **pa** | 17 | zuqxak |
| **E.46** $[(F_5C_6)_2Pt(\mu\text{-}PPh_2)_2Pd(\mu\text{-}OH)_2Pt(PPh_3)_2]$ | 3.562 | 164 |  | **p** | 66 | zodgoo |

[a] All distances in Å, angles in degrees. [b] The *cis* and *trans* prefixes refer to the relative position of the equivalent terminal ligands at the two metal atoms [c] The univocal reference code for each crystal structure in the Cambridge Structural Database.

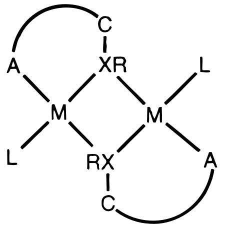
tion, the **ps** structure is found in three cases (**E.14**, **E.28**, and **E.29**). We also note that Okeya et al.[12] obtained two isomers of an anilide-bridged Pd(II) complex forming red plates and orange needles. The two isomers, identified as the *syn* and *anti* conformers, were also found in solution, although no evidence for their interconversion was found in the NMR spectra, indicating a high barrier for this process.

A special case of compounds with asymmetric bridges is that of the complexes bearing bi- or multidentate ligands. This is the case of compound **E.6**, in which ligands of type **7a** favor a bent conformation because the R···R repulsion is replaced by a chemical bond. We can also include in this category compound **E.37**, taking into account that its two bridging hydrazido ligands are connected to a $Li^+$ ion (N−Li = 2.06 Å). In compounds of types **7b**−**d** (**E.15**, **E.17**, **E.27**−**28**, **E.38**−**40**, and **E.44**) the L···R repulsions are totally or in part substituted by chemical bonds, hence $I_{LR}$ is replaced by the difference in chelate ring strain between the bent and planar structures. What is found in the experimental structures is that compounds of types **7b**−**d** forming 5-member chelate rings (**E.15**, **E.38**, and **E.39**) actually present the **be** structure (i.e., with the chelate ring occupying the *endo* positions, as found also for compounds with XR bridges[23]), and those having only 6-member chelate rings are planar (**E.17**, **E.27**,**28**, and **E.44**), thus confirming that the strain associated with the chelate ring also has some say in the relative stability of the planar and bent forms. The exception here corresponds to compound **E.40**, which forms 6-member chelate rings but whose bent structure may be favored by a stacking interaction between the two phenyl substituents of the bridging ligands (at a distance of 4.17 Å between their centroids) as well as by a more attractive $I_{MM}$ term in the case of terminal Me ligands (**E.40**) than for the bulkier terminal chlorides (**E.27**,**28**).

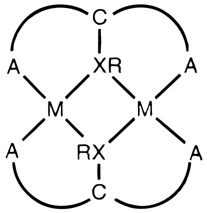
The gold complexes $[Au_2(\mu\text{-}NMe_2)_2Me_4]$ and $[Au_2(\mu\text{-}NHMe)_2Me_4]$ (**E.42** and **E.43**) provide an interesting opportunity to explore the predictive capability of the present calculations, since they have been calculated without any modelization (model compounds **M.20** and **M.29**, Tables 1 and 2) and they differ only in one substituent at each bridge. Yet these compounds



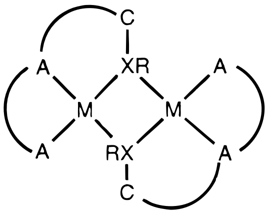
**7a**



**7b**



**7c**



**7d**

crystallize with different conformations (**p** and **be**, respectively). The former is predicted in our calculations to be more stable in the planar conformation by 3.2 kcal/mol, in agreement with the experimental structure. Such a result can be qualitatively explained by the low tendency of Au to form Au$\cdots$Au bonding interactions, combined with the Me$\cdots$Me repulsion between the *exo* substituents that destabilize the bent conformation. In contrast, the latter is predicted by our calculations to be slightly more stable in the **bx** form, but is experimentally found in the **be** conformation. We note that the difference in energy between the different conformers in this case is rather small and probably the presence of a doublet assigned to the amidic hydrogen atom in the $^1$H NMR spectrum[36] is indicative of an equilibrium in solution between the **be** and **bx** conformers.

The structures of three compounds (**E.35**−**36** and **E.41**) are not analyzed here because their structures are far more complex than those in the model complexes used in our calculations. To finish this section, let us just mention the existence of a reduced number of complexes with mixed bridges, one monsubstituted, another one disubstituted, all of which are bent and have as metal atoms Pt, Pd, or Rh.[19,67,68]

## Isomerism and Dynamic Behavior

Although the structural characterization of more than one isomer of the compounds under study is not common, there is a wealth of spectroscopic evidence for the coexistence of more than one conformer in solution. This is consistent with the similar stability of the different conformers found in our calculations. However, a low activation energy is required for the intramolecular interconversion of conformers to occur thermally. As an example, the $^{31}$P{$^1$H) NMR spectrum of compound **E.14** has been interpreted as revealing the presence of six or seven isomers at room temperature.[13] In contrast, variable temperature $^1$H NMR studies show that compound **E.7** exists in solution as a single isomer.[69] In this paper we are concerned about the conformations related to the orientation of the bridging ligand and to the bending around the X- - -X hinge. Hence, we will not discuss additional possibilities of isomerism that arise when the two terminal ligands are different, resulting in transoid and cisoid isomers, which have been reported to interconvert for compounds **E.11**[13] and **E.16**.[20]

To the best of our knowledge, there is only one case in which two isomers have been structurally characterized in the solid state, corresponding to structures **E.27** and **E.28** with **pa** and **ps** conformations in the solid state, respectively. The analogous complex *trans*-$[Pt_2(\mu\text{-}PPh\{CH_2\}_3PPh_2)_2Cl_2]$, for which no X-ray structure has been presented, was also isolated in two isomeric forms that present solution NMR spectra similar to those of the two isomers **E.27** and **E.28**, thus suggesting by analogy that the two isomers detected in solution correspond to the **pa** and **ps** forms. Okeya et al.[12] obtained two isomers of an anilide-bridged Pd(II) complex forming red plates and orange needles, respectively, but no structural characterization was reported. The two isomers, identified by IR and NMR spectroscopy as the *syn* and *anti* conformers, were also found in solution, although no evidence for their interconversion was found in the NMR spectra, indicating a high barrier for isomerization. In other cases, only one isomer (**pa** or **ps**) has been found in the solid state, but the two coexist in solution (compounds **E.12**,[16] **E.29**,[19] and **E.45**,[17] in Table 4). These data are fully consistent with the results of our calculations for compounds with asymmetric bridges (Table 2), for which the **pa** and **ps** conformers appear to be practically isoenergetic.

Since the compounds with asymmetric bridges that are more stable in bent forms are expected to have similar energies in the three bent conformations, and the planar forms are within thermal energy of the former, one can anticipate that such compounds should present dynamic behavior in solution through one of the following pathways:

$$\mathbf{be} \rightarrow \mathbf{ps} \rightarrow \mathbf{bx}$$
$$\mathbf{ba} \rightarrow \mathbf{pa} \rightarrow \mathbf{ba}$$

The rhodium complex **E.4** was seen to be present in solution as both *syn* and *anti* isomers, although only the latter is found in the solid state. Variable temperature $^{31}$P NMR spectra are consistent with a rapid ring inversion of the types just outlined, for which a free energy of activation of 9.9 kcal/mol was calculated from the coalescence temperature.[18] The fact that compound **E.7** has bulky *p*-tolyl substituents at the bridging atoms should enhance the difference in energy between the **be** and **bx** conformers calculated for the similar model compound **M.22**, explaining why in this case only one conformation has been observed in solution. A Rh compound that appears in the **bx** conformation (**E.6**) is prevented from undergoing such dynamic processes because of the bidentate nature of the bridging ligand. The present results suggest that more detailed experimental and theoretical studies on the isomerism and dynamic behavior of these compounds are needed.

## Main 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 of the type $[M_2(\mu\text{-}XR_2)_2L_4]$. Systematic ab initio calculations were performed for the different conformers of complexes in which the metal atom, the bridging atom, the bridge substituent, and the terminal ligands were varied. The agreement between calculated and experimental bond distances and angles is within chemical precision. The nonbonded M$\cdots$M distances are fairly

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well reproduced except when the terminal ligands in the experimental structure are significantly bulkier than in the corresponding theoretical model.

The variation of structural parameters upon bending the two coordination planes around the X- - -X hinge has been analyzed. The MXM bond angles decrease upon bending, but the M−X distance and the XMX angle are not very sensitive to bending. The orientation of the substituents in the bridging ligands is correlated with the bending angle, a fact that can be used to tune the degree of bending through the use of bidentate bridging ligands. Furthermore, the two substituents become asymmetrically distributed above and below the $XM_2$ plane upon bending, and the asymmetry (measured by the angle $\omega$) increases with the degree of bending. The preference for a bent geometry strongly depends on the nature of the metal atoms, being more pronounced for Rh than for Pt or Au. At the same time, the bent conformers of the Rh complexes show smaller values of $\theta$ than Pt or Au compounds with the same set of ligands.

The energy differences calculated for the different conformers of the same molecule can be rationalized by considering several contributions: (a) an increase in energy associated with the decrease in the MXM bond angles upon bending; (b) a stabilization due to the weakly bonding M···M interaction in the bent conformations; (c) an enhanced repulsion between the terminal ligands of the two $ML_2$ fragments; (d) the energy of interaction between the substituents at the two bridging atoms; and (e) the energy of interaction between the terminal ligands and the substituents. The two first terms are essentially electronic in nature, whereas the last three terms correspond to steric repulsions. The ligand−substituent and substituent−substituent repulsions are important in the bent conformers even with Me groups as substituents, but H···H and Me···Me interactions in the planar structures are negligible.

In compounds with symmetric bridges, the introduction of Me substituents at the bridging atoms destabilizes the bent form relative to the planar one. The extent of bending is significantly decreased and the values of $\tau$ are also reduced upon substitution. Compounds with a smaller bridging atom experience stronger effects of the bulkier substituent at the bridging atom. All these effects can be attributed to repulsions between the *exo* substituents and can be correlated with the R···R distances. A structural consequence of the minimization of the Me···Me repulsion in the **bx** conformers is seen in less bent molecules (larger bending angles) than in the corresponding **be** or **ba** conformers, and in larger values of $\tau$ and $\omega$ than in the analogous compounds with symmetric $XMe_2$ bridges. The suppression of steric repulsions $I_{RR}$ or $I_{LR}$ by chemically attaching the two bridging donors or bridging and terminal donors (i.e., using bidentate ligands) may affect the structural choice between bent and planar structures. In particular, it is seen that 5-member chelate rings spanning a terminal and a bridging position favor bent structures, whereas 6-member chelate rings favor planar structures.

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## Appendix

All ab initio calculations were performed with the GAUSSIAN 94 suite of programs.[70] A molecular orbital *ab initio* method with introduction of correlation energy through the second-order Møller-Plesset (MP2) perturbation[71] approach was applied, excluding excitations concerning the lowest energy electrons (frozen-core approach). A basis set with double-$\zeta$ 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 $CH_3$ groups, for which a minimal basis set was used. Test calculations were carried out on $[Pt_2(\mu\text{-}PH_2)_2(PH_3)_4]^{2+}$ with a double-$\zeta$ basis set for the hydrogen atoms, and the geometries of the planar and bent forms as well as their relative energies were seen to be practically identical. More details on the basis set can be found in our previous paper.[23] 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°). For the case of $[Pt_2(\mu\text{-}PH_2)_2(PH_3)_4]^{2+}$ the fully optimized structure was found to be practically identical to that with frozen ligands, the largest deviations being less than 0.01 Å in the M−X distances and less than 1° in the MXM and $\theta$ angles. The relative energy of the bent and planar forms changed by 0.5 kcal/mol with the full optimization. All other geometrical parameters were optimized to find the most stable structure for each compound. 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 fixed the value of the angle $\theta$ at 180° or *ca.* 120°.

The collection of structural data was obtained through a systematic search of the Cambridge Structural Database[21] (version 5.18) for compounds of general formula $[M_2([\mu\text{-}XR_2)_2L_4]$, 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 $\theta$ was obtained as that between the two $MX_2$ planes.

## Abbreviations

acac = acetylacetonato(l−); dppe = 1,2-bis(diphenylphosphino)ethane; dppm = 1,2-bis(diphenylphosphino)methane; hfacac = hexafluoroacetylacetonato(1−); phen = 1,10-phenanthroline; py = pyridine; thf = tetrahydrofuran.

**Supporting Information Available:** A table comparing the main bonding parameters in calculated structures with those in analogous experimental structures. This material is available free of charge via the Internet at http://pubs.acs.org. The atomic coordinates of the 47 optimized structures are also deposited and can be accessed at the following Internet address: http://kripto.qui.ub.es/~gee/suppl/xr2.html. Each table is identified with the label employed for compounds in Tables 1 and 2, together with the acronym for the conformation.

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