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To Bend or Not To Bend: Dilemma of the Edge-Sharing Binuclear Square Planar Complexes of d^8 Transition Metal Ions

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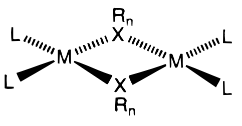
The binuclear complexes of d^8 transition metal ions of type $[L_2M(\mu\text{-}XR_n)_2ML_2]$ ($n = 0$ to 2) show a wide variety of bending angles between the coordination planes of the two metal atoms. A theoretical and structural analysis of those compounds with unsubstituted bridges, $[L_2M(\mu\text{-}X)_2ML_2]$, tries to unravel the factors that determine the degree of bending of such compounds. A rationale is given for the structures of 139 crystallographically independent molecules. A driving force for bending of the molecules is the attractive metal···metal interaction that results from donor−acceptor interactions between the d_{z^2} and p_z orbitals of the two metal atoms and is modulated by the nature of (a) the metal atom, (b) the terminal ligands, and (c) the bridging atoms. In all cases the energy difference between the planar and the bent form is within the 10 kcal/mol range, and steric effects seem to be important in preventing bending only for the bulkiest terminal ligands. For the studied bridging atoms, the stability of the bent form increases in the order O < S > Se > Te and F < Cl < Br < I, and for different metal atoms it increases in the order Ni(II) < Pd(II) < Pt(II) < Rh(I) < Ir(I).

A common situation in the coordination and organometallic chemistry of d^8 transition metal ions is the existence of bis-bridged dimers $[L_2M(\mu\text{-}XR_n)_2ML_2]$ ($n = 0$ to 2) with square planar coordination geometries around the metal atoms (**1**). A peculiar structural feature of such compounds is the wide variety of bending angles found between the two squares (as measured by the angle θ in **2**). This can be illustrated by displaying a histogram of the bending angles found for more than 300 independent molecules of type **1** having un-, mono-, or disubstituted bridges[1] (i.e., $n = 0, 1, 2$; Figure 1). Even if the largest number of structures correspond to esentially planar molecules ($170° < \theta \leq 180°$), there is a significant number of strongly bent molecules. A closer look at Figure 1 allows us to make the following observations: (a) Most of the X-bridged compounds present a planar structure, whereas for the XR and XR_2 bridges the bent compounds are relatively common. (b) In general, the structures are either practically planar ($\theta > 160°$) or strongly bent ($\theta < 150°$), but intermediate bending is practically inexistent. (c) The distribution of the bending angles is quite different for the different metals: Among the compounds with X bridges, those of Ir(I) are bent, those of Rh(I), Pd(II), and Pt(II) present both bent and planar structures, but Ni(II) and Au(III) compounds are only found in the planar form. Is there any regularity? How can a chemist master the bending of a particular complex?



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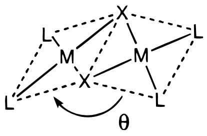

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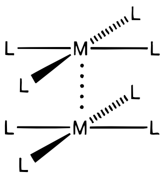

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In an attempt to establish the general rules that govern the bending of the studied binuclear compounds and the conformation of the substituents in the bridging atoms, we have undertaken a theoretical investigation of these families of compounds, together with a structural database analysis. We restrict ourselves in this paper to the discussion of our results for the case of unsubstituted bridges ($n = 0$; X = F, Cl, Br, I, O, S, Se, or Te) for which the most relevant parameter is the choice between planar and bent structures.

Qualitative Theoretical Analysis

Since the square planar d^8-ML_4 complexes are coordinatively unsaturated, the residual bonding capabilities of the metal atoms in such complexes offer a variety of interesting structural possibilities. These compounds are able to bond to additional groups, be they Lewis acids or bases.[2] They can also form dimers or chains through face-to-face stacking of ML_4 units (**3**) with the help of weak M···M interactions,[3−5] related to those found for d^{10} metal complexes.[6] Alternatively, binuclear edge-sharing complexes of the type $[M_2(\mu\text{-}XR_n)_2L_4]$ (**1**, where $n =$

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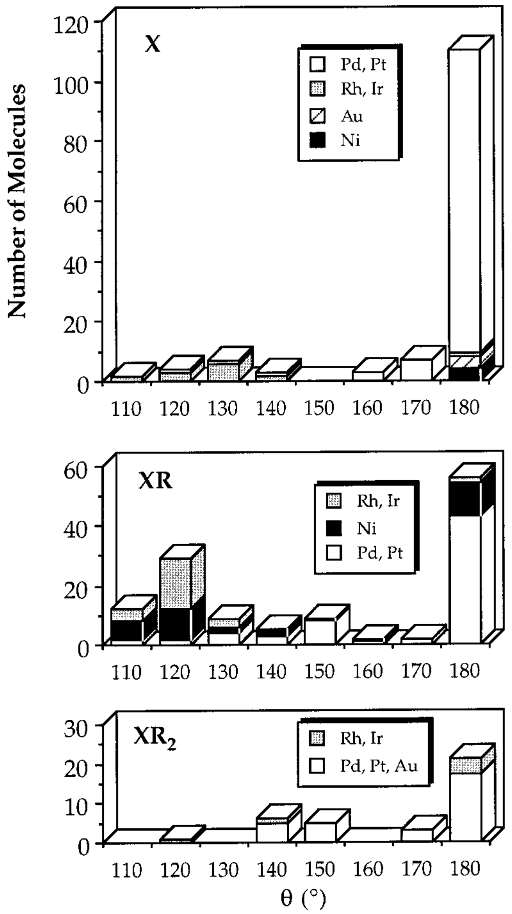
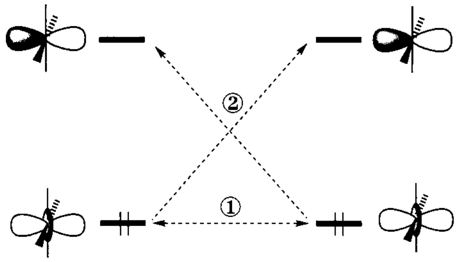


Figure 1. Distribution of the number of molecular structures of edge-sharing binuclear complexes of the type $[L_2M(\mu\text{-}XR_n)_2ML_2]$, where M is Rh(I), Ir(I), Ni(II), Pd(II), Pt(II), and Au(III), as a function of the angle between the two MX_2 planes, θ. The number in the x axis indicates the maximum value for the angles in every interval.

0−3) may present short M···M distances, provided the framework electron count (FEC, the number of electrons involved in the σ-bonding of the M_2X_2 framework) is less than eight.[7] Note that upon bending the M···M distance in the compounds under study become similar to those in the face-to-face dimers or stacks of d^8-ML_4 complexes. This fact suggests that some degree of M···M bonding exists in the bent molecules. Simple model compounds of type **1** (with $n = 0$) used in theoretical ab initio studies,[1,8] such as $[Pt_2(\mu\text{-}S)_2(PH_3)_4]$ and $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$, show a tendency to bend, with a stabilization energy relative to the planar structure of only a few kcal/mol. But, what is the driving force for such bending? A qualitative MO study of the bending motion has been carried out for a Rh model compound, in an attempt to obtain some guidelines for the analysis of the structural data and to assist us in the design of models for ab initio calculations (see Appendix for details on calculations).



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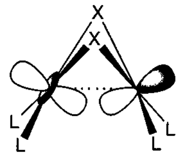
In the face-to-face M_2L_8 dimers **3**, the metal−metal bonding interaction is explained[3,4] as resulting from the combined effect of the repulsion between the electrons in the d_{z^2} orbitals of the two ML_4 monomers (interaction labeled as "1" in **4**) and the donor−acceptor interactions between the d_{z^2} electrons and the empty p_z orbitals (interactions labeled "2" in **4**). In the planar dimers **1** we cannot invoke such interactions, but they may be turned on as the dimer is bent around the X---X hinge (**5**). Hence it is not surprising that the analysis of the overlap populations in $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (OP, calculated at the EH level; Figure 2) indicates that the Rh···Rh interaction, slightly repulsive in the planar molecule (negative Rh···Rh OP), changes little upon bending but finally becomes attractive (i.e., positive OP) if the bending angle is made small enough ($\theta < 140°$).



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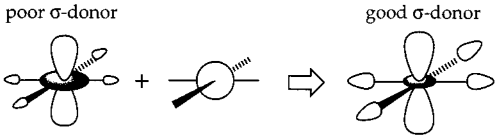
Although EH and HF-SCF calculations for $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ predict the planar form to be more stable than the bent one, the relative stabilities are reversed if electron correlation (at the MP2 level) is taken into account (Figure 3). These results are consistent with previous studies of $d^8 \cdots d^8$ interactions in the stacked dimers of ML_4 complexes (**3**), for which the interaction was found to be attractive when calculated at the MP2 but not at the HF level.[3] The form of the potential energy curve (Figure 3) also tells that a sensible stabilization is gained only for a large degree of bending ($\theta < 160°$). In summary, only for large bending is the M···M interaction attractive enough to make the molecule more stable in its bent form. The existence of a bonding metal−metal interaction in the related bent dimer $[Rh_2(\mu\text{-}SH)_2(cod)_2]$ has been confirmed through the analysis of the Laplacian of the electron density by Poblet et al.[9]

With the simplified orbital interaction diagram **4** we can now analyze the influence of the terminal and bridging ligands on the bonding M···M interactions in the bent molecules. In essence, good σ-donors favor the hybridization of the d_{z^2} orbital of a square planar complex through mixing with the s orbital in the way illustrated in **6**: The better the σ-donor character, the more is the resulting orbital concentrated along the z direction. As a consequence, the donor/acceptor interactions "2" are favored by good σ-donors. In fact, the repulsion "1" should also be larger for good σ-donors, but the two attractive interactions overweigh the only repulsion.



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Also the π-acceptor (or π-donor) nature of the ligands was found to affect the strength of the M···M interaction, because

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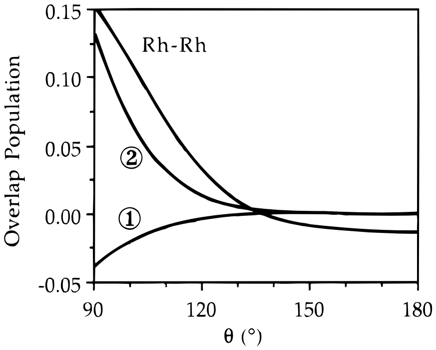

Figure 2. Rh$\cdots$Rh overlap population between two square planar complexes of Rh(I) as a function of the bending angle θ (**2**), as obtained from extended Hückel calculations. (See Appendix for computational details.) Also shown are the contributions to the Rh$\cdots$Rh overlap population from the attractive interaction "2" between the d_{z^2} orbital of one metal atom and the p_z orbital of the other one (see **4**), as well as the contribution from the repulsion "1" between the two d_{z^2} orbitals.

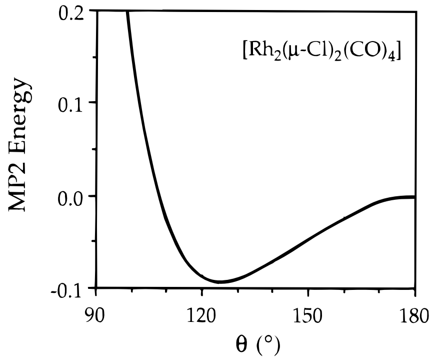

Figure 3. Calculated MP2 (eV) energy for the binuclear compound $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ as a function of the bending angle θ (**2**).

of the mixing of the ligand π^* (or π) orbitals with the metal p_z, therefore affecting in different ways the interactions "2". From our previous study of the stacked dimers[5] one should therefore expect the π-acid ligands to strengthen the M$\cdots$M interaction and the π-basic ligands to weaken it. Such effect might be important enough to determine whether a molecule is bent or not. In fact, our early attempts to study the $d^8\cdots d^8$ interactions using $[PtCl_4]^{2-}$ as a monomer indicated that its face-to-face dimer was unstable toward dissociation at the MP2 level of calculation, whereas our later study of $[PtCl_2(CO)_2]$ gave a bonding energy of 9.9 kcal/mol for the dimer.[3] In the case of the compounds under study, given that the two bridging atoms are by definition π-basic ligands, the presence of π-basic (or poor σ-donor) terminal ligands could hinder molecular bending.

When dealing with simplified model molecules, one should not forget that steric repulsion between bulky terminal ligands at the two metal atoms may become important for a large degree of bending. Given the small values of the metal–metal bonding energies involved (of the order of 10 kcal/mol or less), the repulsion between bulky terminal ligands may eventually be large enough as to hinder the large bending required for the attractive metal–metal interaction. However, we will see below that steric effects are needed to explain the experimental data only for highly bulky ligands, such as PPh_3. Once some qualitative guidelines have been established, we proceed to the evaluation of the least-energy structures for a selected number of model complexes. In that way we should be able to have a better predictive capability as to whether a particular compound should be expected to appear in the planar or the bent form.

Results of ab Initio Calculations

In this section we present the results of ab initio calculations, carried out at the MP2 level (see Appendix for computational details), since Hartree–Fock calculations do not adequately describe the M$\cdots$M contacts. For every selected example, we expect to learn from such calculations whether the bent or the planar structure is the most stable one and also the energy needed for, or gained upon, bending. The advantage of using a computational approach is that one can separately analyze the different factors that often appear simultaneously in an experiment. We will discuss first several model molecules that closely match experimentally characterized compounds and check with these that the computational results reasonably reproduce the experimental data. We will further validate the computational method by checking the effect of improvement in the level of accuracy (i.e., basis set and corrections for electron correlation). Once it is made clear that the theoretical ab initio results agree with the experimental data when little or no modeling is introduced, we will finally present the results for a variety of model compounds in which the bridging ligand, the terminal ligands, or the metal atom are varied in a systematic way.

The geometries for several compounds of type $[M_2(\mu\text{-}X)_2L_4]$ (M = Ni(II), Pd(II), Pt(II), Rh(I), or Ir(I)) optimized at the MP2 level are given in Table 1. The structural parameters for optimized geometries are in excellent agreement with the experimental data for analogous compounds. The largest deviations from the experimental data are observed for $[Pt_2(\mu\text{-}Cl)_2Cl_4]^{2-}$, possibly due to its dianionic character. Let us stress that the computational method employed appears to correctly describe the structures of the compounds under study, even the nonbonded distances such as M$\cdots$M and X$\cdots$X. In particular, in those cases in which a calculated neutral or cationic molecule fully coincides with the experimental one the agreement is excellent.

Since we are interested not only in the structural parameters but also in the energy differences between the planar and bent forms, it is worth checking the reliability of the level of computation used for such purpose. The energy of the less stable form (bent or planar) of each molecule, relative to that of the optimized structure, is given in Table 2 together with the essential structural parameters, the bending angle θ, and the M$\cdots$M distance. For several compounds, the energy at the two alternative structures was recalculated with an improved basis set, adding an f shell to the basis of the metal atoms. The energy differences change little (less than 2.5 kcal/mol), predicting in all cases the bent structure to be slightly more stable (by about 2 kcal/mol) than with the smaller basis set,

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Table 1. Comparison of the MP2-Optimized Geometries for Compounds of the Type $[M_2(\mu\text{-}X_2)L_4]$ (First Line of Each Entry) with the Experimental Data for Related Compounds (Second Line of Each Entry)[a]

compd	θ	M···M	X···X	M−X	M−L	LML	XMX	XML	MXM	ref
$[Ni(\mu\text{-}Cl_2)(PH_3)_4]^{2+}$	179.8	3.166	3.116	2.221	2.206	90.0	89.1	90.4	90.9	
$[Ni_2(\mu\text{-}Cl_2)(PEt_3)_2(C\{CF_3\}{=}CCF_3R)_2]$	180	3.232	3.061	2.237	2.168[b]	91	86	93	94	10, 11
$[Pd_2(\mu\text{-}Cl)_2(PH_3)_4]^{2+}$	179.7	3.446	3.377	2.413	2.297	90.2	88.8	90.5	91.2	
$[Pd_2(\mu\text{-}Cl)_2(PPh_3)_4]^{2+}$	180	3.493	3.200	2.387	2.289	99	85	89	94	12
$[Pt_2(\mu\text{-}S)_2(PH_3)_4]$	120.2	3.096	3.154	2.383	2.286	98.7	82.9	89.2	81.0	
$[Pt_2(\mu\text{-}S)_2(PMe_2Ph)_4]$	121	3.175	3.060	2.340	2.265	*c*	81.6	*c*	85.5	13
$[Pt_2(\mu\text{-}Cl)_2Cl_4]^{2-}$	180.0	3.573	3.283	2.426	2.346	91.6	85.2	91.6	94.8	
$[Pt_2(\mu\text{-}Cl)_2Cl_4]^{2-}$	170−180	3.42−3.45	3.19	2.33	2.28	90	84	93	96	14, 15
trans-$[Pt_2(\mu\text{-}Br)_2(PH_3)_2Me_2]$	110.0	3.128	3.604	2.682[d]	2.067[f]	88.7	86.7	89.5[h]	73.1	
				2.565[e]	2.201[g]			95.1[i]		
trans-$[Pt_2(\mu\text{-}Br)_2(C_4H_6CH_2P^tBu_2)_2)]$	116	3.233	3.423	2.614[d]	2.079[f]	85	84	89[h]	78	
				2.510[e]	2.193[g]			102[i]		16
$[Ir(\mu\text{-}Cl)_2(PF_3)_4]$	108.3	3.023	3.182	2.451	2.115	90.1	89.9	94.5	76.1	
$[Ir(\mu\text{-}Cl)_2(PF_3)_4]$	107.0	2.942	3.144	2.412	2.133	92.7	81.4	92.2	75.2	17
$[Rh(\mu\text{-}Cl)_2(PH_3)_4]$	115.5	3.059	3.294	2.446	2.192	91.3	84.6	92.0	77.4	
$[Rh(\mu\text{-}Cl)_2(PF_3)_4]$	113.5	2.971	3.194	2.388	2.12	94.7	83.9	90.0	76.9	18
$[Rh(\mu\text{-}Cl)_2(CO)_4]$	124.8	3.168	3.278	2.425	1.817	88.9	85.0	93.0	81.5	
$[Rh(\mu\text{-}Cl)_2(CO)_4]$	127	3.138	3.227	2.386	1.840	91	85	91	82	19, 20

[a] All distances in Å, angles in degrees. [b] Ni−P. [c] Not given. [d] Trans to C. [e] Trans to P. [f] Pt−C. [g] Pt−P. [h] Br−Pt−C. [i] Br−Pt−P.

probably because of a better description of the nonbonded $d^8\cdots d^8$ contacts in the bent form. The effect of improving the treatment of electron correlation was checked for $[Pt_2(\mu\text{-}S)_2(PH_3)_4]$ by performing an MP4 (SDTQ) calculation at the two geometries, and the energy difference was seen to change only from 4.8 to 5.5 kcal/mol.

In order to check if the d_{z^2}/p_z orbital mixing is really an important factor for the stabilization of the bent form, we have calculated the bending energy for $[Pt_2(\mu\text{-}S)_2(CO)_4]$ without the platinum 6p orbitals. The stabilization of the molecule upon bending drops from −8.2 kcal/mol when the metal p orbitals are present to −2.6 kcal/mol when the d_{z^2}/p_z orbital mixing is turned off. Furthermore, a contribution of the change in the M−X−M bond angle upon bending to the stabilization of the complexes seems unlikely, according to the bond angle preferences for the X atoms in the H_2X molecules (X = O, S). In effect, a decrease in the H−X−H bond angles by the amount that is found for the binuclear complexes upon bending (e.g., from 95.9 to 81.0° for $[Pt_2(\mu\text{-}S)_2(PH_3)_4]$, Table 2) is found to destabilize the H_2X molecules by 2−4 kcal/mol.

Once we have shown that the computational methodology works reasonably well for both structure and energetics, let us analyze the results for a larger set of model compounds (Table 2) in search for trends and generalities. In all cases the energy difference between the planar and the bent form is within the 10 kcal/mol range. These values suggest that in some cases the steric repulsion between terminal ligands or packing forces can ultimately affect the structural choice. For three compounds, $[Pt_2(\mu\text{-}Te)_2(PH_3)_4]$, $[Pt_2(\mu\text{-}Cl)_2(PH_3)_4]^{2+}$, and $[Pt_2(\mu\text{-}Cl)_2(CO)_4]^{2+}$, the potential energy curve for bending is very shallow and a clear structural preference cannot be proposed. Two interesting results that deserve further study but fall out of the scope of the present work appear for $[Ni(\mu\text{-}S)_2(PH_3)_4]$ and $[Pd_2(\mu\text{-}S)_2(PH_3)_4]$. For these two compounds the planar structure gives a minimum with a short S−S distance (2.044 and 2.223 Å, respectively), a geometry that has a precedent in the two isomers of copper bridged by either two oxo or one peroxo groups.[21−23]

In such compounds, there is a formal change in the metal and bridging atom oxidation state and a bonding situation clearly different from that studied here, which has been previously discussed.[7] Hence, the data given for $[Pd_2(\mu\text{-}S)_2(PH_3)_4]$ in Table 2 with a planar structure were obtained by fixing the S···S distance constant (2.375 Å).

By comparing the data for complexes with the same metal atom and bridging ligands but different terminal ligands, one sees that the bent form is favored in the order $Cl^- < PH_3 \approx CH_3^- \leq CO$. These results are in fair agreement with the expected qualitative cis-influence of the terminal ligands on the metal···metal interaction, based on their σ-donor and π-acceptor properties.[5] This can be illustrated by the series of $[Pt_2(\mu\text{-}Cl)_2L_4]$ complexes. For these compounds the better σ-donors can be associated with increased delocalization of the d_{z^2}

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Table 2. Theoretical ab Initio (MP2) Results for Compounds of Type $[M_2(\mu\text{-}X_2)L_4]$[a]

compd	θ (deg)	M···M (Å)	MXM (deg)	ΔE (kcal/mol)
$[Ni_2(\mu\text{-}Cl)_2(PH_3)_4]^{2+}$	179.8	3.166	90.9	
	118.3	2.859	79.9	8.4
$[Pd_2(\mu\text{-}Cl)_2(PH_3)_4]^{2+}$	179.7	3.446	91.2	
	118.8	3.110	80.5	3.8
$[Pt_2(\mu\text{-}Cl)_2(PH_3)_4]^{2+}$	160.7	3.536	92.8	
	180.0	3.579	94.2	0.0 (0.2)[b]
$[Pd_2(\mu\text{-}S)_2(PH_3)_4]$	117.5	3.090	81.7	
	180.0	3.608[c]	98.8	3.4
$[Pt_2(\mu\text{-}O)_2(PH_3)_4]$	135.2	2.862	90.9	
	180.0	3.012	97.8	4.0 (5.0)[b]
$[Pt_2(\mu\text{-}S)_2(PH_3)_4]$	120.2	3.096	81.0	
	180.0	3.532	95.9	4.8 (7.3)[b]
$[Pt_2(\mu\text{-}S)_2(CO)_4]$	117.1	3.028	78.6	
	180.0	3.521	95.1	8.2
$[Pt_2(\mu\text{-}Se)_2(PH_3)_4]$	115.1	3.155	78.4	
	180.0	3.754	97.9	4.1 (6.8)[b]
$[Pt_2(\mu\text{-}Te)_2(PH_3)_4]$	106.5	3.219	73.9	
	180.0	4.185	103.0	−0.4 (1.9)[b]
$[Pt_2(\mu\text{-}Cl)_2Cl_4]^{2-}$	180.0	3.573	94.8	
	121.6	3.257	83.6	3.9
trans-$[Pt_2(\mu\text{-}Cl)_2(PH_3)_2Me_2]$	126.2	3.216	82.5	
	180.0	3.539	93.3	1.1
trans-$[Pt_2(\mu\text{-}Br)_2(PH_3)_2Me_2]$	110.0	3.128	73.1	
	180.0	3.755	91.7	2.7
$[Pt_2(\mu\text{-}Cl)_2(CO)_4]^{2+}$	151.5	3.464	91.5	
	180.0	3.553	94.5	0.2
$[Rh_2(\mu\text{-}F)_2(PH_3)_4]$	139.1	3.002	92.8	
	180.0	3.169	99.9	0.8
$[Rh_2(\mu\text{-}Cl)_2(PH_3)_4]$	115.5	3.059	77.4	
	180.0	3.543	92.7	4.1
$[Rh_2(\mu\text{-}Cl)_2(CO)_4]$	124.8	3.168	81.5	
	180.0	3.525	93.0	2.2
$[Rh_2(\mu\text{-}Br)_2(PH_3)_4]$	108.3	3.059	73.2	
	180.0	3.696	91.9	6.1
$[Rh_2(\mu\text{-}I)_2(PH_3)_4]$	100.4	3.061	68.4	
	180.0	3.930	92.4	7.4
$[Ir_2(\mu\text{-}Cl)_2(PH_3)_4]$	109.4	3.022	75.9	
	180.0	3.646	95.8	6.1
$[Ir_2(\mu\text{-}Cl)_2(PF_3)_4]$	108.3	3.023	76.1	
	180.0	3.654	96.3	6.2

[a] For each compound the first line corresponds to the most stable structure and its energy is arbitrarily taken as zero. For the geometry given in the second line, the angle θ was fixed at the value given and the rest of the structure was partially optimized. [b] An f shell was added to the basis set of the metal atom. [c] S···S distance for the planar structure kept fixed (see text).

electrons toward the ligands (**6**), as reflected by the Mulliken population of d_{z^2} for Cl^- (1.972), PH_3 (1.919), and CO (1.919). Consistently, the energy of the bent form relative to the planar one is 3.9, 0.0, and −0.2 kcal/mol for L = Cl^-, PH_3, and CO, respectively. Probably the small extra stability of the carbonyl complex compared to the phosphine analogue can be attributed to its π-acceptor character.

If we compare similar complexes in which only the metal atoms are changed, we find that the bent form is more favorable for the heavier elements of each group: Pt > Pd > Ni; Ir > Rh. Among the metals of the same period, the stability of the bent form decreases from left to right of the periodic table. In summary, the following order of stability of the bent structure results: Ni < Pd < Pt < Rh < Ir. The reason for such behavior can be found in the differences in diffuseness of the metal d orbitals. This trend can be explained by analyzing the $<p_z|d_{z^2}>$ and $<d_{z^2}|d_{z^2}>$ overlap integrals between the Slater orbitals (EH calculations), shown in Figure 4. There it is seen that the $<p_z|d_{z^2}>$ overlap, responsible for the attractive interaction "2", increases with increasing diffuseness of the atomic orbitals, i.e., from right to left along a transition metal period and when going down a group. In contrast, the $<d_{z^2}|d_{z^2}>$ overlap, responsible for the repulsion "1", is practically insensitive to the size of the metal atom. Our use of a constant M···M distance of 3.0 Å to evaluate the overlap integrals is supported by the experimental data, which show that the M···M contacts present practically the same distance regardless of the size of the metal ion.[4] The larger sensitivity of the $p_z|d_{z^2}$ overlap to the atomic size is probably due to the larger directionality of p_z, since part of the density of the d_{z^2} orbital is not along the z axis.

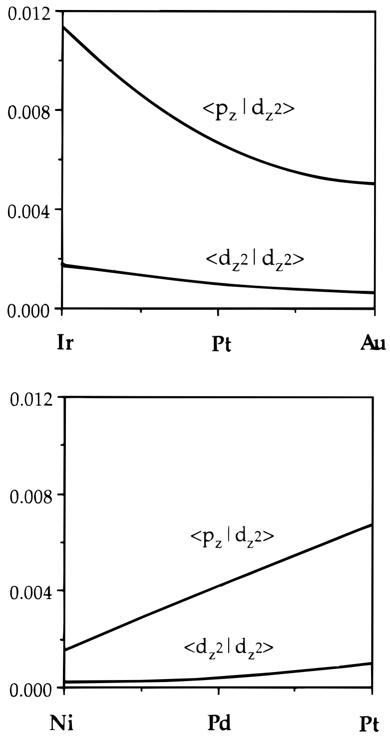

Figure 4. Square of the overlap integrals $<d_{z^2}|p_z>$ and $<d_{z^2}|d_{z^2}>$ between two metal atoms at 3.0 Å (EH) for the coinage metals along the third transition series (above) and down the group 10 (below) of the periodic table.

If bridging halogen atoms are considered (X = F, Cl, Br, I) between Rh atoms with PH_3 as terminal ligands, the expected stability order is observed. According to our qualitative model, the stability of the bent form should increase as the electronegativity of the bridge decreases (i.e., descending down the group). Notice also that the optimized structures present practically the same Rh···Rh distance (~3.1 Å). Since the Rh−X distances increase from F to I, the bending angles θ are progressively smaller. The relationship between electronegativity of the bridging ligands and stability of the bent structure is less clear in the family of chalcogen-bridged Pt compounds with PH_3 as terminal ligands. Here the relative stability of the bent form is seen to be approximately constant for O, S, and Se and drop for Te. Probably another factor is counterbalancing the increased tendency to bend for the heavier, less electronegative chalcogen bridges: The longer M−X distances corresponding to the heaviest bridge require smaller M−X−M bond angles (81, 81, 78, and 74° for X = O, S, Se, and Te, respectively) which make such structures less stable. As found for the halo-bridged Rh compounds, the optimum bending angle θ decreases along the chalcogen group.

Analysis of the Structural Data

Having learned about the factors that influence the structural choice between planar or bent structures from a theoretical point

Table 3. Structural Data for Binuclear Complexes of d^8 Metal Ions of the Type $[L_2M(\mu\text{-}X)_2ML_2]$ (see **1** and **2**)

compd^{a}	M···M (Å)	θ (deg)	refcode	ref
Ni				
$[Ni_2(\mu\text{-}F)_2(C_6F_5)_4]^{2-}$	2.884	180	janwaw	24
$[Ni_2(\mu\text{-}Cl)_2(C_6F_5)_4]^{2-}$	3.276	180	janvup	24
$[Ni_2(\mu\text{-}Cl)_2(PEt_3)_2(C\{CF_3\}{=}CCF_3R)_2]$	3.282	180	buykov10	10, 11
$[Ni_2(\mu\text{-}Cl)_2(SiCl_3)_4]^{2-}$	3.283	180	janwea	24
Rh				
$[Rh_2(\mu\text{-}Cl)_2(PF_3)_4]^{b}$	2.995	115		18
$[Rh_2(\mu\text{-}Cl)_2(CO)_4]^{b}$	3.138	127	fuzbeh01	19, 20
cis-$[Rh_2(\mu\text{-}Cl)_2(CO)_2(PMe_2Ph)_2]$	3.167	125	pmpcrh	25
cis-$[Rh_2(\mu\text{-}Cl)_2(CO)_2(P\{\mathit{calixarene}\}H)_2]^{b}$	3.148	125		26
$[Rh_2(\mu\text{-}Cl)_2(P^{i}Pr_3)_4]$	3.805	180	liksut	27
$[Rh_2(\mu\text{-}Cl)_2(PPh_3)_4]$	3.662	180	tprhea	28
Pd				
$[Pd_2(\mu\text{-}Cl)_2Cl_4]^{2-}$	3.347	165	cajxiu	29
$[Pd_2(\mu\text{-}Cl)_2Cl_4]^{2-}$	3.392	180	vofpub	30
	3.453	180		
$[Pd_2(\mu\text{-}Cl)_2Cl_4]^{2-}$	3.405	180	varkoo	31
$[Pd_2(\mu\text{-}Cl)_2Cl_4]^{2-}$	3.411	180	fehzoh10	32
$[Pd_2(\mu\text{-}Br)_2Br_4]^{2-}$	3.596	180	jajpep	33
$[Pd_2(\mu\text{-}Br)_2Br_4]^{2-}$	3.565	180	volseu	34
$[Pd_2(\mu\text{-}I)_2I_4]^{2-}$	3.796	180	fehzun10	32, 35
trans-$[Pd_2(\mu\text{-}Cl)_2Cl_2(P\{OPh\}_3)_2]$	3.483	180	tapkaw	36
trans-$[Pd_2(\mu\text{-}Cl)_2Cl_2(PBu_3)_2]$	3.484	180	zzzjui01	37
trans-$[Pd_2(\mu\text{-}Cl)_2Cl_2(Me_2C{=}NNMePh)_2]$	3.400	180	amhzpd	38
	3.407	180		
trans-$[Pd_2(\mu\text{-}Cl)_2Cl_2(\mathit{C}H\{COPh\}\{PBu_3\})_2]$	3.479	180	vawyat	39
trans-$[Pd_2(\mu\text{-}Cl)_2Cl_2(P\{CF_3\}_2N{=}PPh_3)_2]$	3.481	180	jewwox	40
trans-$[Pd_2(\mu\text{-}Cl)_2Cl_2(\mathit{C}_6H_3MeNO_2)_2]$	3.492	180	fiphan	41
trans-$[Pd_2(\mu\text{-}Cl)_2Cl_2(\mathit{C}H_2CH{=}N^{i}Pr_2)_2]$	3.493	180	bubriz10	42,43
trans-$[Pd_2(\mu\text{-}Cl)_2Cl_2(PPh_2py\{Ph_2PO\})_2]$	3.497	179	fonfuj	44
trans-$[Pd_2(\mu\text{-}Cl)_2Cl_2(PPh_2R)_2]$	3.503	180	mofrnb	45
trans-$[Pd_2(\mu\text{-}Cl)_2Cl_2(NH_2)_2]^{2-}$	3.541	180	kizveu	46
trans-$[Pd_2(\mu\text{-}Cl)_2Me_2(Me_2S)_2]$	3.511	180	dudvut	47
trans-$[Pd_2(\mu\text{-}Br)_2Br_2(Me_2S)_2]$	3.541	180	pddmsd10	48
trans-$[Pd_2(\mu\text{-}Br)_2Br_2(Pr_2\mathit{S}O)_2]$	3.609	180	gojger	49
trans-$[Pd_2(\mu\text{-}I)_2I_2(Ph_2PC_2H_3)_2]$	3.844	166	wavpoy	50
	3.859	179		
trans-$[Pd_2(\mu\text{-}I)_2I_2(PBu_3)_2]$	3.900	180	yudcab	51
$[Pd_2(\mu\text{-}Cl)_2(PPh_2OH)_2(PPh_2O)_2]^{b}$	3.608	180	hebxer	52
	3.623	180		
trans-$[Pd_2(\mu\text{-}Cl)_2(PhCr\{CO\}_3)_2(PCy_3)_2]^{b}$	3.611	180	konmij	53
$[Pd_2(\mu\text{-}Cl)_2(PPh_2R)_4]^{2+}$	3.546	168	pekzua	54
$[Pd_2(\mu\text{-}Cl)_2(PPh_3)_4]^{2+\ b}$	3.498	180	wangun	12
trans-$[Pd(\mu\text{-}Cl)_2(NO_2)_2(PPr_3)_2]$	3.421	180	kijtom	55
$[Pd_2(\mu\text{-}Cl)_2(P\{EtO\}_2OH)_2(P\{EtO\}_2O)_2]^{b}$	3.486	180	bubfej01	56−58
trans-$[Pd_2(\mu\text{-}Cl)_2(H\mathit{C}\{CO_2Et\}_2)_4]^{2-}$	3.506	175	cigmua	59
trans-$[Pd_2(\mu\text{-}Cl)_2(\mathit{C}H_2CMe_2Ph)_2(PPh_3)_2]$	3.613	180	fisvos	60
trans-$[Pd_2(\mu\text{-}Br)_2(\mathit{C}_6H_4Bu)_2(PTol_3)_2]$	3.795	180	pobveh	61
$[Pd_2(\mu\text{-}Te)_2(PEt_3)_4]$	4.231	180	sispep	62
trans-$[Pd_2(\mu\text{-}I)_2(PPh_3)_2(COPh)_2]$	3.930	180	lanbux	63
Ir				
$[Ir_2(\mu\text{-}Cl)_2(PF_3)_4]^{b}$	2.942	107		17
Pt				
$[Pt_2(\mu\text{-}S)_2(PMe_2Ph)_4]^{b}$	3.175	121		13
$[Pt_2(\mu\text{-}Cl)_2Cl_4]^{2-\ b}$	3.420	170	dmcprp10	14
$[Pt_2(\mu\text{-}Cl)_2Cl_4]^{2-\ b}$	3.448	180	kowcii	64
$[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]^{2-}$	3.528	180	forciy	65
$[Pt_2(\mu\text{-}Br)_2Br_4]^{2-}$	3.590	180	etabpt01	66, 67
$[Pt_2(\mu\text{-}I)_2I_4]^{2-}$	3.793	179	codhim	68
$[Pt_2(\mu\text{-}I)_2I_4]^{2-}$	3.824	180	dozluz	69
trans-$[Pt_2(\mu\text{-}Cl)_2Cl_2(P^{t}Bu_2C_3H_5)_2]$	3.618	180	figpeq	70
trans-$[Pt_2(\mu\text{-}Cl)_2Cl_2(Me_2py)_2]$	3.431	180	cclupt	71
trans-$[Pt_2(\mu\text{-}Cl)_2Cl_2(Et_2\mathit{S}O)_2]$	3.471	180	tankau	15
trans-$[Pt_2(\mu\text{-}Cl)_2Cl_2(AsMe_3)_2]$	3.483	180	cmaspt10	72
trans-$[Pt_2(\mu\text{-}Cl)_2Cl_2(\mathit{C}\{O^{i}Pr\}CH_2{}^{t}Bu)_2]$	3.521	180	cmpcpt20	73, 74
	3.554	180		
trans-$[Pt_2(\mu\text{-}Cl)_2Cl_2(PPr_3)_2]$	3.533	180	cppcpt	75
trans-$[Pt_2(\mu\text{-}Cl)_2Cl_2(PEt_3)_2]$	3.543	180	kanyih	76
cis-$[Pt_2(\mu\text{-}I)_2I_2(CO)_2]$	3.846	180	gitvua	77
trans-$[Pt_2(\mu\text{-}I)_2I_2(C_6H_3\{CH_2NMe_2\}_2)_2]^{2-}$	3.890	180	veckap	78
$Pt_2(\mu\text{-}S)_2(PPh_2py)_4]$	3.555	180	yijnek	79
trans-$[Pt_2(\mu\text{-}Cl)_2(Cl\mathit{Sn}N\{SiMe_3\}_2)_2(PEt_3)_2]$	3.611	180	cuttiu	80
trans-$[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$	3.643	180	cprmpp	81
$[Pt_2(\mu\text{-}Cl)_2(PCy_3)_2(\mathit{C}H_2CH_2PCy_3)_2]^{2+}$	3.730	180	dutpox10	82
trans-$[Pt_2(\mu\text{-}Cl)_2(PEt_3)_2(CF_3\mathit{C}{=}CCF_3SnCl_3)_2]$	3.543	180	cehpek	83
$[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]^{b}$	3.763	180		84
$[Pt_2(\mu\text{-}Te)_2(PEt_3)_4]^{b}$	4.100	180	vumyad	85
$[Pt_2(\mu\text{-}Te)_2(PPh_3)_4]^{b}$	4.104	180	kijvuu	86
Pd and Pt				
trans-$[PdPt(\mu\text{-}Cl)_2Cl_2(PEt_3)_2]$	3.524	180	dalhut	87
$[Pd(C_6F_5)_2(\mu\text{-}Cl)_2Pt(PEt_3)_2]$	3.568	159	jogcir	88
Au				
$[Au_2(\mu\text{-}Cl)_2Cl_4]$	3.425	180		89
$[Au_2(\mu\text{-}Br)_2Br_4]$	3.588	176		90
$[AuBr_2(\mu\text{-}Br)_2AuMe_2]$	3.705	180	mebrau	91

[a] For complex ligands, the atom bonded to the metal is set in italics. [b] To be compared with theoretical data in Table 1.

of view, it is appropriate to analyze the available structural data for several families of compounds (Tables 3−6) with two goals. First, we can check whether the theoretical predictions are obeyed by the real structures. Second, we can see how other factors not considered in the simplified models employed by us, such as steric effects, can affect the structural choice. For the subsequent discussion we will refer to structures with large angles ($\theta > 155°$) as *planar*. The following observations can be made:

(1) Although there is scarce structural data for complexes of the first transition series, all known Ni binuclears are planar. Similarly, only three bent structures could be found in our structural database search for Pd(II) and two for Pt(II) compounds. However, the Pd···Pd distance in the bent Pd(II) compounds (3.42−3.46 Å) are significatnly longer than in the Pt(II) ones (3.18−3.23 Å). In contrast, most of the Rh(I) and Ir(I) compounds present bent structures. All this is in agreement with the metal preference for bending found in our calculations.

(2) All complexes having only halides as terminal ligands are planar. Also compounds with two halide bridges and one terminal halide at each metal atom are planar. This is in keeping with our qualitative model, which indicates that poor σ-donors and π-basic ligands hinder the bending. Also the ab initio calculations predicted that the chloride terminal ligands are less likely to produce bent structures than phosphines or carbonyls.

(3) Only two palladium phosphine compounds appear in Table 1. Even if $[Pd_2(\mu\text{-}S)_2(PH_3)_4]$ is predicted by our calculations to be bent, the experimentally characterized complexes present bulky phosphines (PEt_3 and PPh_3) that sterically prevent those molecules from bending, and also the bridging ligands (Te and Cl, respectively) are not expected to favor bending. A similar situation is found for the Pt phosphine complexes, except

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that in this case one example is known with a less sterically demanding phosphine ($\mathrm{PMe_2Ph}$), which is bent as predicted for the model compound with $\mathrm{PH_3}$. The same trend can be found for Ir and Rh, for which the complexes with the smaller phosphines $\mathrm{PF_3}$ and $\mathrm{PMe_2Ph}$ are bent and those with bulkier ligands ($\mathrm{P^{\mathit{i}}Pr_3}$ or $\mathrm{PPh_3}$) are planar.

(4) Although square planar carbonyl complexes are scarce, those which are collected in Table 1 with four terminal carbonyls or two carbonyls and two phosphines are all bent, in agreement with our qualitative predictions for good σ-donor and π-acid ligands and the ab initio calculations for Rh and Pt tetracarbonyls. If one extends these ideas to other π-acid ligands, such as the olefins, one would expect diolefin complexes to be bent but monoolefin complexes to be planar. The structural data for complexes having one or two olefins per metal atom as terminal ligands are shown in Table 4. Despite the expected good σ-donor and π-acceptor properties of olefins, compounds having Pd or Pt as metal and chloride as bridging ligands are all planar. Only for Rh or Ir compounds with one olefin and one phosphine, or with two olefins, can bent structures be found. In this case one cannot unambiguously predict the structure, and both bent and planar structures can be found for Rh diolefin complexes.

Table 4. Structural Data for Olefine Binuclear Complexes of $\mathrm{d^8}$ Metal Ions of the Type $[\mathrm{L_2M}(\mu\text{-X})_2\mathrm{ML_2}]$ (See **1** and **2**)

compd	M···M (Å)	θ (deg)	refcode	ref
$[\mathrm{Pd_2}(\mu\text{-Cl})_2(\sigma,\eta^2\text{-cyclooctadiene})_2]$	3.525	180	cocdpd10	92
$[\mathrm{Pd_2}(\mu\text{-Cl})_2(\mathrm{H_2}\mathit{C}\{\mathrm{C_2H_3Cl}\}\mathrm{Me}\mathit{C}{=}\mathrm{CH_2})_2]$	3.544	180	dulror	93
$[\mathrm{Pd_2}(\mu\text{-Cl})_2\mathrm{Cl_2}(\eta^2\text{-olefin})_2]$	3.459	151	duxzeb	94
$[\mathrm{Pd_2}(\mu\text{-Cl})_2(\mathrm{H_2}\mathit{C}{=}\mathrm{CH}\mathit{C}\mathrm{R})_2]$	3.420	180	fuhmie	95
$[\mathrm{Pd_2}(\mu\text{-Cl})_2(\mathrm{C_8H_{12}}\{\mathrm{C_2H_4Cl}\})_2]$	3.522	180	bukdoa	96
$[\mathrm{Pd_2}(\mu\text{-Cl})_2(\eta^2\text{-allylnorbornyl})_2)]$	3.584	180	calbpd10	97
$[\mathrm{Pt_2}(\mu\text{-Cl})_2\mathrm{Cl_2}(\eta^2\text{-cyclopentene})_2]$	3.509	180	ccyppt	98
$[\mathrm{Pt_2}(\mu\text{-Cl})_2\mathrm{Cl_2}(\eta^2\text{-cycloheptene})_2]$	3.487	180	chptpt	98
$[\mathrm{Pt_2}(\mu\text{-Cl})_2(\eta^2\text{-ClEt}\mathit{C}{=}\mathrm{CEt}\{\mathrm{CPr}\}_2\mathit{C}\mathrm{O})_2]$	3.713	180	fijmiu	99
$[\mathrm{Pt_2}(\mu\text{-Br})_2\mathrm{Br_2}(\eta^2\text{-cycloheptene})_2]$	3.680	180	pixzeb	100
$[\mathrm{Pt_2}(\mu\text{-Cl})_2\mathrm{Cl_2}(\eta^2\text{-tetramethylallene})_2]$	3.544	180	ptmall10	101
$[\mathrm{Pt_2}(\mu\text{-Cl})_2\mathrm{R_2}(\eta^2\text{-}\mathrm{H_2}\mathit{C}{=}\mathrm{CH_2})_2]$	3.588	180	siznoe	102
$[\mathrm{Rh_2}(\mu\text{-Cl})_2(\mathrm{PHR_2})_2(\eta^2\text{-cyclooctene})_2]$	3.687	180	cifzew	103
$[\mathrm{Rh_2}(\mu\text{-Cl})_2(\mathrm{Ph_2POC(O)H}\mathit{C}{=}\mathrm{CMe_2})_2]$	3.172	120	diwrik10	104
$[\mathrm{Rh_2}(\mu\text{-Cl})_2(\mathrm{Ph_2POC(O)H}\mathit{C}{=}\mathrm{CHC_3H_5})_2]$	3.134	123	fathox	99
$[\mathrm{Rh_2}(\mu\text{-Cl})_2(\eta^2\text{-}\mathrm{H_2}\mathit{C}{=}\mathrm{CHCH{=}CMe_2})_4]$	3.090	116	mpdrhd	105
$[\mathrm{Rh_2}(\mu\text{-Cl})_2(\mathrm{cod})_2]$	3.498	169	rhcoct	106, 107
$[\mathrm{Ir_2}(\mu\text{-Cl})_2(\mathrm{cod})_2]$	2.910	109	qqqcxa02	108

(5) With only two exceptions, all cyclometalated and chelate complexes are practically planar (Table 5). One exception is

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Table 5. Structural Data for Cyclometalated Binuclear Complexes of d^8 Metal Ions of the Type $[L_2M(\mu\text{-}X)_2ML_2]$ (See **1** and **2**)

compd	donors	M···M (Å)	θ (deg)	refcode	ref
trans-$[Pd_2(\mu\text{-}Cl)_2(\mathit{C}H_2CMe_2\mathit{P}{}^{i}Bu_2)_2]$	C, P	3.553	180	bihlot01	46, 109
trans-$[Pd_2(\mu\text{-}Cl)_2(\mathit{C}H_2CMe{=}CH\mathit{P}{}^{t}Bu_2)_2]$	C, P	3.558	180	caffoe	110
trans-$[Pd_2(\mu\text{-}Cl)_2(Mes_2\mathit{P}CHR'CHR''\mathit{C}H_2)_2]$	C, P	3.585	180	vanhex	111
$[Pd_2(\mu\text{-}I)_2(\mathit{C}H_2\{C_6H_4\}\mathit{P}Tol_2)_2]$	C, P	3.929	180	codjag	112
$[Pd_2(\mu\text{-}I)_2(C_4\{CO_2Me\}_4)_2]^{2-}$	C, C	3.912	180	kaswuw	113
trans-$[Pd_2(\mu\text{-}Cl)_2(\mathit{C}_6H_4C\{COPh\}{=}\mathit{N}CH_2Ph)_2]$	C, N	3.553	180	poltal	114
cis-$[Pd_2(\mu\text{-}Cl)_2(py\mathit{C}_6H_4)_2]$	C, N	3.480	173	sohduo	115, 116
trans-$[Pd_2(\mu\text{-}Cl)_2(\mathit{C}_6H_4CH{=}\mathit{N}C_6H_3Me_2)_2]$	C, N	3.424	153	yadneu	117
trans-$[Pd(\mu\text{-}Cl)_2(\mathit{C}H_2C{}^{t}Bu{=}N\mathit{N}MePh)_2]$	C, N	3.434	180	daghau	118
trans-$[Pd_2(\mu\text{-}Cl)_2(\mathit{C}_6H_4NR\mathit{N}R')_2]$	C, N	3.447	179	dunweo	119
trans-$[Pd_2(\mu\text{-}Cl)_2(\mathit{N}Me_2CH_2CMe_2CHCHO)_2]$	C, N	3.471	180	otmppd	120
trans-$[Pd_2(\mu\text{-}Cl)_2(\mathit{C}_6H_4N{=}NC_6H_3Me_2)_2]$	C, N	3.477	180	sixxig	121
	C, N	3.478	180		
trans-$[Pd_2(\mu\text{-}Cl)_2(\mathit{C}HRCHR'O\mathit{N}O)_2]$	C, N	3.489	179	coploi	122
trans-$[Pd_2(\mu\text{-}Cl)_2(\mathit{o}\text{-}\mathit{C}_6H_4CMe\mathit{N}H{}^{i}Pr)_2]$	C, N	3.496	164	jibnox	123
trans-$[Pd_2(\mu\text{-}Cl)_2(Me_2\mathit{N}CH_2CH_2\mathit{C}H_2)_2]$	C, N	3.501	180	dijpan	124
trans-$[Pd_2(\mu\text{-}Cl)_2(\mathit{o}\text{-}\mathit{C}_6H_3\{MeO\}CH_2\mathit{N}Me_2)_2]$	C, N	3.535	180	dagboc	125
trans-$[Pd_2(\mu\text{-}Cl)_2(\mathit{m}\text{-}\mathit{C}_6H_3\{MeO\}CH_2\mathit{N}Me_2)_2]$	C, N	3.509	180	dagbui	125
trans-$[Pd_2(\mu\text{-}Cl)_2(\mathit{p}\text{-}\mathit{C}_6H_3\{MeO\}CH_2\mathit{N}Me_2)_2]$	C, N	3.502	167	dagcap	125
trans-$[Pd_2(\mu\text{-}Cl)_2(\mathit{C}H_2CMe_2CMe{=}\mathit{N}MePh)_2]$	C, N	3.512	180	daggun	118
trans-$[Pd_2(\mu\text{-}Cl)_2(Tol\mathit{N}{=}N\mathit{C}_6H_3OH)_2]$	C, N	3.554	166	songad	126
trans-$[Pd_2(\mu\text{-}Cl)_2(\mathit{C}_6H_4CPh{=}\mathit{N}NHPh)_2]$	C, N	3.575	180	dephov	127
trans-$[Pd_2(\mu\text{-}Br)_2(\mathit{C}H_2C_6H_2Me_2CH{=}\mathit{N}Tol)_2]$	C, N	3.717	180	hantof	128
trans-$[Pd_2(\mu\text{-}Br)_2(Me\mathit{C}_6H_3CH{=}\mathit{N}Cy)_2]$	C, N	3.418	134	lalcik	129
trans-$[Pd_2(\mu\text{-}Br)_2(\mathit{C}_6H_4N{=}\mathit{N}C_6H_3Me_2)_2]$	C, N	3.589	165	peltef	130
trans-$[Pd_2(\mu\text{-}Br)_2(\{MeO\}_2\mathit{C}_6H_2CH{=}\mathit{N}Cy)_2]$	C, N	3.631	180	kimpeb	131
cis-$[Pd_4(\mu\text{-}Br)_4(\{\{MeO\}_3\mathit{C}_6HCH{=}\mathit{N}\}_2C_6H_4)_2]$	C, N	3.662	171	sucyeu	132
trans-$[Pd_2(\mu\text{-}I)_2(\mathit{C}_6H_4N{=}\mathit{N}C_6H_3Me_2)_2]$	C, N	3.790	160	peltij	130
trans-$[Pt_2(\mu\text{-}Br)_2(\mathit{C}_4H_6CH_2\mathit{P}{}^{t}Bu_2)_2]^{a}$	C, P	3.233	116	foybuq	16
trans-$[Pt_2(\mu\text{-}Cl)_2(Mes_2\mathit{P}CHR'CHR''\mathit{C}H_2)_2]$	C, P	3.624	180	vanhib	111
trans-$[Pt_2(\mu\text{-}Cl)_2(Ph_2P(\mathit{C}_6H_4)\mathit{C}HAc)_2]$	C, C	3.599	180	cebtos	133
trans-$[Pt_2(\mu\text{-}Cl)_2(\mathit{C}_6H_4N{=}\mathit{N}Ph)_2]$	C, N	3.598	180	pazpcp	134

[a] To be compared with theoretical data in Table 1.

trans-$[Pt_2(\mu\text{-}Br)_2(\mathit{C}_4H_6CH_2\mathit{P}{}^{t}Bu_2)_2]$ for which the bending angle is 116°. Is there some specificity in the electronic structure of cyclometalated complexes that makes them less susceptible to bending than other compounds? What is so special in the bromo-bridged compound? A closer look at Table 5 indicates that all the cyclometalated complexes of this family have Pd or Pt as metals, which have little tendency to bending. Only in *trans*-$[Pt_2(\mu\text{-}Br)_2(\mathit{C}_4H_6CH_2\mathit{P}{}^{t}Bu_2)_2]$ appear simultaneously terminal and bridging ligands which favor bending. The ab initio calculations on *trans*-$[Pt_2(\mu\text{-}Br)_2(CH_3)_2(PH_3)_2]$ (Table 1) confirm that it is not its cyclometalated nature but the particular choice of metal atom, bridging ligands, and terminal ligands in this compound that favor its bent structure. In this regard, notice that both saturated and unsaturated metallacycles are planar, indicating that the existence of π delocalization throughout the metallacycle is irrelevant for the choice between the planar and bent structures.

Table 6. Structural Data for Binuclear Complexes of d^8 Metal Ions of the Type $[(LL)M(\mu\text{-}X)_2M(LL)]$ (See **1** and **2**) with Chelating Terminal Ligands

compd	M···M (Å)	θ (deg)	refcode	ref
$[Rh_2(\mu\text{-}Cl)_2(\{C_2F_5\}_2\mathit{P}C_2H_4\mathit{P}\{C_2F_5\}_2)_2]$	3.217	128	sukdad	135
$[Rh_2(\mu\text{-}Cl)_2({}^{t}Bu_2\mathit{P}CH_2\mathit{P}{}^{t}Bu_2)_2]$	3.260	132	yuwfeb	136
	3.272	133		
$[Ir_2(\mu\text{-}Cl)_2(\{C_2F_5\}_2\mathit{P}C_2H_4\mathit{P}\{C_2F_5\}_2)_2]$	3.236	128	sukdeh	135
trans-$[Pd_2(\mu\text{-}Cl)_2(\{{}^{t}BuNC\}_2Cl_2\mathit{Rh}\{py\mathit{P}Ph_2\})_2]$	3.658	180	volkow	137
$[Pt_2(\mu\text{-}Cl)_2(\{F_3C\}_2\mathit{P}C(Me)\mathit{P}\{CF_3\}_2)_2]$	3.508	180	gipnau	138
$[Pt_2(\mu\text{-}Cl)_2({}^{t}Bu_2\mathit{P}C_3H_6\mathit{P}{}^{t}Bu_2)]^{2+}$	3.752	180	kotnuc	139
$[Pt_2(\mu\text{-}Te)_2(dppe)_2]$	3.965	180	sodduk	140
$[Pt_2(\mu\text{-}I)_2(en)_2]^{2+}$	3.799	180	fomfiw	141
$[Pt_2(\mu\text{-}I)_2(dppm)_2]^{2+}$	3.880	180	virlox	142
$[Au_2(\mu\text{-}Se)_2(Se_4)_2]^{2-}$	3.656	180	sellie	143

(6) Other chelate complexes appear in Table 6. The structural data for these compounds again reflect the dramatic influence of the nature of the metal atom on the structure. The Rh and Ir compounds (having good σ-donor terminal ligands) are bent, whereas the Pt analogues are planar.

In summary, either the ligands are small enough and the metal−metal interaction favors a strongly bent structure ($\theta < 150°$) or the bulkiness of the ligands inhibits a close approach of the two metal atoms, and the molecule prefers to stay planar ($\theta > 160°$). This duality would explain the nonexistence of partially bent structures ($140° < \theta < 160°$) as seen in Figure 1.

Conclusions

In this contribution we show that binuclear compounds with two metal atoms in a square planar environment (**1**) with eight framework electrons for the M_2X_2 ring may bend around the X---X hinge to form weakly bonding metal···metal interactions

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(**2**). The combined use of theoretical studies and a structural database analysis has allowed us to establish a few rules for the structural choice between planar or bent structures. Such rules, which allow for the rationalization of the structures of 139 crystallographically independent molecules, can be summarized as follows:

(a) The tendency to form bent structures increases with the difusseness of the metal's atomic orbitals, i.e., when descending along a group of the periodic table and from right to left along a period.

(b) Complexes with two good σ-donor (and preferably good π-acid) terminal ligands per metal atom (CO, PR_3, bipy, cod, or other diolefins) favor bent structures, provided that no important steric hindrance occur. As an example, phosphine ligands with at most one bulky substituent (e.g., PMe_3 or PMe_2Ph) favor bent structures, but those with two or three bulky groups (e.g., Ph, ^{t}Bu, ^{i}Pr, or Cy) at the terminal ligands (e.g., PEt_3, $PRPh_2$, PPh_3, dppe, $SiCl_3$) are planar. In contrast, complexes with two or more π-basic or poor σ-donor terminal ligands (halides, amides, thioethers, C_6F_5) favor a planar structure.

(c) Among bridging atoms of the same period, the less electronegative ones favor the bent structure the most. The exception corresponds to the bulkiest bridging atoms (i.e., Te or I), which favor planar structures.

(d) Even if practically all the complexes with chelating ligands, including cyclometalated compounds, are planar, this is the result of the factors a−c.

(e) Except for the neglect of important steric effects, the ab initio MP2 calculations for model compounds match very well the experimental behavior of similar compounds.

Appendix: Computational Details

Extended Hückel calculations[144,145] were used to illustrate the qualitative discussion, taking as model compounds $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ and $[Rh_2(\mu\text{-}Cl)_2Cl_4]^{4-}$. The analysis of the interaction between the fragment molecular orbitals of two square planar moieties upon bending (Figure 2) was carried out by replacing each bridging Cl^- ligand in the latter model by two independent H^- terminal ligands while deleting the overlap between the H atoms and keeping the rest of the molecular geometry untouched. Bonding angles of 90° around the metal atom were assumed, and the following bond distances were used: $Rh-Cl = 2.40$, $Rh-C = 1.80$, $Rh-H = 1.57$, and $C-O = 1.15$ Å. The calculations were carried out with the YAeHMOP[146] program using the modified Wolfsberg−Helmholz formula.[147] Standard atomic parameters were used for Rh,[148] Cl,[149] C, H, and O.[145]

All ab initio calculations were performed with the GAUSSIAN 94 suite of programs.[150] A molecular orbital *ab initio* method with introduction of correlation energy through the Möller−Plesset (MP) perturbation approach,[151] excluding excitations concerning the lowest energy electrons (frozen core approach) was applied. Effective core potentials (ECP) were used to represent the innermost electrons of the metal atoms[152] as well as the electron core of the P, S, Se, Te, Cl, Br, and I atoms.[153] Geometry optimizations were carried out at the second level of the Möller−Plesset theory (MP2) with a basis set of valence double-ζ quality for the metal atoms (associated with the pseudopotential,[153] and a standard LANL2DZ contraction scheme[150]) and valence double-ζ plus *d* polarization functions for the atoms directly attached to the metal (6-31G(d) basis set for C, O, and F atoms[154−156] and the basis set associated with

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the pseudopotential[153] and a standard LANL1DZ contraction,[150] supplemented with a set of *d* polarization functions[157] for P, S, Se, Te, Cl, Br, and I). The oxygen atoms of the carbonyl ligands were also represented by a valence double-$\zeta + d$ polarization function basis set.[154−156] A minimal basis set was used for the H atoms of the PH_3 and CH_3 groups,[158] and a valence double-ζ basis set, for the F atoms of the PF_3 ligands.[154] The internal structure of the phosphine ligands was kept frozen in the optimizations (P−H = 1.42 Å; H−P−H = 93.2°). 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 θ at 180° or *ca.* 120°. Symmetry restrictions were introduced in the optimizations when possible.

In order to check the accuracy and reliability of our results, single point energy-only calculations were carried out for several compounds at the previously optimized geometries by adding an f shell to the basis set of the Pt atom.[159] For the complex $[Pt_2(\mu\text{-}S)_2(PH_3)_4]$, the energy difference was also computed at the MP4(SDTQ)//MP2 level as a check.

The collection of structural data was obtained through a systematic search of the Cambridge Structural Database[160] (version 5.12) for compounds of general formula $M_2(\mu\text{-}X)_2L_4$, in which M was imposed to be a metal at its oxidation state with a d^8 configuration: M = 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.

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