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Molecular Structures of Edge-Sharing Square-Planar Dinuclear Complexes with Unsaturated Bridges

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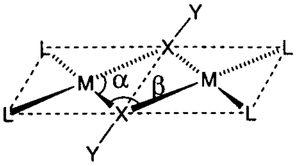
The dinuclear complexes of transition metal ions of type $[M_2(\mu,\eta^1\text{-}XY)_2L_4]$, where XY is an unsaturated ligand that can act as a four-electron or a two-electron donor through the X atom, appear in two molecular conformations depending on whether the coordination planes around the two metal atoms are coplanar or bent. In both structures the geometry of the X atom is planar, corresponding to an sp^2 hybridization. An ab initio theoretical study on 43 representative complexes, complemented with a structural database analysis, provides a rationale for the experimentally observed structures.

The doubly bridged dinuclear complexes of type $[L_2M(\mu\text{-}XY)_2ML_2]$ with an X−Y multiple bond and square-planar coordination geometries around the metal atoms appear in planar (**1**) or bent (**2**) geometries. The orientation of the XY ligand, indicated by the uplift angle τ (that between the X−Y bond and the X- -X vector), is expected to increase with the bending angle θ.[1,2] In addition, some planar complexes may present a short through-ring M···M distance. These compounds form part of the larger family of general formula $[M_2L_4(\mu\text{-}XR_n)_2]$ that are ubiquitous in the organometallic and coordination chemistry of late transition metals. Although there is a wealth of structural information available for these compounds, we are still in need of establishing the rules that govern their molecular structures. In recent work we have theoretically analyzed the molecular conformation of related $[M_2L_4(\mu\text{-}XR_n)_2]$ complexes ($n = 0-2$) in which X is an sp^3 donor.[1−3] Here we wish to extend our study to the $[M_2(\mu,\eta^1\text{-}XY)_2L_4]$ compounds with sp^2 hybridization at the bridging atom and an $X\overset{n}{-}Y$ multiple bond ($n = 2$ or 3) in the bridge, as well as to the hydrido-bridged complexes $[M_2(\mu,\eta^1\text{-}XY)_{2-m}(\mu\text{-}H)_mL_4]$ ($m = 1-2$). We will focus on two main aspects of their structures: (i) the possibility of M···M interactions in the planar M_2X_2 diamond and (ii) the existence of bending of the molecular plane. Although related alkynyl-bridged complexes such as $[M_2(\mu,\eta^2\text{-}C{\equiv}CR)_2L_4]$ are known,[4] the bonding mode of the bridging ligand is different enough to deserve a separate study, and we restrict the present report to compounds of the type $[M_2(\mu,\eta^1\text{-}XY)_2L_4]$ in which the Y atom does not interact with the metals.



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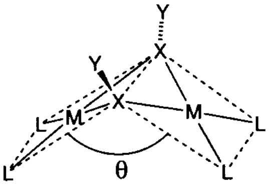

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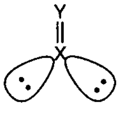
Before discussing the available structural data, we will shortly describe the different bonding situations that appear in these complexes and recall the electron-counting rules that will allow us to classify the compounds as *electron precise* or *electron deficient*. Then we will summarize the available structural information and discuss the results of our ab initio calculations by comparing them with the experimental data.

Electron-Precise and Electron-Deficient Complexes: The Framework Electron Count. Let us consider first those XY bridging ligands that can act as two-orbital−four-electron donors (**3a**), such as azido (N_3^-), vinylidene ($R_2C{=}C^{2-}$), diazenido ($RN{=}N^-$), or other ligands listed in Scheme 1. The σ bonding of the M_2X_2 skeleton in this case can be defined by four framework bonding orbitals obtained as symmetry-adapted combinations of the bridge and metal orbitals (**4a**). Given the square planar geometry of the metal atoms, one has to make provisions for eight electrons per metal atom to occupy the nonbonding d orbitals. Hence, all metal valence electrons in excess of eight, together with the electrons provided by the bridging ligands, constitute the *framework electron count* (FEC).[5−8] Therefore, two four-electron-donor bridging ligands



3a

3b

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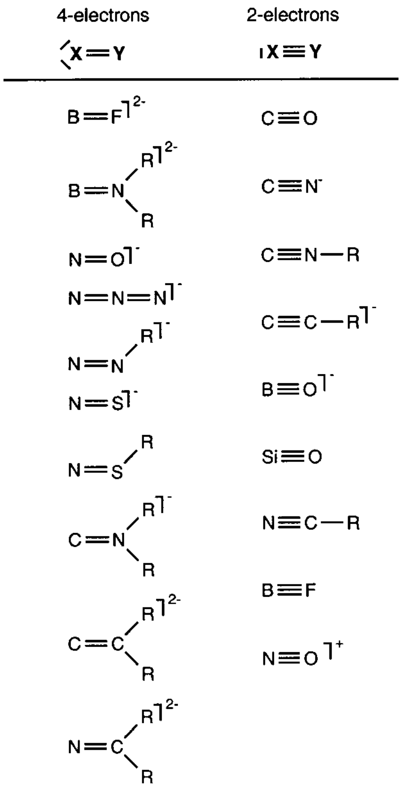
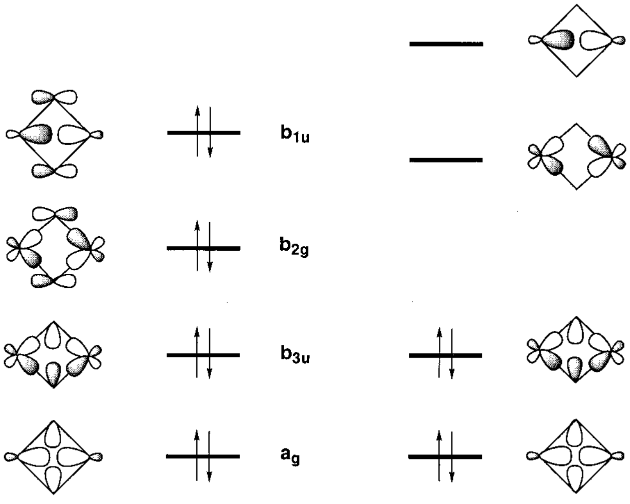
Scheme 1. List of Bridging Ligands Used in the Calculations and Formal Charges Assumed for Electron Counting Purposes in Electron-Precise (4 Electron Donors) and Electron-Deficient (2 Electron Donors) Complexes



X═Y combined with two d^8 metal ions give a FEC of 8, and we will refer to these compounds as *electron-precise* throughout this paper. In such cases, the framework orbitals describe four bonds corresponding to the edges of the M_2X_2 diamond, and relatively long M···M and X···X distances across the ring should be expected.

Consider now X≡Y bridging ligands such as carbonyl or isonitriles that have only one lone pair orbital available for bonding toward the metal atoms (**3b** and Scheme 1). A modified orbital diagram results (**4b**) because there are no b_{1u}- and b_{2g}-type orbitals in the bridging ligands to interact with the metal d, and we are left with metal-centered, nonbonding b_{1u} and b_{2g} orbitals. Hence, for d^8 metal ions b_{1u} and b_{2g} are empty, and the number of framework bonding electrons (FEC) is 4. Since the occupied orbitals have σ and π M−M bonding character whereas the empty ones are σ^* and π^*, a short through-ring M···M distance is predicted.[5−8] In this paper we call these *electron-deficient complexes*, since formally only two electron pairs (FEC = 4) account for the four M−X links and a short M−M distance. The bridging hydrido ligand is also a one-orbital−two-electron donor, and the qualitative orbital diagram of **4b** also applies to hydrido-bridged complexes.[5]



4a **4b**

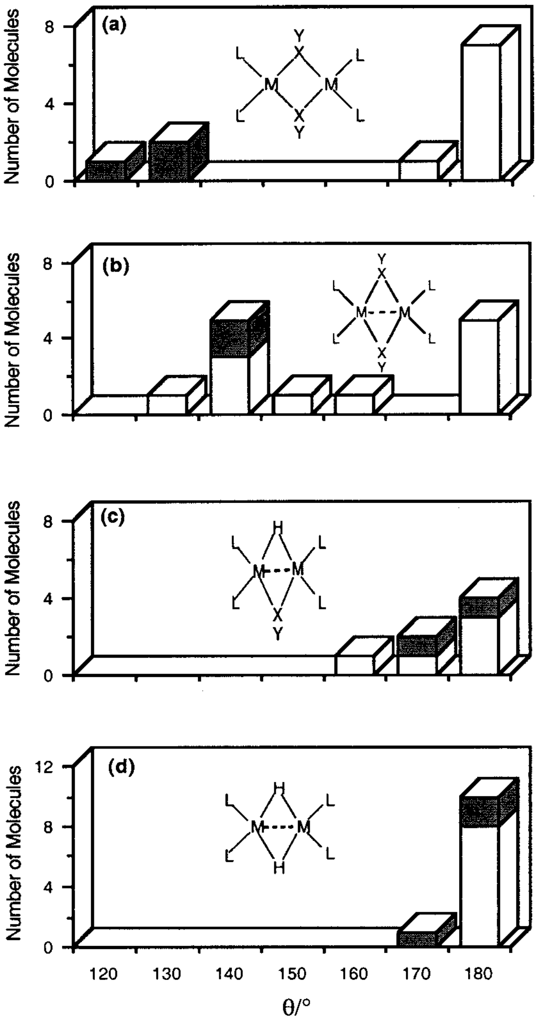


Figure 1. Distribution of the number of molecular structures of type $[M_2(\mu\text{-}XY)_{2-m}(\mu\text{-}H)_mL_4]$ (m = 0−2, XY = unsaturated ligand) as a function of the bending angle θ for the families of (a) electron-precise complexes (FEC = 8); (b) electron-deficient complexes having two XY ligands (m = 0, FEC = 4); (c) electron-deficient complexes with one hydrido bridge (m = 1), and (d) bis(hydrido)complexes (m = 2). In every interval, the number in the horizontal axis indicates the maximum value of the angle θ. Black bars correspond to Rh and Ir compounds, white bars to Ni, Pd, and Pt compounds.

Experimental Structural Data

The experimental structures of electron-precise compounds with unsaturated XY bridges are distributed between the planar and bent forms (Figure 1a), as deduced from a Cambridge Structural Database search.[9] Such behavior is similar to that previously found for the analogous complexes with saturated bridging ligands.[1−3] It is worth stressing that the bending angle θ shows a bimodal distribution with one maximum at θ = 180° and another one at a smaller angle ($\theta \approx 130°$) separated by a

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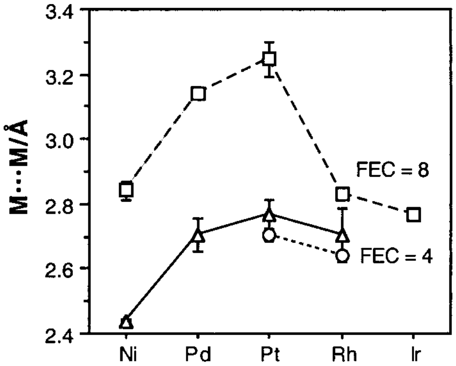


Figure 2. Distribution of average M···M distances for all families of dinuclear complexes studied, for different framework electron counts and metal atoms. The error bars correspond to the standard deviation of the average. Data for electron-precise compounds (FEC = 8, Table 3) are represented by squares, for electron-deficient compounds (FEC = 4) with the electron configuration $a_g^2b_{3u}^2b_{2g}^2$ (**4b**, Tables 5−7) by triangles, and with the electron configuration $a_g^2b_{3u}^2$ by circles (Table 7).

clear gap at intermediate angles, as previously found for saturated XR_n bridges.[1−3] The electron-deficient complexes $[M_2(\mu\text{-}XY)_2L_4]$ (Figure 1b) present also a bimodal distribution centered at θ values of 140° and 180°. The substitution of one XY bridging ligand by a hydride in $[M_2(\mu\text{-}XY)(\mu\text{-}H)L_4]$ complexes dramatically changes the conformational choice, and only planar or slightly bent molecules can be found (Figure 1c), an effect that is enhanced for the bis(hydrido) complexes, for which only practically planar structures are found (Figure 1d).

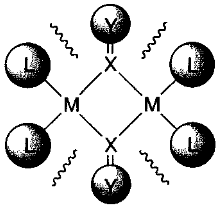
A weakly bonding metal···metal interaction has been shown to provide a driving force for bending in electron-precise complexes,[1−3] while short M···M distances in planar compounds are a fingerprint for electron deficiency.[6] It is therefore interesting to analyze the M···M distances found in compounds with different electron counts (Figure 2). It was seen that for electron-precise complexes (i.e., FEC = 8) the distances increase significantly down the Ni group, whereas essentially the same distances are found for Rh and Ir. On the other hand, the group 9 metals show shorter distances than the corresponding group 10 ones. The shorter distances found for Rh and Ir have been attributed to their stronger metal−metal bonding interaction in the bent molecule.[10] In contrast, short M···M distances are found for all metals in electron-deficient complexes across planar M_2X_2 rings, as expected from the framework electron-counting rules.[6]

Despite the existence of two alternative structures, planar or bent, we are not aware of structurally characterized isomers, although spectroscopic data support their existence. Both planar and bent conformers can be identified in solution for $[M_2(\mu\text{-}N{=}CR_2)_2(tfbb)_2]$ (M = Ir, Rh) and their interconversion detected in the ^1H NMR time scale,[11] even if only one isomer appears in the solid state. A ring inversion was also proposed by Forniés et al. for several compounds of the $[Pt_2(\mu,\eta^1\text{-}C{\equiv}CR)_2L_4]$ family, on the basis of their ^1H and ^{13}C NMR spectra.[12]

According to our previous experience with unsubstituted,[3] monosubstituted,[1] and disubstituted sp^3 bridges,[2] we can anticipate some factors that may affect the structural choice. In the former, a weak metal···metal bonding favors the bent structure, counterbalanced in part by steric repulsion between terminal ligands (Table 1). The tendency to bending 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: Ir > Rh > Pt > Pd > Ni > Au. Also good σ-donor (and preferably good π-acid) terminal ligands favor bent structures.[3] In the compounds with substituted bridges new factors must be considered, such as the conformational preference of the bridging atom or the repulsions between substituents and terminal ligands (R- -R in the *exo* and R- -L in the *endo* conformation).[1] These two latter factors are of less significance in the present study due to the planar configuration of the bridging atom X. In summary, the factors that are expected to influence the choice between planar and bent structures in the presently studied complexes are (i) the M···M and L···L interactions between two ML_2 fragments in the bent form, represented by an interaction term I_{MM}; (ii) the decrease in MXM bond angles upon bending, represented by an energy term V_β; and (iii) the steric repulsion between substituent and terminal ligands in the planar form (**5**), I_{LY}.

Table 1. Theoretical Estimates of the Interaction Energy between Two ML_2 Fragments in the Bent Conformation (I_{MM}, kcal·mol^{-1}) for Several Dinuclear Complexes of the Type $[M_2(\mu\text{-}XR_n)_2(PH_3)_4]^{z+}$ (n = 0−2)[1−3]

XR_n	Ir	Rh	Pt	Pd	Ni
$n = 0$					
Cl^-	−6.1	−4.1	0.0	+3.8	+8.4
Br^-		−6.1			
I^-		−7.4			
O^{2-}			−4.0		
S^{2-}			−4.8	−3.4	
$n = 1$					
HO^-		−6.3	−1.2		+1.3
HS^-	−11.6	−10.9	−4.2	−4.8	−3.9
$n = 2$					
H_2N^-		−7.7	−1.4		
H_2P^-		−8.3	−1.5		
H_2S			+4.1		



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Results of ab Initio Calculations

Ab initio MP2 calculations (see Appendix for computational details) were performed on model complexes $[M_2(\mu\text{-}XY)_{2-m}(\mu\text{-}H)_m(PH_3)_4]^{z+}$ (m = 0−2), $[M_2(\mu\text{-}XY)_2Cl_4]^{z+}$ (where M is Pt or Pd, and XY is one of the bridging ligands presented in Scheme 1 or H^-), and $[Rh_2(\mu\text{-}NCH_2)_2L_4]^{z+}$ (where L is $\eta^2\text{-}C_2H_4$ or CO) in both the planar and bent conformations. The two alternative structures for a total of 43 compounds were optimized with the only restrictions that the geometries of the terminal ligands were kept frozen and the bending angle θ fixed in those structures for which a bent minimum was not found. The atomic coordinates of the minima are supplied as Supporting Information. To facilitate identification of the different model compounds whose formula can be found in Tables 2 and 4, we label them with an **M** (Table 2) or **N** (Table 4) followed by a sequential number. Similarly, the experimentally determined structures will be identified by a capital letter for each class of compounds: **A** (Table 3), **B** (Table 5), **C** (Table 6), and **D** (Table

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Table 2. Theoretical Results for Electron-Precise (FEC = 8) Compounds $[M_2(\mu\text{-}X{=}Y)_2L_4]$ with Four-Electron Bridging Ligands (see Scheme 1)[b]

entry	compound	M···M	θ	α	β	$E_b - E_p$
M.1	$[Pt_2(\mu\text{-}NO)_2(PH_3)_4]^{2+}$	3.214	180	74.5	105.5	
		3.092	134[a]	69.1	98.4	+11.3
M.2	$[Pt_2(\mu\text{-}N_3)_2(PH_3)_4]^{2+}$	3.294	180	75.0	105.0	
		3.061	131[a]	71.6	95.2	+5.3
M.3	$[Pt_2(\mu\text{-}NNH)_2(PH_3)_4]^{2+}$	3.232	180[a]	75.3	104.7	
		3.168	153	74.1	101.9	−0.9
		3.053	132[a]	70.6	96.5	+2.1
M.4	$[Pt_2(\mu\text{-}NS)_2(PH_3)_4]^{2+}$	3.217	180[a]	75.3	104.7	
		3.141	152	74.1	101.4	−1.5
		3.032	132[a]	70.9	96.1	+1.6
M.5	$[Pt_2(\mu\text{-}BF)_2(PH_3)_4]$	3.411	180[a]	64.3	115.7	
		3.313	139	59.3	109.1	−1.6
M.6	$[Pt_2(\mu\text{-}NSH)_2(PH_3)_4]^{4+}$	3.334	180[a]	74.6	105.4	
		3.163	137	72.5	97.4	−4.8
M.7	$[Pt_2(\mu\text{-}NCH_2)_2(PH_3)_4]^{2+}$	3.237	180[a]	75.6	104.4	
		3.065	139	73.2	97.3	−5.3
M.8	$[Pt_2(\mu\text{-}CNH_2)_2(PH_3)_4]^{2+}$	3.208	180[a]	73.0	107.0	
		3.051	136	68.9	99.5	−5.3
M.9	$[Pt_2(\mu\text{-}CCH_2)_2(PH_3)_4]$	3.245	180[a]	73.4	106.6	
		2.994	128	69.4	95.3	−9.5
M.10	$[Pt_2(\mu\text{-}BNH_2)_2(PH_3)_4]$	3.543	180[a]	60.8	119.2	
		3.099	116	56.6	96.8	−14.0
M.11	$[Pd_2(\mu\text{-}N_3)_2Cl_4]^{2-}$	3.221	180	78.6	101.4	
		3.015	129[a]	74.1	92.0	+7.0
M.12	$[Rh_2(\mu\text{-}NCH_2)_2(CO)_4]$	3.231	180[a]	77.3	102.7	
		3.075	141	75.4	96.6	−1.5
M.13	$[Rh_2(\mu\text{-}NCH_2)_2(\eta^2\text{-}C_2H_4)_4]$	3.209	180[a]	77.9	102.1	
		2.872	126	75.4	89.6	−3.8

[a] θ was kept frozen in the calculation. [b] The first line of each entry corresponds to the planar, the second to the bent structure.

7). Before discussing the particular results for each family of compounds, we analyze in this section the data for optimized and related experimental structures and the energy contributions to bending.

Comparison of Theoretical and Experimental Structures. The optimized structural parameters are in general good agreement with the experimental data. For the interested reader, we have collected together calculated and experimental structural data as Supporting Information (Tables S1 and S2). The following trends can be extracted.

(a) Calculated bending angles θ deviate from the experimental ones only when the real ligands are significantly bulkier than those employed in the model complexes. Nevertheless, the conformational preference for a bent or planar structure is in agreement with the observed geometries.

(b) Experimental M···M distances are fairly well reproduced by the calculations, and large deviations can be attributed to the presence of bulky ligands and the corresponding difference in bending angle θ. The maximum deviations are 0.08 (between experimental compound **A.6** and theoretical model **M.6**) and 0.07 (between **C.4** and **N.2**) Å for electron-precise and electron-deficient complexes, respectively.

(c) Calculated M−X, M−L, and X−Y bond lengths are in good agreement with the experimental ones. The difference of 0.03 Å between the calculated and experimental C═O distance in **N.14** and **B.1**, for instance, is just 3 times the experimental standard deviation. Not unexpectedly, larger deviations (∼0.2 Å) appear for the M−H distances of the hydrido-bridged complexes, experimentally determinated by X-ray diffraction, as well as for associated structural parameters.

(d) Calculated L−M−L bond angles deviate significantly from the experimental ones only when a bidentate ligand is modeled by two monodentate ones (**M.13** vs **A.1**, **N.2** vs **C.4**, **N.15** vs **D.8**, **N.1** vs **D.5**, **D.7**, and **D.8**) or when bulky substituents are replaced in the calculation by hydrogen atoms (e.g., PPh_3 in **A.5** and **A.6**, compared to PH_3 in **M.4** and **M.6**).

(e) Calculated ring angles, X−M−X and M−X−M, deviate at most 4° from the experimental ones, corresponding to the case of the **N.15** model molecule and the experimental **B.8** structure, and is related to the different L−M−L bond angles associated with monodentate and bidentate terminal ligands, respectively.

Energy Contributions. For the compounds with XY bridges, the difference in energy between the planar and the bent structures can be associated with three contributions corresponding to (i) the change in MXM (β) bond angles (V_β), (ii) the interaction between the two ML_2 fragments (I_{MM}), and (iii) the interaction between the substituent Y and the terminal ligands in the planar conformation (I_{LY}):

$$E_b - E_p = I_{MM} + 2V_\beta + 2I_{LY} \tag{1}$$

Some I_{MM} values found in our previous work on analogous systems with saturated bridges are given in Table 1.

To evaluate the relative importance of the second term (V_β), we have calculated the energy associated with changes in H−C−H bond angles in the simple model H_2CO. This molecule can be thought of as a CO^{2-} that acts as a four-electron donor toward two Lewis acids (H^+ ions) that assume in this model the role of the metal ions in the dinuclear complexes presently studied. The energy minimum for this molecule is found at 114.1°, consistent with the sp^2 hybridization (120°) at the carbon atom, and the energy varies in an almost linear way between 80° and 100°. Other XY groups tested show a similar behavior, with only a small shift of the minimum energy angle (119.5° for H_2NO^+ and 117.1° for $H_2NCH_2^+$) and an almost coincident energy profile. We do not put much emphasis on the numerical results, since the more ionic character of the M−X bonds compared to the H−X ones should affect the angular depen-

Table 3. Experimental Structural Data for Electron-Precise (FEC = 8, All Orbitals in **4a** Occupied) Dinuclear Complexes of the Type $[M_2(\mu,\eta^1\text{-}X{=}Y)_2L_4]$

	compound	M···M/Å	α/deg	β/deg	θ/deg	ref	refcode
A.1	$[Rh_2(\mu\text{-}N{=}CPh_2)_2(tfbb)_2]$	2.827	76.2	87.4	123	11	LIFMIW
	$[Rh_2(\mu\text{-}N{=}CPh_2)_2(tfbb)_2]$	2.835	76.3	87.4	123		LIFMIW
A.2	$[Ir_2(\mu\text{-}N{=}CPh_2)_2(cod)_2]$	2.764	75.6	84.1	116	15	NUZDAN
A.3	$[Ni_2(\mu\text{-}NSNS)_2(CN)_2]^{2-}$	2.862	79.6	100.4	180	16	BIZKIE
A.4	$[Ni_3(\mu\text{-}NSNS)_4]^{2-}$	2.819	80.6	97.8	162	17	CIJVIA
A.5	$[Pt_2(\mu\text{-}NSNS)_2(PPh_3)_2]$	3.212	77.0	103.0	180	18	DAPRAN
A.6	$[Pt_2(\mu\text{-}NSNS)_2(PPh_3)_2]$	3.218	76.5	103.5	180	19	DEBXAJ
A.7	$[Pt_2(\mu\text{-}NSeNSe)_2(PPh_3)_2]$	3.227	75.0	105.0	180	20	KIKDAJ
A.8	$[Pt_2(\mu\text{-}NNH)_2(PPh_3)_4]^{2+}$ [a]	3.326	70.0	110.0	180	21	IPTAPT
A.9	$[Pd_2(\mu\text{-}N_3)_2(N_3)_4]^{2-}$	3.142	76.6	103.4	180	13	PASAZP
A.10	$[Pd_2(\mu\text{-}N{=}CHC_6H_4PPh_2)_2Cl_2]$	3.140	79.9	100.1	180	22	

[a] Disordered crystal with $[Pt_2(\mu\text{-}NH_2)_2(PPh_3)_4]^{2+}$.

Table 4. Theoretical Results[a] for Electron-Deficient Compounds $[M_2(\mu\text{-H})_m(\mu,\eta^1\text{-X}{\equiv}Y)_{2-m}L_4]$ ($m = 0-2$)[e]

		$z = 0$ ($e = 6$)					$z = 2$ ($e = 4$)				
	compound	M···M	θ	α	β^c	$E_b - E_p$	M···M	θ	α	β^c	$E_b - E_p$
N.1	$[Pt_2(\mu\text{-H})_2(PH_3)_4]^{z+}$	2.852	180	72.7	107.3		2.681	180	82.7	97.3	
		2.792	124^b	58.5	101.1	+12.0	2.649	118^b	63.2	94.0	+12.8
N.2	$[Pt_2(\mu\text{-H})(\mu\text{-CO})(PH_3)_4]^{(1+z)+}$	2.787	180	83.9	106.4, 85.8		2.796	179	89.7	106.4, 74.2	
		2.747	123^b	69.9	100.7, 83.0	+12.4	2.758	119^b	74.6	101.2, 70.5	+7.5
N.3	$[Pt_2(\mu\text{-SiO})_2(PH_3)_4]^{(2+z)+}$	2.935	179	102.9	77.1		2.977	179	104.9	75.1	
		2.866	114^b	87.3	74.7	+10.1	2.853	109^b	90.9	69.5	+5.5
N.4	$[Pt_2(\mu\text{-CO})_2(PH_3)_4]^{(2+z)+}$	2.789	178	95.7	84.3		2.981	180^b	98.4	81.6	
		2.754	121^b	81.4	82.6	+6.4	2.951	140	94.3	79.5	−0.3
							2.921	116^b	85.7	76.9	+0.7
N.5	$[Pt_2(\mu\text{-NO})_2(PH_3)_4]^{(4+z)+}$	2.949	179	93.7	86.3						
		2.923	123^b	79.3	85.4	+5.2	[d]				
N.6	$[Pt_2(\mu\text{-BO})_2(PH_3)_4]^{z+}$	2.780	173	99.4	80.4		2.717	179	102.8	77.2	
		2.761	118^b	84.1	79.0	+3.0	2.709	115^b	86.4	75.8	+7.5
N.7	$[Pt_2(\mu\text{-CNH})_2(PH_3)_4]^{(4+z)+}$	2.816	180^b	96.3	83.7		2.907	180^b	99.5	80.5	
		2.767	126	84.9	82.0	−4.3	2.823	114	85.6	76.2	−6.4
N.8	$[Pt_2(\mu\text{-CN})_2(PH_3)_4]^{z+}$	2.906	180^b	95.1	84.9		2.873	180^b	95.5	84.5	
		2.813	120	82.0	81.7	−6.7	2.870	165	94.8	84.3	−0.0
							2.813	120^b	82.0	81.8	+4.6
N.9	$[Pt_2(\mu\text{-NCH})_2(PH_3)_4]^{(2+z)+}$	3.178	180^b	91.6	88.4		3.623	180^b	80.6	99.4	
		2.910	107	75.0	79.4	−14.0	3.101	115	75.8	83.5	−7.7
N.10	$[Pt_2(\mu\text{-CCH})_2(PH_3)_4]^{z+}$	2.910	180^b	94.9	85.1		2.922	180^b	92.9	87.1	
		2.777	113	78.4	80.6	−14.4	2.826	125	82.4	83.8	−6.6
N.11	$[Pt_2(\mu\text{-BF})_2(PH_3)_4]^{(2+z)+}$	2.729	180	96.1	83.9		2.740	180^b	103.5	76.5	
		2.701	121^b	81.7	82.2	+13.2	2.714	148	100.9	75.3	−0.3
N.12	$[Pt_2(\mu\text{-CO})_2Cl_4]^{(2+z)-}$	2.705	180	94.9	85.1		2.671	179	101.4	78.6	
		2.667	125^b	82.4	83.7	+6.0	2.608	118^b	88.7	75.7	+4.5
N.13	$[Pt_2(\mu\text{-CNMe})_2Cl_4]^{(2+z)-}$	2.742	180	94.1	85.9		2.690	180	100.3	79.7	
		2.702	128^b	82.7	84.7	+6.5	2.645	121^b	88.9	77.0	+8.4
N.14	$[Pd_2(\mu\text{-CO})_2Cl_4]^{(2+z)-}$	2.744	180	95.3	84.7		2.761	180^b	103.0	77.0	
		2.690	126^b	84.2	82.9	+4.7	2.752	163	102.3	76.7	+0.0
							2.691	118^b	91.3	73.8	+2.5
N.15	$[Pd_2(\mu\text{-CNH})_2Cl_4]^{(2+z)-}$	2.794	180	94.1	85.9		2.769	171	101.6	78.1	
		2.731	127^b	83.3	83.9	+5.5	2.694	127^b	90.5	74.8	+2.9

[a] Distances in Å, angles in deg, energies in kcal.mol^{-1}. [b] θ kept frozen in the calculation. [c] For compounds with mixed bridges, the first β value corresponds to the H^-, the second one to the CO bridge. [d] Dissociates. [e] Angular parameters defined in **1** and **2**. E_b and E_p are the calculated energies of the bent and planar forms, respectively (kcal·mol^{-1}). e is the number of electrons in the frontier orbitals **4b**.

Table 5. Structural Data for Dinuclear Electron-Deficient Complexes of the Type $[M_2(\mu\text{-XY})_2L_4]$ with Six Electrons in the Frontier Orbitals **4b**

	compound	M···M/Å	α/deg	β/deg	θ/deg	ref	refcode
B.1	$[Pd_2(\mu\text{-CO})_2Cl_4]^{2-}$	2.685	95.4	84.6	180	31	BAHMOM
	$[Pd_2(\mu\text{-CO})_2Cl_4]^{2-}$	2.709	94.3	85.7	180		BAHMOM
B.2	$[Pd_2(\mu\text{-CO})_2(SO_3F)_2]$[a]	2.694	94.0	86.0	180	32	PINCIY
B.3	$[Pd_2(\mu\text{-CO})_2(AcO)_2]_2$	2.663	95.7	84.3	155	33,34	COPDAC10
B.4	$[Pd_2(\mu\text{-CNC}_6H_3Me_2)_2Cl_2(py)_2]$	2.661	97.2	82.8	130	35	DUSDEA
B.5	$[Pd_2(\mu\text{-CN}^tBu)_2(AcO)_2]_2$	2.655	96.5	83.5	137	24	PIBHOX
	$[Pd_2(\mu\text{-CN}^tBu)_2(AcO)_2]_2$	2.664	96.2	83.8	141		PIBHOX
B.6	$[Pd_2(\mu\text{-CNC}_6H_3Me_2)_2(AcO)_2]_2$	2.657	96.8	83.2	133	36	LAWTEI
	$[Pd_2(\mu\text{-CNC}_6H_3Me_2)_2(AcO)_2]_2$	2.667	96.1	83.9	140		LAWTEI
B.7	$[Pd_2(\mu\text{-CNC}_6H_2Me_3)_2(napy)_4]^{2+}$	2.745	90.1	89.9	180	37	TOHRIR
B.8	$[Pd_2(\mu\text{-CNC}_6H_2Me_3)_2(HBpz_3)_2]$[a]	2.757	89.9	90.1	180	38	HAYMUP
B.9	$[Rh_2(\mu\text{-CO})_2(PPh_3)_4]$	2.630	88.6	82.0	133	39	TPCDRH10
B.10	$[Rh_2(\mu\text{-CNC}_6H_4Cl)_2(P\{O^iPr\}_3)_4]$	2.641	89.5	81.1	132	40	FERXOP

[a] Weak interaction with an extra ligand in apical position at 2.666 (**B.2**) and 2.693 Å (**B.8**).

dence of the energy. The main qualitative idea that can be extracted from these calculations is that the decrease in the MXM bond angle that accompanies bending of the dinuclear complex has an energetic cost of around 1 kcal·mol^{-1} per degree (twice that amount if two bridges are considered).

In all electron-precise complexes, β decreases upon bending, and a destabilizing contribution of V_β to the total energy can be expected. Since the β angles associated with bent molecules is typically around 90°, one should expect V_β values in the range 5−20 kcal·mol^{-1}. Therefore, in a first approximation we would predict that most electron-precise complexes should be planar, except for Rh and Ir, which give stronger M···M bonding interactions. The experimental data (Figure 1a) confirm this prediction, since only Rh or Ir compounds seem to give bent structures, whereas Pd and Pt appear only in the planar conformation. We will see later, however, that the nature of the ligands may also affect the choice between a planar or bent structure.

For electron-deficient compounds, the experimental values of β decrease by only a few degrees upon bending, and similar calculated results are obtained for $[Pd_2(\mu\text{-CO})_2Cl_4]^{2-}$ (Table 4). We can thus estimate V_β values of around 3 kcal·mol^{-1}, and the $2V_\beta$ term in eq 1 is of the same order of magnitude as the I_{MM} contributions estimated in our previous work (Table 1). One should therefore expect subtle differences to determine the structural choice for electron-deficient compounds, with the steric factor I_{LY} playing a decisive role. A look at the distribution of experimental structures (Figure 1b) shows that this is the

Table 6. Structural Data for Electron-Deficient Dinuclear Complexes of the Type $[M_2(\mu\text{-H})(\mu\text{-XY})L_4]$ with Six Electrons in the Frontier Orbitals **4b**

	compound	M···M/Å	α/deg	β/deg[a]	θ/deg	ref	refcode
C.1	$[Ni_2(\mu\text{-H})(\mu\text{-CO})(tmeda)_2]^+$	2.441	77.8	119.9,84.5	179	41	ZARPUD
C.2	$[Pd_2(\mu\text{-H})(\mu\text{-CO})(bipy)_2]^+$	2.691	82.0	108.4,87.6	177	42	TILGUQ
C.3	$[Pd_2(\mu\text{-H})(\mu\text{-CO})(dippp)_2]^+$	2.767	71.3	128.5,86.2	159	43	KONSAH
C.4	$[Pt_2(\mu\text{-H})(\mu\text{-CO})(dppe)_2]^+$	2.716	76.5	122.4,84.6	180	44	CAJKAZ
C.5	$[Pt_2(\mu\text{-H})(\mu\text{-CO})(dppf)_2]^+$	2.790	81.0	107.8,87.3	163	45	KAFGED
C.6	$[Rh_2(\mu\text{-H})(\mu\text{-NO})(P^iPr_3)_4]$	2.746	80.4	106.8,92.4	179	46	PELGIW
C.7	$[Rh_2(\mu\text{-H})(\mu\text{-NCHMe})(dippe)_2]$	2.799	84.1	102.7,86.8	164	47	VUSYUD

[a] The first β value corresponds to the hydrido bridge, the second to the unsaturated bridge.

Table 7. Structural Data for Electron-Deficient Bis(hydrido) Complexes of General Formula $[M_2(\mu\text{-H})_2L_4]$, Where *e* Is the Number of Electrons in the Frontier Orbitals **4b**

	compound	*e*	M···M/Å	α/deg	β/deg	θ/deg	ref	refcode
D.1	$[Ni_2(\mu\text{-H})_2(dtbpe)_2]$	6	2.433	79.4	100.6	180	48	HOPNUV
D.2	$[Ni_2(\mu\text{-H})_2(dippp)_2]$	6	2.440	81.4	98.3	172	49	PUPWEC
D.3	$[Ni_2(\mu\text{-H})_2(dcpp)_2]$	6	2.441	78.8	101.1	176	50	HPCHPN
D.4	$[Pd_2(\mu\text{-H})_2(dippp)_2]$	6	2.824	85.3	94.7	179	51	WEWMIU
D.5	$[Pt_2(\mu\text{-H})_2(dfepe)_2]^a$	6	2.793	76.6	103.4	180	52	TODSOU01
D.6	$[Pt_2(\mu\text{-H})_2(SiEt_3)_2(PCy_3)_2]^a$	4	2.692	81.7	98.3	180	53	HYPSPT10
D.7	$[Pt_2(\mu\text{-H})_2(dcpp)_2]^{2+a}$	4	2.698	81.4	98.6	180	54	TEPFEZ
D.8	$[Pt_2(\mu\text{-H})_2(dtbpp)_2]^{2+a}$	4	2.728	80.0	100.0	180	54	TEPFID
D.9	$[Rh_2(\mu\text{-H})_2(P\{O^iPr\}_3)_4]$	4	2.647	85.8	94.2	180	55,56	IPXHRH01
D.10	$[Rh_2(\mu\text{-H})_2(dippe)_2]$	4	2.627	80.5	97.5	160	57	SAXYOF
	$[Rh_2(\mu\text{-H})_2(dippe)_2]$	4	2.629	83.2	96.8	180		SAXYOF

[a] Angle values estimated for a Pt−H distance of 1.78 Å.[58]

case, and bent or planar structures can be obtained for different metals.

The I_{LY} term in the presently studied compounds is similar to the steric repulsion term I_{LR} in complexes with saturated bridges. The latter has been found to be important only in bent structures of $[M_2(\mu\text{-XR})_2L_4]$ complexes (L = PH_3 or Me) with *endo* substituents.[1] Such repulsion appears to be small (less than ∼2 kcal·mol^{-1}) in these compounds when R = H and increases by about 3 kcal·mol^{-1} for R = Me. Notice that in the compounds studied here this ligand···substituent repulsion is important only in the coplanar structure **5**.

Discussion of Results for Electron-Precise Complexes

In electron-precise complexes there is no direct metal···metal bonding across the planar M_2X_2 ring. But as the molecule is bent around the X- -X hinge, the metal···metal distance decreases below the van der Waals radii sum,[1−3] and a weak attractive interaction may appear. This situation is similar to that found for the face-to-face dimers and chains of d^8-ML_4 square planar complexes, for which the M···M attraction can be explained through interactions involving occupied d_{z^2} and empty p_z orbitals.[10]

The calculated energy differences between the bent and planar geometries are presented in Table 2. For Pd and Pt complexes, which have little tendency to form metal−metal contacts (I_{MM} term in eq 1), the results indicate that the planar form is more stable than the bent one when the Y atom of the bridge is an unsubstituted element of the second period. When Y is larger (e.g., sulfur) or substituted (as in CCH_2 or NCH_2), the bent form is stabilized, presumably due to an increase in the bridge−terminal ligand repulsion term (I_{LY} in eq 1). If the substituent at the Y atom is linear, as for the azido bridge N_3^-, the steric hindrance is minimum and still planar forms are preferred. In summary, the stability of the bent form increases according to the following series of bridging ligands:

$$NO^- < N_3^- < NNR^- \approx NS^- < BF^{2-} < NSR \approx NCR_2^- \approx CNR_2^- < CCR_2^{2-} < BNR_2^{2-}$$

The most salient feature of this series is that, for a given bridging atom X, the stability of the bent form increases with decreasing electronegativity of the substituent Y. Conversely, for a given Y, the bent form is more stable as the electronegativity of X decreases.

The analysis of the calculated parameters for these compounds (Table 2) shows that upon bending the metal···metal distance decreases by about ∼0.2 Å and the X−M−X angle decreases by ∼4° for most compounds. Similar variations were previously obtained for an analogous complex with the methoxide bridging ligand, $[Pt_2(\mu\text{-OMe})_2(PH_3)_4]^{2+}$, for which the bent geometry was calculated to be more stable than the planar one. These changes are complemented with the decrease of β by 6−12°, depending on the degree of bending.

Interesting structural effects can be seen for some bridging ligands: for the azide anion, N_3^-, an asymmetry of the two N−N bonds clearly shows up in the optimized distances ($N^\beta-N^\gamma$ = 1.16 and $N^\alpha-N^\beta$ = 1.24 Å, to be compared with experimental values of 1.14 and 1.24, respectively[13]), indicating an important weight of the $N{\equiv}N^+{-}N^{2-}$ resonance form and consistent with the atomic charges calculated through a Mulliken population analysis. However, this ligand seems still to be acting as a four-electron donor, consistent with the Lewis structure shown in Scheme 1, since a long through-ring metal−metal distance is calculated, in contrast with the short distances predicted for compounds with X≡Y bridges discussed in the next section. Also the $^-N{=}SH^+$ zwitterionic form of the NSH ligand seems to have an important weight, since the N−S distance (1.58 Å) is shorter than that of a N−S single bond (see below). For the aminoboryl ligand (BNH_2^{2-}, isoelectronic with vinylidene) the long, calculated B−N distance (1.42 Å) is in agreement with that reported by Baerends et al. (1.40 Å).[29]

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For the electron-precise complexes of the second and third transition metal series (Table 3), the M···M distance is ca. 3.2 Å in the planar form. Upon bending, it decreases down to ~2.8 Å, a typical distance for weak metal···metal interactions, in good qualitative agreement with the computational results. Although nickel complexes present distances of about 2.8 Å already in the planar isomer, it cannot be attributed to a bonding M···M interaction but to the smaller atomic radius of Ni,[3] as indicated by acute X−M−X bond angles (~80°).[6]

Let us now compare the experimental molecular conformations with the theoretical expectations. Given the weak M···M attraction for M = Ni, Pd, and Pt, the most favorable conformation for their compounds is expected to be planar, as found for **A.3**−**10**. The calculations show that azido N_3^- (**M.2**) and diiminido HN═N⁻ (**M.3**) ligands prefer a planar or nearly planar conformation, as found in the experimental structures **A.8** and **A.9**. In the presence of an azavinylidene (NCR_2) bridging ligand, compounds **A.1**−**2** are bent, as predicted for the model Rh compounds **M.12** and **M.13**. The analogous Pt complex, **M.7**, also predicted to be bent, seems an interesting synthetic goal, since no bent Pt compounds with unsaturated bridges have been so far characterized.

All compounds with the disulfurdinitrido(2−) ligand $SNSN^{2-}$ or its selenium analogue present planar structures (**A.3**−**7**). These results must be attributed to the suppression of the I_{LY} repulsion term (eq 1, see **5**) when a bidentate ligand occupies both the Y and L positions. The short distances of less than 1.58 Å for the N−S and S−N bonds involving the bridging N atom in these complexes agree with a π-delocalized description of their bonding, in contrast with the greater values (1.66 Å) found in N−S bonds of terminal ligands (Allen et al.[14] reported experimental distances of 1.52−1.56 and 1.63−1.71 Å, respectively). These ligands can be modeled with either NS⁻ (**M.4**) or NSH (**M.6**). The NS⁻ ligand shows long N−S bond distances (1.61 Å) and little tendency toward bending. The N−S bond length is shorter in NSH (1.58 Å, close to the experimental value) and prefers a slightly bent geometry. We can conclude that the $SNSN^{2-}$ ligand is intermediate between the two model ligands with a small tendency toward bending, but the bulky phosphine PPh_3 and the chelate nature of the $SNSN^{2-}$ ligand favor the planar form.

Consider bridging ligands such as NO and BF. These ligands can be considered either as two- or four-electron donors, depending on the formal charge ascribed to them in the complex, as shown in Scheme 1. Therefore, in $[Pt_2(\mu\text{-}NO)_2(PH_3)_4]^{2+}$ (**M.1**) and $[Pt_2(\mu\text{-}BF)_2(PH_3)_4]$ (**M.5**), the long, calculated through-ring M−M distances are consistent with the bridging ligands being four-electron donors (i.e., NO⁻ and BF^{2-}), combined with formal oxidation states Pt(2+), thus resulting in a FEC of 8. This issue will be reconsidered in the next section, after the results for analogous compounds with less electrons are presented.

Discussion of Results for Electron-Deficient Complexes

As discussed in the introductory section, complexes of d^8 ions with two-electron donor bridges (e.g., CO, NO⁺, hydride, or other ligands displayed in the right column of Scheme 1)[5] should present a bonding interaction between two antipodal atoms even in the planar form. An interesting question that arises is whether bent structures are feasible for these compounds in which short M···M distances are already present in the planar form.

Compounds with Two X≡Y Bridges. The results of ab initio calculations for these compounds are presented in Table 4. Among the electron-deficient compounds, those having as bridging ligands cyanide, alkynyl, or isocyanide clearly prefer the bent form. In contrast, complexes with bridging ligands of type XO always have a planar geometry. Also the hydride ligand favors the planar structure, in excellent agreement with the experimental inexistence of bent hydrido-bridged structures (Figure 1c,d).

For the Pt complexes with strictly four framework electrons ($z = 2$ in Table 4), the following series summarizes the preferences for a bent structure:

$$H^- < BO^- < SiO \approx CN^- \leq CO \approx BF < CNR \approx {}^-CCR \approx NCR$$

For the analogous complexes with two more electrons (i.e., $z = 0$ in Table 4), the b_{2g} orbital (**4b**) is occupied, but since it has M−X nonbonding character, we still have FEC = 4. Even if the structural parameters are quite similar despite the two-electron difference, the preference for the bent structure is significantly modified:

$$BF < H^- \approx SiO < CO < NO^+ < BO^- < CNR < CN^- < NCR \approx {}^-CCR$$

Calculations on the prototypical carbonyl-bridged complexes $[M_2(\mu\text{-}CO)_2L_4]$ (**N.4**, Table 4) have been reported by several authors,[23,24] who confirmed the presence of a metal···metal bonding interaction, in agreement with the short distances found by us. The optimized distances and angles are consistent with the experimental data for related complexes (Supporting Information, Table S2). The results of our calculations for Pd and Pt complexes with PH_3 as terminal ligand and different bridging ligands (Table 4) tell that the bent structure is more stable with bridging ligands substituted at the Y atom, but the planar one is preferred for the diatomic bridges, similarly with what was found above for the electron-precise complexes. The fact that the bent form is preferred for electron-deficient compounds, which have bonding metal···metal interactions already in the planar form may be an additional indication that the I_{LY} term is important in determining the bending of the molecular plane. Compounds with chloride terminal ligands show a preference for the planar conformation, in agreement with our previous findings for the related family having unsubsituted bridges.[3]

The variations of the geometrical parameters upon bending are similar for the different bridging ligands under consideration: (i) the X−M−X bond angles α decrease some 15°; (ii) metal···metal distances decrease by less than 0.1 Å, (iii) the nonbonded X···X distance decreases by about ~0.3 Å, and (iv)

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only a slight decrease is observed for β (of about 2°). A special case is that of the aminoboryl and fluoroboryl ligands, for which the calculations predict long M···M distances in both forms, planar and bent. Hence, although the destabilizing V_β contribution is only a few kcal·mol^{-1}, the strong distortion of the X$-$M$-$X bond angles required by bending (not considered in eq 1) probably represents an important contribution to the instability of the bent structure.

The calculated bond distances in the bridging ligands are consistent with experimental information. In those cases for which no experimental data are available for comparison, the bond distances agree well with the standard values reported by Orpen et al.[25] In an example with a SiO bridging ligand,[26,27] the calculated Si$-$O distance (1.54 Å) is typical of a double bond, comparable to that in the related experimental structure[28] (1.51 Å). Several boryl ligands have been proposed recently as alternatives to carbonyl chemistry,[27,29,30] among which BO$^-$ can be considered a two-electron donor. The calculated B$-$O distance in the oxoboryl-bridged complex **N.6** (1.23 Å) is clearly indicative of multiple bonding (cf. experimental values of 1.22$-$1.24 Å[29]). For the case of the fluoroboryl bridge, we have already commented above that it can be considered either as the two-electron donor B$\equiv$F or as a four-electron donor B$=$F^{2-} by readjusting the electron count of the metal atoms. The B$-$F calculated distances nicely show this dichotomy: in compounds **N.11**, $[Pt_2(\mu\text{-}BF)_2(PH_3)_4]^{2+}$ and $[Pt_2(\mu\text{-}BF)_2(PH_3)_4]^{4+}$, the bridges act as two-electron B$\equiv$F donors toward Pt(II) atoms and present short B$-$F distances (1.247 and 1.299 Å, respectively), whereas in **M.5**, $[Pt_2(\mu\text{-}BF)_2(PH_3)_4]$, the bridges act as four-electron donors (i.e., formally B$=$F^{2-}) toward Pt(II) atoms and show a longer B$-$F distance (1.37 Å). These distances compare well with those reported for free BF[28] (1.263 Å) and when acting as terminal ligand in models of mononuclear[27,29,30] complexes (1.25$-$1.29 Å). Similarly, the calculated N$-$O bond distances for **M.1** (1.22 Å) and **N.5** (1.17 Å) are in good agreement with a description of the bridging ligand as NO$^-$ and NO$^+$, respectively (see Scheme 1).

If we compare now the planar or bent conformation of the experimental structures with the results of our calculations, the following observations can be made. Palladium complexes (**B.1**$-$**3**) have planar structures, as predicted for the $[Pd_2(\mu\text{-}CO)_2Cl_4]^{2-}$ model (**N.14**); only the acetato complex **B.3** is somewhat bent, probably forced by its polynuclear nature. Complexes with isonitriles as bridging ligands (**B.4**$-$**6**) prefer bent structures, in agreement with our calculations (**N.7**). Only two compounds are planar, probably due to steric requirements in **B.7** and to a weak apical interaction of the chelate ligand in **B.8**. We note that isonitrile-bridged Pd complexes are more strongly bent (133$-$141° in **B.5**$-$**6**) than carbonyl-bridged ones (155° in **B.3**), probably due to the importance of the I_{LY} term (eq 1) in the former case and to the stronger preference of isonitrile bridges for a bent structure compared to carbonyl bridges (see Table 4). Two Rh compounds found in the bibliography (**B.9** and **B.10**) are bent, as predicted for the isoelectronic Pd and Pt compounds.

Complexes with One or Two Hydrido Bridges. The model electron-deficient complex with one hydrido bridge (**N.2**) and FEC $= 6$ is predicted to be planar (Table 4). The increase in energy associated with bending is probably due to the large changes required in the XMX and MXM (β) angles. Experimentally, all related structures are nearly planar ($\theta \geq 159°$, Table 6). Deviations from planarity in these complexes appear only in the presence of bulky substituents at the terminal ligands (**C.3** and **C.5**) and can be attributed to steric repulsions (I_{LY} in eq 1, **5**). Similar results are found for bis(hydrido)-bridged complexes with two additional electrons in the b_{2g} orbital ($z = 0$ in Table 4), both theoretically (**N.1**) and experimentally (**D.1**$-$**5**, Table 7). We can see that the geometries are very similar regardless of whether such an orbital is occupied ($z = 0$) or empty ($z = 2$, **D.6**$-$**10** in Table 7), with sizable variations of the angle β (up to 5°) upon bending.

Comparison of calculated and experimental structural data for electron-precise and electron-deficient complexes shows that the metal···metal distances for group 10 metals are shorter in the latter case, consistent with the existence of a through-ring attractive interaction (Figure 2). Notice that this interaction appears in both the planar and bent forms of all electron-deficient complexes and involves similar distances regardless of the degree of bending (i.e., 2.69$-$2.80 Å for Pd, Pt, and Rh complexes, Tables 5$-$7). This distance does not change with the bridging ligand and depends only on the metal (i.e., 2.43$-$2.44 Å for Ni compounds).

Additional data that supports the poor tendency of the bis(hydride) complexes to bend come from the effect of Lewis acids. The planar $[Pd_2(\mu\text{-}H)_2(dippp)_2]$ complex (**D.4**, $\theta = 179°$) preserves its planarity upon addition of alkaline salts in thf ($\theta = 172°$ and 166° for $LiBF_4$ and $NaBF_4$, respectively).[51,59] In contrast, the addition of $LiBF_4$ to $[Pt_2(\mu\text{-}X)_2(PPh_3)_4]$ results in

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a bent geometry ($123° < \theta < 139°$ for X = O, S),[60−65] in agreement with our theoretical studies[3] that predict the bent structure to be more stable by 4−5 kcal·mol^{-1}.

Dynamic Behavior

There is spectroscopic evidence[11,12] for the coexistence in solution of different conformers of the dinuclear compounds under study. This is consistent with the relatively small energy differences between the planar and bent forms found in our calculations. However, for such intramolecular reactions to occur thermally, a low activation energy is needed. Since the compounds with rhodium and iridium are more stable in the bent form and the planar form is within thermal energy of the former, one can anticipate that such compounds should present dynamic behavior in solution through a bent → planar → bent pathway, and the energy barrier for this process can be estimated from the energies of the planar and bent forms:

$$E_a \approx E_p - E_b \tag{2}$$

Such values (Table 2) are rather small ($E_a \leq 4$ kcal·mol^{-1}). Consistently, variable ^{1}H NMR spectra of $[M_2(\mu\text{-NCR}_2)_2\text{-(diolefin)}_2]$ (M = Ir, Rh, **A.1**) in the olefinic region are consistent with a M_2N_2 ring inversion, although the activation energy has not been reported.[11] In contrast, complexes of metals with less tendency to form M···M contacts, such as $[Pd_2(\mu\text{-CO})_2(SO_3F)_2]$, do not show a planar-bent isomerization, but rather a dynamic behavior corresponding to the exchange of bridging and terminal carbonyls.[32]

An interesting related phenomenon is the ring inversion reported for $[Pt_2(\mu,\eta^2\text{-CCR})_2L_4]$ based on NMR spectra.[12] Forniés et al. proposed that such isomerization proceeds via formation of a $[Pt_2(\mu,\eta^1\text{-CCR})_2L_4]$ intermediate. A crude estimate for the activation energy of such a process deduced from our calculations gives 6.6 kcal·mol^{-1}, in fair agreement with the experimental energy barrier of about 10 kcal·mol^{-1} obtained from the NMR spectra for a PtRh dimer.[66]

Conclusions

The combined use of theoretical studies and a structural database analysis has allowed us to establish the general trends for the structural choice between the planar and bent conformers in dinuclear compounds of square planar transition metals with bridges of the type $[M_2(\mu,\eta^1\text{-XY})_{2-m}(\mu\text{-H})_mL_4]$ ($m = 0-2$), where XY is an unsaturated ligand.

A systematic ab initio study was carried out for the planar and bent forms of complexes in which the bridging ligand, the terminal ligands, and the metal atoms were varied. Comparison of the relative energies of the different conformers allows one to estimate different contributions. In general, the predicted conformation for a particular molecule is in good qualitative agreement with its experimentally determined structure. Simplifications introduced in the theoretical model, especially replacement of a bulky phosphine by PH_3, may alter the relative stabilities of the different conformers within a few kcal·mol^{-1}.

In electron-precise compounds, due to a geometrically imposed decrease in MXM bond angles upon bending, only complexes with strong M···M contacts (Rh or Ir) are expected to present a bent structure. For electron-deficient complexes, the planar form is favored for the most electronegative bridging ligands, although the choice of metal, terminal ligands, or substituents at the bridges can alter such preference. Thus, compounds with cyanide, alkynyl, or isocyanide bridging ligands prefer the bent form, whereas XO-bridged complexes always have a planar geometry. In complexes with PH_3 terminal ligands, the bent structure is more stable with bridging ligands substituted at the Y atom, but the planar one is preferred for the diatomic bridges. Mono- and bis-hydrido-bridged complexes are predicted to be planar, in good agreement with available experimental structures. Complexes with four electrons in the frontier orbitals present a lesser tendency than those with six electrons toward bent geometries.

The main structural effects of bending in electron-deficient complexes with two-electron-donor bridges such as CO are (i) the X−M−X bond angle decreases some 15°; (ii) metal···metal distances do not significantly change, (iii) the X···X distance decreases, and (iv) only a slight decrease is observed for the M−X−M angle.

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Appendix

Computational Details. All ab initio calculations were performed with the GAUSSIAN94 suite of programs.[67] A molecular orbital ab initio method with introduction of correlation energy through the second-order Møller−Plesset (MP2) perturbation approach was applied,[68] excluding excitations concerning the lowest energy electrons (frozen core approach). A basis set with double-ζ quality for the valence orbitals was used for all atoms, supplemented by polarization functions with effective core potentials for the innermost electrons, except for the H atoms of the PH_3 groups, for which a minimal basis set was used.[69]

More details on the basis set can be found in a previous paper.[1] For compounds with bridging hydrides, $[M_2(\mu\text{-H})_2(PH_3)_4]$ and $[M_2(\mu\text{-H})(\mu\text{-CO})(PH_3)_4]$, a 6-31G** basis set was used for the bridging atoms.

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The internal structures of the phosphine ligands were 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, and symmetry restrictions were introduced in the optimizations when possible. 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°.

Structural Database Search. The collection of structural data was obtained through a systematic search of the Cambridge Structural Database[9] (version 5.20) for compounds of general formula $[M_2(\mu\text{-}XY)_{2-m}(\mu\text{-}H)_mL_4]$ ($m = 0, 1, 2$), in which M was imposed to be a metal having square-planar coordination (Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Ru, or Os) and X was allowed to be any element of groups 13−17. The bending angle θ was calculated as that between the two MX_2 planes. For the hydrido ligands not localized in the crystal structure determination, the angles have been estimated from standard M−H distances reported by Teller and Bau[58] in the idealized molecule for the local symmetry.

Abbreviations. bipy = 2,2′-bipyridine; cod =1,5-cyclooctadiene; dcpp = 1,3-bis(dicyclohexylphosphino)propane; dfepe = 1,3-bis(bis(perfluoroethyl)phosphino)ethane; dippe = 1,2-bis(diisopropylphosphino)ethane; dippp = 1,3-bis(diisopropylphosphino)propane; dppe = 1,2-bis(diphenylphosphino)ethane; dppf = 1,1′-bis(diphenylphosphino)-ferrocene; dtbpe = 1,2-bis(ditertbutylphosphino)ethane; dtbpp = 1,3-bis(ditertbutylphosphino)propane; napy = 1,8-naphthyridine; py = pyridine; pz = pyrazole; tfbb = tetrafluorobenzobarrelene; tmeda = *N*,*N*,*N*′,*N*′-tetra(methyl)ethylenediamine

Supporting Information Available: Tables comparing the main bonding parameters in calculated and analogous experimental structures are deposited (Tables S1 and S2). This material is available free of charge via the Internet at http://pubs.acs.org. The atomic coordinates of the 43 optimized structures, identified with the label employed for compounds in Tables 2 and 4, are also deposited and can be accessed at the following Internet address: http://kripto.qi.ub.es/~gee/suppl/xy.html.

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