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Article

Chalcogen–Chalcogen Bonds in Edge-Sharing Square-Planar d^8 Complexes. Are They Possible?

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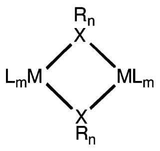
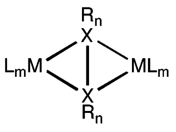
A theoretical study of the formation of X–X bonds in complexes with the general formula $[M_2(\mu\text{-}X)_2L_4]$ (M = group 10 and X = group 16 elements) having d^8 transition-metal atoms is presented. The existence of two energy minima for some complexes, with short and long X–X distances, is shown by density functional theory calculations, and the factors responsible for it are analyzed, including a strong influence of the nature of the metals and ligands on the relative stability of the two isomers. The influence of the bite angle of chelating terminal ligands and the nature of the donor atom on the relative stabilities of the two isomers are also discussed.

Introduction

The M_2X_2 core in doubly bridged dinuclear complexes $[L_mM(\mu\text{-}XR_n)_2ML_m]$ can adopt three different structures: (a) with no bonding between opposite atoms as in **1a**, (b) with X−X bonding interaction as in **1b**, and (c) with M−M interaction as in **1c**. The existence of bonding between antipodal atoms in binuclear complexes obeys qualitative rules based on the occupation of framework molecular orbitals (FEC).[1−5] The absence of through-ring interaction is found for eight framework electrons, corresponding to four M−X framework bonds (**1a**), whereas the presence of X−X (**1b**) or M−M (**1c**) bonding is anticipated for less than eight framework electrons. In general, the changes in the number of electrons for the M_2X_2 rings, with the concomitant changes in ring bonding, can be produced in several ways: (a) electrochemically, by varying the number of electrons, giving oxidized or reduced species without any additional change in the coordination sphere of the metals;[6] (b) stereochemically, by varying the orientation of ligands in the coordination sphere of the metal,[3,7] e.g., by rotating the two terminal ligands from square-planar to tetrahedral geometry;[2] (c) by varying the coordination number through association or dissociation of terminal ligands,[4,7] e.g., moving from square-planar to square-pyramidal or octahedral coordination by adding one or two axial ligands.



1a



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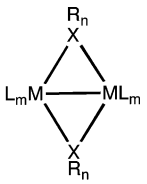

1c

In all three cases the isomerization of the M_2X_2 core is related to a chemical modification made on the system. Surprising results have been found for platinum−silicon four-membered rings in $[L_2M(\mu\text{-}XR_n)_2ML_2]$ complexes with square-planar coordination geometries around the metal

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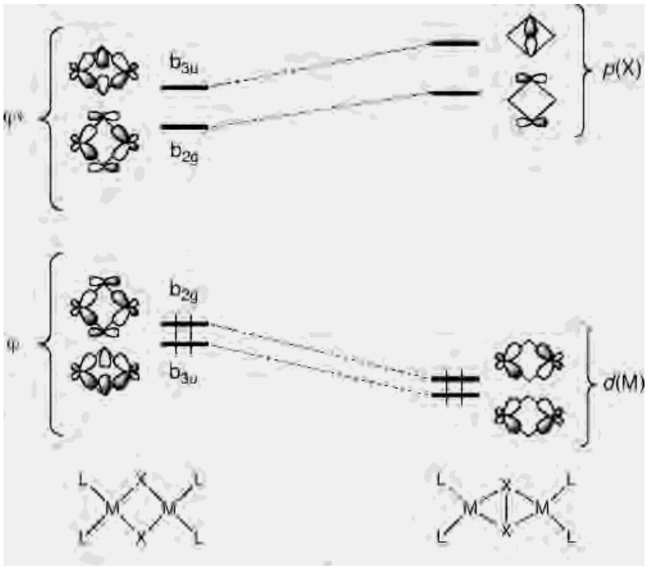
atoms and silylene bridges. These compounds prefer short Si···Si distances (about ∼2.6 Å) in apparent contradiction with the general rules that predict a *normal* diamond with no bonding interaction across the ring for an eight-electron skeleton. This apparent violation of the framework electron rules has been attributed to an electron localization effect caused by the low electronegativity of the bridging ligands, schematically shown in **2**.[2,3,5] The σ-bonding in regular diamonds **1a** is described with four framework bonding orbitals, labeled φ. The localization of two of these occupied orbitals, b_{2g} and b_{3u} in the D_{2h} group (**2**, left), is strongly sensitive to electronegativity differences between metal and bridge fragments, and for small differences both are essentially metal d orbitals, whereas the combinations centered at bridging atoms having X···X antibonding character are empty (**2**, right). As a result, each metal center retains a pair of electrons in the d orbitals (formally d^8 ions become d^{10} ions) and only four electrons are left for the ring framework bonding, with the formation of Si−Si interaction as a η^2-silene-bridged compound in **3**.



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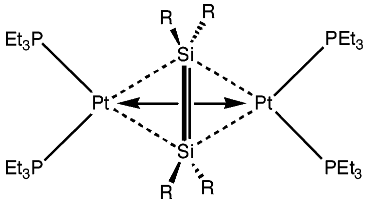


3

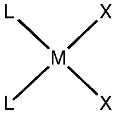
Such a localization of electrons in one of the two atom sets appears also in some bioinorganic systems such as the active site of hemocyanin or the oxygen evolving complex of photosystem II, in which a dioxygen molecule is activated (**1b** → **1c**)[7] or generated (**1c** → **1b**),[8] respectively. A ruthenium(III) compound, $[Ru_2(\mu\text{-}Cl)_2Cl_2(Cp^*)_2]$,[9] has been reported in which two ring isomers (**1a** and **1c**) coexist due to the different localization of electrons in the d orbitals. For group 10 metals a limited number of structures with short X−X distances have been reported, which can be rationalized by the qualitative rules stated above. In $[Pt_2(\mu\text{-}Te)_2(PEt_3)_4]^{2+}$ (Te−Te = 2.70 Å)[10] and $[Pd_2(\mu\text{-}As)_2(PPh_3)_4]$ (As−As = 2.27 Å),[11] the framework electron count is only six and short distances are expected. In $[Ni_2(\mu\text{-}X)_2(\{Ph_2PCH_2\}_3CMe)_2]$, with X = S (S−S = 2.21 Å)[12] and Te (Te−Te = 2.80 Å),[13] a tridentate terminal ligand is present, and thus, the geometry cannot be described as square-planar. However, with the exception of these cases and the Si−Si complexes already cited, all the doubly bridged square-planar d^8 bimetallic complexes characterized correspond to **1a** compounds, and neither structures with X−X bonds nor coexistence of the two isomers has been reported.

Chalcogenides have a strong propensity to act as bridging ligands, and a number of bimetallic group 10 complexes with bridging chalcogen atoms have been characterized.[14] The possibility of bridging dichalcogenide ligands is an open question. The presence of significant X···X interactions in the four-membered Ni_2X_2 rings of $[Ni_2(\mu\text{-}X)_2(\eta^5\text{-}Cp)_2]$ complexes (X = S, Se, Te) has been demonstrated recently.[15]

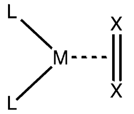
In this work we apply density functional theory (DFT) to study the bonding in $[M_2(\mu\text{-}X)_2L_4]$ compounds. The goal of this work is to theoretically investigate the possible existence of isomers with X_2 ligands in $[M_2(\mu\text{-}X)_2L_4]$ complexes where M and X are elements of groups 10 and 16, respectively, for which preliminary data suggest an interesting source of chemical reactivity.[3] We present a systematic DFT study to analyze the influence of the metal, the bridging atoms, and the nature of the terminal ligands on the stability of X−X bonded structures. For comparative purposes monomeric compounds $[(R_3P)_2M(X_2)]$ have also been considered.

Results and Discussion

Monomeric Compounds. We first study some complexes with general formula $[L_2MX_2]$ (M and X are elements of groups 10 and 16, respectively), for which two alternative molecular structures have been considered (**4**). Despite the absence of X−X bonds in dinuclear complexes, several examples of molecular structure **4b** in mononuclear $[L_2M(\eta^2\text{-}X_2)]$ complexes have been reported.[16,17] In contrast,



4a



4b

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Table 1. Theoretically Optimized[a] Structures of $[(PH_3)_2MX_2]$ Complexes (M = Ni, Pd, and Pt; X = O, S, Se, and Te)[b]

compound	isomer	X···X	M−X	M−P	P−M−P	E_{rel}
$[(H_3P)_2NiO_2]$	**4b**	1.391	1.815	2.233	105.9	
	4a	2.854	1.664	2.312	91.0[c]	+60.6
$[(H_3P)_2PdO_2]$	**4b**	1.355	2.042	2.365	102.7	
	4a	3.137	1.827	2.439	97.3	+65.4
$[(H_3P)_2PtO_2]$	**4b**	1.403	2.025	2.301	98.8	
	4a	3.059	1.825	2.426	91.1	+45.4
$[(H_3P)_2NiS_2]$	**4b**	2.088	2.221	2.221	106.7	
	4a	3.524	2.115	2.304	90.8	+75.0
$[(H_3P)_2PdS_2]$	**4b**	2.075	2.397	2.363	105.3	
	4a	3.709	2.245	2.460	89.9	+72.0
$[(H_3P)_2PtS_2]$	**4b**	2.109	2.404	2.306	102.5	
	4a	3.694	2.247	2.429	87.2	+60.9
$[(H_3P)_2NiSe_2]$	**4b**	2.353	2.348	2.219	105.4	
	4a	3.718	2.254	2.306	89.3	+70.9
$[(H_3P)_2PdSe_2]$	**4b**	2.345	2.516	2.362	105.4	
	4a	3.901	2.381	2.455	89.3	+67.6
$[(H_3P)_2PtSe_2]$	**4b**	2.376	2.521	2.306	102.7	
	4a	3.895	2.382	2.418	87.0	+59.1
$[(H_3P)_2NiTe_2]$	**4b**	2.712	2.541	2.221	103.6	
	4a	4.000	2.463	2.310	87.6	+67.5
$[(H_3P)_2PdTe_2]$	**4b**	2.711	2.694	2.365	105.0	
	4a	4.175	2.581	2.458	88.1	+63.9
$[(H_3P)_2PtTe_2]$	**4b**	2.741	2.697	2.311	102.8	
	4a	4.179	2.585	2.411	86.3	+58.1

[a] Distances in angstroms, angles in degrees, energies in kilocalories per mole. [b] The first line of each entry corresponds to the $M(\eta^2\text{-}X_2)$ isomer **4b**, the second one to the $M(\eta^1\text{-}X)_2$ structure **4a** (not a minimum (C_{2v} symmetry enforced)). [c] Calculated with the P−Ni−P angle frozen during optimization.

no compound with structure **4a** seems to have been characterized in the solid state, although this structure has been proposed to appear in catalytic processes that imply the activation of a dioxygen molecule by zerovalent group 10 metals, especially palladium.[17,18] The **4a** → **4b** interconversion has been analyzed by means of qualitative molecular orbital arguments for the related case of an ethylene ligand splitting into two methylene ligands.[19]

The main parameters for the calculated geometries of complexes $[(H_3P)_2M(X_2)]$ are shown in Table 1. In all the studied cases the $M(\eta^2\text{-}X_2)$ isomer is much more stable than the $M(\eta^1\text{-}X)_2$ isomer. The energy difference between **4b** and **4a** structures decreases on descending down either the metal or the chalcogen groups, with the exception of oxygen, i.e., Ni > Pd > Pt and S > Se > Te ≫ O. The only exception is the $Pd(\eta^1\text{-}O)_2$ complex, in which the P−Pd−P angle is also out of range. From the large energy differences obtained it appears that the only mononuclear species that could be synthesized are those of type **4b** (see below).

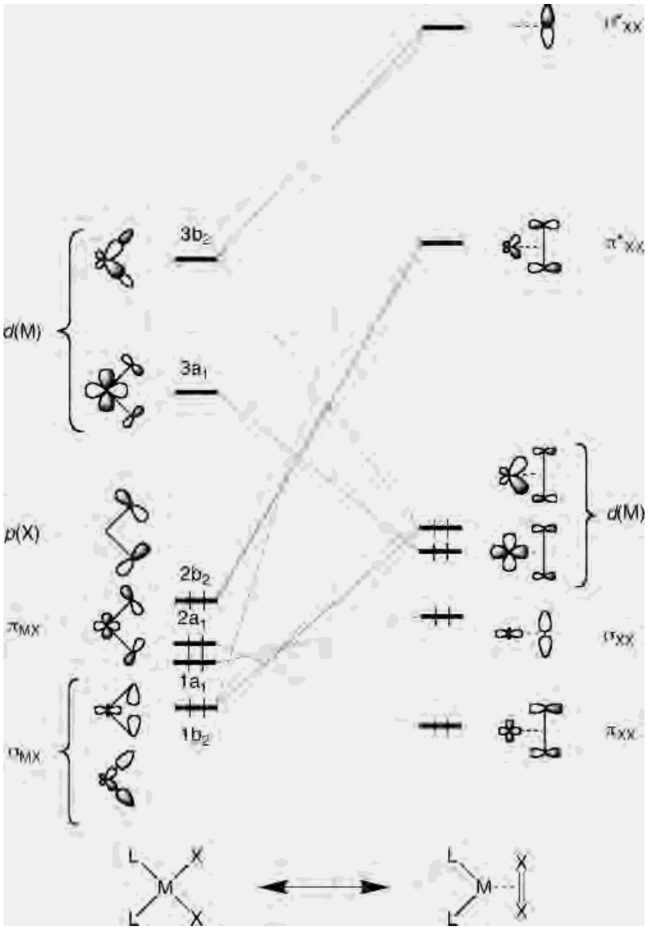

Figure 1. Simplified diagram of the framework orbitals of $[L_2M(X)_2]$ (left) and $[L_2M(\eta^2\text{-}X_2)]$ (right) for isomers **4a** and **4b** of $[(H_3P)_2PdS_2]$, classified in the C_{2v} group. The back-bonding interaction is not shown for simplicity.

The bonding in complexes $[L_2M(\eta^2\text{-}X_2)]$ having structure **4b** can be described by the Dewar−Chatt−Duncason model[20] in much the same way as for the olefin−d^{10}-ML_2 complexes, in agreement with their diamagnetic behavior.[16,21] The metal adopts a trigonal-planar geometry in which two positions are occupied by phosphines and the third position is occupied by an unsaturated η^2-X_2 ligand oriented coplanar to the P−M−P plane to maximize the π interaction. In these systems the existence of a X═X double bond is consistent with our qualitative analysis, since σ and π orbitals centered at the X atoms are occupied, both of a_1 symmetry, whereas the corresponding antibonding combinations of b_2 symmetry are empty (see Figure 1, right).[19] Also, a d^{10} electronic configuration must be assigned to the transition metal because the five d orbitals are formally occupied. The analysis of the Kohn−Sham orbitals and their populations confirms this bonding description in which X_2 acts as a two-electron donor to an sp^2 orbital of the d^{10}-ML_2 fragment, complemented by a back-bonding interaction from the metallic fragment to the $\pi_\perp$ orbital of the diatomic molecule (not shown in Figure 1 for simplicity). The occupations of the d(M) and p(X) orbitals, calculated by a natural population analysis (about 9.0 and 4.5, respectively), are consistent with formal charges M^+ and X_2^-. Also, the frequency analysis of $\nu_{st}(XX)$ shows an intermediate value between those of X_2 and X_2^{2-} (i.e., 1114, 549, 314, and 219 cm^{-1} for X = O, S, Se, and Te, respectively, in $[(H_3P)_2Pd(\eta^2\text{-}X_2)]$).[22]

The electronic structure of the alternative form having an $M(\eta^1\text{-}X)_2$ unit (**4a**) can be considered as a result of an oxidative addition, because two d orbitals are now empty

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Table 2. Main Structural Parameters[a] for Experimental Structures of $[(PR_3)_2MX_2]$ Type and Related Compounds (M = Group 10 Metal, X = Group 16 Element)

compound	X···X	M−X	M−L	L−M−L	ref	refcode
$[(^t\mathrm{BuNC})_2\mathrm{Ni}(\mathrm{O}_2)]$	1.448	1.809	1.840[c]	91.8	33	OBICNI
$[(^t\mathrm{Bu}_2\mathrm{PhP})_2\mathrm{Pd}(\mathrm{O}_2)]$	1.372	2.054	2.359	115.4	21	PDOXBP
$[(^t\mathrm{Bu}_2\mathrm{PhP})_2\mathrm{Pt}(\mathrm{O}_2)]$	1.432	2.019	2.290	113.1	21	PTOXBP
$[(\mathrm{Ph}_3\mathrm{P})_2\mathrm{Pt}(\mathrm{O}_2)]$	1.505	2.006	2.233	101.2	34	TPPOTP
$[(\mathrm{Ph}_3\mathrm{P})_2\mathrm{Pt}(\mathrm{O}_2)]$[b]	1.45	2.01	2.27	101.2	35	DOTPHP
$[(\mathrm{Ph}_3\mathrm{P})_2\mathrm{Pt}(\mathrm{O}_2)]$[b]	1.26	1.95	2.25	100	36	TPPOPT
$[(\mathrm{S}_2\mathrm{WS}_2)\mathrm{Ni}(\mathrm{S}_2)]^{2-}$	2.038	2.186	2.189[c]	106.8	37	TIZHOZ
$[(\mathrm{Me}_2\{\mathrm{R}_3\mathrm{C}_6\mathrm{H}_2\}\mathrm{P})_2\mathrm{Pt}(\mathrm{S}_2)]$	2.077	2.343	2.268	106.9	38	XIGDAS
$[(\mathrm{Se}_2\mathrm{WSe}_2)\mathrm{Ni}(\mathrm{Se}_2)]^{2-}$	2.328	2.299	2.289[c]	111.0	39	JAGBOI
$[(\mathrm{Me}_2\{\mathrm{R}_3\mathrm{C}_6\mathrm{H}_2\}\mathrm{P})_2\mathrm{Pt}(\mathrm{Se}_2)]$	2.336	2.457	2.266	107.8	38	XIGDEW
$[(\mathrm{MeC}\{\mathrm{CH}_2\mathrm{PPh}_2\}_3)\mathrm{Ni}(\mathrm{Te}_2)]$	2.665	2.570	2.226(71)[d]	94.4(20)[d]	40	FONMUQ
$[(\mathrm{PhP}\{\mathrm{C}_2\mathrm{H}_4\mathrm{PPh}_2\}_2)\mathrm{Ni}(\mathrm{Te}_2)]$	2.669	2.556	2.189(48)[d]	101.0(99)[d]	40	FONMOK

[a] Distances in angstroms, angles in degrees. [b] Poor structure resolution having an *R* factor greater than 8% (DOTPHP, 10.3%; TPPOPT, 12.0%). [c] Nonphosphine ligands. [d] The terminal ligand acts as a tridentate ligand, and the mean and standard deviation are shown for the three donor atoms.

due to the electron transfer that has taken place to form two X^{2-} ligands (Figure 1, left). The result is a d^6 ion with a square-planar coordination. Several d^6 complexes can be found in the literature with this geometry: $[\mathrm{FeCl}_2(\mathrm{OCHNH}_2)_2]$,[23] $[\mathrm{RuCl}_2(\mathrm{CNAr})_2]$,[24] [Fe(Pc)] (where Pc is a phthalocyanato[25] or porphyrinato[26] dianion). In addition to the two σ(MX) bonds, there is an occupied $2a_1$ orbital of M−X π-bonding character, resulting in a value of 1.5 for the M−X bond order. The existence of coplanar π bonds has also been described previously for oxo anions with trigonal-planar geometry around a metal, such as $[\mathrm{Fe}_2\mathrm{O}_5]^{6-}$ and $[\mathrm{Co}_2\mathrm{O}_4]^{4-}$ having d^6 and d^7 configurations, respectively.[27] In principle, the crossing between $3a_1$ and $2b_2$ orbitals (Figure 1) should be responsible for the existence of two minima corresponding to isomers **4a** and **4b**. However, structure **4a** is not a minimum in the potential energy surface since an imaginary frequency has been found in the vibrational analysis that corresponds to a twist of the MX_2 fragment toward a tetrahedral coordination of the metal. We suspect that such a structure can be stabilized by coordinating solvent molecules in axial positions, forming a $[MX_2(PH_3)_2(\mathrm{solvent})_2]$ species. Alternative stabilization of **4a** can be obtained by adding two electrons to the $3a_1$ orbital, the metal then formally becoming a d^8 ion.

In agreement with the bonding description above, the isomers having $M(\eta^2\text{-}X_2)$ core **4b** present strong X−X bonds, with X−X distances shorter than twice the atomic radius (Table 1). The X−X distances follow the order Pd < Ni < Pt, and the P−M−P angles range from 99° to 107°. Notice that in η^2-O_2 complexes the O−O distance is shorter than that of typical single bonds, suggesting that some double bond character is retained, whereas the X−X bonds in η^2-S_2, η^2-Se_2, and η^2-Te_2 are close to or slightly longer than a standard single bond.[28] The calculated Wiberg bond indexes for these X−X bonds are in the range 1.19−1.38. The weak bonding of dioxygen to the palladium fragment agrees with experimental[21] and theoretical[29] reports. The M−X Wiberg bond indexes (∼0.52, ∼0.43, and ∼0.47 from Ni, Pd, and Pt, respectively) are consistent with weak M−X bonds, and also the known reversibility of the dissociation process.[21] Only the complexes $[(H_3P)_2M(\eta^2\text{-}O_2)]$ with M = Pt, Pd,[29,30] and Ni[29] had been previously studied by theoretical calculations at the DFT level, with results in agreement with the present calculations, especially for the variations within the periodic group. Similar results had been obtained by Fantucci et al. at the HF level for M = Pt.[31]

Longer nonbonding X···X distances are obtained for isomers **4a**, with a shortening of 0.1−0.2 Å of the M−X bond and a lengthening of M−P distances by about ∼0.1 Å. A distorted square-planar geometry can be defined for the complex, in which large X−M−X angles (108−118°) arise from the repulsion between chalcogenide ligands, whereas L−M−L angles are near 90° (86−91°). The Pd-$(\eta^1\text{-}O)_2$ complex constitutes the only exception, with a value of the P−Pd−P angle of 97°. The influence of P−M−P angles on the X−X bonds of $M(\eta^2\text{-}O_2)$ complexes has been previously discussed as a key factor that controls the electronic transfer from the metal to the X_2 ligand.[21]

Some structural data on mononuclear $L_2M(X_2)$ compounds (M = group 10 metal, X = group 16 atom) can be found in the literature. Through a search of the Cambridge Structural Database, the complexes collected in Table 2 were retrieved. Only the structures of isomers of the **4b** type, with X−X

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(22) The X−X stretching frequencies corresponding to a single bond have been calculated at 654, 361, 200, and 137 cm^{-1} in X_2^{2-} for X = O, S, Se, and Te, respectively (X−X distances of 1.63, 2.30, 2.59, and 2.96 Å). For double bonds, the corresponding frequencies calculated in X_2 molecules in the triplet state (singlet state in parentheses) are 1657 (1642), 697 (692), 375 (372), and 247 (245) cm^{-1}, respectively (distances of 1.21, 1.94, 2.22, and 2.59 Å).

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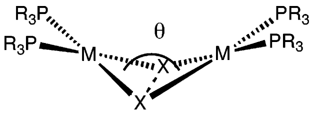
bonds, have been reported. The theoretical trend found for the X−X distances (Pd < Pt) is also found in three $[(R_3P)_2M(\eta^2\text{-}O_2)]$ compounds (M = Pt or Pd). A correlation between the P−Pt−P angle and the X−X bond length can also be appreciated. In general, these compounds have been obtained with bulky phosphines such as PPh_3 or P^tBu_2Ph, with large P−Pt−P angles. The O−O bonds are equal or shorter than in the peroxide anion.[32] For M = Ni, only a compound with isonitriles as terminal ligands has been reported.

Less data were found for other group 16 elements. Recently, disulfur and diselenium bis(phosphine)platinum compounds with short X−X distances have been reported.[38] The presence of bulky phosphines as terminal ligands conceivably increases the P−Pt−P angle and stabilizes the $Pt(\eta^2\text{-}X_2)$ isomer. Similarly, disulfur and diselenium nickel complexes of general formula $[X_2W(\mu\text{-}X)_2Ni(\eta^2\text{-}X_2)]^{2-}$ have been characterized, in which the two terminal ligands are substituted by a WX_4^{2-} complex. The angle imposed by the tetrahedral anion in $W(\mu\text{-}X)_2Ni$ rings favors a $Ni(\eta^2\text{-}X_2)$ bonding mode. Among ditellurium compounds, only nickel complexes having Te−Te distances shorter than the calculated distances have been structurally characterized, but the presence of a tridentante phosphine as terminal ligand in such a complex increases the coordination number of the metal atoms and may influence the Te⋯Te distance.

Dinuclear Compounds. The precedent study has revealed that the η^2-X_2 bonding mode is favored in mononuclear complexes. This fact is in sharp contrast with the experimental evidence that no bridging η^2-X_2 ligands have been reported in bimetallic complexes. We have investigated the dimers of type $[M_2(\mu\text{-}X)_2(PH_3)_4]$ (M = Ni, Pd, and Pt; X = O, S, Se, and Te) in search for the possible existence of two minima, with short and long X−X distances (i.e., bonding and nonbonding through-ring interactions).

Dinuclear square-planar complexes with $M_2(\mu\text{-}X)_2$ rings can present a planar ($\theta = 180°$) or bent ($\theta < 180°$) M_2X_2 core (**5**). The study of the structural features of such



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compounds with terminal PH_3 ligands showed that the degree of bending is weak ($\theta \approx 150°$) and the contribution of the bending to the stabilization is less than 2 kcal·mol^{-1}. Moreover, the degree of bending decreases on descending down the group and is also disfavored by bulky terminal ligands.[41] When a bent minimum has been obtained in our calculations, we have also performed a restricted optimization at the planar geometry, by freezing θ at 180°, to model a possible real structure with bulky substituents in the phosphine ligands.[41] The results of our calculations are shown in Table 3.

Table 3. Theoretically Optimized[a] Structures of $[(PH_3)_4M_2X_2]$ Complexes (M = Ni, Pd, and Pt; X = O, S, Se, and Te)

compound	isomer	M⋯M	X⋯X	M−X	M−P	P−M−P	θ	E_{rel}
$[(H_3P)_4Ni_2O_2]$	**1b**[b]	3.592	1.466	1.940	2.209	109.1	180.0	
	1a[c]	2.662	2.441	1.806	2.267	101.5	180.0	−38.0
	1a	2.626	2.437	1.807	2.263	101.8	159.7	−38.1
	1ts[d]	3.368	1.648	1.875	2.240	106.0	180.0	+2.9
$[(H_3P)_4Pd_2O_2]$	**1b**	4.127	1.406	2.180	2.362	109.9	180.0	
	1a[c]	2.976	2.662	1.996	2.347	101.2	180.0	−8.3
	1a	2.861	2.616	1.997	2.344	102.2	142.7	−9.7
	1ts[d]	3.634	1.853	2.040	2.389	101.9	180.0	+21.4
$[(H_3P)_4Pt_2O_2]$	**1b**	4.182	1.438	2.211	2.288	112.2	180.0	
	1a[c]	3.038	2.636	2.011	2.292	98.4	180.0	−47.5
	1a	2.955	2.601	2.012	2.291	98.9	148.5	−48.3
	1ts[d]	3.804	1.774	2.099	2.312	102.4	180.0	+14.4
$[(H_3P)_4Ni_2S_2]$	**1a**[e]	3.352	2.909	2.219	2.255	98.5	180.0	
$[(H_3P)_4Pd_2S_2]$	**1b**	4.424	2.193	2.469	2.379	109.1	180.0	
	1a[c]	3.636	3.052	2.373	2.375	100.3	180.0	−0.7
	1a	3.486	3.090	2.374	2.373	100.1	150.5	−0.8
	1ts[d]	4.081	2.502	2.394	2.391	105.1	179.7	+1.6
$[(H_3P)_4Pt_2S_2]$	**1a**[c]	3.579	3.181	2.394	2.321	98.4	180.0	
	1a[e]	3.391	3.170	2.395	2.319	98.6	141.6	−0.8
$[(H_3P)_4Ni_2Se_2]$	**1a**[e]	3.669	2.914	2.343	2.247	99.7	180.0	
$[(H_3P)_4Pd_2Se_2]$	**1b**[e]	4.331	2.621	2.531	2.384	105.4	180.0	
$[(H_3P)_4Pt_2Se_2]$	**1a**[c]	3.786	3.285	2.506	2.326	98.5	180.0	
	1a[e]	3.622	3.291	2.507	2.325	98.3	146.6	−0.3
$[(H_3P)_4Ni_2Te_2]$	**1b**[e]	4.089	3.019	2.541	2.235	100.9	180.0	
$[(H_3P)_4Pd_2Te_2]$	**1b**[e]	4.487	2.988	2.696	2.386	104.3	180.0	
$[(H_3P)_4Pt_2Te_2]$	**1a**[e]	4.149	3.387	2.678	2.335	99.1	180.0	

[a] Distances in angstroms, angles in degrees, energies in kilocalories per mole. [b] Not a minimum, it evolves to a η^1:η^1-OO complex (symmetry has been imposed). [c] Not a minimum (calculated with the bending angle fixed at 180°). [d] Geometry of the transition state for **1a** ↔ **1b** interconversion. [e] Only one isomer has been found.

Two energy minima are obtained for the oxo complexes, with the $M_2(\mu\text{-}X)_2$ regular isomer always being much more stable than that with a X−X bond, their relative stability decreasing in the order Pt > Ni ≫ Pd. The small energy difference between **1a** and **1b** for palladium must be related to a higher inaccessibility of the oxidation state M^{II} in **1a**, as shown by the larger second ionization potential of Pd (19.43), compared to Ni (18.17) and Pt (18.56 eV). For the sulfur compounds only the **1a** minimum is obtained in our calculation of nickel and platinum complexes, whereas in $[Pd_2(\mu\text{-}S)_2(PH_3)_4]$ minima for **1a** and **1b** structures are found with an energy difference of less than 1 kcal·mol^{-1}. For the selenium and tellurium complexes only one minimum is obtained for the three metals, although of different type depending on the metal. Platinum−selenium and −tellurium compounds are predicted to have a long X−X distance with no antipodal interaction,[42] whereas related palladium compounds have clearly bonding X−X distances. Nickel complexes present the isomer with long distance for selenium and with short distance for tellurium. To discuss the kinetic

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Table 4. Calculated Energy of the Isomers and Transition State of $[Pd_2(\mu\text{-}S)_2(PH_3)_4]$ Calculated with Different Computational Levels at the B3LYP-Optimized Structures, Relative to That of the **1b** Isomer[a]

isomer	B3LYP	CCSD	CCSD(T)
1b	0.0	0.0	0.0
1a	−0.8	−7.1	−6.5
1ts	+1.6	+0.4	+0.4

[a] Energies in kilocalories per mole.

stability of the two isomers, in the systems where both **1a** and **1b** have been found as minima, the transition state has been localized for the **1a** → **1b** interconversion. In the M_2O_2 complexes high energy barriers are found, with values of 41.0, 31.1, and 62.6 kcal·mol^{-1} for Ni, Pd, and Pt, respectively. For the reverse **1b** → **1a** reaction, the barriers are 2.9 (Ni), 21.4 (Pd), and 14.4 (Pt) kcal·mol^{-1}, although the nickel compound evolves to a new species with the $\{Ni_2(\mu,\eta^1:\eta^1\text{-}O_2)\}$ core. Taking into account the relative stabilities of **1a** and **1b** and the energy barriers for their interconversion, only the Pd_2O_2 case appears as a candidate for the detection of the two isomers. This tendency of palladium to stabilize the two structures is still enhanced in the Pd_2S_2 system, where the two almost isoenergetic minima are separated by an energy barrier of only 2.3 kcal·mol^{-1} (1.6 for the reverse **1b** → **1a** isomerization).

To assess the validity of the B3LYP results, the energies of both isomers and the transition state for their interconversion for the $[Pd_2(\mu\text{-}S)_2(PH_3)_4]$ system have been recalculated using highly correlated CCSD and CCSD(T) methods, gathered in Table 4. It is clear from these results that obtaining an accurate estimation of the relative energies of these isomers is a difficult task that cannot be warranted with the computational methodology available for the system with real ligands. However, our CCSD(T) results, which give an energy difference of only 6.5 kcal·mol^{-1} between the two isomers, with a very low energy barrier for the interconversion, make us feel confident about the possible existence of two structures in a real system.

The bonding analysis in a regular M_2X_2 diamond (**1a**) has shown the absence of X−X and M−M interactions, consistent with the presence of eight electrons for four M−X bonds (Figure 2, left).[2] However, when the X−X distance is shortened, the avoided crossing between two framework orbitals of b_{3u} symmetry results in important changes in their compositions due to the extensive mixing. One becomes localized at the bridging atoms with σ^*(XX) character, the other one at the metals, becoming a d nonbonding orbital (Figure 2, right), which must be responsible for the transfer of 0.38 (X = O) or 0.24 (X = S) electron from each X atom to Pd (as obtained from a natural population analysis). The bonding orbital $1b_{1u}$ is also stabilized due to its π(XX) character, but it does not lose its framework bonding character. As a result, the M_2X_2 diamond is described as an electron-deficient system with only six electrons, and a net bonding interaction between the two bridging atoms results, if weaker than that found in the mononuclear analogue $[L_2M(\eta^2\text{-}X_2)]$.

Regarding **1b** isomers, the weaker X−X bond found in dinuclear compounds compared to mononuclear compounds is reflected in the optimized X−X distances (Tables 1 and 3), which are ~0.05, 0.12, 0.28, and ~0.30 Å longer for dinuclear O, S, Se, and Te complexes, respectively. Calculated Wiberg bond indexes also show a weakening of X−X bonds, from 1.33 in mononuclear **4b** to 1.13 in the binuclear **1b** for Pd complexes, and similar values are obtained for Ni and Pt. The vibrational analysis shows a frequency corresponding to the X−X stretching, at values intermediate between those of double and single bonds, although lower than those of the corresponding mononuclear compounds.[22] For palladium−sulfur complexes, this frequency decreases from 549 (mononuclear **4b**) to 429 (dinuclear **1b**) cm^{-1}, and similar variations are obtained in oxo complexes of Pd (from 1114 to 973 cm^{-1}) and Pt (from 1001 to 917 cm^{-1}), and heavier palladium dichalcogenide complexes (Se, from 314 to 219 cm^{-1}; Te, from 219 to 181 cm^{-1}). In agreement with the electron-deficient description of the M_2X_2 ring having six framework electrons, the M−X distances are also longer than in related mononuclear species, consistent with changes in the Wiberg bond index from 0.43 (**4b**) to 0.30 (**1b**) for palladium complexes (0.48 in **1a**). Another important parameter changes markedly in both isomers: the P−M−P

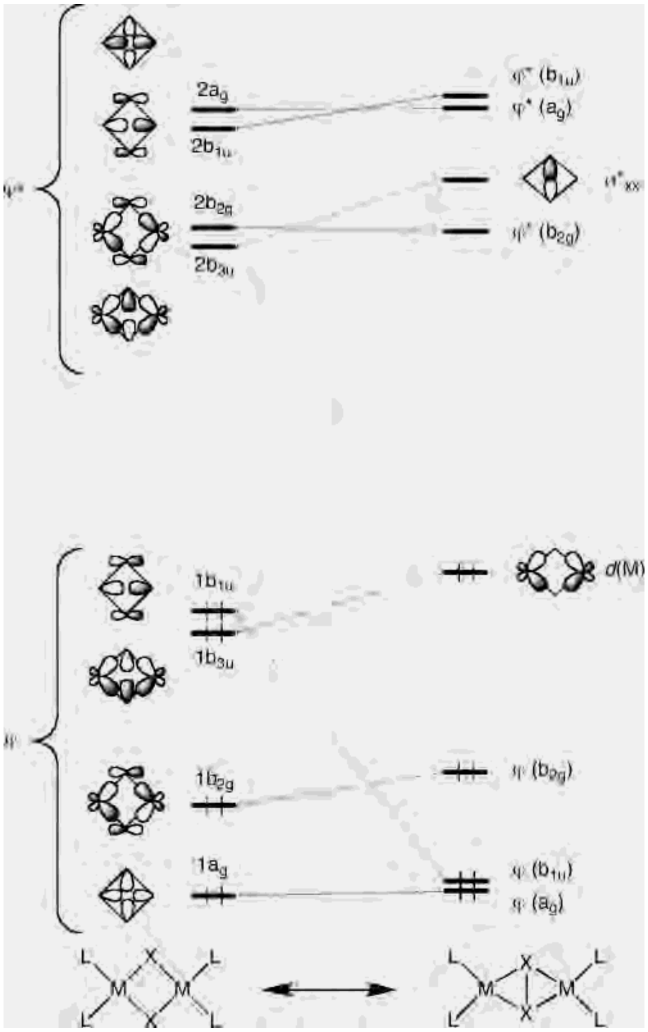

Figure 2. Simplified diagram of the framework orbitals in two forms of M_2X_2 rings in $[L_4M_2(\mu\text{-}X)_2]$ (left, **1a**) and $[L_4M_2(\mu,\eta^2\text{-}X_2)]$ (right, **1b**). The labels represented correspond to the $[(H_3P)_4Pd_2S_2]$ model with D_{2h} symmetry.

Table 5. Main Experimental Structural Parameters[a] for $[M_2(\mu\text{-}X)_2L_4]$ Complexes and Related Compounds (M = Group 10 Metal, X = Group 16 Element)

compound	M···M	X···X	M−X	M−L	L−M−L	θ	ref	refcode
$[(dippe)_2Ni_2S_2]$	2.941	3.077	2.197	2.148	89.9	140.9	44	CONJAQ
$[(MeC\{CH_2PPh_2\}_3)_2Ni_2S_2]$	3.865	2.209	2.226	2.238(14)[b]	93.0(15)[b]	180.0	12	CAWFIP
$[(Ph_3P)_4Pt_2S_2]$	3.177	2.693	2.089	2.228	98.7	168.3	43	QINYUH
$[(Me_2PhP)_4Pt_2S_2]$	3.175	3.060	2.340	2.265	99.4	121.0	45	QQQCOA
$[(Ph_2Ppy)_4Pt_2S_2]$	3.355	3.004	2.327	2.276	103.0	180.0	46	YIJNEK
$[(dppe)_2Pt_2S_2]$	3.292	3.134	2.350	2.245	102.4	138.3	47	NILDAN
$[(Ph_3P)_4Pt_2Se_2]$	3.763	3.136	2.449	2.277	99.5	180.0	42	TIMHOM
$[(MeC\{CH_2PPh_2\}_3)_2Ni_2Te_2]$	4.348	2.802	2.587	2.193(36)[b]	95.7(19)[b]	180.0	13	DIVDIV
$[(N\{C_2H_4PPh_2\}_3)_2Pd_2Te_2]$	4.365	2.917	2.635	2.334	102.4	180.0	48	BAQBOK
$[(Et_3P)_2Pd_2Te_2]$	4.231	3.066	2.612	2.325	107.8	180.0	49	SISTEP
$[(dppe)_2Pd_2Te_2]$	4.021	3.319	2.607	2.286	86.1	180.0	50	HOQKON
$[(Ph_3P)_4Pt_2Te_2]$	4.104	3.258	2.620	2.291	100.5	180.0	51	KIJVUU
$[(Et_3P)_4Pt_2Te_2]$	4.100	3.263	2.620	2.284	106.1	180.0	10	VUMYAD
$[(Et_3P)_4Pt_2Te_2]^{2+}$	3.648	2.697	2.635	2.273	98.5	107.4	10	VUMYEH
$[(Et_3P)_4Pt_2Te_2]^{2+}$	3.647	2.697	2.637	2.275	98.3	107.1	10	VUMYIL
$[(dppe)_2Pt_2Te_2]$	3.965	3.465	2.633	2.251	86.0	180.0	52	SODDUK

[a] Distances in angstroms, angles in degrees. [b] The terminal ligand acts as a tridentate ligand, and the mean and standard deviation are shown for the three donor atoms.

bond angle decreases about 8−14° from X−X bonded isomers **1b** to regular **1a** isomers, except in the Ni_2O_2 compound. No remarkable differences in the M−P bond distances are found between the two isomers, indicated also by a nearly constant Wiberg bond index of about 0.33.

The experimental data reported in the references for $[M_2X_2L_4]$ complexes are shown in Table 5. Isomers with long X−X distances are found for X = S (3.00−3.13 Å), Se (3.14−3.25 Å), and Te (3.32−3.47 Å). These compounds present in general a planar geometry, but some complexes with a bent M_2X_2 ring are found for X = S,[14] in agreement with the tendency toward bending expected for the group 16 compounds.[41] All these compounds present eight framework electrons, and nonbonding X−X interaction must be expected. In contrast, complexes with six framework electrons such as $[Pt_2(\mu\text{-}Te)_2(PEt_3)_4]^{2+}$ (entries VUMYEH and VUMYIL)[10] clearly present X−X bonds. The value of 2.70 Å for the Te−Te distance is cleary shorter than 3.26 Å found for the parent complex $[Pt_2(\mu\text{-}Te)_2(PEt_3)_4]$ (refcode VUMYAD).[10] Another compound we must comment on here due to the presence of the shortest S···S distance is $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (refcode QINYUH).[43] The values of 2.69 Å for S···S and 2.09 Å for Pt−S, 0.25 Å shorter than in related complexes (∼2.34 Å), make us suspect that this compound is partially oxidized. The precipitation of crystals after two months from a solution under dinitrogen with unidentified solvent molecules disordered in the crystal would support this hypothesis, and a redetermination of its crystal structure would be of interest.

Although dinuclear compounds with eight framework electrons should be expected to have long through-ring X···X distances, a few exceptions are known. We have found only four compounds presenting a short X···X distance, all of them with a planar geometry (θ = 180°) in agreement with our calculations. Two of them (entries BAQBOK and SISTEP)[48,49] contain Pd_2Te_2 rings with P−Pd−P angles larger than 102°, in agreement with our theoretical results (Te−Te ≤ 3.07 Å, compared to the calculated value 2.99 Å). The other two are nickel compounds with three-coordinated terminal ligands cited in the Introduction (CAWFIP and DIVDIV, having S and Te bridges, respectively). It is worth comparing our results with the recently reported structures of $[Ni_2(\mu\text{-}X)_2(\eta^5\text{-}Cp)_2]$ complexes (X = S, Se, Te), although they are not of the $[M_2X_2L_4]$ type. Our values are in good agreement with the X-ray distances of 2.75, 2.86, and 3.05 Å for S···S, Se···Se, and Te···Te, respectively, which were interpreted as indicative of a weakest X···X interaction for S and strongest for Te.[15]

An interesting piece of structural data can be found by comparing the geometries of $[M_2(\mu\text{-}Te)_2(PR_3)_4]$ complexes (M = Pd, Pt) with different terminal ligands. For the palladium compounds, two complexes are found with P−Pd−P angles of 108° and 86°, for $PR_3 = PEt_3$ and dppe/2, respectively, with an important difference of 0.25 Å in their Te···Te distances (3.07 vs 3.32 Å). Similarly, the platinum complexes with P−Pt−P angles of 101−106° ($PR_3 = PPh_3$, PEt_3) show a shortening of 0.21 Å in the Te···Te distance with respect to that at 86° (PR_3 = dppe/2) (3.26 vs 3.47 Å). However, both distances are too long to consider the existence of any Te···Te bonding interaction in the platinum compounds.

The M_2X_2 rings can also be found in some metal chalcogenides and derivatives having $\{M(\mu\text{-}X)_2\}_\infty$ chains **6**, made by fusing together M_2X_2 diamonds. In these cases, the

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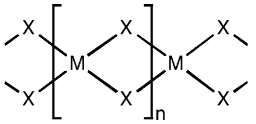

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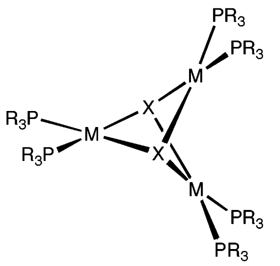
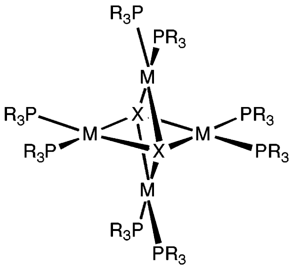
L−M−L and X−M−X angles are identical (79−91°) and close to the values expected for regular isomers **1a** without antipodal bonding interaction. In all compounds (Table 6), distances and angles are in agreement with calculated parameters for dinuclear complexes (Table 3). Only $BaNiO_2$ (ICSD entry 15760)[53] presents a quite long X···X distance. The great degree of bending of the Ni_2O_2 unit of 116° due to an attractive Ni···Ni interaction may induce such a lengthening of the O···O distance.[41]

Polynuclear Complexes. We have also investigated the effect of increasing the nuclearity of the complex on the X···X interaction by adding ML_2 groups as shown in **7**. The



7a



7b

formation of trimetallic species $[M_3L_6(\mu\text{-}X)_2]$ by coordination of an ML_2 unit to the X bridges has often been reported.[14] From the results of Table 3, which show the palladium−sulfur complex to be the most favorable case for presenting two isomers, we have selected the fragment $\{Pd(PH_3)_2\}^{2+}$ to complete the environment of the S_2 unit in $[Pd_2(\mu\text{-}S)_2(PH_3)_4]$ for trinuclear and tetranuclear complexes $[\{(H_3P)_2Pd\}_n(\mu\text{-}S)_2]^{(2n-4)+}$ ($n = 3$ in **7a** and $n = 4$ in **7b**). In both cases (see the Supporting Information), only one isomer with a nonbonding X···X distance is calculated to be stable as found experimentally[14] (S···S distances are 3.06 and 2.93 Å, respectively). Optimized **7a** presents practically the same geometrical parameters as the dinuclear compound of Table 3, whereas **7b** shows very weak Pd−S bonds due to the square-pyramidal geometry of the tetracoordinated sulfur atoms present in the Pd_4S_2 core. Structures with the S−S distance fixed at 2.20 Å are found to be about 26 kcal·mol^{-1} above the minimum. As shown in Figure 3, one can only expect an equilibrium between bonded and nonbonded X−X isomers for bimetallic complexes.

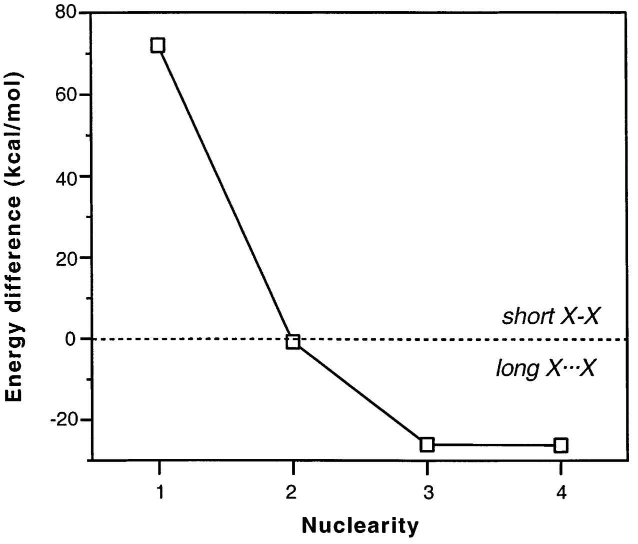


Figure 3. Calculated energy difference (kcal·mol^{-1}) between forms having long and short S···S distances in compounds $[\{(H_3P)_2Pd\}_n(\mu\text{-}S)_2]^{(2n-4)+}$ as a function of the number of palladium atoms ($n = 1-4$). Points under the zero line correspond to isomer **1a** being more stable than **1b**.

Table 6. Main Experimental Structural Parameters[a] for Metal Chalcogenides Having $\{M(\mu\text{-}X)_2\}_\infty$ Chains and Other Compounds with Similar Structures in the Solid State (M = Ni, Pd, and Pt; X = O, S, Se, and Te)

compound	M···M	X···X	M−X	X−M−X	θ	ref	ICSD code
Li_2NiO_2	2.779	2.599	1.903	86.2	180.0	54	25000
$BaNiO_2$	2.378	2.868	2.002	91.5	116.5	53	15760
PdO	3.036	2.663	2.019	82.5	180.0	55, 56	29281
Li_2PdO_2	2.986	2.769	2.034	85.8	180.0	57	61199
K_2PdO_2	3.119	2.740	2.076	82.6	180.0	58	06158
PtO	3.040	2.670	2.023	82.6	180.0	55	26599
Na_2PtO_2	3.119	2.685	2.058	81.4	180.0	59	25018
PdS	3.389	3.028	2.332	81.0	145.6	60	61063
Na_2PdS_2	3.539	3.146	2.368	83.3	179.3	61	87220
PtS	3.470	3.055	2.312	82.7	180.0	62	41376
Na_2PtS_2	3.548	3.112	2.360	82.5	177.6	61	87219
K_2PtS_2	3.590	3.059	2.358	80.9	180.0	63	26258
Rb_2PtS_2	3.640	3.005	2.360	79.1	180.0	63	26259
Na_2PtSe_2	3.686	3.288	2.470	83.5	180.0	64	40429
K_2PtSe_2	3.733	3.149	2.442	80.3	180.0	64	40430
Rb_2PtSe_2	3.753	3.234	2.477	81.5	180.0	64	40431
K_2PtTe_2	3.949	3.502	2.639	83.1	180.0	64	40432

[a] Distances in angstroms, angles in degrees.

In general, our calculated parameters for optimized structures are in agreement with the experimental parameters for mononuclear, dinuclear, and trinuclear compounds. As an example, X···X distances for the two isomers are shown in Figure 4. We can observe a good correlation between calculated and experimental distances. A good separation is found between bonded and nonbonded X···X distances for a given chalcogen. For each isomer type, the X···X distance increases from O to Te, as expected.

Ligand Design for Dinuclear Complexes. Our study of $[M_2X_2L_4]$ compounds using model terminal ligands (L =

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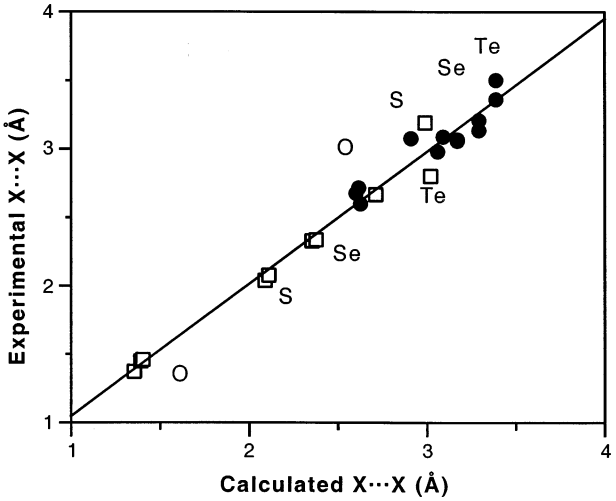
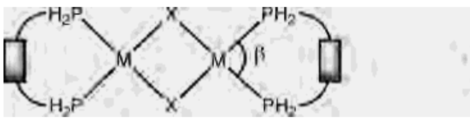


Figure 4. Scatterplot of experimental and calculated X···X distances in complexes of types [MX_2L_2] (Tables 1 and 2), [$M_2X_2L_4$] (Tables 3 and 4), and [$M_3X_2L_6$] (see the Supporting Information). The data for extended structures (Table 6) are plotted versus the calculated data for the related dinuclear complexes. Structures with an X−X bond are represented by open squares, those without X−X bonding by circles.

PH_3) points to the Pd_2S_2 ring as the best case for further study, since the two isomers **1a** and **1b** are almost isoenergetic (see Table 4). Given the strong influence exerted by the terminal ligands on M_2X_2 rings, it can be expected that this energy difference could be fine-tuned by a proper choice of the terminal ligands. We attempt to design complexes that could stabilize the structure with a bonding X−X interaction. To investigate the influence of terminal ligands, we have analyzed two factors: (a) the geometrical constraints of terminal ligands and (b) the nature of the donor atoms.

It is well-known that steric factors can determine the molecular structure and chemical properties of compounds.[65,66] Since the optimized structures of Table 3 show large P−M−P angles in the isomers with an X−X bond, we wish to find out whether structures **1b** can be stabilized by using chelating terminal ligands with large bite angles. We have therefore analyzed the influence of the P−M−P bite angle[67−69] of the terminal ligands on the relative stabilities of structures **1a** and **1b**. In this study we have replaced the two monodentate PH_3 ligands by the series of chelating diphosphines shown in the Chart 1 to modify the P−M−P angles (β in **8**) in compounds of the type [$Pd_2(\mu\text{-}S)_2(H_2P{-}spacer{-}PH_2)_2$]. To that end we have selected several saturated diphosphines, dpm, dpe, dpp, and dpb,[67,68] an important chiral diphosphine, diop,[70] several unsaturated diphosphines, dpen, dpbn,[68] bisbi,[70,71] and stiffer dpab and dpnap,[68] other diphosphines with somewhat more rigid spacers such as dpf[67] and norphos,[70,71] related diphosphites, obisbi and dpobn,[72] and, finally, large-bite-angle xanthene-derived diphosphines based on hetereoaromatic rings, dpephos, xantphos, oxantphos, and dpfphos.[66,69,73]



8

The structural data of the optimized structures are presented in Table 7. For the eighteen diphosphines considered, two energy minima have been found, one with an S−S bond (S−S $\approx$ 2.2 Å) and another one without S···S interaction (3.0 < S···S < 3.4 Å). The **1a** isomer is more stable than **1b** in all cases, with the only exception the dpm ligand, whose small bite angle causes a poor Pd−P interaction reflected in the long Pd−P distance (2.45 Å, compared to 2.32−2.39 Å for most compounds). Notice that, despite the small difference in the geometry of the Pd_2S_2 ring, the energy difference between the two isomers changes appreciably by modifying the terminal ligands, covering a range of 15 kcal·mol^{-1} (only 7 kcal·mol^{-1} if we consider only planar structures **1a**). In most cases, given the relative energies between the two isomers, we anticipate that their interconversion may occur thermally because a low energy barrier is expected, as in the related complex having monodentate phosphines.

The distances and angles within the Pd_2S_2 diamond are similar to those in the simpler model having PH_3 groups as terminal ligands. Whereas the isomer with a short S−S distance always presents a planar Pd_2S_2 ring (θ = 180°), the **1a** isomers are bent (θ = 121−149°) except for the dpm complex, for which the **1a** isomer is more stable with a planar ring. In the cases that give a bent **1a** isomer, we have frozen the corresponding planar geometry to simulate bulky R substituents at the phosphorus atoms that are known to stabilize planar rings. The results reported here show that bending of the Pd_2S_2 ring is an additional factor that stabilizes isomer **1b** with no S···S interaction. All in all, the studied systems appear to be more flexible than thought and can respond to changes in the bite angle by modifying the Pd−P distance or bending the Pd_2S_2 ring.

It has been recently demonstrated that the reductive elimination rate of RCN from the complexes [(diphosphine)-Pd(R)(CN)] increases significantly with increasing diphosphine bite angle.[65] However, the most remarkable result of the present calculations is that there is no universal correlation between the bite angle of the terminal bidentate ligand and the energy difference between isomers **1a** and **1b**, although the results can be grouped into two families. On one hand, we have those ligands in which the two phosphine groups are linked by a carbon skeleton with only single or

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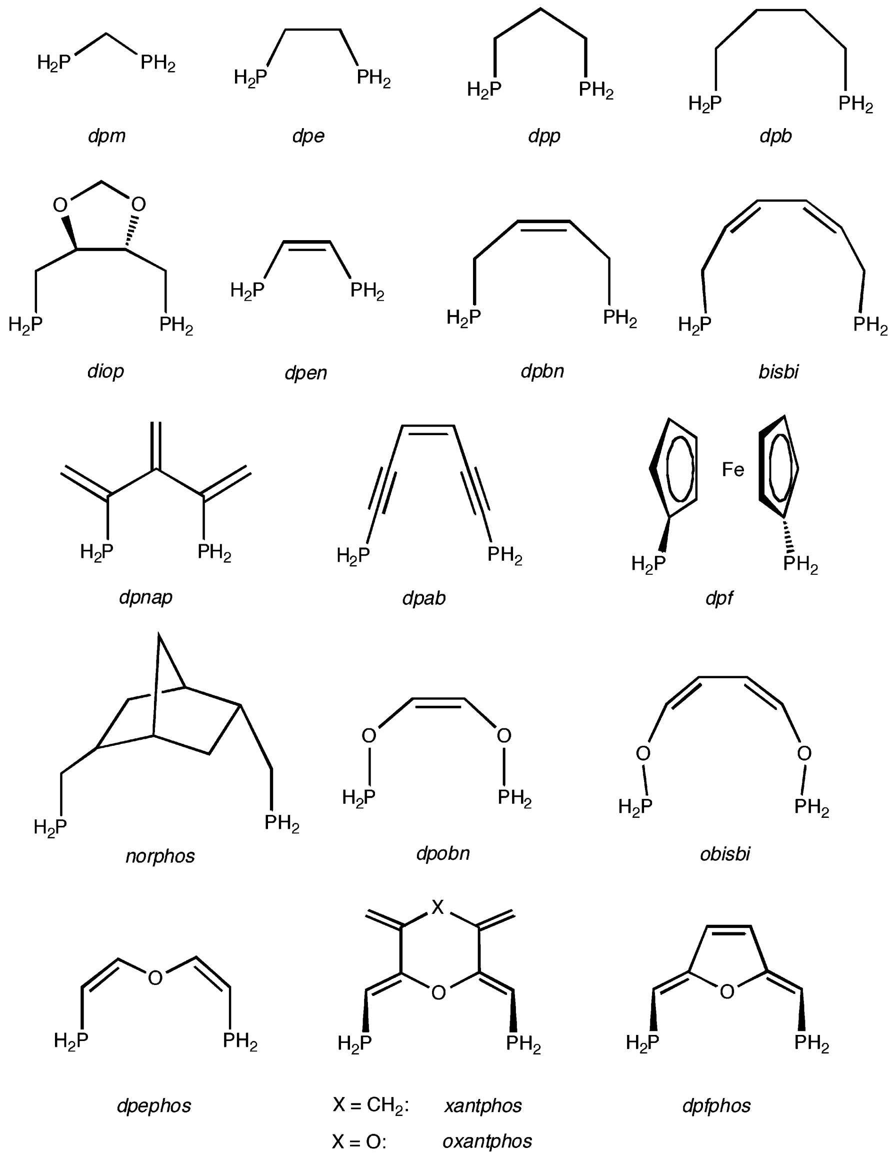
Chart 1



double carbon−carbon bonds (dpm−bisbi; see Chart 1 and Table 7), which show a dependence of the energy difference between the two isomers on the bite angle (Figure 5): large bite angles favor the isomer with a long S···S distance, whereas smaller bite angles tend to equalize the energies of the two isomers. No correlation between bite angle and energy difference is found for the rest of the diphosphines that incorporate some extra rigidity via double and triple bonds (dpnap or dpab), a ferrocene (dpf) or a norbornane skeleton (norphos), or ether functions in the spacer linking the two phosphine groups (dpobn−dpfphos). It is interesting to notice that xanthene-derived ligands (dpephos−dpfphos, represented by times signs in Figure 5) with the same bite angle as a diether ligand (dpobn and obisbi, open squares in Figure 5) make the S−S bonded isomer significantly less unstable, probably because the ether group in the former case can interact with the palladium atom. Within each family of diphosphine ligands with ether spacers, the energy difference between the two isomers is practically insensitive to bite angle variations of about 12°. We must conclude that the chemical nature of spacers between the two phosphorus donor atoms also plays an important role to stabilize each structure.

The study with bidentate phosphines has shown that the Pd−P distance, which is related to the P → M donation, affects the energy difference between the two isomers. Indeed, in the only case for which **1b** is favored (dpm), a long Pd−P distance is found. It can be expected that the nature of the donor atom bonded to the metal also influences this parameter. We have substituted donor atoms of the phosphine ligands by other pnicogens, $[Pd_2(\mu\text{-}S)_2(PnH_3)_4]$ (Pn = group 15 element), and the main parameters for optimized geometries are shown in Table 8. The Pd_2S_2 unit keeps a structure similar to that in the reference PH_3 complex, having a slight lengthening of Pd−S and shortening of S···S distances in all calculated isomers, together with the expected increase of the Pd−Pn distance as Pn goes down in the group. However, an important change in the relative stabilities of the two isomers is obtained for this series of complexes. For ammonia, only structure **1a** is predicted, whereas **1b** is not a minimum and lies ~22 kcal·mol^{-1} above when the S−S

Table 7. Theoretically Optimized^a Structures for $[Pd_2(\mu\text{-}S)_2(H_2P{-}\text{spacer}{-}PH_2)_2]$ Complexes^b

diphosphine	isomer	Pd···Pd	S···S	Pd−S	Pd−P	P−Pd−P	θ	E_{rel}
dpm	**1b**	4.332	2.224	2.435	2.452	72.1	180.0	
	1a	3.695	2.913	2.352	2.449	71.7	180.0	+0.5
dpe	**1b**	4.386	2.217	2.457	2.376	86.9	180.0	
	1a^c	3.586	3.112	2.374	2.363	85.1	180.0	−2.7
	1a	3.279	3.182	2.377	2.349	85.7	136.4	−3.4
dpp	**1b**	4.392	2.221	2.461	2.362	96.3	180.0	
	1a^c	3.560	3.163	2.381	2.345	93.4	180.0	−5.2
	1a	3.229	3.216	2.387	2.335	95.8	132.5	−5.7
dpb	**1b**	4.399	2.220	2.464	2.359	103.9	180.0	
	1a^c	3.566	3.166	2.385	2.344	99.3	180.0	−5.8
	1a	3.275	3.191	2.386	2.338	100.1	134.7	−10.2
diop	**1b**	4.422	2.204	2.470	2.359	104.9	180.0	
	1a^c	3.570	3.160	2.384	2.347	100.8	180.0	−4.5
	1a	3.244	3.192	2.386	2.340	101.9	132.3	−5.9
dpen	**1b**	4.383	2.216	2.455	2.372	86.4	180.0	
	1a^c	3.595	3.097	2.372	2.362	84.7	180.0	−2.0
	1a	3.286	3.175	2.376	2.347	85.2	136.7	−2.8
dpbn	**1b**	4.428	2.201	2.472	2.372	104.6	180.0	
	1a^c	3.575	3.153	2.384	2.358	100.4	180.0	−3.9
	1a	3.179	3.206	2.390	2.345	102.5	127.5	−5.8
bisbi	**1b**	4.407	2.211	2.465	2.384	110.2	180.0	
	1a^c	3.607	3.104	2.379	2.375	103.5	180.0	−4.4
	1a	3.280	3.130	2.388	2.376	112.4	130.8	−13.7
dpnap	**1b**	4.310	2.271	2.436	2.350	83.1	180.0	
	1a^c	3.552	3.156	2.376	2.321	83.4	180.0	−6.1
	1a	3.301	3.187	2.377	2.315	84.2	138.8	−6.9
dpab	**1b**	4.447	2.185	2.477	2.384	111.7	180.0	
	1a^c	3.580	3.150	2.384	2.377	107.3	180.0	−1.8
	1a	3.171	3.189	2.389	2.368	109.9	126.1	−4.7
dpf	**1b**	4.417	2.206	2.469	2.373	104.5	180.0	
	1a^c	3.575	3.154	2.384	2.364	101.4	180.0	−4.3
	1a	3.234	3.185	2.386	2.357	102.4	131.0	−5.6
norphos	**1b**	4.427	2.204	2.473	2.377	113.9	180.0	
	1a^c	3.631	3.087	2.383	2.374	107.6	180.0	−4.0
	1a	3.434	3.108	2.383	2.376	107.6	143.8	−4.4
dpobn	**1b**	4.434	2.202	2.475	2.335	102.2	180.0	
	1a^c	3.451	3.345	2.403	2.299	100.5	180.0	−6.3
	1a	3.021	3.384	2.411	2.281	103.6	123.2	−12.4
obisbi	**1b**	4.441	2.198	2.478	2.352	114.0	180.0	
	1a^c	3.548	3.203	2.390	2.340	107.9	180.0	−5.8
	1a	3.041	3.315	2.411	2.322	117.3	120.6	−10.6
dpephos	**1b**	4.393	2.214	2.459	2.389	105.1	180.0	
	1a^c	3.612	3.085	2.375	2.382	100.7	180.0	−3.5
	1a	3.464	3.106	2.375	2.383	100.7	149.0	−3.7
xantphos	**1b**	4.391	2.217	2.459	2.380	102.5	180.0	
	1a^c	3.599	3.106	2.377	2.373	99.2	180.0	−3.8
	1a	3.426	3.124	2.377	2.375	99.2	146.0	−4.0
oxantphos	**1b**	4.394	2.211	2.460	2.391	104.0	180.0	
	1a^c	3.610	3.085	2.374	2.387	100.5	180.0	−3.0
	1a	3.466	3.108	2.375	2.387	100.6	149.7	−3.2
dpfphos	**1b**	4.397	2.197	2.457	2.497	111.1	180.0	
	1a^c	3.664	2.986	2.363	2.511	108.3	180.0	−0.6
	1a	3.235	3.093	2.372	2.508	115.6	128.2	−3.2

^{a} Distances in angstroms, angles in degrees, energies in kilocalories per mole. ^{b} The first line of each entry corresponds to the $M(\eta^2\text{-}X_2)M$ isomer **1b**, the second to the *planar* $M(\eta^1\text{-}X)_2M$ structure **1a** (see the text), and the third to the *optimized* $M(\eta^1\text{-}X)_2M$ structure. ^{c} Not a minimum, calculated with the bending angle fixed at 180°.

distance is fixed at 2.20 Å. Nevertheless, for Pn = As or Sb both isomers are obtained, and their relative stability is inverted with respect to that of the PH_3 system. Thus, the influence of the donor atoms of terminal ligands is crucial to stabilize one or the other isomer. Recently the efficiency of bidentate arsine ligands in rhodium− and platinum−tin-catalyzed hydroformylation has been pointed out, and rationalized in terms of their wide natural bite angles.[74]

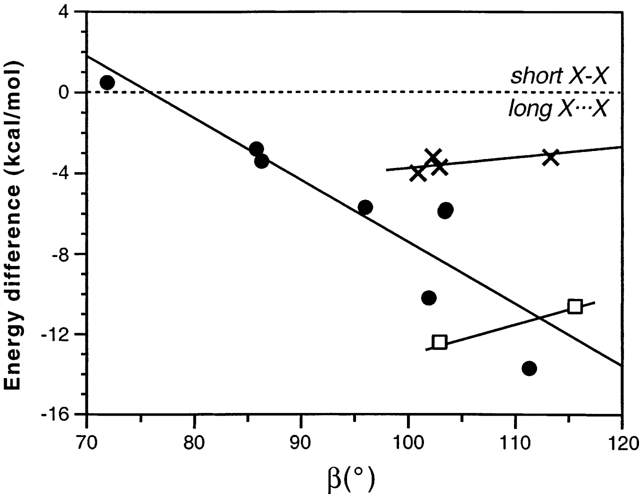


Figure 5. Calculated energy difference (kcal·mol^{-1}) between forms **1a** and **1b** in $[Pd_2(\mu\text{-}S)_2(H_2P{-}\text{spacer}{-}PH_2)_2]$ as a function of the bite angle of the open chain terminal bidentate diphosphines dpm−bisbi, represented by circles (see Chart 1). Points under the zero line correspond to isomer **1a** being more stable than **1b**. Also, the four phosphines derived from xanthene are represented by times signs (dpephos−dpfphos), and the two diphosphites (dpobn and obisbi) by open squares.

Table 8. Theoretically Optimized^a Structures for $[Pd_2(\mu\text{-}S)_2(PnH_3)_4]$ Complexes Where Pn Is a Group 15 Element^b

PnH_3	isomer	Pd···Pd	S···S	Pd−S	Pd−Pn	Pn−Pd−Pn	θ	E_{rel}
NH_3	**1b**^{c}	4.211	2.200	2.376	2.281	100.7	180.0	
	1a^d	3.460	3.159	2.343	2.208	98.1	180.0	−21.3
	1a	3.281	3.133	2.343	2.207	98.5	140.8	−22.0
AsH_3	**1b**	4.416	2.187	2.435	2.486	108.7	180.0	
	1a^d	3.664	2.996	2.352	2.488	100.5	180.0	+1.1
	1a	3.495	3.046	2.352	2.486	100.3	149.5	+1.0
SbH_3	**1b**	4.453	2.169	2.477	2.639	110.4	180.0	
	1a^d	3.666	3.001	2.369	2.650	102.0	180.0	+3.4
	1a	3.375	3.089	2.371	2.643	102.0	139.5	+3.0

^{a} Distances in angstroms, angles in degrees, energies in kilocalories per mole. ^{b} The first line of each entry corresponds to the $M(\eta^2\text{-}X_2)M$ isomer **1b**, the second to the *planar* $M(\eta^1\text{-}X)_2M$ structure **1a** (see the text), and the third to the *optimized* $M(\eta^1\text{-}X)_2M$ structure. ^{c} Not a minimum, calculated with a fixed S−S distance. ^{d} Not a minimum, calculated with the bending angle fixed at 180°.

Conclusions

The study of mononuclear complexes of group 10 metals with two chalcogenide ligands has shown that $M(\eta^2\text{-}X_2)$ structures with X−X bonds are clearly more favorable than open $M(X)_2$ structures with long X···X distances. In contrast, for dinuclear complexes with bridging chalcogen ligands, in addition to the usual $M_2(\mu\text{-}X)_2$ structures with long through-ring X···X distances, $M_2(\eta^2\text{-}X_2)$ structures with X−X bonds are possible. In several cases both minima have been found, whereas in other cases only one minimum exists. The presence of one or two minima and their relative stabilities are strongly dependent on the nature of the metal, the bridging atoms, and the terminal ligands.

The existence of the two isomers can be rationalized by an electron localization effect which converts a framework molecular orbital with $\sigma^*(XX)$ character into an essentially d orbital, with the consequent formation of a $\sigma(XX)$ bond. The importance of this effect is related to the tendency of the chalcogen to retain its electrons, and thus to its electronegativity. Accordingly, the stability of the X−X interac-

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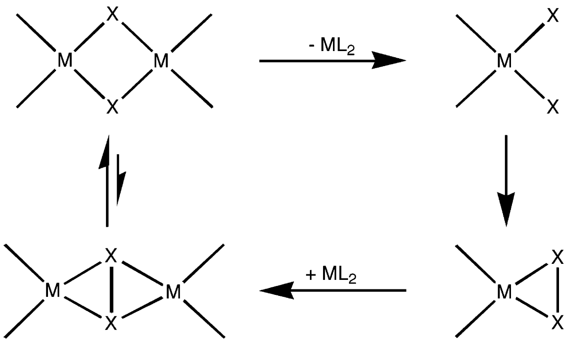
tion decreases with the electronegativity of X, being weakest for oxygen and strongest for tellurium. The choice of the bridging ligand is the main factor that accounts for the presence of one or two minima. For the smaller X (O, S) the increase in the X−X distance on going from structure **1a** to **1b** is large, and two minima can exist. On the contrary, only one minimum is found for Se and Te. The effect of the metal is clearly appreciated by looking at the nature of the Se and Te minima. For palladium, only X−X bonded complexes are found, whereas no X−X interaction is found in platinum complexes. For nickel, whereas the selenium compound shows a regular **1a** ring, the tellurium compound can be described as having a Te−Te bond. Palladium is thus, being the metal with the largest second ionization potential, best placed to give an $M_2(\eta^2\text{-}X_2)$ structure, due to its difficulty in reaching the formal oxidation state M^{II}.

Our study using PH_3 groups as terminal ligands indicates the possible coexistence of both isomers for Pd_2S_2 rings. We have used this core to undertake a systematic study of the effect of terminal ligands on the relative stabilities of **1a** and **1b** isomers. Contrary to what we expected, we have found that aliphatic chelating diphosphines with large bite angles stabilize preferentially the isomer with a long S···S distance, while for other diphosphines there is no clear-cut correlation between bite angle and isomer stability. The flexibility of these systems to compensate the constraint imposed by the bite angle appears as the main reason for such behavior. Xanthene-derived diphosphines, however, seem to stabilize the isomer with a S−S bond more than other diphosphines with the same bite angle. An additional factor is the extra stabilization gained in some cases by bending the $M_2(\mu\text{-}X)_2$ core and developing a metal−metal interaction. The nature of the donor atom of the terminal ligand has a strong influence on the relative stabilities of both isomers. The structure with S−S bonds is found to be the most stable one for AsH_3 and SbH_3 terminal ligands.

The present theoretical study has shown that it could be possible to synthesize dinuclear group 10 complexes with bridging η^2-dichalcogen ligands. Its preparation and characterization is thus a challenge for experimental chemists. Comparison of the present results for mono- and dinuclear complexes also suggests that the dimerization and dissociation steps might be involved in the X−X bond formation and cleavage reactions, as schematically indicated in **9**.



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Appendix

Computational Details. Density functional calculations were carried out using the GAUSSIAN98 package.[75] The hybrid DFT method known as B3LYP was applied, in which the Becke three-parameter exchange functional[76] and the Lee−Yang−Parr correlation functional were used.[77] Effective core potentials (ECPs) were used to represent the innermost electrons of the metal atoms and the basis set of valence double-ζ quality associated with the pseudopotentials known as LANL2DZ.[78] A similar description was used for heavy elements (P, S, As, Se, Sb, and Te),[79] supplemented with an extra d-polarization function.[80] The basis set for the light elements was 6-31G for C, O, and H of phosphine ligands[81] and 6-31G* for O and N directly attached to the metal.[82] A series of structures have been computed adding an extra f-polarization function at the Pd atom,[83] and the results, provided as Supporting Information, are seen to be chemically identical with those without f functions. The geometries were fully optimized using gradient techniques. The nature of the stationary points was characterized by frequency analysis (minima and transition states). Their electronic structures were analyzed through natural bond order analysis.[84] For comparative purposes, the relative energies of some structures that do not correspond to an energy minimum were

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obtained by optimizing with a fixed value of one geometrical parameter (the frozen parameters are indicated in Tables 1, 3, 7, and 8). For instance, in complexes with bent M_2X_2 cores, an optimization was performed by keeping the dihedral angle θ fixed at 180°. In an attempt to reduce the computational requirements in the large systems, symmetry was introduced in the optimizations of bulky diphosphines. To check the validity of the B3LYP relative energies of **1a** and **1b**, coupled cluster[85] calculations have been performed at the optimized B3LYP geometries (see Table 4).

Structural Analysis. The experimental collection of structural data was retrieved from the Cambridge Structural Database (version 5.23, April 2002).[86] Our search included compounds with several cores having metal atoms of groups 10 and 16. Additional data have been searched in the Inorganic Crystal Structure Database (release 2001/1)[87] for binary and ternary compounds of general formulas MX_2 and A_nMX_2.

Supporting Information Available: Table S1 comparing the main bonding parameters for trinuclear complexes in calculated and experimental structures and Table S2 with optimized structures of the $[Pd_2X_2(PH_3)_4]$ complexes (X = O, S, Se, Te) with an extra f-polarization function at the palladium atoms. This material is available free of charge via the Internet at http://pubs.acs.org.

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