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Molecular Structure and Isomerization in Square-Planar Edge-Sharing Dinuclear Complexes with Alkynyl Bridges

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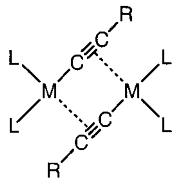
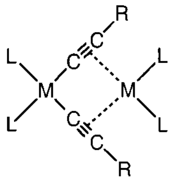
The dinuclear transition-metal complexes of the type $[M_2(\mu\text{-}C{\equiv}CR)_2L_4]$, in which each metal atom is in a square-planar environment, appear in different molecular conformations depending on (a) the coordination mode of the alkynyl ligands and (b) the angle between the coordination planes around the two metal atoms. An ab initio theoretical study on representative complexes for all isomers, complemented with a structural database analysis, provides a rationale for the experimentally observed structures.

The doubly bridged dinuclear alkynyl complexes $[L_2M(\mu\text{-}C{\equiv}CR)_2ML_2]$, with a square-planar coordination sphere around the metal atoms, present different molecular structures as shown in **1**.[1−5] The most frequent coordination mode of the alkynyl bridges for the platinum-group metals is σ,π (**1a**,**b**),[1,3] in which each alkynyl ligand acts as a four-electron donor. In this case two possibilities appear, depending on the relative orientation of the two alkynyl ligands (**1a**,**b**). Alternatively, the alkynyl ligand can act as a two-electron donor in the η^1 mode typical of bridging carbonyls (**1d**),[3,6] and we can also foresee the possibility of the two ligands each acting in a different coordination mode (**1c**). Despite the amount of available structural data for these complexes,[3,4] a full understanding of the factors that determine the molecular geometry of a particular compound has not been achieved. Semiempirical studies have been carried out by Jemmis and Kumar on metallocene complexes.[7] These authors studied the **1d** to **1a** interconversion for the case of $[Zr_2(\mu\text{-}C{\equiv}CR)_2Cp_4]$ through extended Hückel calculations and discussed the bonding in such a complex. More recently, Mealli, Godinho, and Calhorda[8] reported density functional calculations on alkynyl-bridged copper(I) complexes which present a trigonal coordination sphere, at odds with the square-planar metals studied here.



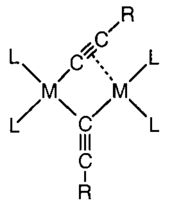
η^2,η^2 (*Rectangular*)

1a



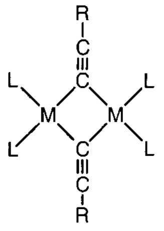
η^2,η^2 (*V-shaped*)

1b



η^1,η^2

1c



η^1,η^1

1d

Despite the structural variability shown in **1**, we are not aware of structurally characterized isomers, although spectroscopic data support their existence. Hence, in many cases, the synthesis of these complexes proceeds through a rearrangement of the coordination modes of alkynyl ligands in the starting mononuclear complex,[4] even if only one isomer appears in the solid state. The interconversion of isomers can be detected in solution from the ^{1}H, ^{13}C, and ^{19}F NMR spectra, and a ring inversion was proposed by Forniés et al. as a likely mechanism for such isomerization process.[9,10]

The bending angles θ (see **2**) of the studied compounds as obtained from a Cambridge Structural Database search[11] are shown in Figure 1, from which the following

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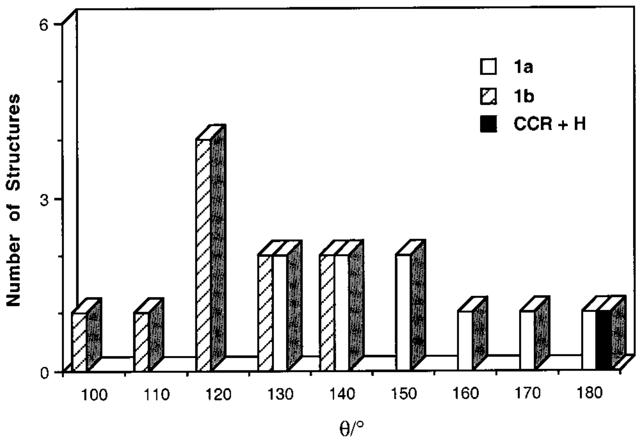
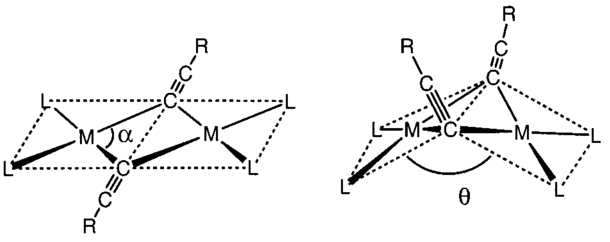


Figure 1. Distribution of the number of molecular structures for alkynyl complexes. In every interval, the number indicates the maximum value of the bending angle θ.



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trends can be established: (i) the rectangular skeleton **1a** appears either in the planar or bent form, (ii) the asymmetric V-shaped isomer (**1b**) is found only in the bent form, showing a larger degree of bending (smaller value of θ) than **1a**, and (iii) when one alkynyl ligand is substituted by a hydride, only the planar form is found. Such behavior is in contrast with our previous findings for related complexes with saturated bridges,[12−15] for which a bimodal distribution of bending angles was found with both planar and strongly bent structures but no structures were found at intermediate bending angles. Our structural database search for other bridging ligands coordinated in the μ,η^2 mode to two square-planar metal centers was unsuccessful.

Let us consider now two aspects of the molecular structure of the compounds under study from a theoretical point of view: the possible existence of a short metal−metal distance in the dinuclear unit and the angle formed between the coordination planes of the two metal atoms. When two d^8 metals are bridged by two four-electron-donor ligands, long metal···metal distances can be expected, corresponding to a description of the four edges of the M_2X_2 diamond as two-electron bonds.[16,17] In this case, the metal···metal distance decreases upon bending around the two bridging atoms, eventually becoming shorter than the sum of the van der Waals radii,[12−15] and an attractive interaction may appear, similar to that found for the face-to-face dimers and chains of d^8-ML_4 complexes.[18] However, when two bridges provide six (**1c**) or four (**1d**) electrons to d^8 metals, a short metal−metal distance across the diamond is expected in the planar dinuclear complex.[17]

With regard to the choice between a bent or a coplanar structure, theoretical studies were carried out in our group previously for related $[M_2(\mu\text{-}XR_n)_2L_4]$ and $[M_2(\mu\text{-}XY)_2L_4]$ complexes, where XR_n ($n = 0{-}2$) has an sp^3 donor atom and XY an sp^2 donor atom.[12−15] According to our previous experience with such systems, we can anticipate the factors that may affect the structural choice in the present case. In the first place, a weak metal···metal bonding interaction and the absence of steric repulsion between terminal ligands favor a bent structure. The preference for the bent structure increases with increasing size of the metal atom: i.e., when descending down a periodic group and from right to left along a period, Ir > Rh > Pt > Pd > Ni > Au. The presence of good σ-donor terminal ligands, and preferably good π-acceptors, favors bent forms. For complexes with substituted bridges, the conformational preference of the bridging atom or the repulsions of substituents and terminal ligands also influence the choice between planar and bent structures. Because the last factors are only significant for the planar form in the complexes studied here,[15] the energy contributions that may be expected to influence the choice between the planar and bent structures are (i) the interaction between two ML_2 fragments in the bent form, including M···M and L···L interactions (we will refer to the energy associated to these interactions as I_{MM}), and (ii) the repulsion between substituent and terminal ligands in the planar form (I_{LR}). We do not expect the metal−bridge bonding to be affected because of the cylindrical character of the π system of the alkynyl ligands.

In this paper we present an ab initio theoretical study for compounds of the type $[M_2(\mu,\eta^y\text{-CCR})(\mu,\eta^z\text{-CCR})L_4]$ (y, $z = 1, 2$) in an attempt to contribute a better understanding of the relative stabilities of their conformers. We focus on the two structural aspects that are of interest for alkynyl-bridged complexes: the bending of M_2X_2 skeleton and the coordination mode of the alkynyl ligand. We will obtain in this work some qualitative guidelines to make predictions if a complex should be expected to be bent or planar and information about their fluxional behavior.

Theoretical Results

Relative Stabilities of Isomers 1a−d. The most relevant calculated parameters in the planar and bent geometries are collected in Table 1. As an example, the optimized structures of the four isomers of $[Pt_2(\mu\text{-}C{\equiv}CH)_2(CH_3)_4]^{2-}$ (**M.4**) are shown in Figure 2. Two important trends can be deduced from our calculations about the relative stabilities of the different geometries analyzed. On one hand, the bent form is more stable than the planar one in all cases except for **M.4d**. On the other hand, **1a** is the most stable isomer, whereas **1d** is always the most unstable one. These trends

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Table 1. Calculated Energies and Main Structural Parameters for $[M_2(\mu\text{-C}{\equiv}\text{CH})_2L_4]$ Compounds[a]

	compd	M···M, Å	θ, deg	α, deg	E_{rel}, kcal mol^{-1}	$E_b - E_p$, kcal mol^{-1}
M.1a	$[Pt_2(\mu,\eta^2\text{-CCH})_2(PH_3)_4]^{2+}$	3.581	180[b]	87.2	7.8	
		3.252	123	83.2	0.0	−7.8
M.1b	$[Pt_2(\mu,\eta^2\text{-CCH})_2(PH_3)_4]^{2+}$	3.640	180[b]	90.2	18.4	
		3.099	113	88.0	4.5	−13.9
M.1c	$[Pt_2(\mu,\eta^2\text{-CCH})(\mu\text{-}\eta^1\text{-CCH})(PH_3)_4]^{2+}$	3.272	180[b]	88.5	17.9	
		2.967	121	83.2	6.5	−11.4
M.1d	$[Pt_2(\mu,\eta^1\text{-CCH})_2(PH_3)_4]^{2+}$	2.922	180[b]	87.1	18.6	
		2.826	125	83.8	12.0	−6.6
M.2a	$[Pt_2(\mu,\eta^2\text{-CCH})_2(\eta^2\text{-}C_2H_4)_4]^{2+}$	3.584	180[b]	86.8	3.3	
		3.133	115	83.4	0.0	−3.3
M.2b	$[Pt_2(\mu,\eta^2\text{-CCH})_2(\eta^2\text{-}C_2H_4)_4]^{2+}$	3.650	180[b]	86.5	15.2	
		2.914	102	83.9	5.2	−10.0
M.2c	$[Pt_2(\mu,\eta^2\text{-CCH})(\mu\text{-}\eta^1\text{-CCH})(\eta^2\text{-}C_2H_4)_4]^{2+}$	3.252	180[b]	89.2	12.2	
		2.917	119	84.0	2.5	−9.7
M.2d	$[Pt_2(\mu,\eta^1\text{-CCH})_2(\eta^2\text{-}C_2H_4)_4]^{2+}$	2.931	180[b]	92.3	11.2	
		2.809	125	82.8	5.4	−5.8
M.3a	$[Pt_2(\mu,\eta^2\text{-CCH})_2(CF_3)_4]^{2-}$	3.825	180[b]	81.4	2.1	
		3.576	140	81.3	0.0	−2.1
M.3b	$[Pt_2(\mu,\eta^2\text{-CCH})_2(CF_3)_4]^{2-}$	3.959	180[b]	79.7	16.1	
		3.320	120	81.5	7.3	−8.8
M.3c	$[Pt_2(\mu,\eta^2\text{-CCH})(\mu\text{-}\eta^1\text{-CCH})(CF_3)_4]^{2-}$	3.542	180[b]	81.9	22.7	
		2.957	113	82.7	12.9	−9.8
M.3d	$[Pt_2(\mu,\eta^1\text{-CCH})_2(CF_3)_4]^{2-}$	3.171	180[b]	86.9	30.1	
		2.807	114	81.4	19.6	−10.5
M.4a	$[Pt_2(\mu,\eta^2\text{-CCH})_2Me_4]^{2-}$	3.743	180[b]	84.2	0.3	
		3.653	154	83.7	0.0	−0.3
M.4b	$[Pt_2(\mu,\eta^2\text{-CCH})_2Me_4]^{2-}$	3.803	180[b]	83.9	6.3	
		3.532	138	83.6	4.5	−1.8
M.4c	$[Pt_2(\mu,\eta^2\text{-CCH})(\mu\text{-}\eta^1\text{-CCH})Me_4]^{2-}$	3.165	180[b]	98.2	13.4	
		2.882	117	90.2	9.6	−3.8
M.4d	$[Pt_2(\mu,\eta^1\text{-CCH})_2Me_4]^{2-}$	2.779	175	101.5	11.0	
		2.746	118[b]	88.6	13.4	+2.4

[a] For each isomer the first line corresponds to the planar form and the second line to the bent geometry. [b] θ has been frozen in the calculation.

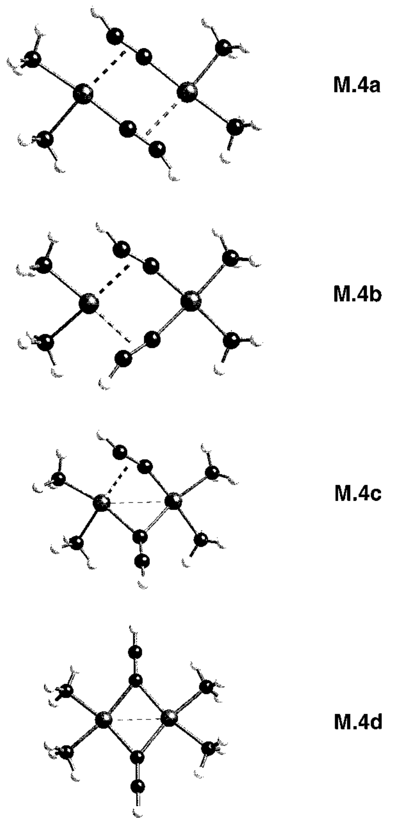


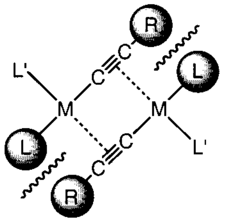
Figure 2. Optimized molecular structures of the four isomers of the model compound $[Pt_2(\mu\text{-C}{\equiv}\text{CH})_2(CH_3)_4]^{2-}$.

indicate that the one or two alkynyl ligands bonded in an η^1 fashion to both metal atoms are unstable with respect to the η^2 complexes, a finding that can be associated with the electron-deficient nature of the η^1-alkynyl group as a bridging ligand.[15] This behavior is related in the M···M distances in the planar form, which are larger than 3.5 Å in **1a** and **1b** but close to 3 Å in **1d** compounds, with intermediate distances in **1c** compounds.

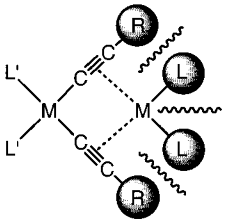
Discussion of Optimized Structural Data. Two main differences are found between isomers **1a** and **1b**: (a) the rectangular-shaped isomer **1a** is always more stable than the V-shaped **1b** for planar and bent forms and (b) bending in the V-shaped isomers is more stabilizing than in the rectangular isomers. For all studied compounds the V-shaped isomer **1b** presents a larger degree of bending and, consequently, shorter M···M distances than the rectangular **1a** isomer. One can see that the metal···metal distance decreases upon bending up to 0.5 Å and the bond angle α decreases by up to 10° for most of the compounds. Similar variations were obtained previously for the related $[M_2(\mu\text{-}XR_n)_2(PH_3)_4]$ complexes with saturated bridges.[12−15]

We can explain the trends observed in both forms on the basis of repulsion between terminal and bridging ligands. In **1b**, two sets of L−M−L angles for the metal and terminal ligands can be found, due to the asymmetry of both metals. One ML_2 unit approaches the R groups, and the repulsion R···L favors the approach of the two L groups, creating a new L···L repulsion due to the congestion on a side of the molecule as shown in

3b, whereas the second ML′$_2$ unit is situated on a more open side. This repulsion L···L is reflected in the angles L−M−L, which increase between 3.0 and 8.0° upon bending, whereas L′−M−L′ changes less than 0.3°. The latter values are similar to those found in **1a**, where only the repulsions R···L can be considered important. However, both ML$_2$ units in **1a** experience such repulsion at only one ligand, as shown in **3a**, and the optimized geometry shows a rocking distortion of the terminal ligands for each metal. The deviation of each fragment can be represented by the angle between the symmetrical position and the bisector of both ligands, the value in the planar form being 6−10° and decreasing to 4−6° in the bent geometry. In conclusion, following the premise above, the planar geometry **1b** is always unstable and its bending energy is also increased by the repulsion L···L, whereas in the bent form the stabilizing contribution of the M···M contact can be added.



3a



3b

Comparison of Theoretical and Experimental Structures. We wanted to check the reliability of the computational results by comparing the calculated and experimental structural data. For the interested reader, we have collected together calculated and experimental structural data as Supporting Information (Table S1). In general, the optimized structural parameters are in good agreement with the experimental data and the following trends can be outlined.

(a) The calculated bending angles θ between two MX$_2$ planes deviate from the experimental ones only when experimental ligands are significantly bulkier than assumed in the model complexes. Nevertheless, the predicted conformational preference for a bent or planar structure is in agreement with the observed geometries in all cases.

(b) Calculated M···M distances are fairly well reproduced, and large deviations can be attributed to bulky ligands and the resulting differences in bending angles θ.

(c) Calculated bond lengths are in good agreement with the experimental lengths. The largest deviations for the M−C$^{\alpha}$, M−π (centroid of the C≡C bond), C$^{\alpha}$−C$^{\beta}$, M−L$_{\sigma}$ (ligand trans to η^1-C≡CR), and M−L$_{\pi}$ (ligand trans to η^2-C≡CR) bonds are 0.030, 0.140, 0.051, 0.085, and 0.061 Å, respectively. The calculated M−π bond length is particularly long compared to experimental data for isomers **1b** but is at most 0.09 Å longer than the experimental values for **1a**. This is probably due to steric congestion on one side of the molecule (**3b**).

(d) Calculated ring angles involving metals and bridging ligands deviate at most 3.3° from the experimental ones, the largest deviations corresponding to experimental complexes with significantly bulkier ligands than in the calculated models.

(e) Calculated L−M−L bond angles deviate significantly from the experimental ones only when the experimental ligand is bidentate but the theoretical model bears two monodentate ligands.

Analysis of the Energy Contributions. For the compounds of type [M$_2$(μ,η^2-C≡CR)$_2$L$_4$], the difference in energy between the planar and bent structures can be associated with the repulsion between R and L groups in the planar form (I_{LR}) and to the interaction between the two ML$_2$ fragments in the bent geometry (I_{MM}):[15]

$$E_b - E_p = I_{MM} + 2I_{LR} \tag{1}$$

Notice that the I_{MM} term includes not only the M···M attractive interaction but also the L···L repulsion, as well as the energy differences between planar and bent structures associated with changes in the bond angles of the metal−alkynyl ring. The repulsive I_{LR} term has been previously found to be important only in bent structures of [M$_2$(μ-XR)$_2$L$_4$] complexes with the substituents in the endo conformation.[13] Such repulsion appears to be small in those compounds with L = PH$_3$, Me and R = H (≤2 kcal mol^{-1}) and increases by about 3 kcal mol^{-1} for R = Me. For compounds with the η^2 coordination mode, one can anticipate a non-negligible repulsion between the substituent and the ligand in the planar conformer, as shown in **3**.

Analysis of Experimental Data

The experimental structural data for the alkynyl complexes are shown in Table 2. The η^1 mode of coordination gives the least stable isomer for the four studied complexes (**M.1d**−**M.4d**, Table 1). Consistently, this isomer is not found among the experimental structures (Table 2). Such a coordination mode appears only in compounds in which one square-planar metal fragment ML$_2$ is substituted by the isolobal TiCp$_2$ group, as in [(C$_6$F$_5$)$_2$Pt(μ,η^1-C≡C^{t}Bu)$_2$TiCp$_2$],[19] as happens also in complexes with alkynyl bridges between two TiCp$_2$ fragments.[5]

As for the preference between planar or bent conformations, the bent structure appears in most of the Pt complexes, in agreement with the results of our calculations. The exceptions to this general rule are compounds **E.13** and **E.17**. The only non-diplatinum complexes known have Rh or Ir occupying either one (**E.1**, **E.9**, **E.14** and **E.15**) or both (**E.16**) of the metal positions. Since Rh and Ir complexes are known to present stronger metal···metal bonding interactions,[12] an enhanced preference for the bent structure in such complexes should be expected in comparison to the platinum-only case, as experimentally found for **E.1**, **E.14**, and **E.16** (Table 2). The **E.13** compound presents a planar structure, while our calculations on **M.1a** and **M.3a** predict a bent structure. A look at the molecular structure indicates that the phenyl rings of the alkynyl bridges and the C$_6$F$_5$ terminal ligands form stacking interactions (C···C distance of 3.11 Å) that replace the steric repulsion in **3** by weakly attractive interactions,[31,32] although the Pt···Pt distance is 0.22 Å longer than in its analogue without phosphines (**E.12**).

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Table 2. Structural Data for Dinuclear Complexes with Alkynyl Bridges[a]

	compd[b]	M···M, Å	α, deg	*θ*, deg	ref	refcode
E.1	$\mathrm{[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2Rh(cod)]^-}$ (**1b**)	2.889	83.1	98	20	MAWJEZ
E.2	$\mathrm{[(Ph_3P)_2Pt(\mu\text{-}C{\equiv}C^tBu)_2Pd(C_3H_5)]^+}$ (**1b**)	3.026	87.1	112	21	TOWJAQ
E.3	$\mathrm{[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CSiMe_3)_2Pd(C_3H_5)]^-}$(**1b**)	3.050	87.1	114	22	WEZWAZ
E.4	$\mathrm{[(^tBuC_2PPh_2)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pd(C_6F_5)_2]}$ (**1b**)	3.157	87.2	125	23	PODGAQ
E.5	$\mathrm{[(^tBuC_2PPh_2)_2Pt(\mu\text{-}C{\equiv}CPh)_2\{Pt(C_6F_5)_2\}_2]}$ (**1b**)	3.197	79.7	112	23	PODLOJ
	$\mathrm{[(^tBuC_2PPh_2)_2Pt(\mu\text{-}C{\equiv}CPh)_2\{Pt(C_6F_5)_2\}_2]}$ (**1b**)	3.222	79.9	114		PODLOJ
E.6	*cis*-$\mathrm{[Pt_2(\mu\text{-}C{\equiv}CPh)_2(C_6F_5)_2(dppe)]}$ (**1b**)	3.270	83.2	126	9	KUMPOX
E.7	$\mathrm{[(Et_3P)Cp^*Rh(\mu\text{-}C{\equiv}CSiMe_3)_2Pt(\mu\text{-}C{\equiv}CSiMe_3)_2Pt(C_6F_5)_2]^{2-}}$ (**1b**)	3.367	81.4	134	24	
E.8	$\mathrm{[Pt_3(\mu\text{-}C{\equiv}CPh)_4(C_6F_5)_4]^{2-}}$ (**1b**)	3.399	82.5	138	25	LEHKOY
	$\mathrm{[Pt_3(\mu\text{-}C{\equiv}CPh)_4(C_6F_5)_4]^{2-}}$ (**1a**)	3.431	81.8	136		LEHKOY
E.9	$\mathrm{[(cod)Rh(\mu\text{-}C{\equiv}CSiMe_3)_2Pt(\mu\text{-}C{\equiv}CSiMe_3)_2Ir(cod)]}$ (**1b**, *Rh−Pt*)	3.003	82.8	106	10	
	$\mathrm{[(cod)Rh(\mu\text{-}C{\equiv}CSiMe_3)_2Pt(\mu\text{-}C{\equiv}CSiMe_3)_2Ir(cod)]}$ (**1a**, *Pt−Ir*)	3.611	80.1	159		
E.10	*trans*-$\mathrm{[Pt_2(\mu\text{-}C{\equiv}CC(OMe)EtMe)_2(C_6F_5)_2(PPh_3)_2]}$ (**1a**)	3.359	82.4	129	26	
E.11	*trans*-$\mathrm{[Pt_2(\mu\text{-}C{\equiv}CC(OH)Ph_2)_2(C_6F_5)_2(PPh_3)_2]}$ (**1a**)	3.407	80.4	129	26	
E.12	$\mathrm{[Pt_2(\mu\text{-}C{\equiv}CPh)_2(C_6F_5)_4]^{2-}}$ (**1a**)	3.431	83.0	141	9	KUMPUD
E.13	*trans*-$\mathrm{[Pt_2(\mu\text{-}C{\equiv}CPh)_2(C_6F_5)_2(PPh_3)_2]}$ (**1a**)	3.651	82.2	180	27	HEDLEH
E.14	$\mathrm{[(Me_3SiC{\equiv}C)_2Pt(\mu\text{-}C{\equiv}CSiMe_3)_2Ir(cod)]^-}$ (**1a**)	3.538	80.5	147	10	
E.15	$\mathrm{[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CSiMe_3)_2Ir(cod)]^-}$ (**1a**)	3.639	79.7	163	20	MAWJID
E.16	$\mathrm{[Ir_2(\mu\text{-}C{\equiv}CSiMe_3)_2(cod)_2]}$ (**1a**)	3.339	82.1	134	28	VAKWOT
E.17	*trans*-$\mathrm{[Pt_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)(C_6F_5)_2(PPh_3)_2]}$[c]	2.815	93.8	178	29	NUWTUU

[a] All compounds present an η^2 coordination mode of the bridging ligands (**1a**,**b**). [b] For molecular topologies see **1**: cod = 1,5-cyclooctadiene; dppe = 1,2-bis(diphenylphosphino)ethane. [c] Bond angles involving H atoms have been estimated for a Pt−H distance of 1.78 Å.[30]

Two structures with η^2 ligands have been experimentally identified: V-shaped (**1b**) in **E.1**−**E.7** and rectangular (**1a**) in **E.10**−**E.16**. More interesting, in the trinuclear compounds **E.8** and **E.9** one ring has the rectangular and the other the V-shaped form. In agreement with the calculations, the V-shaped isomers are more strongly bent ($98 < \theta < 138°$) than the rectangular ones ($129 < \theta < 180°$). Notice that the phosphine ligand in the Pt complexes is always found to be cis with respect to the σ-alkynyl ligand (L′ in **3**, compounds **E.2**, **E.4**−**E.6**, **E.10**, **E.11**, and **E.13**), thus avoiding steric phosphine···R repulsions.

The presence of one hydrido bridge implies that only six electrons are available for σ-bonding within the MHCM ring (i.e., the framework electron count (FEC) is 6) and a short M···M distance should be expected,[17] as actually found. The presence of metal−metal bonding is confirmed by a decreased distance in comparison with analogous complexes with FEC = 8.[15] In Table 2 we find a mixed-ligand complex that has one hydrido and one μ,η^2-alkynyl bridging ligand (**E.17**). The larger tendency of bridging hydrido complexes to present a planar form,[15] together with the presence of bulky phosphines, may favor such a geometry in this compound.

The cyclooctadiene ligand in **E.15** can be modeled by two ethylene ligands, as in the **M.2** isomers. For this model, the planar and bent forms are very close in energy (Table 1) only for the **1a** isomer, which is the experimentally found structure. In contrast, **E.1** is found as a bent **1b** isomer, for which the model calculations (**M.2b**, Table 1) predict the bent form to be more stable by 10 kcal mol^{-1}.

Dynamic Behavior: Some Hints

As summarized in the introductory section of this paper, there is spectroscopic evidence for the coexistence in solution of different conformers of the binuclear compounds under study. This is consistent with the similar stabilities of different conformers found in our calculations. However, for such intramolecular reactions to occur thermally, a low activation energy is needed. The interconversion of the different conformers can proceed through the pathways presented in Scheme 1. Hence, we can obtain a rough estimate of the activation energies as differences in energy between the different forms involved in each process.

Since, according to the present calculations, the compounds with η^2-alkynyl are more stable in the bent form and the planar form is within thermal energy, one can anticipate that such compounds should present dynamic behavior in solution through a bent-planar-bent interconversion pathway (pathway A in Scheme 1), and the energy barrier or this process, $E_a{}^A$, can be estimated from eq 2.

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

The ring inversion for the η^2-alkynyl complexes has been proposed on the basis of NMR spectra in a couple of cases.[9,10] We can also get a crude estimate of the activation energy from our calculations (eq 2), obtaining upper limits of 7.8 and 13.9 kcal mol^{-1} for rectangular- and V-shaped isomers, respectively, and 6.6 kcal mol^{-1} for the η^1-alkynyl complexes. The substitution of the terminal phosphine ligands by a less bulky methyl favors the ring inversion, decreasing the barrier in all

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Scheme 1

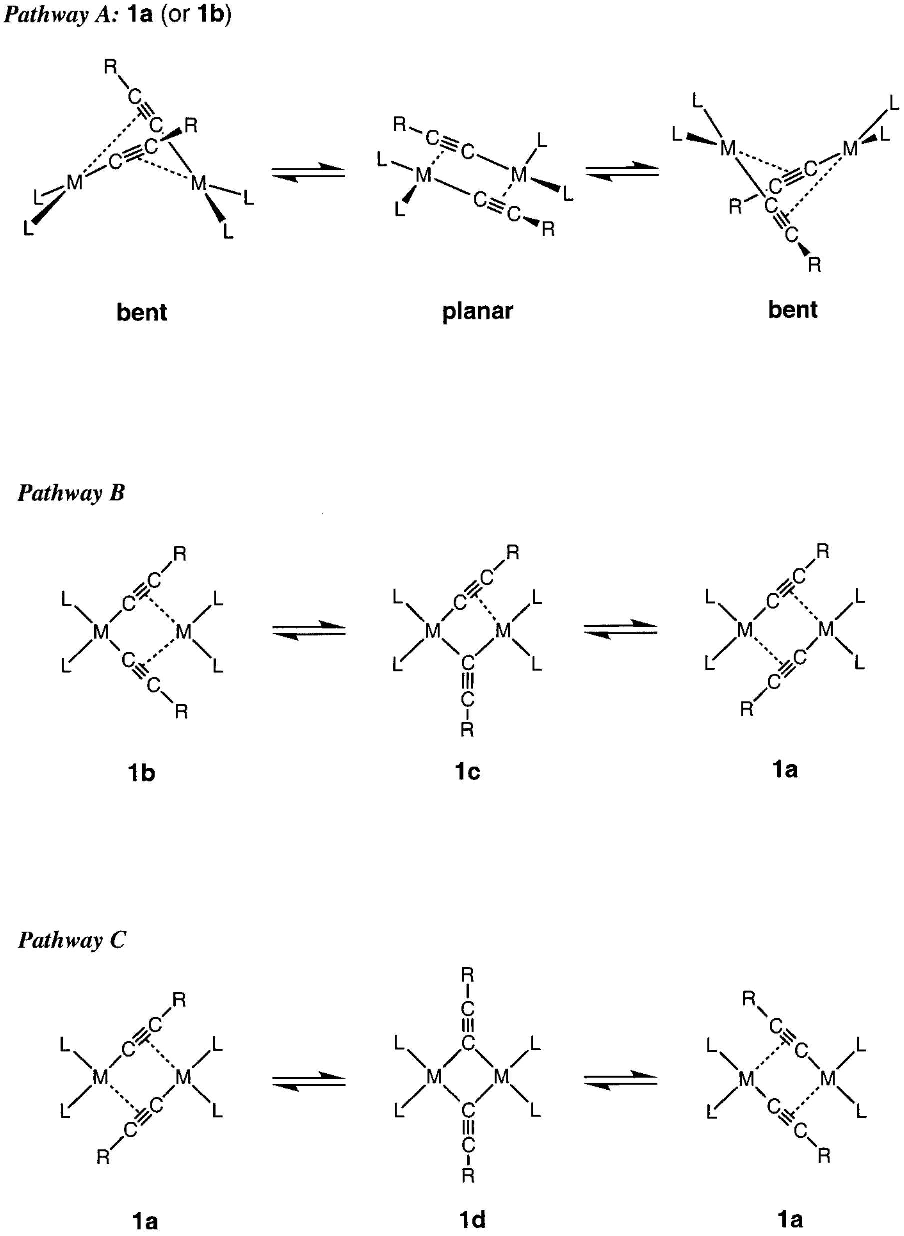

Table 3. Energy Barrier (in kcal mol^{-1}) for Dynamic Processes in Alkynyl Complexes [$Pt_2(\mu$-C≡CH$)_2L_4$] with Different Terminal Ligands (See Scheme 1)[a]

compd	term. ligand	$E_a{}^A$(**1a**)	$E_a{}^A$(**1b**)	$E_a{}^B$	$E_a{}^C$
M.1	PH_3	7.8	13.9	2.0	12.0
M.2	C_2H_4	3.3	10.0		5.4
M.3	CF_3^-	2.1	8.8	5.6	19.6
M.4	Me^-	0.3	1.8	5.1	11.0

[a] The energies have been estimated for pathways A (**1a** and **1b** isomers), B, and C by eqs 2−4, respectively.

isomers to less than 4 kcal mol^{-1} (Table 3), due to decreased repulsion. These values agree with the experimental energy barrier of about 10 kcal mol^{-1} measured by NMR for the PtRh dimer **E.1**.[20] We note that ring inversion is not observed when the second metal is tetrahedral,[23] where the $d^8\cdots d^8$ interaction between metal atoms is absent.

A second type of dymamic process can occur in the [$L_2M(\mu,\eta^2$-C≡CR$)_2ML_2$] complexes involving an isomerization of the coordination mode of the alkynyl ligands ($\eta^2 \rightarrow \eta^1 \rightarrow \eta^2$), which can take place in combination with the ring inversion (pathway B in Scheme 1). In fact, the platinum compounds with η^2-alkynyl bridges are calculated to have similar energies in the bent conformation, and those compounds are likely to present dynamic behavior in solution.

All compounds with V-shaped bridges (**E.1**−**E.7**) are synthesized from the *cis*-bis(alkynyl) complexes of the type [L_2Pt(C≡CR$)_2$], which behave as bidentate ligands toward a second metal that carries two labile ligands.[9,21−23] In contrast, the rectangular isomers (**E.10**−**E.13**) can be obtained from *trans*-bis(alkynyl) complexes, for which a ligand rearrangement is observed.[26,27,33] For the trinuclear complexes **E.8** and **E.9**, synthesized from [Pt(C≡CR$)_4]^{2-}$, one could expect the formation of two V-shaped rings, but a rearrangement leads to the existence of one V-shaped and one rectangular unit

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within the trinuclear molecule.[10,25] This result suggests a relatively facile transformation of isomer **1b** into **1a**,[9,10,20] in agreement with our finding that the rectangular isomer is more stable than the V-shaped one. A likely mechanism for this process is that of pathway B (Scheme 1), and its activation energy can be described by

$$E_a{}^B \approx E(\mathbf{1c}) - E(\mathbf{1a}\text{ or }\mathbf{1b}) \quad (3)$$

which can be deduced from the results of our calculations. The results for the Pt phosphine complex (Table 3) indicate a quite low barrier (2 and 6.5 kcal mol^{-1} for the **b** → **a** and **a** → **b** processes, respectively), in agreement with the experimental result reported by Forniés et al.,[9,10] who note that the isomerization is faster than the ring inversion. In contrast, complexes having methyl as terminal ligands present larger values of $E_a{}^B$. The nature of the terminal ligand is seen to significantly affect the relative energies of the different isomers. Hence, whereas a similar barrier is calculated with η^2-ethylene ligands, the activation energies are somewhat higher for CH_3 and CF_3 terminal ligands (5.1 and 5.6 kcal mol^{-1}, respectively), although still low enough to allow for dynamic behavior.

Another dynamic process involving rearrangement of the alkynyl coordination modes is the interconversion of the two alternative rectangular forms **1a** (pathway C, Scheme 1), which has been detected by NMR for a Pt−Ir heteronuclear compound.[10] A crude estimate of the activation energy for such a process can be obtained as the energy difference between geometries **1d** and **1a** from our calculations on model compound **M.4** (11.0 kcal mol^{-1}). That barrier is decreased when the terminal ligand is an olefin and the complex is in a bent form (5.4 kcal mol^{-1} for **M.2a** → **M.2d**). A somewhat higher free energy of activation (12.2 kcal mol^{-1}) has been experimentally found for the analogous compound with cyclooctadiene as terminal ligand (**E.14**),[10] probably because its higher steric bulk prevents bending, as seen by the fact that complexes with cod are much less bent (**E.9**, **E.14**, and **E.15**):

$$E_a{}^C \approx E(\mathbf{1d}) - E(\mathbf{1a}) \quad (4)$$

The irreversible isomerization of η^2 to η^1 has been observed in the preparation of heterodinuclear complexes with early transition metals.[19] Mealli, Godinho, and Calhorda[8] have calculated a barrier for such a process in the trigonally coordinated Cu(I) analogue to be 7 kcal mol^{-1}, whereas Erker et al.[34] have reported a barrier of 12−15 kcal mol^{-1} for $[Cp_4Zr_2(\mu\text{-}C{\equiv}CR)_2]$. No fluxional behavior has been reported so far for the mixed hydrido−alkynyl complexes.[29]

Conclusions

The combined use of theoretical studies and a structural database analysis has allowed us to establish some guidelines for understanding the structural choice between the possible conformers in binuclear compounds of d^8 transition metals with σ,π bridging ligands of types $[M_2(\mu\text{-}C{\equiv}CR)_2L_4]$, in which the alkynyl ligand presents η^1 or η^2 coordination.

A systematic ab initio study was carried out for the different conformers of complexes in which the coordination modes of the bridging ligand and the terminal ligands were varied. Comparison of the relative energies of the different conformers allows one to estimate different contributions. In general, our predicted conformation for a particular molecule is in good qualitative agreement with its experimentally determined structure. Simplifications introduced in the theoretical model, especially by replacing bulkier substituents with hydrogen, may alter the relative stabilities of the different conformers within a few kilocalories per mole. An analysis of the experimental data confirms the general trends revealed by the theoretical study.

Furthermore, isomer **1a** is always found to be the most stable in the bent form for model compounds, whereas **1c** and **1d** are higher in energy due to the electron-deficient nature of η^1-bridged complexes. Our results suggest that important repulsions between bridge substituents and terminal ligands in complexes with η^2 ligands favor the higher stability of isomer **1a** relative to **1b**. For a given molecule, the steric repulsion in **1b** can be decreased via a greater degree of bending.

Some hints on the possible mechanisms of dynamic processes can be obtained by comparing energies of different conformers: (a) ring inversion of alkynyl complexes may be prevented by bulky terminal ligands, (b) interconversion of σ,π isomers observed in alkynyl complexes may proceed through a bent $\eta^1{:}\eta^2$ intermediate, and (c) the interconversion of alternative $\eta^2{:}\eta^2$ isomers **1a** detected for a heteronuclear complex is more likely to proceed through the $\eta^1{:}\eta^1$ intermediate **1d**.

Experimental Section

Computational Details. All ab initio calculations were performed with the GAUSSIAN94 suite of programs.[35] A molecular orbital ab initio method with introduction of correlation energy through the second-order Møller−Plesset (MP2) perturbation approach was applied,[36] 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 terminal ligands, for which a minimal basis set was used.[37] More details on the basis set can be found in a previous paper.[13] The internal structures of the phosphine (P−H = 1.420 Å; H−P−H = 93.2°), methyl (C−H = 1.092 Å; H−C−H = 110.2°), perfluoromethyl (F−C−F = 104.4°), and ethylene (C−H = 1.087 Å; C−C−H = 120.6°; H−C−H = 114.5°) ligands were kept frozen in the optimizations. All other geometrical parameters were optimized to find the most stable structure for each compound. To evaluate the energy differences between the bent and planar geometries, optimizations were performed for the least stable structure of

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each compound, keeping the bending angle θ fixed at 180° for the planar form or at ca. 120° for the bent form.

Ab initio MP2 calculations were performed on model complexes $[Pt_2(\mu\text{-}C{\equiv}CH)_2L_4]^{n+}$ ($L = PH_3$, CH_3, CF_3, and $\eta^2\text{-}C_2H_4$) in planar and bent forms (**2**) for each isomer shown in **1**. A total of 32 structures of 4 compounds were optimized, with the only restrictions that the terminal ligands were kept frozen and the bending angle was kept fixed in 16 structures. The atomic coordinates of the 16 minima are supplied as Supporting Information. To facilitate identification of the different model compounds whose formulas can be found in Tables 1 and 2, we label them with an **M** (Table 1) followed by a sequential number and a lower case letter indicating the type of isomer according to the labeling scheme in **1**. Similarly, the experimentally determined structures are identified by a capital letter **E** (Table 2).

Structural Database Search. The collection of structural data was obtained through a systematic search of the Cambridge Structural Database[11] (version 5.22) for compounds of general formula $[M_2(\mu,\eta^y{:}\eta^z\text{-}C{\equiv}CR)_2L_4]$ and $[M_2(\mu,\eta^z\text{-}C{\equiv}CR)(\mu\text{-}H)L_4]$ (y, $z = 1, 2$), in which M was imposed to be a metal at its oxidation state with a d^8 configuration: Co(I), Rh(I), Ir(I), Ni(II), Pd(II), Pt(II), Au(III), Ru(0), and Os(0). The bending angle θ was obtained as that between the two MX_2 planes, where X is C for the η^1-bonded metal and the centroid of the C≡C bond in the case of the η^2-bonded metal. For the hydride ligands not localized in the crystal structure determinations, the angles have been estimated from standard M−H distances reported by Teller and Bau[30] in the molecule with idealized local symmetry.

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Supporting Information Available: A table comparing the main bonding parameters in calculated and analogous experimental structures (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org. The atomic coordinates of the 16 optimized structures, identified with the label employed for compounds in Table 1, have also been deposited and can be accessed at the following Internet address: http://kripto.qi.ub.es/~gee/suppl/ccr.html.

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