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Articles

Theoretical Overview of Pd(I) and Pt(I) Dimers with Bridging Phosphido Ligand(s)

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A review of all of the known structural stereotypes of dimeric Pt(I) or Pd(I) systems with at least one bridging phosphido group is presented. The nature of the direct metal−metal interaction is affected by the number, nature, and disposition of the various coligands. It appears that in some cases a bent M−M bond is by itself a center of nucleophilicity. On the other hand, it is experimentally known that the bridging phosphido ligand is a competing nucleophile, giving rise to an *agostic* interaction in Pd_2, but not in Pt_2, derivatives. MO theory is used to outline the major electronic features and correlation between different prototypes. Besides a qualitative approach based on the EHMO method, DFT and MP2 methods were used to reproduce the experimental structures and to explore the possibility of unknown tautomers.

Introduction

The chemistry of dimeric Pt(I) or Pd(I) systems with bridging phosphido groups has been revitalized in recent years thanks to the work of Leoni, Pasquali, et al.[1] In this paper we summarize all of the molecules, deposited in the Cambridge Structural Database,[2] which contain the three-membered ring M_2P. Occasionally, the original publications have also reported some kind of theoretical analysis. In this paper, we attempt to provide an overview of the chemical bonding and the implicit reaction capabilities of the various species under the unifying concepts of perturbation theory. When necessary, ab initio MP2 and DFT calculations were carried out to reproduce basic experimental trends. The DFT calculations were employed to give quantitative support to the various MO architectures built up from the simple extended Hückel calculations.

Result and Discussion

Table 1 presents the relatively small number of different stereotypes (**a**−**h**) which have been identified for dimers containing the $M_2(\mu\text{-}PR_2)$ unit, M = Pt, Pd. This selection is limited to 16-electron metal centers with planar coordination. The gross features of the selected compounds **1**−**25** (their identities are listed Table 1)[3−25] can be described as follows.

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(1) See, for example, the references in the following: (a) Leoni, P.; Papucci, S.; Pasquali, M. *Polyhedron* **1998**, *17,* 3145. (b) Leoni, P.; Pieri, G.; Pasquali, M. *J. Chem. Soc., Dalton Trans.* **1998**, 657.

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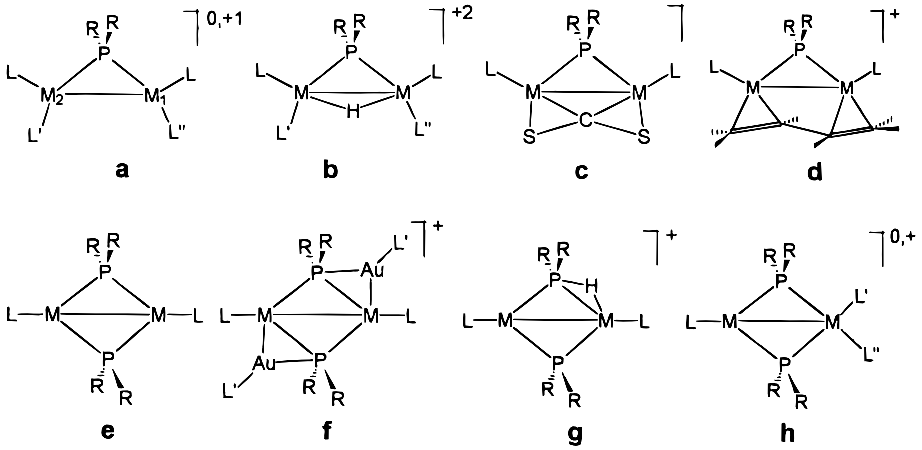
10.1021/ic990275j CCC: $18.00

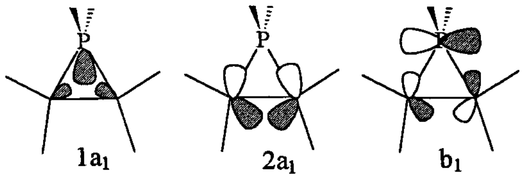
Table 1. Binuclear Pd and Pt Complexes Which Contain the Inner Core $M_2(\mu\text{-}PR_2)$ and Appear in the Cambridge Structural Database (April 1998)[2]



type	compd refcode and no.	M	R	L	L′/L″	M_1-M_2	$M-P_{br}$	ref
a	HASLES, **1**	Pd	^{t}Bu	P^tBu_2Et	O_3SCF_3	2.648	2.227	3
a	JIFHAH, **2**	Pd	Ph	PPh_3	dippm[a]	2.688	2.248	4
a	LANNAP, **3**	Pd	^{t}Bu	PH^tBu_2	2CO	2.682	2.272	5
a	POMPOW, **4**	Pd	^{t}Bu	$PHCy_2$	$2PHCy_2$	2.834	2.267	6
a	POMPUC, **5**	Pd	^{t}Bu	PMe_3	$2PMe_3$	2.692	2.254	6
a	TAQBES, **6**	Pd	^{t}Bu	$PHCy_2$	$PHCy_2 + CO$	2.744	2.273	7
a	TEXKOW, **7**	Pd	^{t}Bu	PMe_3	dppm[b]	2.687	2.262	8
a	TEXKUC, **8**	Pd	^{t}Bu	η^1-dppm	dppm[b]	2.722	2.291	8
a	VIGDEU, **9**	Pd	^{t}Bu	PH^tBu_2	$\eta^4\text{-}OC_6H_5$	2.662	2.255 2.260	9
a	not avail., **10**	Pd	Ph	PPh_3	$Ph_2P(C_6H_4)$	2.655	2.260	10
b	JELCUY, **11**[c]	Pt	Ph	PPh_2OH	PPh_2O^-	2.907	2.305	11
b	CARFOQ, **12**[d]	Pt	Ph	PPh_3	$PPh_3 + Ph$	2.900	2.250 2.160	12
b	DOJGOY, **13**	Pt	Ph	PPh_3	$PPh_3 + Ph$	2.885	2.239 2.289	13
c	ZEPMUC, **14**	Pd	^{t}Bu	PPh_3	CS_2	2.708	2.269	14
d	HASLAO, **15**	Pd	^{t}Bu	PH^tBu_2	butadiene[e]	2.751	2.273	3
d	TAQBIW, **16**	Pd	^{t}Bu	$PHCy_2$	butadiene[e]	2.713	2.253	7
e	FUVMAK, **17**	Pd	^{t}Bu	PMe_3	P^tBu_2	2.571	2.330	15
e	HEMPEU, **18**	Pd	Cy	PCy_2OPh	PCy_2	2.620	2.317	16
e	VONTIB, **19**	Pd	^{t}Bu	PH^tBu_2	P^tBu_2	2.594	2.335	17
e	DPTPPT, **20**	Pt	Ph	PPh_3	PPh_3	2.604	2.31	18
e	not avail., **21**	Pt	^{t}Bu	PH^tBu_2	CO	2.613	2.312[h]	19
f	SAXPUC, **22**	Pt	Ph	PPh_3	PPh_2	2.660	2.315	20
g	KOSTIV, **23**	Pd	^{t}Bu	PH^tBu_2	PH^tBu_2[f]	2.611	2.31	21−25
h	not avail., **24**	Pt[g]	^{t}Bu	PH^tBu_2	H, PH^tBu_2	2.640	2.290	22
h	YEXXUU, **25**	Pd,Pt[g]	Ph	PPh_3	Ph, Ph	2.658	2.354[i] 2.243[j]	23

[a] dippm = $^iPr_2PCH_2P^iPr_2$. [b] dppm = $Ph_2PCH_2PPh_2$. [c] Total charge = 0 on account of two anionic ligands. [d] Total charge = +1 on account of one anionic ligand. [e] but1 = 2-methyl-1,3-butadiene. [f] Agostic interaction. [g] d^8 metals. [h] Average value. [i] $Pt-P_{br}$ distance. [j] $Pd-P_{br}$ distance.

Chart 1



Type a. LL′M(μ-PR$_2$)MLL′ complexes (1−10). By considering the in-plane L and L′ ligands as the donors of two σ electron pairs, the bonding within the M_2P framework stems from three occupied MOs (i.e., $1a_1$, b_1, and $2a_1$), schematically shown in Chart 1. The first level stems from the interactions of *radial* orbitals, and the other two stem from the *tangential* ones. Moreover, only the electrons in the $2a_1$ MO can be thought as belonging to d^9 metals (singly occupied d_π orbital of the typical L_2M fragment[24]) while the other filled bonding levels originate from the σ and p_π *lone pairs* of the phosphido bridge. The level pattern is analogous to that of σ-aromaticity in cyclopropane,[25] which has been adapted also to triangular metal clusters.[26]

Types b−d. LL′M(μ-PR$_2$)(μ-acceptor)MLL′ Complexes (11−16). Formally, these species derive from those of type **a** when an electrophilic atom or group is added over the M−M linkage. The nucleophilicity of the latter is consistent with the filled MO $2a_1$ in the frontier region (Chart 1). In actuality, there is no experimental evidence that the protonation of a type **a** complex leads straightforwardly to one of type **b** containing a bridging hydride. Most probably the required oxidative addition process is a difficult one. Nonetheless the Pt_2 complexes **11**−**13** (obtainable through different routes) are formally consistent with the above picture (oxidation of the metal atoms from d^9-d^9 to d^8-d^8 and evolution of the single M−M bond into a weaker three-center (M_2H)/two-electron interaction).

The idea of nucleophilicity of the M−M linkage in the species

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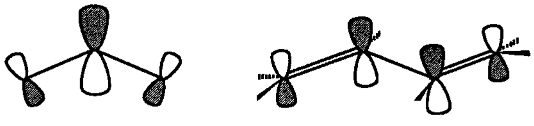
(26) Mealli, C. *J. Am. Chem. Soc.* **1985**, *107*, 2245.

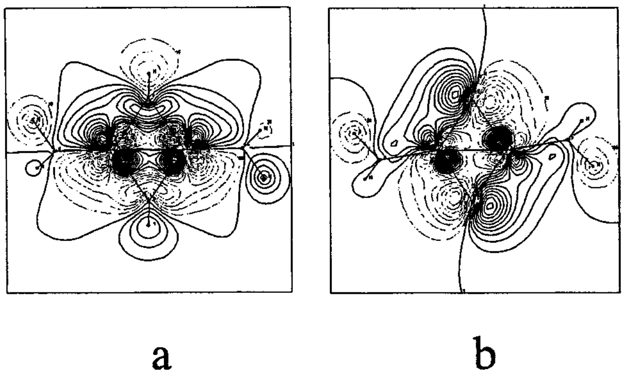
Chart 2



of type **a** is corroborated by the existing complexes **14−16** where small molecules with residual electrophilicity in their central region are added up. In particular, the molecules carbon disulfide and butadiene are well tailored to donate two σ lone pairs and to accept backdonation into an overall π^* level which is cylindrically symmetric in the middle region. The drawings in Chart 2 show the empty CS_2 and C_4H_6 combinations which can interact with the Pd_2 combination $2a_1$. Allyl, cyclopentadienyl, and other conjugated organic groups may exert similar functionality. Although no structural characterization of the latter adducts has been reported for phosphido-bridged systems, structures with a bridging halide ligand are available.[27]

General theoretical ideas have been reported[28] that substantiate the above models. In particular, a qualitative MO analysis of the CS_2 adduct **14** has been presented.[29] Also there are ab initio studies for the allyl derivative with one halide in place of the phosphido bridge.[30] We have tried to reproduce, at DFT and MP2 levels, C_{2v} models of **14** with the simplest H substituents at all of the phosphorus atoms.[31] Although the optimized structure is substantiated by no imaginary frequency, the agreement between the experimental and calculated CS_2 geometry is not excellent. In particular, the bridging CS_2 group is insufficiently bent (by at least 8° with respect to the experimental value of 145.6°) so that the Pd−C distances are too long (by ca. 0.2 Å). It is known that the routine MP2 and DFT approaches may produce unsatisfactory results in peculiar cases such as the present one. It has been pointed out[32] that whenever the ionic component of the bonding is overestimated it may be necessary to evaluate properly *the dynamic correlation* between the ground and the excited states. Indeed, we plan a collaborative work[33] to perform CASSCF[34] calculations for a model of **14**. Electronic correlation problems are typically found in polyhapto-bonded CS_2 metal complexes. At the EHMO level, for instance, the repulsion between *in plane* sulfur lone pairs is always overestimated and prevents a sufficient bending of the triatomic.[35−37]

Chart 3



Type e. LM(μ-PR$_2$)$_2$ML (17−21). In these species, a second phosphido bridge formally replaces two terminal L ligands in the complexes of type **a**. We have optimized the models of the Pt and Pd analogues in C_s symmetry at the DFT level. While the platinum structure has a quasi D_{2h} skeleton [with linear P_{term}−Pt−Pt vectors and a rhomboidal $Pt_2(\mu\text{-}P)_2$ unit], the palladium analogue has slightly asymmetric Pd−P_{bridge} distances and nonlinear P_{term}−Pd−Pd angles.[38] It is noteworthy that the latter deformation has a minimum energy gain of <1 kcal/mol with respect the optimized C_{2v} structure (with one imaginary frequency).

Consistent with the local trigonal coordination of the metals, the highest pair of filled MOs consists of the two symmetry combinations of the d_{xy} orbitals with an inverted order (DFT level) for Pt_2 and Pd_2 species, respectively. While the HOMO of the former (see drawing **a** in Chart 3) is the *in-phase* combination destabilized by the *radial* phosphido orbitals, the *out-of-phase* combination (**b**) lies higher in the Pd_2 analogue and involves a significant contribution of the *tangential* P orbitals. The inversion is not caused by the slight deformation of the Pd_2P_2 rhombus but is attributable to the different diffuseness of the d metal orbitals themselves. Potentially, a HOMO, with different percentages of metal and phosphido character, can determine the reactivity of the given species toward electrophiles (see below).

Since the L−M−M−L grouping is almost collinear, the M−M bond stems from the σ interaction between two hybrid $x^2 - y^2$ orbitals, their antibonding combination being empty. Importantly, the M−M bonding MO is no more bent as it was $2a_1$ (see Chart 1) and, in comparison with the compounds **1−10** (type **a**), the M−M separation in **17−21** appears definitely shorter. In contrast, the two highest filled MOs, with dπ and dπ^* characters (Chart 3), concentrate electron density at the metals and are the cause for the observed nucleophilicity of the species.

Type f. LPt(μ-PR$_2$AuL)$_2$PtL (22). A clear example of the nucleophilicity of the dimers of type **e** is clearly shown by the

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(31) Selected distances (Å) and angles (deg) from DFT and MP2 (in parentheses) calculations: Pd−Pd = 2.789 (2.830); Pd−P_{bridge} = 2.290 (2.328); Pd−P_{term} = 2.347 (2.349); Pd−C = 2.495 (2.485); Pd−S = 2.648 (2.535); C−S = 1.614 (1.642); Pd−P_{bridge}−Pd = 75.00 (74.87); Pd−Pd−P_{term} = 161.95 (159.67); C−S−C = 163.18 (153.63).

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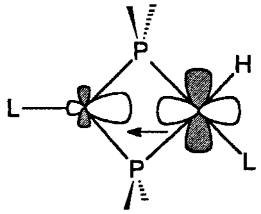
(37) Galindo, A.; Mealli, C. *Inorg. Chem.* **1996**, *35*, 2406.

(38) A selection of the optimized geometrical parameters (Å and deg) for the Pd_2 and Pt_2 models of **e**-type complexes are as follows (the corresponding experimental values of the structures **18** and **20** are given in parentheses): Pd_1−Pd_2 = 2.687 (2.620); Pd_1−P_{bridge} = 2.414 (2.317); Pd_2−P_{bridge} = 2.432 (2.316); Pd−P_{term} = 2.333 (2.236); Pd_1−P_{bridge}−Pd_2 = 67.09 (68.87); Pd_1−Pd_2−P_{term} = 170.52 (173.9). Pt_1−Pt_2 = 2.696 (2.604); Pt_1−P_{bridge} = 2.402 (2.31 av); Pt−P_{term} = 2.280 (2.23 av); Pd_1−P_{bridge}−Pd_2 = 68.35 (68.54).

Chart 4



reactivity toward LAu^+ fragments. Two of the latter are jointly added by one metal and one phosphido group although the Pt−Au interactions seem comparatively stronger than the P−Au ones.[20] The resulting structure of **22** is qualitatively in agreement with the ideas outlined above as also the original authors pointed out the nucleophilicity of the filled d_π orbital combinations in the frontier region of the precursor.[20] The overall electronic features of **22** are probably worth a complete theoretical analysis at the ab initio level.

Type g. LPd(*μ*-PR$_2$)$_2$(*μ*-PR$_2$H)PdL (23). The elegant studies of Leoni, Pasquali, et al.[5] have shown that the protonation of the Pd_2 species LPd(μ-PR$_2$)$_2$PdL (R = ^{t}Bu) (type **e**) leads ultimately to compounds of type **g** (see Table 1). NMR spectroscopy and the X-ray structure of **23** indicate that a PH linkage is engaged in an *agostic* type interaction[39] while the phosphine ligand (formed in situ) bridges the metal atoms. In other words, the phosphido p_π electron pair (see MO b_1 in Chart 1) which is used to saturate the metals in the species **a**−**e** is now engaged with the added proton. One metal atom is only partially saturated by the electron density of the PH linkage itself. We will address below in more detail the electronic structure of this species together with those of the stereotypes **h**.

Type h. LM(*μ*-PR$_2$)$_2$ML$_2$ (24 and 25). Leoni, Pasquali, et al. have obtained the Pt_2 complex **24** with one hydride among the terminal ligands.[22] This type of structure also has been observed in the Pt−Pd dimer **25**, with two terminal phenyl ligands on the Pt atom.[23] Irrespective of the metal, the structure observed for **24** can be considered a tautomer of **23** (*agostic* type **g**). In principle, if a proton is added to a complex of type **e**, it may not stay linked to the P bridging atom but shift to a terminal position thus forming a hydride because of the oxidative addition process. Accordingly, the two d^8 metals (square and trigonal planar, respectively) would be joined via the dative M−M bond from the nonbonding $x^2 - y^2$ lone pair of the former to an empty σ hybrid of the latter (Chart 4). In any event, the above migration process is questionable because the *agostic* derivative of type **g** (**23**) is obtainable through the direct acidification of a Pd_2 species of type **e** but the corresponding Pt_2 compound **24** (type **h**) is formed through a quite different route. The latter starts from an already d^8−d^8 dimer, L$_2$Pt(μ-PR$_2$)$_2$PtL$_2$, which contains no M−M bond.[22]

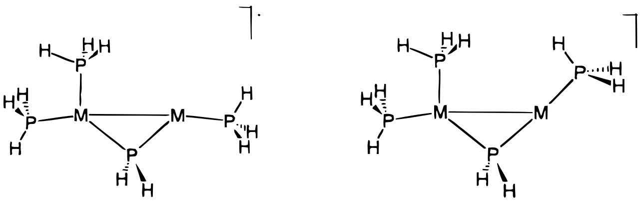
In previous HF and DFT treatments of both the Pd_2 and Pt_2 dimers **23** and **24** (CH_3 groups were used in place of ^{t}Bu ones) only the positions of the phosphorus H substituents were optimized over the skeleton of the heavier atoms, obtained from X-ray structures.[22] Significantly, the P−H *agostic* tautomer is reproduced for the Pd_2 species while the structure with a terminal hydride ligand (type **h**) is preferred by the Pt_2 analogue. As mentioned, the result is in good agreement with the different nature of the HOMO pointed out for the Pd_2 and Pt_2 precursors of type **e** (Chart 3) as the potentiality of the phosphorus p_π orbital as a donor is finely tuned up.

Table 2. Energy and Selected Structural Parameters[a] of the Four Optimized Models with Formula $(PH_3)_2M_2(PH_2)(PH_2H_n)H_{1-n}$, M = Pd, Pt, n = 0,1[b] (Experimental Values Are Reported in Parentheses When Available)[c]

	type **g**	type **h**	type **i**		type **j**	
	Pd	Pt	Pd	Pt	Pd	Pt
M_1-M_2	2.699	2.727	2.768	2.778	2.779	2.774
M_1-P_1	2.361	2.326	2.401	2.331	2.421	2.336
M_2-P_2	2.378	2.274	2.406	2.344	2.360	2.277
M_1-P_3	2.696	2.368	3.700	3.715	4.096	4.003
M_2-P_3	2.372	2.297	2.390	2.340	2.418	2.363
M_1-P_4	2.356	2.456	2.287	2.236	2.295	2.288
M_2-P_4	2.329	2.293	2.289	2.249	2.302	2.294
$H-M_1$	2.054	1.636				
H_1-P_3	1.469	2.559				
$M_1-M_2-P_2$	177.6	176.4	164.9	164.8	153.2	156.3
$M_1-M_2-P_3$	63.8	55.4	91.4	92.7	103.8	103.0
$M_1-P_4-M_2$	70.4	70.0	74.4	76.6	74.4	73.6
$M_2-M_1-P_1$	162.9	145.7	164.9	170.8	106.5	110.8
$H-M_1-M_2$	84.8	130.1				
ΔEs (Pd species)	0.00		0.88		2.23	
ΔEs (Pt species)		0.00		4.48		5.79

[a] Distances (Å), angles (deg), energy (kcal/mol). [b] Atomic labeling can be interpreted as follows. P_1 and P_2 refer to the terminal phosphines linked to the metals M_1 and M_2, respectively. P_3 and P_4 are the bridging phosphorus atoms (P_3 is occasionally involved in the *agostic* interaction with the H bound to atom M_1). [c] The position of the relevant H atom could not be determined from the X-ray analyses. Hence, the PM(μ-P)$_2$MP skeletons appear to have a higher pseudo symmetry.

Chart 5



i **j**

We have attempted full MP2 optimizations of the model compounds **23** and **24** with H substituents at the P atoms. The results are summarized in the first two columns of Table 2. The stereoisomers **g** and **h** have been optimized for the Pd_2 and Pt_2 dimers, respectively, and there is no evidence that the alternative stereoisomer exists in either case. This result agrees with the greater propensity of platinum to undergo oxidative addition, in line with the larger enthalpy expected for the Pt−H vs Pd−H linkage.[40] In general, the agreement between calculated and experimental structures is relatively good although the calculated M−M and M−P distances are long.

As reported in Table 2, two additional tautomers, **i** and **j** (Chart 5), could be optimized for either the Pd_2 or Pt_2 derivative. In any case, the energetics of **i** and **j** are a few kilocalories/mole higher than those of the models **23** and **24** (types **g** and **h**, respectively) but the calculated frequencies confirm their reliability as minima of the PES. The isomer **j**, which lies higher in energy, seems chemically reasonable. In fact, analogously to Chart 4, the linearly coordinated d^{10} metal (right side) may use its populated z^2-type orbital for donation into an empty σ hybrid of the facing d^8 metal (T- shaped). On the other hand, the presence of two terminal PR_3 ligands on the same side of

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Chart 6

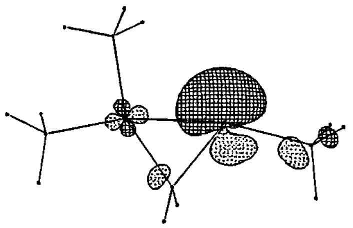
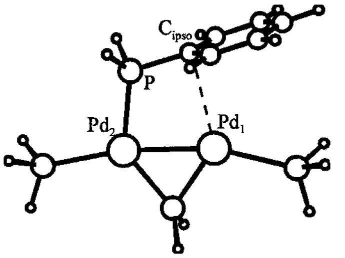


Chart 7



the M−M bond may cause a steric problem which is small only in presence of H substituents. Alternatively, an appropriate diphosphine chelate ligand could avoid the hindrance. More surprising is the isomer of type **i** because of the vacant coordination site at the rightmost metal atom. According to EHMO calculations,[41] an empty metal hybrid (illustrated in Chart 6 by a CACAO drawing[42]) lies relatively low in energy and confers a clear-cut electrophilicity to the system.

There are many stable compounds of type **a** (**1**−**10**) with an added terminal ligand with respect to the species **i**. Significantly, the hybrid of Chart 6 seems clearly directed toward one phosphorus atom of the fully coordinated metal rather than to the site of the missing ligand. Indirect support for this stabilizing interaction comes from the experimental structure of the dimer $[(dppp)Pd]_2^{+2}$, dppp = $PPh_2(CH_2)_3PPh_2$, where two noncollinear, and apparently unsaturated, chelate L_2M fragments adhere to each other.[43] On each side of the Pd−Pd vector, one phosphine of a dppp ligand occupies a semibridging position. According to the results of ab initio calculations, the authors[43] observed residual interactions between the latter P atom and the more remote metal. Since a phenyl substituent of the semibridging phosphine lies roughly parallel to the Pd−Pd linkage, the interaction of the *ipso* carbon with the metal was also hypothesized but found negligible. Similar considerations apply also to the optimized structure of type **i** even though the relevant Pd−Pd−P angle (involving the upper phosphine in Chart 7) is significantly more open than that found in $[(dppp)Pd]_2^{+2}$ (92° vs 75°).

Also, the NMR data in solution[14] for $[(Ph_3P)Pd(\mu\text{-}P^tBu_2)Pd(PPh_3)_2]^+$ (whose crystal structure is not available) seem to exclude any extrastabilization due to the potential interaction of the phenyl C_{ipso} atom and one metal (see a possible model in Chart 7). Indeed, evidence for this interaction is found in other monomeric Pd or Pt complexes which would be otherwise unsaturated.[44] In another comparable case, the M−C_{ipso} interaction was unseen in solution, but was detected from the ^{13}C NMR solid state spectra.[45] For a most recent achievement see Note Added in Proof.

The DFT optimization of the C_s model presented in Chart 7 also produced a Pd_1−C_{ipso} distance of 2.601 Å with a correspondingly small but positive overlap population. However, this structure appeared unreliable after a calculation of the frequencies (two imaginary values). Further attempts of optimization in C_1 symmetry showed a clear propensity of the phenyl ring to rotate about the P−C_{ipso} axis, and no convergence was attained. In our opinion, also the latter unsuccessful computations are chemically meaningful to dismiss an extra stability possibly due to the Pd−C_{ipso} interaction and need to be pointed out.

Conclusions

In this paper, we have reviewed all of the structural prototypes determined for Pd_2 and Pt_2 dimers containing at least one bridging phosphido group and having each metal in a planar coordination environment (16-electron configuration). Calculations, carried out by using the Gaussian 94 package[41] (MP2 and DFT levels), reproduce known experimental structures, suggest unknown structural tautomers, or dismiss alternative chemical hypotheses. Moreover, the qualitative concepts of perturbation theory and the graphs derived from EHMO calculations[41,42] highlight the basic interactions and allow one to correlate the different members in this class of compounds.

Computational Details

All ab initio calculations were performed with the GAUSSIAN94 package.[46] Unless specified in the text, the models have hydrogen substituents on the phosphorus atoms. The molecular geometries were determined using the density functional (DFT) and/or the Moeller Plesset (MP2) methods. For the DFT calculations we used Becke's 1988 functional[47] and the correlation functional of Lee, Yang, and Parr.[48] The standard double-ζ basis set (LANL2DZ) and effective core potential (ECP) have been used for the heavy elements (Pt, Pd, P, S).[49] The basis set for the phosphorus and sulfur atoms were augmented with a d-polarization function with $\alpha = 0.387$ and $\alpha = 0.503$, respectively.[50] An all-electron description at the D95 level was used for the elements of the first row, and a d-polarization function was added for the carbon atoms. Frequency calculations were performed to characterize the stationary points.

Some difficulty was encountered when optimizing structures of type **g**, namely, those where H atoms adopt *agostic* coordination with a Pd metal atom (i.e., a model of the experimental structure **23**). The best results have been obtained at the MP2 level starting from different

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guessed structures. The optimized structure could be obtained only upon the introduction of a 6-31G(d)* basis set for the *agostic* H atom alone.

In order to obtain more accurate energies for the comparison of the isomers of type **g** or **h**, **i**, and **j**, single points of the optimized structures were calculated at the MP2 level using the LANL2DZ basis set for Pt or Pd elements and the 6-311G(d)** basis set for all of the other atoms (see Table 2).

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Note Added in Proof. X-ray evidence for Pd−C_{ipso} interactions in unsaturated Pd_2 dimers with terminal phenylphosphine ligands has been recently presented by Professor H. Kurosawa at the XIIIth FECHEM Meeting (Lisbon, 29 Aug through 3 Sept 1999).

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