

Mixed P–N and As–N Bis-Ylide Palladium Complexes: Cooperative Intramolecular Interactions, Conformational Preferences, and C–H Bond Activations[†]

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The mixed ylide–pyridinium salts $[\text{Ph}_3\text{P}=\text{C}(\text{H})\text{C}(\text{O})\text{CH}_2\text{NC}_5\text{H}_5]\text{Cl}$ (**2a**) and $[\text{Ph}_3\text{As}=\text{C}(\text{H})\text{C}(\text{O})\text{CH}_2\text{NC}_5\text{H}_5]\text{Br}$ (**15**) have been prepared by reaction of the P and As ylides $[\text{Ph}_3\text{P}=\text{C}(\text{H})\text{C}(\text{O})\text{CH}_2\text{Cl}]$ and $[\text{Ph}_3\text{As}=\text{C}(\text{H})\text{C}(\text{O})\text{CH}_2\text{Br}]$ (**14**), respectively, with pyridine. These ylides react with Pd(II) salts in the presence of bases, affording the four-membered C,C-chelated complexes *cis*- $[\text{PdCl}_2\{\eta^2\text{-Ph}_3\text{EC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{NC}_5\text{H}_5\}]$ (E = P (**3**), As (**16**)) as single diastereoisomers (meso form, *RS/SR*). Density functional theory (DFT) calculations revealed that the same conformational preferences are present in free mixed bis-ylides. We have established the presence of two cooperative intramolecular interactions of moderate strength by means of Bader analysis of the electron density on model free bis-ylides: the 1,4-E $\cdots$ O interactions (E = P, As) and the 1,6-CH $\cdots$ O hydrogen bonds. The intramolecular 1,4-As $\cdots$ O interactions have been fully characterized for the first time. These interactions play a key role in determining the preferred conformations, which then are transferred to the complexes. Complex **3** reacts with AgClO_4 to give the dinuclear species $[\text{Pd}(\mu\text{-Cl})\{\eta^2\text{-Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{NC}_5\text{H}_5\}]_2(\text{ClO}_4)_2$ (**4**), which further reacts with L ligands to give $[\text{PdCl}\{\eta^2\text{-Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{NC}_5\text{H}_5\}\text{L}](\text{ClO}_4)$ (L = PPh_3 (**6**), PPhMe_2 (**7**)) as single geometric isomers. The molecular structure of **6** has been determined by X-ray diffraction methods. Complex **6** evolves in refluxing NCMe to give the ortho-metalated derivative $[\text{PdCl}(\text{C}_6\text{H}_4\text{-2-PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{CH}_2\text{NC}_5\text{H}_5)(\text{PPh}_3)]\text{ClO}_4$ (**18**). In addition, ylide **2a** reacts with PtCl_2 in refluxing 2-methoxyethanol to give the ortho-platinated complex $[\text{Pt}(\mu\text{-Cl})(\text{C}_6\text{H}_4\text{-2-PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{CH}_2\text{NC}_5\text{H}_5)](\text{Cl})_2$ (**20**). The role of the electronic and steric factors in the cleavage of the halide bridging system in **4** and in the ortho-metalation reactions affording **18** and **20** is also discussed.

Introduction

The synthesis and reactivity of α -stabilized bis-ylide complexes containing the unit $[\text{Pd}(\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{PPh}_3)]$ have pointed out two behaviors worthy of note. The first one is the diastereoselective coordination of the bis-ylide ligand to the metal center through the two C_α atoms, giving complexes in which only the meso form (*R*S**) is obtained.^{1,2} This selectivity is related to the presence of strong conformational preferences in the free bis-ylides, whose origin lies in the establishment of intramolecular 1,4-P $\cdots$ O interactions.^{3,4} The same selectivity

is observed in the C,C coordination of pyridinium ylides, although in this case the origin of the conformational preferences resides in the presence of intramolecular 1,6-C–H $\cdots$ O=C hydrogen bonds of moderate intensity.⁵ On the other hand, the bis-ylide C,C-bonded to the Pd(II) center in $[\text{Pd}(\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{PPh}_3)]$ easily rearranges into the ortho-metalated $[\text{Pd}(\text{C}_6\text{H}_4\text{-2-PPh}_2\text{-C}(\text{H})\text{C}(\text{O})\text{CH}_2\text{PPh}_3)]$ unit through a C–H bond activation reaction followed by an intramolecular acid–base process.^{6–8} Similar ortho-metalated complexes can be obtained from Pt(II) derivatives.^{9,10} This rearrangement can be promoted by thermal means or by addition of ligands, and it seems to be closely related to the intramolecular steric repulsions between the bulky phosphonium fragments and/or to the incoming ligands.⁶

The work here reported describes the synthesis of mixed bis-ylide derivatives of the type $[\text{Ph}_3\text{E}=\text{C}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{NC}_5\text{H}_5]$ (E

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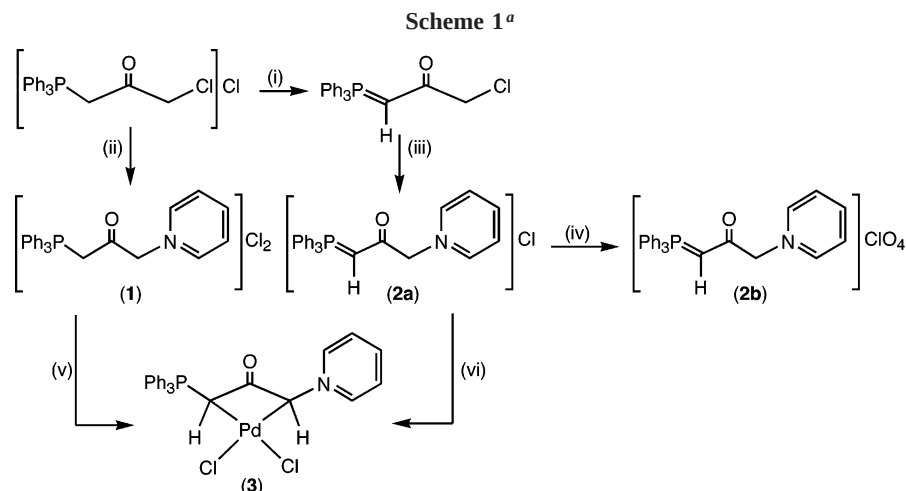
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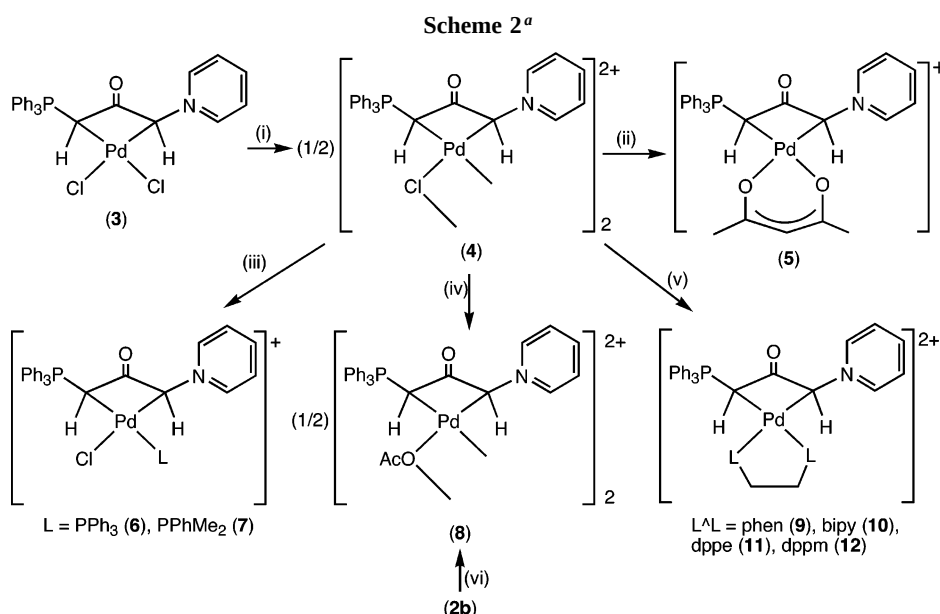
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^a Legend: (i) Na₂CO₃, MeOH/H₂O; (ii) py, DMA, reflux; (iii) py, THF, reflux; (iv) NaClO₄, -NaCl, CH₂Cl₂/Me₂CO; (v) Pd(OAc)₂, -2 HOAc, CH₂Cl₂; (vi) PdCl₂(NCMe)₂, NEt₃, -[HNEt₃]Cl, MeOH.



^a Legend: (i) AgClO₄, -AgCl, CH₂Cl₂/Me₂CO; (ii) Tl(acac), -TlCl, CH₂Cl₂; (iii) L, CH₂Cl₂; (iv) AgOAc, -AgCl, CH₂Cl₂; (v) AgClO₄, -AgCl, THF, L^ΛL; (vi) Pd(OAc)₂, -HOAc, MeOH, reflux.

= P, As) and presents two main objectives. The first is the determination of their coordinating properties: that is, whether the interactions governing the conformational preferences of the P-ylides and the N-ylides are complementary or competitive. With this aim, we have performed DFT calculations (at the B3LYP level)¹¹ on the mixed bis-ylides and their complexes. The second objective is the study of the reactivity of complexes containing the mixed bis-ylide [Pd(Ph₃EC(H)C(O)C(H)NC₅H₅)] (E = P, As) and the influence of the different steric and electronic factors present in the two halves of the molecule, especially in the ortho-metalation reactions.

Results and Discussion

1. Synthesis of Bis-Ylide Complexes. The mixed phosphonium–pyridinium salt [Ph₃PCH₂C(O)CH₂NC₅H₅]Cl₂ (**1**) has

been prepared by reaction of the precursor [Ph₃PCH₂C(O)CH₂Cl]Cl (prepared according to literature methods)¹² with pyridine (1:1 molar ratio) in refluxing DMA (*N,N*-dimethylacetamide). A similar reaction starting from the corresponding ylide [Ph₃PC(H)C(O)CH₂Cl], but in refluxing THF, affords the P-ylide–N-pyridinium salt [Ph₃PC(H)C(O)CH₂NC₅H₅]Cl (**2a**), which can be easily transformed to the perchlorate salt [Ph₃PC(H)C(O)CH₂NC₅H₅]ClO₄ (**2b**) by anion metathesis, following published methods.¹³ All of these reactions are summarized in Scheme 1. The synthesis of the arsonium salts and ylide derivatives has been carried out following similar procedures, which are presented in Scheme 3. The reaction of 1,3-dibromo-2-propanone with an excess of AsPh₃ (1:3 molar ratio) in refluxing THF affords the arsonium salt [Ph₃AsCH₂C(O)CH₂Br]Br (**13**) in very good yield. The treatment of 1,3-dichloroacetone with AsPh₃ under the same reaction conditions does not afford the expected chloride derivative. An increase of the molar ratio of AsPh₃ to dibromoacetone (up to 10:1 molar ratio) does not

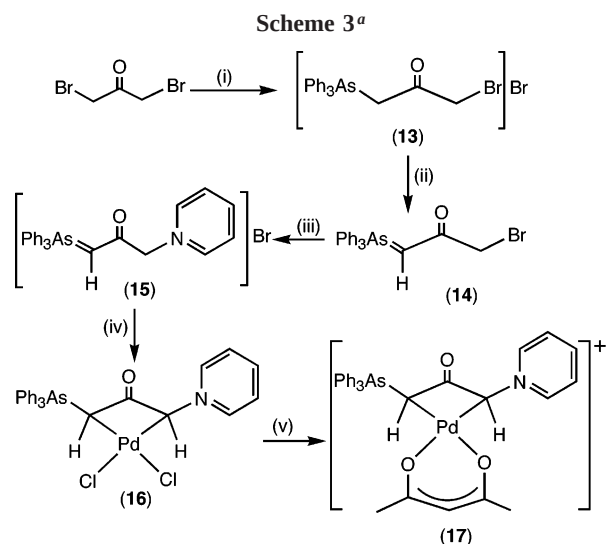
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^a Legend: (i) AsPh₃, THF, reflux; (ii) Na₂CO₃, MeOH/H₂O; (iii) py, excess, THF, reflux; (iv) PdCl₂(NCMe)₂, NEt₃, –[HNEt₃]Cl, MeOH; (v) AgClO₄, Tl(acac), –AgCl, –TlCl, CH₂Cl₂/Me₂CO.

promotes the bis substitution to give the bis-arsonium salt, even when harsh reaction conditions (refluxing DMA) were employed. The arsonium salt **13** can be transformed into the ylide **14** by deprotonation with Na₂CO₃ under very mild conditions, which in turn reacts with pyridine (1:1 molar ratio) in refluxing THF, resulting in the formation of the ylide–pyridinium salt **15**. All of these compounds were characterized through their analytic and spectroscopic data (see the Experimental Section). Full assignment of all ¹H NMR resonances has been carried out with the help of 2D ¹H–¹H COSY experiments and by using selective 1D NOESY and ROESY sequences. Full assignment of all ¹³C{¹H} NMR signals has been carried out through measurement of 2D ¹H–¹³C HSQC experiments. This applies for all compounds described in this work.

Either the treatment of **1** with Pd(OAc)₂ (1:1 molar ratio) in CH₂Cl₂ or the reaction of **2a** with PdCl₂(NCMe)₂ in MeOH and in the presence of base (NEt₃) (1:1:1 molar ratio) affords the mononuclear derivative cis-[Cl₂Pd(Ph₃PC(H)C(O)C(H)NC₅H₅)] (**3**), while reaction of **15** with PdCl₂(NCMe)₂ and NEt₃ (1:1:1 molar ratio) in MeOH gives the corresponding arsenic derivative cis-[Cl₂Pd(Ph₃AsC(H)C(O)CHNC₅H₅)] (**16**) (see Schemes 1 and 3, respectively). Complexes **3** and **16** show correct elemental analyses and mass spectra in accord with a mononuclear stoichiometry. The IR spectra of **3** and **16** show intense absorptions at 1588 (**3**) and 1589 cm^{–1} (**16**), respectively, due to the carbonyl stretch. This band is shifted to high energy with respect to the bands for the starting ylides (1565 (**2a**), 1557 cm^{–1} (**15**)), suggesting their C,C bonding.¹⁴ The position of this absorption falls in the same region as that observed in related complexes: 1590 cm^{–1} in pyridinium bis-ylides,⁵ 1587 cm^{–1} in phosphonium bis-ylides,² and 1585 cm^{–1} in imidazolium bis-ylides.¹⁵ The ³¹P{¹H} NMR spectrum of **3** shows a single signal at 23.82 ppm, shifted downfield with respect to its position in **2a**, and giving additional proof of the C,C bonding of the bis-ylide.¹⁴ The ¹H NMR spectra of **3** and **16** show the presence of a unique set of signals, suggesting the presence of a single reaction product. The C,C bonding of the mixed bis-ylides [Ph₃EC(H)C(O)C(H)NC₅H₅] (E = P, As) to a Pd(II) center in a mono-

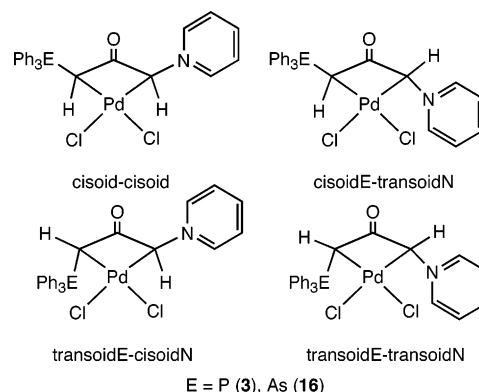


Figure 1. Carbonyl group pointing up toward the molecular coordination plane.

nuclear complex should form a four-membered ring with a non-planar PdC₃O core, by analogy with those reported for bis-ylides of P and N.^{2,15} For this structure one can expect, in principle, four different stereoisomers (Figure 1) arising from the different orientations of the EPh₃ and NC₅H₅ fragments with respect to the carbonyl group. While the patterns of signals in the ¹H NMR spectra of **3** and **16** do not allow us to discard any possibility, since the molecules have no elements of symmetry, the observation of strong NOE effects between the signals at 4.22 ppm (C(H)P) and 5.73 ppm (C(H)N) in **3** and between the signals at 4.54 ppm (C(H)As) and 5.89 ppm (C(H)N) in **16** strongly suggest a cisoid-cisoid arrangement of the EPh₃ and NC₅H₅ fragments, since this arrangement is sterically less hindered than the transoid-transoid one. As we will discuss in the following sections, the cisoid-cisoid stereochemistry is further supported by theoretical calculations and X-ray diffraction data.

2. The Mixed Bis-Ylides [H₃E=C(H)C(O)C(H)NC₅H₅] (E = P, As) and Their Complexes. DFT Studies. We have recently studied in detail the symmetric P and N bis-ylides, and we have shown how the selectivity observed in their coordination modes can be related to the presence of conformational preferences which are, in origin, related to the establishment of different types of intramolecular interactions.^{3–5} The mixed bis-ylides presented here, derived from **2** and **15**, contain well-differentiated halves, with respect to the C=O bond axis. One half contains a pyridinium group, for which 1,6-C–H···O=C hydrogen bond interactions have been previously characterized.⁵ The other half contains positively charged E heteroatoms (P, As) which are able to interact with the negatively charged carbonyl oxygen, giving 1,4-E···O intramolecular interactions. These interactions have been completely characterized by theoretical methods in the case of the P-ylides.^{3,4}

The behavior of bis-ylides derived from **2** and **15** has been studied by DFT methods at the B3LYP level.^{11,16} The obtained results clearly show a cooperative effect between the different interactions described above, each one operating in each half of the molecule. For the two ylides, three extreme conformations

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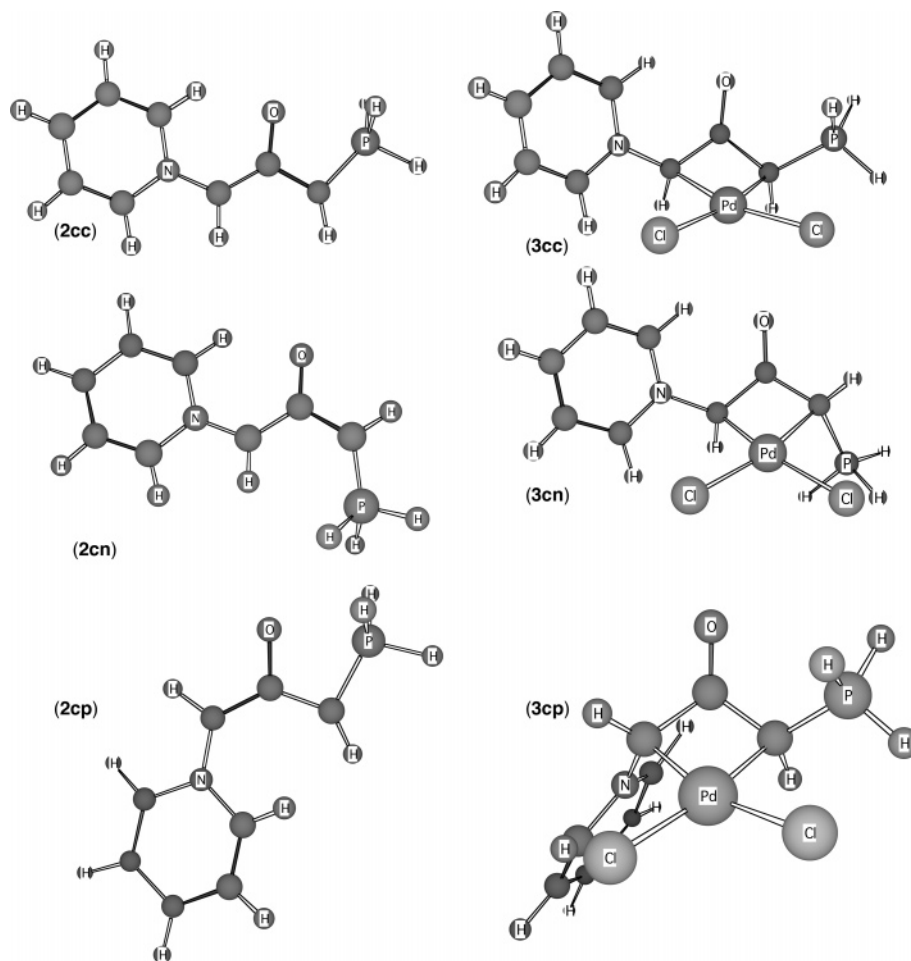


Figure 2. Computed DFT structures for the bis-ylides **2** and their corresponding complexes **3**.

have been optimized (see Figures 2 and 3 and Table 1), denoted as P-cisoid-N-cisoid (**2cc**), P-transoid-N-cisoid (**2cn**), and P-cisoid-N-transoid (**2cp**). The corresponding As-ylides have been denoted as **15cc**, **15cn**, and **15cas**. The optimized structures have been characterized as minima by analytically computing the Hessian matrix. The all-transoid geometries are not stable, probably due to strong steric repulsions, and they evolve during the optimization process to the **2cn** or **15cn** structure. The most relevant fact is that, in all cases, the most stable structure is the cisoid-cisoid isomer, and this fact is in very good agreement with the NMR data. Thus, in the case of the P-ylide, the most stable isomer (**2cc**) shows energy differences with the other structures which are $\Delta E(\mathbf{2cp}-\mathbf{2cc}) = 27.6 \text{ kJ mol}^{-1}$ and $\Delta E(\mathbf{2cn}-\mathbf{2cc}) = 47.3 \text{ kJ mol}^{-1}$. Similar results are obtained for the As-ylide **15**: the isomer **15cc** is the most stable structure, the isomers **15cas** and **15cn** being higher in energy than **15cc** by 27.1 and 52.2 kJ mol^{-1} , respectively. These results strongly suggest that the intramolecular interactions responsible for the conformational preferences in “pure” free P or N bis-ylides (the same interaction in both halves of the bis-ylide) are also operating in the mixed free bis-ylides. Moreover, the effect of these interactions in the mixed free bis-ylides should be additive, since the cisoid-cisoid arrangement is more stable than the cisoid-transoid isomer.

The geometric characterization of the different isomers of mixed bis-ylides **2** and **15** follows the expected patterns, similar to those already reported in pure bis-ylides.^{3–5} Nevertheless, some key features merit some comments. Compounds **2cc** and **15cc** are rigorously planar, (see Table 1) and both of them show the presence of a 1,6-C–H $\cdots$ O=C hydrogen bond ($d(\text{O}\cdots\text{H})$

$= 1.980$ and $1.983 \text{ \AA}$ for **2cc** and **15cc**, respectively).⁵ The presence of a short 1,4-P $\cdots$ O contact in **2cc** can also be inferred from the nonbonding distance $d(\text{P}\cdots\text{O}) = 2.411 \text{ \AA}$, which is shorter than that found in the cisoid-cisoid isomer of $[\text{H}_3\text{P}=\text{C}(\text{H})\text{C}(=\text{O})\text{C}(\text{H})=\text{PH}_3]$ ($2.511 \text{ \AA}$).³ Other parameters are similar to those reported previously. Compounds **2cp**, **2cn**, **15cas**, and **15cn** show a slight deviation from planarity. The presence of a 1,6-C–H $\cdots$ O=C hydrogen bond in **2cn** and **15cn**⁵ is also evident, and it seems to be somewhat stronger than those observed in **2cc** and **15cc**, as suggested by the shortening of the O $\cdots$ H distance. As one goes from **2cc** to **2cp**, the P $\cdots$ O distance notably shortens (from $2.411 \text{ \AA}$ to $2.169 \text{ \AA}$), which indicates an even stronger P $\cdots$ O interaction in **2cp**. Finally, the intramolecular arsenium–oxygen distances for compounds **15cc** and **15cas** are 2.449 and $2.339 \text{ \AA}$, respectively. Both distances are shorter than the sum of the van der Waals radii ($3.40 \text{ \AA}$).¹⁷ In addition, the bond angles $\text{AsC}_\alpha\text{C}_\beta$ and $\text{C}_\alpha\text{C}_\beta\text{O}$ show values of 101.0 and 113.4° for **15cc** and 98.0 and 112.2° for **15cas**. These structural parameters strongly suggest that a 1,4-As $\cdots$ O intramolecular nonbonding interaction, similar to that reported for P-ylides,^{3,4} can be established between the positive As atom and the negatively charged carbonyl oxygen. Moreover, this type of interaction has already been proposed in several contributions,¹⁸ although, as far as we know, it has never been characterized.

Here, we employ Bader’s atoms in molecules (AIM) theory to characterize these intramolecular As $\cdots$ O interactions and to

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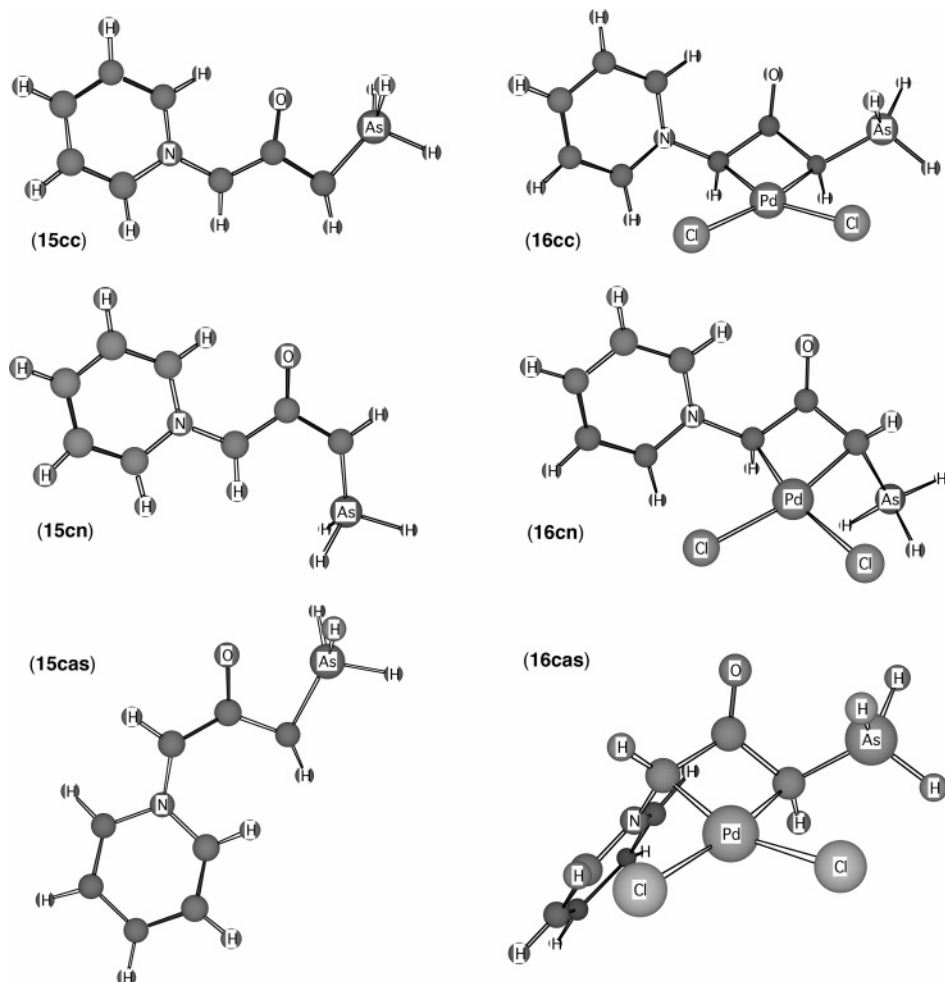


Figure 3. Computed DFT structures for the bis-ylides **15** and their corresponding complexes **16**.

Table 1. Relative Energies (kJ mol⁻¹) and Bond Distances (Å) and Angles (deg) for **2**, **3**, **15**, and **16**

	<i>E</i> _{rel}	N–C _α	O···H	O···H–C	N–C _α –C _β –O	E–C _α ^a	O···E ^a	E–C _α –C _β –O ^a
2cc	0.0	1.373	1.980	131.8	0.0	1.710	2.411	0.0
2cp	27.6	1.368			–171.8	1.730	2.169	–2.0
2cn	47.3	1.373	1.957	131.5	2.3	1.688		–166.5
15cc	0.0	1.371	1.983	131.8	0.0	1.831	2.449	0.0
15cas	27.1	1.366			–169.3	1.846	2.339	–3.1
15cn	52.2	1.371	1.953	102.4	1.7	1.809		–168.5
3cc	0.0	1.445	2.012	132.7	–1.8	1.768	2.923	11.0
3cp	40.2	1.465			127.8	1.767	2.917	12.0
3cn	29.7	1.450	1.997	132.2	–7.6	1.759		–132.0
16cc	0.0	1.445	2.013	132.7	–1.7	1.895	2.962	9.4
16cas	40.6	1.461			129.2	1.896	2.947	10.1
16cn	34.5	1.451	1.994	132.4	–8.1	1.884		–130.1

^a E = P, As.

analyze the bonding nature of the free mixed bis-ylides **2** and **15**. For the structures **15cc** and **15cas** the existence of an intramolecular As···O interaction was confirmed by the topological analysis of the electron density. This type of interaction was characterized by a bond critical point (bcp) in the electronic

charge density ($\rho(r)$), further proving the existence of the As···O interaction. Analogously, the 1,4-P···O intramolecular interactions for **2cc** and **2cp** and the 1,6-CH···O=C hydrogen bonds for **2cc**, **2cn**, **15cc**, and **15cn** were characterized by localization of their corresponding bcp's and rcp's. The variation in bonding nature of P–N and As–N bis-ylides was analyzed by means of the numerical values of the bcp's in charge density ($\rho(r)$), the Laplacian of the charge density ($\nabla^2\rho(r)$), and the ellipticity (ϵ) together with the $-\nabla^2\rho(r)$ graphical representation. Table 2 collects the numerical values, and Figure 4 displays the graphics.

The interaction behaviors of 1,4-P···O and 1,4-As···O contacts are very similar. The values of $\nabla^2\rho(r)$ are low and positive (0.102 and 0.104 au for **2cc** and **15cc**, respectively), indicating a closed-shell interaction of electrostatic nature. For both species the map of the Laplacian shows a similar pattern compatible with an electrostatic interaction (Figure 4). One maximum of charge concentration (indicated by arrows), corresponding to one of the oxygen lone pairs, points toward the charge-depleted valence shell of the phosphorus or arsenic atoms, which are polarized toward the oxygen. We have previously estimated the strength of P···O interaction on simple ylides, which amounts to about 40 kJ mol⁻¹.³ In agreement with this value, the isomer **2cc** is 47.3 kJ mol⁻¹ more stable than **2cn**, in which the P···O interaction is lost. We observe a closely related energetic pattern for mixed As bis-ylides, the **15cc** isomer being 52.2 kJ mol⁻¹ lower in energy than **15cn**. Thus, we can state that the strength and nature of the 1,4-As···O interaction are very similar to those of a 1,4-P···O moderate electrostatic-type interaction. In the case of ylide C–E bonds (E = P, As),

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Table 2. Topological Properties^a (in au) at the Bond and Ring Critical Points and Distances (in Å) of the Mixed Bis-Ylide Structures **2cc**, **2cp**, **15cc**, and **15cas**

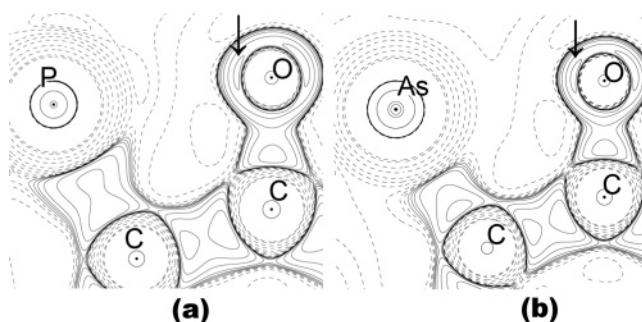
		2cc	2cp	15cc	15cas
E...O	<i>d</i>	2.411	2.169	2.449	2.339
	$\rho(r)$	0.039	0.064	0.040	0.051
	$\nabla^2\rho(r)$	0.102	0.068	0.104	0.115
E–C _α –C _β –O	$\rho(r)$	0.039	0.055	0.038	0.044
	$\nabla^2\rho(r)$	0.137	0.252	0.163	0.203
E–C _α	<i>d</i>	1.710	1.730	1.831	1.846
	$\rho(r)$	0.188	0.184	0.165	0.162
	$\nabla^2\rho(r)$	0.075	0.040	–0.097	–0.097
	ϵ	0.347	0.272	0.276	0.247

^a The topological properties are electron charge density ($\rho(r)$), Laplacian ($\nabla^2\rho(r)$), and ellipticity (ϵ).

it has already been proved that P and As atoms form covalent yet significant polar interactions of similar nature.¹⁹ For these mixed P and As bis-ylides we also observe large values of $\rho(r)$ and ϵ together with low values of $\nabla^2\rho(r)$, which are compatible with previous descriptions. In summary, we expect a very similar behavior for P–N and As–N bis-ylides.

The structural parameters and the topological properties of $\rho(r)$ of the 1,6-C–H...O interactions in the cisoid pyridinium halves show the same trends as the previously studied pyridinium ylides.⁵ For them the interaction could be unambiguously assigned to true hydrogen bonds, making use of a set of criteria based on AIM theory. Despite the inherent weakness of the C–H...O=C bonds, we classified those hydrogen bonds as moderate interactions (about 50 kJ mol^{–1}) by means of an intramolecular adaptation of Grabowski's complex parameter. Moreover, those hydrogen bonds were responsible for most of the conformational preferences observed in N-ylides. In mixed P–N and As–N bis-ylides the conformational preferences of cisoid-cisoid over N-transoid isomers are significantly lower: 27.6 and 27.1 kJ mol^{–1} for **2cc** and **15cc**, respectively. It may seem that here the hydrogen-bond interaction is weaker than in the case of "pure" N bis-ylides. However, upon the loss of the 1,6-C–H...O interactions, the 1,4-P–O and 1,4-As–O interactions of the other halves are reinforced in **2cp** and **15cas**. The P–O and As–O distances are shortened by 0.24 and 0.11 Å, respectively. Moreover, the P–O and As–O interaction in **2cp** and **15cas** show larger values of $\rho(r)$ at the bcp than in their corresponding cisoid-cisoid isomers (Table 2). It has been shown that $\rho(r)$ at the bcp is related to the bond strength; thus, the larger the value of $\rho(r)$ at the bcp, the stronger the bond. Therefore, we can conclude that most of the conformational preferences observed in these mixed bis-ylides come as a result of the two additive moderate intramolecular interactions (1,4-P...O interaction and 1,6-C–H...O hydrogen bond), which are preferred to only one stronger interaction.

We have also recently shown that the conformational preferences in the free bis-ylides are directly transferred to the corresponding metallic complexes.^{4,5} This fact seems also to be operating here, since the cisoid-cisoid stereochemistry suggested by experimental data in complexes **3** and **16** corresponds also to the most stable conformation of the free mixed bis-ylides. To study this issue in more detail, the three extreme conformations for each C,C-chelating complexed bis-ylide (**3cc**, **3cn**, **3cp**, **16cc**, **16cn**, and **16cas**; see Figures 2 and 3 and Table 1) have been optimized, and each optimized structure has been characterized as a minimum by analytically computing the Hessian matrix. As expected, the lowest energy isomers are **3cc**

**Figure 4.** Laplacian contour maps, in the plane containing the E–C–C–O skeleton (E = P, As), for the structures **2cc** (a) and **15cc** (b). Dashed lines correspond to $\nabla^2\rho(r) > 0$ (regions of charge depletion) and solid lines to $\nabla^2\rho(r) < 0$ (regions of charge concentration).

and **16cc**, in good agreement with the NMR data. The N-cisoid isomers **3cn** and **16cn** show energy differences with respect to the cisoid-cisoid isomers which amount to 29.7 and 34.5 kJ mol^{–1}, respectively. These values are clearly smaller than those obtained for the corresponding free ylides (about 50 kJ mol^{–1}). Upon coordination, the P–O and As–O distances in cisoid-cisoid structures become significantly longer, around 0.5 Å for both species. This indicates that in **3cc** and **16cc** the C_α pyramidalizes and the 1,4-E...O interactions weaken because of charge transfer to the metal and loss of charge conjugation. Hence, when the weakened P–O and As–O interactions turn off in P- and As-transoid isomers (**3cn** and **16cn**), the energy differences between **cc** and **cn** isomers become substantially lower. In addition, we do not discard the notion that other subtle effects may play a role in tuning the relative energies of these complexes. On the other hand, the E-cisoid isomers **3cp** and **16cas** show energy differences somewhat higher than those found in the corresponding free ylides (see Table 1). This could be the result of two effects of opposite sign. First, the interaction distances of the hydrogen bond in **3cc** and **16cc** (O...H = 2.012 and 2.013 Å, respectively) are slightly longer than those for the corresponding free bis-ylides (O...H = 1.980 and 1.983 Å, respectively). Hence, when the hydrogen bond interactions are turned off, the energy increase of the N-transoid isomer (**3cp** and **16cas**) is lower than in free bis-ylides. Second, on going from cisoid-cisoid to N-transoid isomers, the E...O distances are only slightly shortened (around 0.02–0.03 Å; see Table 1), in marked contrast with that observed for free bis-ylides. As a consequence, there is no reinforcement of the 1,4-E...O interactions upon loss of the hydrogen bond, which causes higher relative energies of E-cisoid complexed isomers (**3cp** and **16cas**) in comparison to the corresponding free bis-ylides. Despite all this, the experimentally observed diastereoisomeric specificity of the complexes seems to be predetermined by the conformational preferences of the free mixed P–N and As–N bis-ylides, in which two cooperative interactions play a key role.

3. Reactivity of *cis*-[Cl₂Pd(Ph₃EC(H)C(O)C(H)NC₅H₅)] (E = P (3**), As (**16**)).** Complex **3** reacts smoothly with AgClO₄ (1:1 molar ratio) to give the corresponding bridging chloride derivative [Pd(μ-Cl){Ph₃PC(H)C(O)C(H)NC₅H₅}]₂(ClO₄)₂ (**4**), which is obtained as a mixture of two isomers characterized by NMR spectroscopy—two different sets of signals due to the ylidic protons and two different ³¹P peaks. Assuming that the configuration of the two ylidic carbon atoms bonded to the palladium center is maintained,² a sensible explanation for the presence of the two isomers is the formation of the geometric isomers shown in Figure 5, in which the two PPh₃ groups, and hence the two pyridine groups, can be in a pseudo-cis or pseudo-

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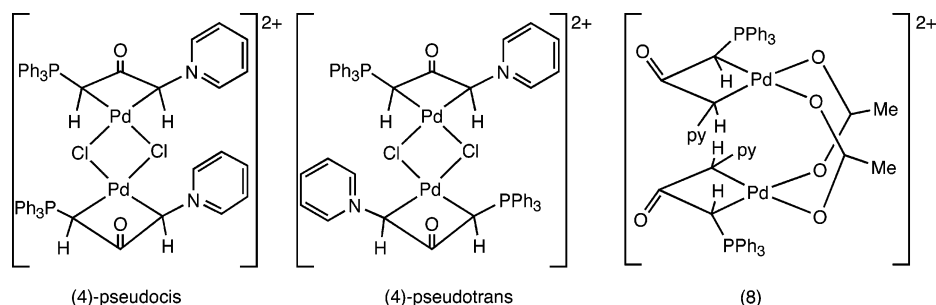


Figure 5. Proposed geometric isomers for complexes **4** and **8**.

trans arrangement. Complex **4** is an adequate starting compound to further explore the reactivity of bis-ylide complexes and shows the expected reactivity of bridging halide systems (Scheme 2). This bridging system can be easily cleaved by the reaction of **4** with neutral ligands *L* (1:2 molar ratio), to give the complexes $[\text{PdCl}\{\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{NC}_5\text{H}_5\}(\text{L})](\text{ClO}_4)$ (*L* = PPh_3 (**6**), PPhMe_2 (**7**)) in good yield. The reaction proceeds with good conversions only when phosphine ligands are used. Attempted cleavages with pyridine ligands always give equilibrium mixtures of all species (**4**, pyridine, and the final monomer), even in the presence of an excess of pyridine. The chloride ligands can be replaced by other anionic ligands: for instance, by reaction with $\text{Ti}(\text{acac})_3$ (1:2 molar ratio) to give the *O,O'*-acetylacetonato derivative **5** or by reaction with AgOAc (*OAc* = acetate) (1:2 molar ratio) to give the dinuclear species $[\text{Pd}(\mu\text{-OAc})\{\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{NC}_5\text{H}_5\}]_2(\text{ClO}_4)_2$ (**8**). Complex **8** can also be obtained by reaction of the perchlorate **2b** with $\text{Pd}(\text{OAc})_2$. The chloride ligands can also be replaced by other neutral chelating ligands *L*∧*L* through reaction of **4** with AgClO_4 and *L*∧*L* (1:2:2 molar ratio), giving the mononuclear dicationic complexes $[\text{Pd}\{\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{NC}_5\text{H}_5\}(\text{L}\wedge\text{L})](\text{ClO}_4)_2$ (*L*∧*L* = phen (**9**), bipy (**10**), dppe (**11**), dpmm (**12**)). In contrast to the clear reactivity shown by the phosphorus complex **3**, that of the arsenic derivative **16** is not straightforward. Although the reaction of **16** with AgClO_4 and $\text{Ti}(\text{acac})_3$ (1:1:1 molar ratio) gives cleanly the *O,O'*-acac complex **17** in moderate yield, we have not been able to isolate any other derivative with this As-containing mixed bis-ylide. In all attempted cases, intractable dark brown oils were obtained, from which no identifiable species could be isolated. For this reason, this area of the bis-ylides was not further investigated.

The characterization of complexes **4–12** and **17** has been carried out on the basis of their analytic and spectroscopic parameters (see the Experimental Section). All complexes show correct elemental analyses and mass spectra and also show the expected bands in their IR spectra in accord with the presence of different functional groups (acac, PR_3 , AcO, etc.). The NMR spectra of the acac derivatives **5** and **17** reflect the asymmetry of the C,C-bonded bis-ylide and show the expected nonequivalence of the methyl groups, while those of **6** and **7** show peaks corresponding to the presence of a single product. That is, the cleavage of the halide bridging system in **4** promoted by *L* is highly selective, and **6** and **7** are obtained as only one geometric isomer. The trans arrangement of the *L* ligand and the ylidic carbon atom of the $\text{C}(\text{H})\text{PPh}_3$ group, proposed in Scheme 2, can be inferred from the NMR data. The ^1H NMR spectra of **6** and **7** show the signal due to the $\text{C}(\text{H})\text{N}$ proton as a singlet, while that due to the $\text{C}(\text{H})\text{P}$ proton appears as a doublet of doublets, with values of the coupling constant $^3J_{\text{PH}}$ (~9.5 Hz) similar to those observed in related situations.^{6,8} In the same way, the ^{13}C NMR spectrum of **7** shows the resonance attributed to the $\text{C}(\text{H})\text{P}$ carbon as a doublet of doublets, also

with a value of the coupling constant $^2J_{\text{PC}}$ (~75 Hz) similar to those observed in related situations.^{6,8} Selective NOESY-1D experiments in **7** give the definitive proof of the proposed stereochemistry. The saturation of the singlet signal at 5.60 ppm in the ^1H NMR spectrum of **7**, attributed to the $\text{C}(\text{H})\text{N}$ proton, promotes an intense NOE effect on the signal of the other ylidic $\text{C}(\text{H})\text{P}$ proton (3.94 ppm), on the ortho protons of the pyridinium group (8.30 ppm), and on the methyl protons of the PPhMe_2 ligand (1.54, 1.57 ppm). Additional characterization of these types of complexes comes from the X-ray molecular structure of **6** (see below). This selective bonding of the *L* ligand in the position trans to the $\text{C}(\text{H})\text{PPh}_3$ group seems to be strongly related to the different steric hindrances exerted by each ylide unit. Obviously, the $\text{C}(\text{H})\text{NC}_5\text{H}_5$ moiety shows much lower steric requirements than the bulky $\text{C}(\text{H})\text{PPh}_3$ group; thus, it is sensible to assume that a second bulky unit (the *L* ligand) would be better accommodated cis to the pyridinium group than cis to the phosphonium group, to minimize intramolecular repulsive interactions. This fact has additional consequences on the reactivity of **6** and **7** (see item 5).

The NMR spectra of **8** show, regardless of the synthetic method, a unique set of resonances, meaning that it is obtained as a single isomer. This somewhat surprising behavior is in contrast to that shown by **4**, which is obtained as a mixture of pseudo-cis and pseudo-trans geometric isomers (see Figure 5). The simple consideration of the planar structure of the μ -chloride derivative **4**, by comparison with related complexes,² toward the open-book structure usually shown by the μ -acetate complexes²⁰ could give a simple reasoning for the observed behavior. The molecular planes of the fragments $[\text{Pd}\{\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{NC}_5\text{H}_5\}]$ should be, by analogy, arranged in an almost parallel way and also should be almost stacked (see Figure 5). It is clear that the stereochemistry which minimizes the steric repulsions between the “upper” plane and the “lower” plane is that containing different ylide units on the same half of the molecule (with respect to a plane containing the two Pd atoms and the two CO groups); that is, the $\text{C}(\text{H})\text{NC}_5\text{H}_5$ unit of the upper plane is arranged above the $\text{C}(\text{H})\text{PPh}_3$ group of the lower plane. Obviously, two bulky $\text{C}(\text{H})\text{PPh}_3$ groups on the same half of the molecule should be a more unstable geometry, due to intramolecular repulsions, as was observed in the related derivative $[\text{Pd}(\mu\text{-OAc})\{\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{PPh}_3\}]_2(\text{ClO}_4)_2$.⁶

The NMR spectra of **10–12** are in good agreement with the structures shown in Scheme 2 and reflect the asymmetry of the C,C-bonded bis-ylide: the halves of the bipy ligand appear as nonequivalent in the ^1H NMR spectrum of **10**, as well as the two P atoms of the chelating ligands dppe (**11**) and dpmm (**12**). The observed chemical shifts of the phosphorus atoms in the

(20) More than 90 X-ray structures containing the $\text{Pd}_2(\mu\text{-OAc})_2$ unit were found in the CCDC; all of them showed an “open-book” ligand arrangement. Allen, F. H.; Kennard, O. *Chem. Des. Automation News* **1993**, 8, 31.

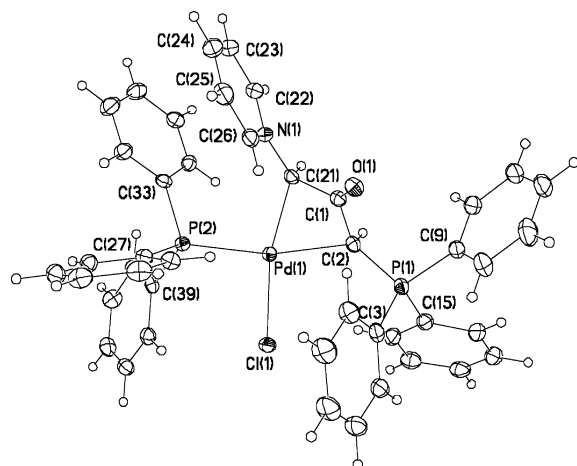


Figure 6.

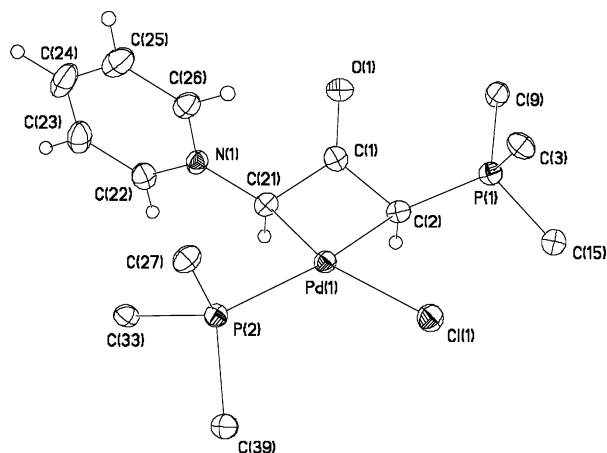


Figure 7.

^{31}P NMR spectra (very deshielded for dppe and very shielded for dpmm) are typical for a P,P-chelating bonding in both cases.^{6,21}

At first sight, the reactivity of **4** seems to be as expected, following the usual patterns for a dinuclear complex with halide bridges.²² However, the comparison of this reactivity with that reported for $[\text{Pd}(\mu\text{-Cl})\{\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{PPh}_3\}]_2(\text{ClO}_4)_2$ shows very remarkable differences, although, in principle, the two complexes are closely related. As has been described, $[\text{Pd}(\mu\text{-Cl})\{\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{PPh}_3\}]_2(\text{ClO}_4)_2$ undergoes an intramolecular C–H activation process in refluxing NCMe, giving the ortho-metallated $[\text{Pd}(\mu\text{-Cl})(\text{C}_6\text{H}_4\text{-2-PPH}_2\text{-C}(\text{H})\text{C}(\text{O})\text{CH}_2\text{PPh}_3)]_2(\text{ClO}_4)_2$, while the thermal treatment of **4** under the same reaction conditions does not promote any observable change, and **4** is recovered unaffected. On the other hand, the cleavage of the chloride bridging system in $[\text{Pd}(\mu\text{-Cl})\{\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{PPh}_3\}]_2(\text{ClO}_4)_2$ by voluminous L ligands (PPh_3) or the reaction of the solvate $[\text{Pd}\{\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{PPh}_3\}(\text{S})_2](\text{ClO}_4)_2$ ($\text{S} = \text{THF}$, NCMe) with classical bulky $\text{L}\wedge\text{L}$ didentate ligands also promoted an ortho-metallation process, giving the corresponding $[\text{PdCl}(\text{C}_6\text{H}_4\text{-2-PPH}_2\text{-C}(\text{H})\text{C}(\text{O})\text{CH}_2\text{PPh}_3)\text{L}](\text{ClO}_4)$ or $[\text{Pd}(\text{C}_6\text{H}_4\text{-2-PPH}_2\text{-C}(\text{H})\text{C}(\text{O})\text{CH}_2\text{PPh}_3)(\text{L}\wedge\text{L})](\text{ClO}_4)_2$ complexes. In the case of **4**, the cleavage reaction gives stable complexes (e.g., **6** or **7**) and the bidentate ligands can also be incorporated in the

Table 3. Crystal Data and Structure Refinement Details for $6 \cdot 3\text{CH}_2\text{Cl}_2$

empirical formula	$\text{C}_{47}\text{H}_{43}\text{Cl}_8\text{NO}_5\text{P}_2\text{Pd}$
fw	1153.76
temp (K)	100(1)
radiation (λ , Å)	Mo K α (0.710 73)
cryst syst	orthorhombic
space group	$\text{Pna}2_1$
a (Å)	19.7194(2)
b (Å)	24.8788(2)
c (Å)	10.03120(10)
V (Å ³)	4921.26(8)
Z	4
D_{calcd} (Mg/m ³)	1.557
μ (mm ⁻¹)	0.923
cryst size (mm ³)	$0.34 \times 0.29 \times 0.08$
no. of rflns collected	82 228
no. of indep rflns	11 262 ($R_{\text{int}} = 0.0352$)
no. of data/restraints/params	11 262/1/577
goodness of fit on F^2	1.022
final R indices ($I > 2\sigma(I)$)	$R1 = 0.0297$, $wR2 = 0.0755$
R indices (all data)	$R1 = 0.0314$, $wR2 = 0.0763$
abs structure param	0.000(16)
largest diff peak, hole (e Å ⁻³)	0.986 and -0.542

coordination sphere of the Pd atom without change in the bis-ylide, as it is evident from the synthesis of **9–12**. Moreover, we have described that the acetate-bridged $[\text{Pd}(\mu\text{-OAc})\{\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{PPh}_3\}]_2(\text{ClO}_4)_2$ spontaneously rearranges in solution to give the dinuclear $[(\text{C}_6\text{H}_4\text{-2-PPH}_2\text{-C}(\text{H})\text{COCH}_2\text{-PPh}_3)\text{Pd}(\mu\text{-OAc})_2\text{Pd}\{\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{PPh}_3\}](\text{ClO}_4)_2$. However, the related complex **8**, with a mixed P,N bis-ylide, has shown very good stability in solution. Since all ortho-metallation processes mentioned here (thermal, ligand-induced, or spontaneous) were strongly dependent on steric factors, and due to the fact that the bis-ylide $[\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{PPh}_3]$ is clearly bulkier than the mixed bis-ylide $[\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{NC}_5\text{H}_5]$, it seems reasonable to assume that the lack of reactivity of complexes **4–12** towards the ortho-metallation is due mainly to this steric difference. Thus, the mixed bis-ylide can accommodate bulky ligands in a more efficient way than the pure P bis-ylide, resulting in fewer significant intramolecular repulsions and, hence, in a higher stability.

The X-ray molecular structure of **6**, which contains the C,C-coordinated bis-ylide $[\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{NC}_5\text{H}_5]$ and an ancillary PPh_3 ligand, provides additional valuable structural information.

4. X-ray Crystal Structure of $[\text{PdCl}\{\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{NC}_5\text{H}_5\}(\text{PPh}_3)]\text{ClO}_4 \cdot 3\text{CH}_2\text{Cl}_2$ ($6 \cdot 3\text{CH}_2\text{Cl}_2$). Drawings of the cationic organometallic part are given in Figures 6 and 7, relevant crystallographic parameters are given in Table 3, and selected bond distances and angles are collected in Table 4. The complex crystallizes in the hemimorphic, polar, orthorhombic space group $\text{Pna}2_1$, with one organometallic and three solvent molecules in the asymmetric unit. Then, only one diastereoisomer is present.

The Pd atom is located in a very distorted square planar environment, surrounded by the two ylidic C atoms C(2) and C(21), the P atom of the PPh_3 ligand P(2), and the chlorine atom Cl(1). Two important facts are worthy of note. The first one is the evident C,C-chelating coordination of the bis-ylide ligand and the pseudocisoid conformations of the stabilized P-ylidic (dihedral angle $\text{O}(1)\text{--C}(1)\text{--C}(2)\text{--P}(1) = -4.2(1)^\circ$) and N-ylidic fragments (dihedral angle $\text{O}(1)\text{--C}(1)\text{--C}(21)\text{--N}(1) = 6.3(1)^\circ$). The absolute configurations for the ylidic C atoms shown in Figures 6 and 7 are $S_{\text{C}(2)}$ and $R_{\text{C}(21)}$. Thus, once again,^{2–9} a meso form is obtained. Since only one isomer has been detected in solution (for this complex and for all the other complexes reported here), we can conclude that these configura-

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for 6·3CH₂Cl₂

Pd(1)–C(21)	2.080(3)	Pd(1)–C(2)	2.179(3)
Pd(1)–P(2)	2.2853(6)	Pd(1)–Cl(1)	2.3552(6)
Pd(1)–C(1)	2.379(2)	C(1)–O(1)	1.234(3)
C(1)–C(2)	1.464(4)	C(1)–C(21)	1.491(4)
C(2)–P(1)	1.763(3)	P(1)–C(3)	1.786(3)
P(1)–C(15)	1.797(3)	P(1)–C(9)	1.801(3)
C(21)–N(1)	1.444(3)	N(1)–C(26)	1.355(4)
N(1)–C(22)	1.356(4)	C(22)–C(23)	1.368(4)
C(23)–C(24)	1.377(5)	C(24)–C(25)	1.383(5)
C(25)–C(26)	1.374(4)	P(2)–C(33)	1.815(3)
P(2)–C(27)	1.823(3)	P(2)–C(39)	1.829(3)
C(21)–Pd(1)–C(2)	67.40(10)	C(21)–Pd(1)–P(2)	99.20(7)
C(2)–Pd(1)–P(2)	165.98(7)	C(21)–Pd(1)–Cl(1)	165.39(7)
C(2)–Pd(1)–Cl(1)	98.22(7)	P(2)–Pd(1)–Cl(1)	95.32(2)
O(1)–C(1)–C(2)	126.3(2)	O(1)–C(1)–C(21)	125.6(2)
C(2)–C(1)–C(21)	106.3(2)	C(1)–C(2)–P(1)	116.84(19)
C(1)–C(2)–Pd(1)	78.88(14)	P(1)–C(2)–Pd(1)	126.75(13)
C(2)–P(1)–C(3)	112.66(12)	C(2)–P(1)–C(15)	107.66(12)
C(3)–P(1)–C(15)	109.39(13)	C(2)–P(1)–C(9)	110.63(13)
C(3)–P(1)–C(9)	108.67(13)	C(15)–P(1)–C(9)	107.70(13)
N(1)–C(21)–C(1)	115.0(2)	N(1)–C(21)–Pd(1)	125.83(17)
C(1)–C(21)–Pd(1)	81.76(15)	C(26)–N(1)–C(22)	120.3(2)
C(26)–N(1)–C(21)	120.6(2)	C(22)–N(1)–C(21)	119.1(2)

tions are also preserved in solution. These results are in perfect agreement with the NMR results in solution and also with the theoretical calculations. The second noteworthy fact is the cis bonding of the PPh₃ ligand with respect to the N-ylidic fragment H₅C₅NC(H). This fact is also in good agreement with the NMR data and strongly suggests a cleavage of the halide bridge and a further coordination of an incoming ligand driven by steric factors.

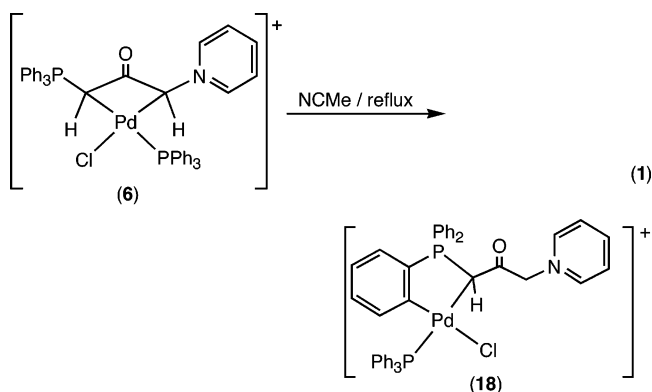
The geometrical parameters of the organometallic cation are similar to those reported previously for related complexes. The Pd–C bond distances are different from each other, since they are reflecting the different trans influences of the trans ligands. Thus, the Pd–C bond distance trans to the chlorine atom (Pd(1)–C(21) = 2.080(3) Å) is identical within experimental error with those found in the dinuclear [Pd(μ-Cl)(Ph₃PC(H)C(O)C(H)PPh₃)₂](ClO₄)₂ (ranging from 2.053(11) to 2.078(11) Å),² while that trans to the phosphine ligand is clearly longer (Pd(1)–C(2) = 2.179(3) Å) and is identical within experimental error with that found in [Pd(C₆H₄-2-PPh₂C(H)C(O)CH₂PPh₃)-(PPh₃)(NCMe)](ClO₄) (2.161(8) Å).⁶ The pseudo-cisoid conformations of both ylidic fragments are also characterized by (i) the intramolecular P–O distance (P(1)···O(1) = 3.047(3) Å) and (ii) the intramolecular hydrogen bond (O(1)···H(26) = 2.410(3) Å; O(1)···C(26) = 2.826(3) Å; O(1)···H(26)–C(26) = 102.7(1)°), which are similar to those reported in related complexes.^{3–5} The Pd–P and Pd–Cl bond distances are typical,^{23a} as are the internal bond distances on the bis-ylide ligand,^{23b} and do not merit further comment.

The chelating bond angle C(21)–Pd(1)–C(2) (67.40(10)°) is identical within experimental error with those found in [Pd(μ-Cl)(Ph₃PC(H)C(O)C(H)PPh₃)₂](ClO₄)₂ (68.8(4) and 68.0(5)°).² On the other hand, the C(2)–Pd(1)–Cl(1) bond angle (98.22(7)°) is closer to those found in [Pd(μ-Cl)(Ph₃PC(H)C(O)C(H)PPh₃)₂](ClO₄)₂ (101.0(3) and 102.6(3)°),² probably due to the steric hindrance of the PPh₃ ligand. The pyridine ring appears to be slightly rotated with respect to the N(1)–C(21) bond, this fact being characterized by the torsion angle C(26)–N(1)–C(21)–C(1) (–48.6(2)°) and by the angle between the

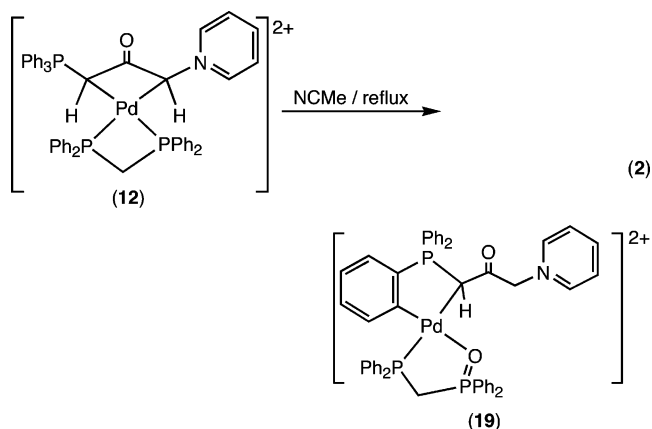
best least-squares planes defined by N(1)–C(21)–C(1)–O(1) and C(26)–N(1)–C(21)–C(1) (39.0(2)°). It is also interesting to note that the calculated bond distances and angles in the species **3cc** are in good agreement with those determined in **6** by X-ray diffraction methods (for values, see Tables 1 and 4).

5. Ortho-Metalation Reactions on Pd(II) and Pt(II) Complexes. We have already established one of our main objectives—the conformational preferences operating on pyridinium N-ylides and on phosphonium P-ylides have a complementary behavior. We have also described the different reactivities of complexes containing the bis-ylide [H₅C₅NC(H)C(O)C(H)=PPh₃] with respect to those with the bis-ylide [Ph₃P=C(H)C(O)C(H)=PPh₃], mainly due to steric factors. In particular, the ortho-metalation of the bis-ylide seems to be a very restricted process. Despite all the difficulties found in promoting a C–H activation reaction due to the general high stability of the C,C-bonded mixed bis-ylide, some systems could be activated through thermal processes.

The thermal treatment of complex **6** in refluxing NCMe for 24 h gives, after workup, the ortho-metalated [PdCl(C₆H₄-2-PPh₂C(H)C(O)CH₂NC₅H₅)(PPh₃)](ClO₄) (**18**) (see the Experimental Section and eq 1). As reported previously,^{6,10} the reaction

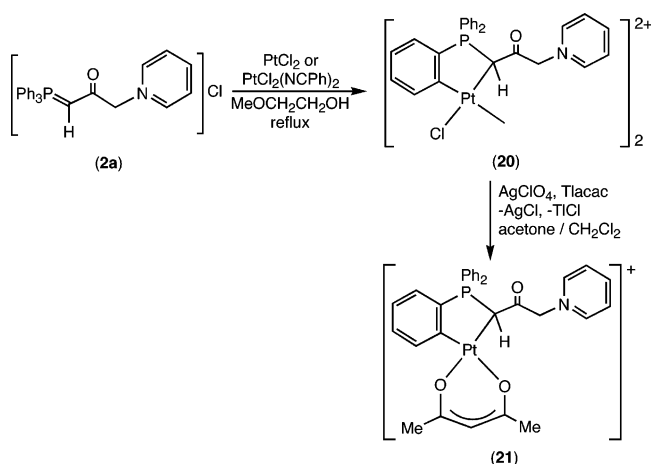


solvent in these processes is critical. The refluxing of **6** (24 h) in CHCl₃ or ClCH₂CH₂Cl leaves the starting material unchanged, and refluxing in 2-methoxyethanol produces its immediate decomposition. The ancillary ligand seems also to be important. Thus, the treatment of **7** under the same reaction conditions (NCMe) also produces the complete decomposition of the starting material. When **9–12** were subjected to the same thermal treatment, only **12** was successfully transformed into [Pd(C₆H₄-2-PPh₂C(H)C(O)CH₂NC₅H₅)(dppm-O)](ClO₄)₂ (**19**) (see eq 2), while the starting compounds were recovered in all other cases. From these results, it is clear that the C–H activation process in the bonded mixed bis-ylide is less versatile than those observed in other bis-ylides.



(23) (a) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, D.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1–S83. (b) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, 685 (S1–S19).

Scheme 4



The C–H bond activation can be promoted even by direct refluxing of a simple metal complex with the corresponding ylide or phosphonium salt.²⁴ This process has been attempted by starting from the ylide–pyridinium salts **2a,b** and Pd(II) and Pt(II) salts. The reactions of $\text{Pd}(\text{OAc})_2$ or $\text{PdCl}_2(\text{NCMe})_2$ with **2a,b** have already been described and afford **3** or **8** (see Schemes 1 and 2). The same processes under other reaction conditions (refluxing MeOH or $\text{MeOCH}_2\text{CH}_2\text{OH}$) give decomposition. However, the reaction of **2a** with $\text{PtCl}_2(\text{NCPh})_2$ (1:1 molar ratio) in refluxing $\text{MeOCH}_2\text{CH}_2\text{OH}$ for 24 h gives $[\text{Pt}(\mu\text{-Cl})(\text{C}_6\text{H}_4\text{-2-PPH}_2\text{C}(\text{H})\text{C}(\text{O})\text{CH}_2\text{NC}_5\text{H}_5)](\text{Cl})_2$ (**20**) in moderate yield (see Scheme 4). This reactivity is different from that reported for the P bis-ylide.^{9,10} Complex **20** reacts very clearly with AgClO_4 and $\text{Tl}(\text{acac})$ (1:2:2 molar ratio) to give $[\text{Pt}(\text{acac-O,O}')(\text{C}_6\text{H}_4\text{-2-PPH}_2\text{C}(\text{H})\text{C}(\text{O})\text{CH}_2\text{NC}_5\text{H}_5)]\text{ClO}_4$ (**21**), which is more soluble than **20** and could be completely characterized. The thermal rearrangement of hindered Pd(II) complexes **6** and **12** and direct synthesis in the case of the Pt(II) complex **20** seem to be the only ways to obtain ortho-metalated derivatives from the mixed bis-ylide.

The characterization of **18–21** was carried out on the basis of their analytical and spectroscopic data. All complexes show satisfactory elemental analyses and mass spectra. The ^1H NMR spectra of **18** and **19** show the presence of, among others, seven well-spread and well-resolved signals: (i) four multiplets in the low-field region (6.5–7.0 ppm), corresponding to the PdC_6H_4 unit; (ii) an AB spin system (5.5–6.5 ppm), corresponding to the diastereotopic protons of the NCH_2 group; (iii) a multiplet (4.5–5.2 ppm) assigned to the ylidic proton $\text{PdC}(\text{H})\text{P}$. These facts, together with the shift to high frequencies of the carbonyl stretch (from 1600 to 1630 cm^{-1}),⁶ which corresponds to a change from the bis-ylide situation to an ylide–pyridinium one, are the key features for the identification of the ortho-metalated unit and the pyridinium cation.

In this aspect, the rearrangement of $[\text{Pd}(\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{NC}_5\text{H}_5)]$ to give the metalated species $[\text{Pd}(\text{C}_6\text{H}_4\text{-2-PPH}_2\text{-C}(\text{H})\text{C}(\text{O})\text{CH}_2\text{NC}_5\text{H}_5)]$ is formally very similar to that reported for the transformation of $[\text{Pd}(\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{PPh}_3)]$ into the $[\text{Pd}(\text{C}_6\text{H}_4\text{-2-PPH}_2\text{-C}(\text{H})\text{C}(\text{O})\text{CH}_2\text{PPh}_3)]$ group.⁶ The C–H bond activation step, which gives the $[\text{Pd}(\text{C}_6\text{H}_4\text{-2-PPH}_2\text{C}(\text{H})\text{C}(\text{O}))]$ fragment, is followed by an acid–base reaction in which the

remaining ylide unit captures the proton resulting from the ortho metalation and is transformed into a pyridinium group. For complex **18** the trans arrangement of the ylidic carbon atom and the PPh_3 ligand is similar to those found in related complexes⁶ and can be inferred from the observation of a $^3J_{\text{PH}}$ coupling constant of about 8.4 Hz. In the case of complex **19**, the oxidation of the dppm ligand is not an uncommon process^{6,25} and has been described in related reactions. By analogy, we propose the structure shown in eq 2, in which the oxygen is trans to then ortho-metalated C atom. The presence of the oxidized P atom is clearly seen through the observation of a signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 58.05 ppm. On the other hand, the mass spectrum (FAB+) of **20** suggests its dinuclear nature due to the observation of a peak at m/z 1287, with the correct isotopic distribution for the stoichiometry $[\text{C}_{52}\text{H}_{44}\text{-Cl}_3\text{N}_2\text{O}_2\text{P}_2\text{Pt}_2]$; that is, a cationic dinuclear complex with halide bridges and a chloride as a counterion, arising from **20** by loss of the other chloride. An ortho-metalated structure such as that depicted in Scheme 4 for **20** should give, in principle, up to four possible isomers distinguishable by NMR methods—two diastereoisomers (RR/SS and RS/SR) in two different geometric orientations, syn and anti. The NMR spectra of **20** show in each case two identical sets of signals (2.50/1 molar ratio), corresponding to the two possible diastereoisomers (RR/SS and RS/SR) of only one geometric isomer (anti or syn). We can propose an anti arrangement of the two ortho-platinated unit based on two arguments. (i) We have previously shown that the syn geometries are mainly obtained as kinetic isomers, under mild reaction conditions, while the anti geometries are obtained as thermodynamic isomers under strong reaction conditions;⁹ the synthesis of **20** corresponds clearly to the second case. (ii) Moreover, the difference in chemical shifts ($\Delta\delta$) for the ylidic protons in the ^1H NMR spectrum of **20** (0.09 ppm) is very similar to that reported in the literature for other related anti complexes (ranging from 0.06 to 0.08 ppm).^{6,9} Even if a moderate diastereoselective excess is obtained in the synthesis of **20** (de = 42.8%), we have not been able to assign unambiguously a given conformation to each set of data due to extensive overlapping of signals in the aromatic region of the ^1H NMR spectrum. The presence of the ortho-platinated $[\text{Pt}(\text{C}_6\text{H}_4\text{-2-PPH}_2\text{-C}(\text{H})\text{C}(\text{O})\text{CH}_2\text{NC}_5\text{H}_5)]$ fragment can be adequately characterized in a more soluble and less overlapped environment. Further derivatization of **20** by treatment with AgClO_4 and $\text{Tl}(\text{acac})$ (1:2:2 molar ratio) gives the corresponding acac derivative $[\text{Pt}(\text{acac-O,O}')(\text{C}_6\text{H}_4\text{-2-PPH}_2\text{C}(\text{H})\text{C}(\text{O})\text{CH}_2\text{NC}_5\text{H}_5)]\text{ClO}_4$ (**21**), which can be fully characterized. The ^1H NMR spectrum show the aforementioned well-resolved pattern of seven signals, corresponding to the PtC_6H_4 , $-\text{NCH}_2-$, and $\text{PtC}(\text{H})\text{P}$ fragments, in addition to other expected peaks due to the bis-ylide and acac ligands. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum provides fundamental evidence of the presence of the PtC_6H_4 unit, since it show six different signals assigned to the six chemically nonequivalent C atoms, from which the ortho-metalated carbon C_1 appears at 140.70 ppm, typical for this type of C atom in Pt(II) complexes.⁹ In accord with these data, we propose the structure shown in Scheme 4 for **21**.

Conclusions

The synthesis and characterization of palladium complexes with the mixed bis-ylide $[\text{H}_5\text{C}_5\text{NC}(\text{H})\text{C}(\text{O})\text{C}(\text{H})=\text{EPh}_3]$ ($\text{E} = \text{P}, \text{As}$) are reported. The resulting complexes are obtained as unique diastereoisomers in the meso form. The two ylidic

(24) (a) Illingsworth, M. L.; Teagle, T. A.; Burmeister, J. L.; Fultz, W. C.; Rheingold, A. L. *Organometallics* **1983**, 2, 1364. (b) Vicente, J.; Chicote, M. T.; Fernández-Baeza, J. *J. Organomet. Chem.* **1989**, 364, 407. (c) Gracia, C.; Marco, G.; Navarro, R.; Romero, P.; Soler, T.; Urriolabeitia, E. P. *Organometallics* **2003**, 22, 4910. (d) Petz, W.; Kutschera, C.; Neumüller, B. *Organometallics* **2005**, 24, 5038.

(25) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, 16, 2127.

fragments show in these complexes the same conformational preferences as those characterized in pure P or N bis-ylide complexes. The mixed bis-ylides and their corresponding complexes have been studied by means of DFT calculations and by Bader analysis of electron density. As in pure P and N bis-ylides, the 1,4-P $\cdots$ O and 1,6-CH $\cdots$ O=C intramolecular interactions were characterized by localization of their corresponding bond and ring critical points. In addition, we have characterized a new 1,4-As $\cdots$ O intramolecular interaction, which is very similar in nature to the previously determined 1,4-P $\cdots$ O moderate electrostatic-type interaction. Both types of interactions (1,4-E $\cdots$ O and 1,6-CH $\cdots$ O=C) take place simultaneously in cisoid-cisoid isomers **2cc** and **15cc**, playing a key role in the higher stabilization of these isomers. Moreover, the cisoid-cisoid conformational preferences of the free mixed PN and AsN bis-ylides are transferred to the complexes, as was the case for pure P and N bis-ylides. Thus, it seems clear that the two types of interactions operate in a cooperative way. The reactivity of the complexes containing the [Pd{Ph₃PC(H)C(O)C(H)NC₅H₅}] unit shows striking differences from the analogous [Pd{Ph₃PC(H)C(O)C(H)PPh₃}] unit, probably because of a combination of steric and electronic effects. For instance, the ortho-palladation of the bis-ylide is only achieved by refluxing of the bis-ylide complexes in the presence of bulky ligands. The ortho-platination of the mixed bis-ylide is, however, easily achieved by direct reaction of PtCl₂ with the mixed salt [H₅C₅NCH₂C(O)C(H)=PPh₃]Cl.

Experimental Section

Safety Note. *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared, and they should be handled with great caution.³⁴

Synthesis of [Ph₃P=C(H)C(O)CH₂NC₅H₅]Cl (2a**).** A clear solution of [Ph₃P=C(H)C(O)CH₂Cl] (3.000 g, 8.5 mmol) and pyridine (6.8 mL, 85 mmol) in THF (15 mL) was refluxed for 30 h. After the reaction time, the solid (**2a**) was filtered, washed with cold THF (20 mL) and Et₂O (50 mL), and dried by suction. Yield: 3.110 g (85%). ¹H NMR (CD₂Cl₂, δ): 4.26 (d, 1H, C(H)P, ²J_{PH} = 22.0 Hz), 5.66 (s, 2H, CH₂N), 7.45–7.67 (m, 15H, PPh₃), 7.92 (t, 2H, H₃, py, ³J_{HH} = 6.8 Hz), 8.31 (t, 1H, H₄, py, ³J_{HH} = 7.7 Hz), 9.18 (d, 2H, H₂, py, ³J_{HH} = 6.0 Hz). ³¹P{¹H} NMR (CD₂Cl₂, δ): 15.44.

Synthesis of cis-[Cl₂Pd{Ph₃PC(H)C(O)C(H)NC₅H₅}] (3**).** **Method A.** To a suspension of **1** (0.313 g, 0.67 mmol) in CH₂Cl₂ (20 mL) was added Pd(OAc)₂ (0.150 g, 0.67 mmol). The resulting red-orange solution was stirred at room temperature for 30 min. During this time a deep yellow solid (**3**) precipitated, which was filtered, washed with additional CH₂Cl₂ (10 mL) and Et₂O (50 mL), and dried by suction. Yield: 0.298 g (78%).

Method B. To a solution of **2a** (0.300 g, 0.69 mmol) in MeOH (15 mL) were added NEt₃ (97 μ L, 0.69 mmol) and PdCl₂(NCMe)₂ (0.180 g, 0.69 mmol) at room temperature. A deep yellow solid (**3**) precipitated almost instantaneously. This solid was filtered, washed with MeOH (10 mL) and Et₂O (25 mL), and dried in vacuo. Yield: 0.381 g (96%). ¹H NMR (DMSO-*d*₆, δ): 4.22 (s, br, 1H, C(H)P), 5.73 (s, br, 1H, C(H)N), 7.61–7.63 (m, 6H, H_m, PPh₃), 7.71–7.76 (m, 3H, H_p, PPh₃), 7.78–7.90 (m, br, 6H, H_o, PPh₃), 7.98 (t, 2H, H₃, py, ³J_{HH} = 7.0 Hz), 8.45 (t, 1H, H₄, py, ³J_{HH} = 7.7 Hz), 9.01 (d, 2H, H₂, py, ³J_{HH} = 6.0 Hz). ³¹P{¹H} NMR (DMSO-*d*₆, δ): 23.82.

Synthesis of [Pd(μ -Cl){Ph₃PC(H)C(O)C(H)NC₅H₅}]₂(ClO₄)₂ (4**).** To a suspension of **3** (1.000 g, 1.746 mmol) in CH₂Cl₂ (40 mL) was added AgClO₄ (0.362 g, 1.75 mmol). The resulting yellow suspension was stirred at room temperature for 30 min with

exclusion of light and then filtered over Celite. The clear deep yellow solution was evaporated to dryness, and the oily residue was treated with Et₂O (50 mL) and continuous stirring, giving **4** as a yellow solid. This solid was filtered, washed with additional Et₂O (50 mL), and dried in vacuo. Yield: 1.102 g (99% yield). The characterization of **4** by NMR showed the presence of a mixture of two isomers in 2.25/1 molar ratio. ¹H NMR (CD₂Cl₂, δ): 3.97 (s, br, C(H)P, both isomers), 5.78 (s, br, C(H)N, minor isomer), 5.99 (s, br, C(H)N, major isomer), 7.51–7.79 (m, PPh₃ + H₃(py), both isomers), 8.26 (s, br, H₄, py, both isomers), 8.86 (s, br, H₂, py, minor isomer), 8.95 (s, br, H₂, py, major isomer). ³¹P{¹H} NMR (CD₂Cl₂, δ): 24.19 (minor isomer), 23.74 (major isomer).

Synthesis of [PdCl(PPh₃){Ph₃PC(H)C(O)C(H)NC₅H₅}]ClO₄ (6**).** To a suspension of **3** (0.200 g, 0.157 mmol) in CH₂Cl₂ (20 mL) was added PPh₃ (0.082 g, 0.314 mmol). The initial yellow suspension dissolved in a few seconds, but the stirring was maintained for 30 min at room temperature. After the reaction time, the resulting yellow solution was evaporated to dryness and the residue was treated with Et₂O, giving **6** as a yellow solid. This solid was filtered, washed with Et₂O (10 mL), and dried in vacuo. Yield: 0.230 g (81%). ¹H NMR (CD₂Cl₂, δ): 4.22 (ddd, 1H, C(H)P, ²J_{PH} = 6.4, ³J_{PH} = 9.9, ⁴J_{HH} = 0.9 Hz), 5.99 (s, br, 1H, C(H)N), 7.05 (t, 2H, H₃, py, ³J_{HH} = 7.2 Hz), 7.19–7.23 (m, 6H, H_m, PPh₃), 7.28–7.32 (m, 3H, H_p, PPh₃), 7.35–7.41 (m, 6H, H_o, PPh₃), 7.44–7.52 (m, 6H, H_m, PPh₃), 7.54–7.61 (m, 3H, H_p, PPh₃), 7.77 (t, 1H, H₄, py, ³J_{HH} = 7.2 Hz), 7.80–7.87 (m, 6H, H_o, PPh₃), 8.27 (dd, 2H, H₂, py, ³J_{HH} = 5.9, ⁴J_{HH} = 1.2 Hz). ³¹P{¹H} NMR (CD₂Cl₂, δ): 23.68 (d, 1P, Pd–PPh₃, ³J_{PP} = 4.7 Hz), 26.30 (d, 1P, C(H)PPh₃).

Synthesis of [Ph₃As=C(H)C(O)CH₂Br] (14**).** To a solution of Na₂CO₃ (0.233 g, 2.2 mmol) in H₂O (15 mL) was added rapidly a solution of **13** (2.300 g, 4.40 mmol) in MeOH (15 mL). A white solid (**14**) precipitated almost instantaneously. The mixture was diluted with additional water (30 mL) and further stirred at room temperature for 15 min. After the reaction time, the ylide **14** was filtered, washed with cold water (10 mL), and dried in vacuo. Yield: 1.440 g (74%). ¹H NMR (CDCl₃, δ): 3.87 (s, 2H, CH₂Br), 4.44 (s, 1H, As=CH), 7.56 (t, 6H, H_m, AsPh₃, ³J_{HH} = 7.6 Hz), 7.65 (t, 3H, H_p, AsPh₃, ³J_{HH} = 7.2 Hz), 7.70 (d, 6H, H_o, AsPh₃, ³J_{HH} = 7.6 Hz).

Synthesis of [Ph₃As=C(H)C(O)CH₂NC₅H₅]Br (15**).** Compound **15** was prepared by following a synthetic procedure similar to that reported for **2a**. Yield: 0.566 g (60% yield). ¹H NMR (CD₂Cl₂, δ): 5.56 (s, vbr, 1H, C(H)As), 6.08 (s, 2H, CH₂N), 7.66 (t, 6H, H_m, AsPh₃, ³J_{HH} = 7.0), 7.73 (t, 3H, H_p, AsPh₃, ³J_{HH} = 7.2), 7.84 (d, 6H, H_o, AsPh₃, ³J_{HH} = 7.2), 7.89 (t, 2H, H₃, py, ³J_{HH} = 6.8), 8.43 (t, 1H, H₄, py, ³J_{HH} = 7.6), 9.61 (d, 2H, H₂, py, ³J_{HH} = 6.0).

Synthesis of cis-[Cl₂Pd{Ph₃AsC(H)C(O)C(H)NC₅H₅}] (16**).** To a solution of **15** (0.200 g, 0.38 mmol) in MeOH (20 mL) were added NEt₃ (54 μ L, 0.39 mmol) and PdCl₂(NCMe)₂ (0.100 g, 0.38 mmol) at room temperature. A light brown solid (**16**) precipitated almost instantaneously. This solid was filtered, washed with MeOH (5 mL) and Et₂O (25 mL), and dried in vacuo. Yield: 0.177 g (75%). ¹H NMR (DMSO-*d*₆, δ): 4.54 (s, br, 1H, CHAs), 5.89 (s, br, 1H, CHN), 7.59–7.86 (m, 15H, PPh₃), 7.99 (t, 2H, H₃, py, ³J_{HH} = 6.9), 8.45 (t, 1H, H₄, py, ³J_{HH} = 7.2), 9.07 (s, br, 2H, H₂, py).

Synthesis of [PdCl(C₆H₄-2-PPh₂C(H)C(O)CH₂NC₅H₅)(PPh₃)]ClO₄ (18**).** A suspension of **6** (0.200 g, 0.222 mmol) in dry NCMe (20 mL) was refluxed for 24 h. At this point, some decomposition (black Pd⁰) is evident. Once it was cooled, the orange-brown suspension was filtered over Celite and the resulting solution was evaporated to dryness. The residue was suspended in MeOH (15 mL), and the suspension was stirred at room temperature for 12 h. A small fraction of an insoluble solid (mainly starting product **6**) was filtered and discarded. The alcoholic solution was evaporated to dryness, and the residue was treated with Et₂O (20 mL) and

vigorous stirring, giving **18** as an orange solid. Yield: 0.150 g (75%). ^1H NMR (CD_2Cl_2 , δ): 4.49 (dd, 1H, PdC(H)P, $^3J_{\text{PH}} = 8.4$, $^2J_{\text{PH}} = 1.2$ Hz), 5.71 (d, 1H, CH_2N , $^2J_{\text{HH}} = 16.0$ Hz), 6.33 (d, 1H, CH_2N , $^2J_{\text{HH}} = 16.0$ Hz), 6.48 (t, 1H, C_6H_4 , $^3J_{\text{HH}} = 7.6$ Hz), 6.60 (m, br, 1H, C_6H_4), 6.79 (m, 1H, C_6H_4), 6.91 (dd, 1H, C_6H_4 , $^3J_{\text{HH}} = 7.6$, $^3J_{\text{HH}} = 8.0$ Hz), 7.07 (t, 2H, H_3 , py, $^3J_{\text{HH}} = 7.2$ Hz), 7.17–7.82 (m, 23H, $\text{PPh}_3 + \text{PPh}_2$), 8.02 (m, 2H, H_o , PPh_2), 8.23 (t, 1H, H_4 , py, $^3J_{\text{HH}} = 7.6$ Hz), 8.93 (d, 2H, H_o , py, $^3J_{\text{HH}} = 6.0$ Hz). $^{31}\text{P}\{-^1\text{H}\}$ NMR (CD_2Cl_2 , δ): 16.19 (d, 1P, C_6H_4 -2- PPh_2 , $^3J_{\text{PP}} = 15.9$ Hz), 32.22 (d, 1P, Pd- PPh_3).

Computational Details. Calculations were performed using the GAUSSIAN98 series of programs.¹⁶ Density functional theory (DFT) was applied with the B3LYP functional.¹¹ Effective core potentials (ECP) were used to represent the innermost electrons of the palladium atom.^{11,26} The basis set for Pd was that associated with the pseudopotential, with a standard double- ζ LANL2DZ contraction.¹⁶ The C, N, O, Cl, As, and P atoms were represented by means of the 6-31G(d) basis set, whereas the 6-31G basis set was employed for the H atoms.²⁷ All geometry optimizations were full, with no restrictions. Stationary points located in the potential energy hypersurface were characterized as true minima through vibrational analysis. The topological properties of the electron density were investigated using the XAIM 1.0 program²⁸ using the B3LYP density, as described in AIM theory.²⁹

Crystal Structure Determination and Data Collection of 6- $3\text{CH}_2\text{Cl}_2$. Yellow crystals of adequate quality for X-ray measure-

ments were grown by slow diffusion of Et_2O into a CH_2Cl_2 solution of the crude compound at low temperature (-18°C). These crystals readily lose solvent; thus, they were always handled in the mother liquor. A single crystal (dimensions specified in Table 3) was very quickly mounted at the end of a quartz fiber in a random orientation, covered with Magic Oil, and placed under the cold stream of nitrogen. Data collection was performed at 100 K on an Oxford Diffraction Xcalibur2 diffractometer using graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). A hemisphere of data was collected on the basis of three ω -scan or ϕ -scan runs. The diffraction frames were integrated using the program CrysAlis RED,³⁰ and the integrated intensities were corrected for absorption with SADABS.³¹

Structure Solution and Refinement. The structures were solved and developed by Patterson and Fourier methods.³² All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed at idealized positions and treated as riding atoms. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The structures were refined to F_o^2 , and all reflections were used in the least-squares calculations.³³

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Supporting Information Available: Text giving full experimental details, and a CIF file and tables giving data collection parameters, atomic coordinates, complete bond distances and angles, and thermal parameters for **6- $3\text{CH}_2\text{Cl}_2$** . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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