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Article

Palladium Complexes of a Phosphorus Ylide with Two Stabilizing Groups: Synthesis, Structure, and DFT Study of the Bonding Modes[†]

Larry R. Falvello,[‡] Juan Carlos Ginés,[‡] Jorge J. Carbó,[§] Agustí Lledós,*,[||] Rafael Navarro,[‡] Tatiana Soler,[⊥] and Esteban P. Urriolabeitia*,[‡]

Departamento de Compuestos Organometálicos, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza - CSIC, 50009 Zaragoza, Spain, Departament de Química-Física i Inorgánica, Universitat Rovira i Virgili, 43007 Tarragona, Spain, Departament de Química, Edifici Cn, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain, and Servicios Técnicos de Investigación, Facultad de Ciencias Fase II, 03690 San Vicente de Raspeig, Alicante, Spain

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The phosphorus ylide ligand [$Ph_3P{=}C(CO_2Me)C({=}NPh)CO_2Me$] (**L1**) has been prepared and fully characterized by spectroscopic, crystallographic, and density functional theory (DFT) methods (B3LYP level). The reactivity of **L1** toward several cationic Pd^{II} and Pt^{II} precursors, with two vacant coordination sites, has been studied. The reaction of [$M(C{\wedge}X)(THF)_2$]ClO_4 with **L1** (1:1 molar ratio) gives [$M(C{\wedge}X)$(**L1**)]ClO_4 [M = Pd, $C{\wedge}X$ = $C_6H_4CH_2NMe_2$ (**1**), *S*-$C_6H_4C(H)MeNMe_2$ (**2**), CH_2-8-C_9H_6N (**3**), C_6H_4-2-NC_5H_4 (**4**), *o*-$CH_2C_6H_4P$(*o*-tol)$_2$ (**6**), η^3-C_3H_5 (**7**); M = Pt, $C{\wedge}X$ = *o*-$CH_2C_6H_4P$(*o*-tol)$_2$ (**5**); $M(C{\wedge}X)$ = $Pd(C_6F_5)(SC_4H_8)$ (**8**), $PdCl_2$ (**9**)]. In complexes **1**–**9**, the ligand **L1** bonds systematically to the metal center through the iminic N and the carbonyl O of the stabilizing CO_2Me group, as is evident from the NMR data and from the X-ray structure of **3**. Ligand **L1** can also be orthopalladated by reaction with $Pd(OAc)_2$ and LiCl, giving the dinuclear derivative [$Pd(\mu$-$Cl)$(*C*$_6H_4$-2-$PPh_2{=}C(CO_2Me)C(CO_2Me){=}$*N*Ph)]$_2$ (**10**). The X-ray crystal structure of **10** is also reported. In none of the prepared complexes **1**–**10** was the C_α atom found to be bonded to the metal center. DFT calculations and Bader analysis were performed on ylide **L1** and complex **9** and its congeners in order to assess the preference of the six-membered N,O metallacycle over the four-membered C,N and five-membered C,O rings. The presence of two stabilizing groups at the ylidic C causes a reduction of its bonding capabilities. The increasing strength of the Pd–C, Pd–O, and Pd–N bonds along with other subtle effects are responsible for the relative stabilities of the different bonding modes.

Introduction

The chemistry of metal complexes with ylides is a subject of present interest.[1] The α-stabilized phosphorus ylides [$Ph_3P{=}C(H)R$] [R = CN, C(O)R′; R′ = Me, Ph, OMe, NMe_2] have proven to be versatile ligands toward transition metals because of the presence of different functional groups in their molecular skeleton.[1a–s] This versatility has allowed the characterization of coordinated ylides in different bonding modes: C-coordinated (through the C_α atom), O-bonded (through the carbonyl O), N-bonded (through the N of the cyano group), or even situations in which the same ylide shows a combination of bonding modes.[1] An interesting fact is that, despite the presence of several potential donor atoms on the same ylide, they always behave as ambidentate ligands.[1]

We are interested in the bonding properties of polyfunctional phosphorus ylides, and we have now focused our attention on the doubly stabilized ylides. The presence of functional groups containing donor atoms expands the bonding abilities of the ylides. The introduction of an additional stabilizing functional group can be achieved through several simple synthetic procedures: acylation,[2] reactivity toward alkynes or other unsaturated compounds,[3] reactivity of iminophosphoranes with alkynes,[4] retro-Wittig reactions,[5] and other less common processes.[6] These types of ylides have been the subject of intensive research from a

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[†] Dedicated to Professor Victor Riera on the occasion of his 70th birthday.

* To whom correspondence should be addressed. E-mail: agusti@klingon.uab.es (A.L.), esteban@unizar.es (E.P.U.). Fax: (+34) 976761187.

[‡] Universidad de Zaragoza.

[§] Universitat Rovira i Virgili.

[||] Universitat Autònoma de Barcelona.

[⊥] Facultad de Ciencias Fase II.

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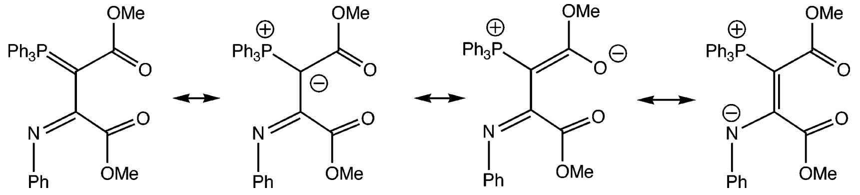

Figure 1. Resonance forms of the ylide **L1**.

purely organic point of view. However, metal complexes of doubly stabilized phosphorus ylides are scarcely explored, and few examples have been characterized crystallographically.[7] The reaction of mercury(II) halides HgX_2 (X = Cl, Br, I) or uranium(VI) salts with $Ph_3P{=}C[C(O)Me][C(O)Ph]$ (ABPPY) gives mono- and dinuclear complexes in which the ylide bonds to the metal center through the acetyl O.[7a,d] The reactivity of the ABPPY ylide toward HgX_2 complexes is different from that observed with the stabilized ylide $Ph_3P{=}C(H)C(O)Ph$ (BPPY) because the latter coordinates selectively through the C_α atom.[8] Meanwhile, the reaction of $PtCl_2(NCC_6F_5)_2$ with $Ph_3P{=}C(H)CO_2Me$ gives, among other products, the imine−ylide complex $[PtCl_2\{NH{=}C(C_6F_5)C({=}PPh_3)C(O)Me\}_2]$,[7b] coordinated to the Pt center through the imine N atom. All of these examples share a common feature, which is the fact that the ylidic C_α atom is not involved in the coordination to the metals.

Aiming to expand our knowledge of the bonding properties of doubly stabilized phosphorus ylides, we have studied the reactivity of the ylide $[Ph_3P{=}C(CO_2Me)C({=}NPh)CO_2Me]$ (**L1**)[4] toward bis-solvates of Pd^{II} and Pt^{II}. In this ylide, there are three functional groups with a total of six donor atoms. Despite the polydenticity of **L1**, N,O-chelate complexes were obtained selectively. C_α-bonded complexes were not observed in any of the cases studied. This paper reports the results of the observed reactivity and aims to explain, on the basis of density functional theory (DFT) calculations, why the C_α atom is not bonded to the metal center.

Results and Discussion

1. Synthesis and Reactivity of L1. The ylide **L1** was obtained following previously reported procedures[4] with minor modifications (see the Experimental Section). The IR spectrum of **L1** shows three strong absorptions at 1734, 1647, and 1571 cm^{-1}, assigned to the carbonyl stretch of the β-remote nonconjugated CO_2Me group, to the C=O stretch in the α-resonance-stabilized CO_2Me unit,[9] and to the C=N iminic stretching,[10] respectively. The absorptions due to the resonance-stabilized C=N and C=O bonds appear at lower energies than expected, in accord with the charge delocalization through the N−C−C(P)−C−O system (Figure 1).

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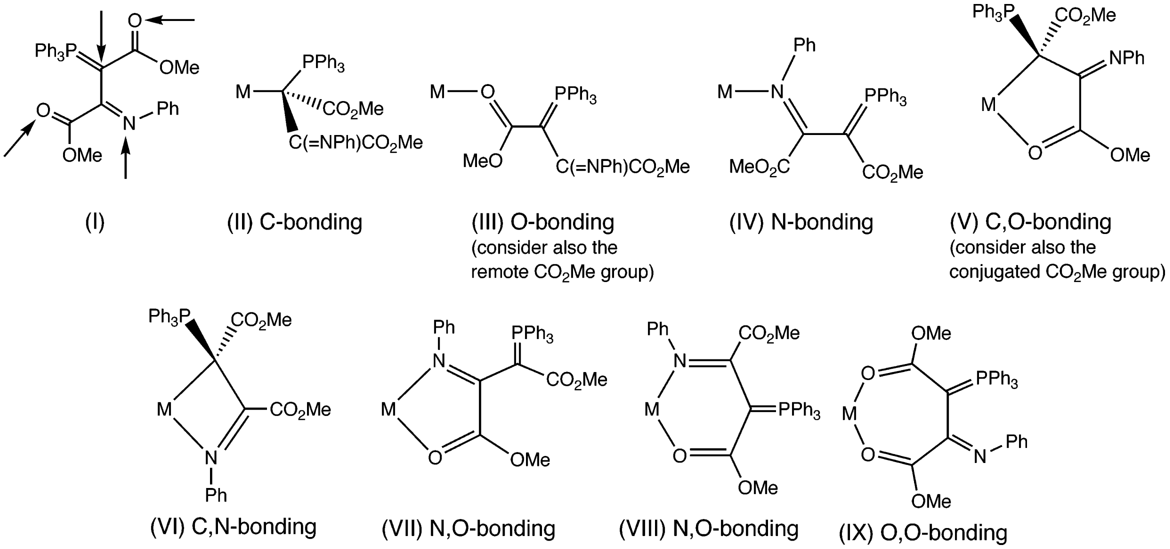
Chart 1



(I) (II) C-bonding (III) O-bonding (IV) N-bonding (V) C,O-bonding

(VI) C,N-bonding (VII) N,O-bonding (VIII) N,O-bonding (IX) O,O-bonding

The position of the $^{31}P\{^1H\}$ NMR signal (17.37 ppm) is in good agreement with the presence of the ylidic P═C bond,[9] as well as the doublet peak in the $^{13}C\{^1H\}$ NMR spectrum at 59.19 ppm ($^1J_{PC}$ = 119.6 Hz). Signals attributed to the carbonyl and imine groups are also observed in the $^{13}C\{^1H\}$ NMR spectrum at 160.33 (C═N), 166.56 (C═O nonresonant with the P═C bond), and 168.47 (C═O resonant) ppm. Full assignment of the ^{13}C NMR signals (in **L1** and in all complexes) was performed with the help of heteronuclear single quantum coherence and multiple-bond $^1H-^{13}C$ correlations.

The cationic precursors $[M(C{\wedge}X)(THF)_2]ClO_4$ (THF = tetrahydrofuran) were prepared by the reaction of the corresponding dinuclear derivatives $[M(\mu\text{-}Cl)(C{\wedge}X)]_2$ with $AgClO_4$ (1:2 molar ratio; C∧X = ancillary ligands; see eq 1) in THF at room temperature. After elimination of the silver halide, the freshly prepared solutions of $[M(C{\wedge}X)(THF)_2]ClO_4$ were treated with ylide **L1** (1:1 molar ratio), resulting in the formation of the cationic mononuclear complexes $[M(C{\wedge}X)(\mathbf{L1})]ClO_4$ (**1**−**8**). Complex **9** was synthesized by the reaction of $Li_2[PdCl_4]$ with **L1** in methanol. The elemental analyses of complexes **1**−**9** are in good agreement with the stoichiometries shown in eq 1, and their mass spectra (positive ion fast atom bombardment, FAB^+) show in all cases the presence of the cationic fragment with the correct isotopic distribution. Because of the presence of at least four potential donor atoms (see Chart 1, I), no less than eight possible bonding modes can be envisaged (Chart 1, II−IX). The spectroscopic data of **1**−**9** allow their structure and, moreover, their stereochemistry to be ascertained.

The NMR spectra of complexes **1**−**9** show the following general features: (i) in all cases, only one set of signals is observed (even at low temperature, CD_2Cl_2, 183 K), with this fact suggesting that all products are obtained as single isomers; (ii) the pattern of resonances for complexes **1** and **3**−**6** shows that the molecular plane is a plane of symmetry; (iii) for **1**−**9**, the position of the P signal in the $^{31}P\{^1H\}$ NMR spectra is slightly deshielded (range 18−22 ppm) with respect to the free ligand **L1** (17.37 ppm); (iv) also in all cases, the signal due to the ylidic C atom (P═C) appears, in the $^{13}C\{^1H\}$ NMR spectra, in a narrow range of frequencies (65−72 ppm), close to that in the starting compound **L1** (59.19 ppm) and, moreover, with a coupling constant (average $^1J_{PC}$ = 117 Hz) very similar to that observed for **L1** ($^1J_{PC}$ = 119.6 Hz). This set of observations allows us to discard those bonding modes containing a C-bonded ylide (proposals II, V, and VI in Chart 1) because C coordination produces a clear deshielding of the ^{31}P signal[9] and a shielding of the signal due to the ylidic C_α atom in the ^{13}C NMR spectra, together with a notable decrease in the value of the $^1J_{PC}$ coupling constant, due to the hybridization change.[9] Moreover, C coordination should lead to the obtention of diastereoisomers in **2** (not observed) and to the loss of the molecular plane of symmetry in **1**, **3**, **5**, and **6**. The structures III and IV in Chart 1 can also reasonably be discarded because of the following facts: (i) the stoichiometry of the complexes shows clearly the presence of only one ligand per M atom; thus, it seems very likely that the ligand **L1** (which has four potential donor atoms) behaves as a chelating ligand; (ii) moreover, no solvent molecules (which could also be coordinated to the metal center) are observed in the NMR spectra; (iii) finally, the IR data show absorptions due to the presence of an ionic, noncoordinated ClO_4^- as the counterion.[11]

The discrimination between structures VII−IX (Chart 1) can be easily achieved from the IR data. The IR spectra of **1**−**9** show, for all studied complexes, the presence of a strong band in the range 1730−1750 cm^{-1} (mainly in the very narrow range 1730−1735 cm^{-1}) and another broad band in the range 1570−1610 cm^{-1}. It is sensible to suppose that the former is due to the carbonyl stretch of the CO_2Me unit nondelocalized by resonance because of its very close position with respect to that observed in free **L1** (1734 cm^{-1}). This observation suggests that this carbonyl group is not involved in coordination to the metal center (otherwise, a

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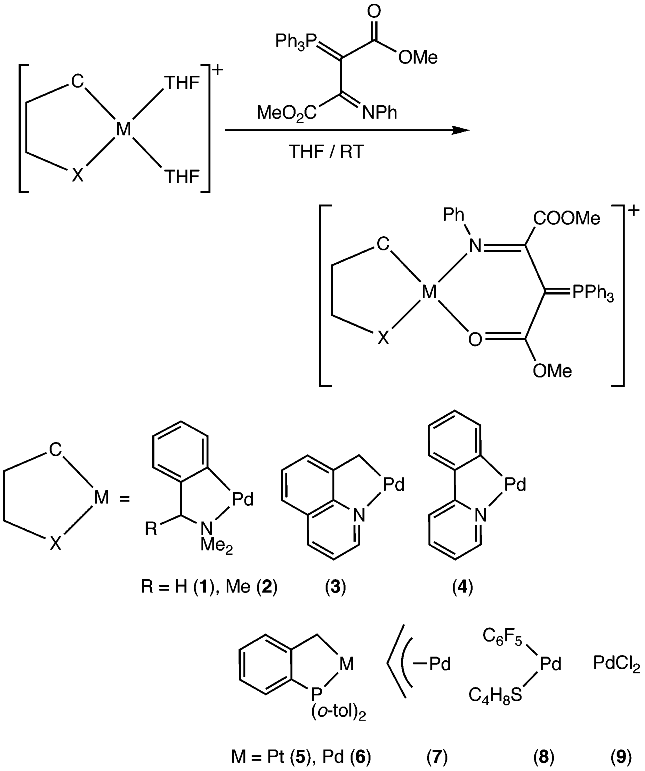
[11] Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd ed.; Wiley: New York, 1963; pp 111 and 175−177.

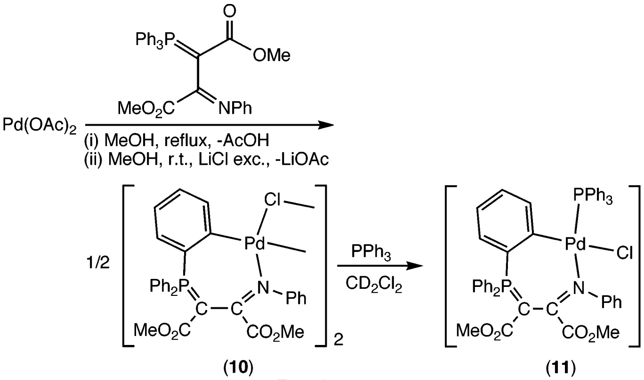
decrease in this carbonyl frequency should be observed) and that structures VII and IX (Chart 1) can also be discarded. Only structure VIII, a six-membered chelate ring formed by coordination of the iminic N atom and the stabilized carbonyl O, fits with all spectroscopic parameters. It is interesting to note that achievement of the optimal orientation in this bonding mode implies the rotation (at least) of the C═N bond around the $C_\alpha-C_\beta$ bond. An additional argument in favor of the N,O-chelating coordination comes from the deshielding observed for the ^{13}C NMR signals due to the iminic N═C and the stabilized carbonyl C═O carbon atoms (see the Experimental Section).[9,12] In fact, this coordination mode of the ligand is also in very good agreement with the resonance forms envisaged in Figure 1. For all of these reasons, we propose the N,O-coordination mode shown in eq 1 for ligand **L1**.



Equation 1

The asymmetry of ylide **L1** should give, a priori, two possible geometric isomers when N,O-bonded to the metal atom of precursors **1**−**6** and **8**. However, as has been stated, only one set of signals is observed in the NMR spectra over a wide range of temperatures, meaning that each compound is obtained as a single isomer. The C-trans-O arrangement proposed in eq 1 is supported by the observation in the 2D ^1H NOESY spectrum of complex **3** of a cross-peak between the H_{ortho} protons of the NPh group (6.94 ppm) and the methylene protons of the $PdCH_2$ unit of the 8-mq ligand (2.94 ppm). The O bonding of a keto-stabilized ylide trans to C is a common feature of this type of chemistry.[1,9] On the basis of these data and because of the close similarity of the C,N-orthopalladated ligands in complexes **1**−**4**, it is sensible to propose the same arrangement (C-trans-O) for all of them. This hypothesis was confirmed through the determination of the X-ray structure of **3** (see below). In the case of complexes **5** and **6**, the key feature is the observation of a clear nuclear Overhauser enhancement (NOE) effect (in the 2D ^1H NOESY spectra) between the H_{ortho} protons of the NPh group and the methylene protons of the metalated MCH_2 units. For complex **8**, the ^1H NOESY spectrum does not show NOE correlations between the protons of the SC_4H_8 ligand and the protons of the **L1** ligand. However, this fact cannot be considered as a positive argument in favor of a given structure. Consequently, the 2D $^{19}F-^1H$ NOESY spectrum of **8** was measured (see the Experimental Section). This spectrum shows three very clear heteronuclear NOE effects: a NOE between the F_{ortho} nuclei of the C_6F_5 ligand and the SCH_2 protons of the tetrahydrothiophene ligand and NOEs between the F_{ortho} nuclei of the C_6F_5 ligand and the H_{ortho} and H_{meta} protons of the NPh unit. The structure depicted in eq 1 ($C = C_6F_5$; $X = SC_4H_8$) for complex **8** matches all of these facts.

Further reactivity of ligand **L1** was attempted. The treatment of **L1** with $Pd(OAc)_2$ (OAc = acetate; 1:1 molar ratio) in methanol, followed by the addition of an excess of LiCl, gives the orthometalated dinuclear derivative $[Pd(C_6H_4\text{-}2\text{-}PPh_2{=}C(CO_2Me)\text{-}C(CO_2Me){=}NPh\text{-}\kappa\text{-}C,N)(\mu\text{-}Cl)]_2$ (**10**) in moderate yield (see eq 2). Complex **10** gives correct elemental analysis for the proposed stoichiometry. The ^1H NMR spectrum of **10** shows, in the aromatic region, four well-separated signals (6.57, 6.72, 6.77, and 6.93 ppm) corresponding to the four protons of the cyclopalladated phenyl ring. In addition, resonances corresponding to the other expected groups (PPh_2, NPh, and OMe) are also observed. The presence of the metalated phenyl ring can also be inferred from the $^{13}C\{^1H\}$ NMR spectrum because five different peaks (two partially overlapped) can be observed in the 120−130 ppm region together with an additional deshielded signal (153.01 ppm), which is attributed to the metalated C.[13] The $^{13}C\{^1H\}$ NMR spectrum also shows that the ylidic carbon atom C_α is not bonded to the Pd atom because the assigned signal appears as a doublet ($^1J_{PC}$ = 125.1 Hz) at 61.35 ppm, that is, in a position very similar to that observed for the free ligand **L1** (59.19 ppm) and with



Equation 2

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[12] Bravo, J.; Cativiela, C.; Navarro, R.; Urriolabeitia, E. P. *J. Organomet. Chem.* **2002**, *650*, 157.

virtually the same coupling (${}^1J_{PC} = 119.6$ Hz). The metallacycle is closed by coordination of the iminic N atom, forming a seven-membered ring, as can be inferred from the position of the iminic C resonance (164.56 ppm), deshielded from its position in the free ylide (160.33 ppm). The ${}^{31}P\{{}^1H\}$ NMR spectrum of **10** shows a signal at 9.56 ppm, shielded with respect to its position in free **L1** (17.37 ppm). This fact is an additional proof of the absence of interaction between the ylidic C_α atom and the Pd atom because C bonding promotes a deshielding of the corresponding signal.[13] All of these facts are in very good agreement with the structure depicted in eq 2 for **10**. This structure has been confirmed by X-ray diffraction methods.

The cyclopalladation of α-stabilized phosphorus ylides is not a very unusual reaction, and several examples have already been described.[1,13] However, in all reported cases, the metallacycle is closed forming a five-membered ring in which the donor atoms are the arylic C atom, that which has undergone the C−H bond activation process, and the ylidic C atom. This is not our case because the reluctance of the ylidic C_α atom to bind to the transition metal results in the formation of a seven-membered cycle, instead of the, in principle, more stable five-membered ring. Seven-membered metallacycles are very scarce, as can be seen from a search in the Cambridge Structural Database.[14] Of the most common metallacycles (four through seven members), a very low percentage (1.7%) have seven members (12 entries out of 691 having Pd with C and N donor atoms). This percentage increases slightly (2.6%) when considering all possible transition metals (49 entries out of 1890 with C and N donor atoms). The reactivity of **10** seems to be similar to that observed for other classical C,N-cyclopalladated derivatives. For instance, **10** reacts with PPh_3 (1:2 molar ratio, room temperature, CD_2Cl_2) to give the mononuclear **11**, by cleavage of the halide bridging system (see eq 2). When the reaction was performed with an excess of PPh_3 (1:4 molar ratio), **11** and unreacted PPh_3 were the only species detected in solution, this fact demostrating a noteworthy stability of the cycle. No other reactions were attempted.

In conclusion, the ylide **L1** coordinates as a neutral ligand to Pd^{II} and Pt^{II} solvates through the iminic N atom and through the resonance-stabilized carbonyl O. The orthometalation of **L1** can easily be achieved, with the concomitant formation of an unusual C_{aryl},N seven-membered ring. Despite the presumed nucleophilic properties of the ylidic carbon C_α, this atom does not coordinate to the metal center in any of the cases studied.

2. Crystal Structures of L1, 3, and 10·0.5CHCl$_3$. Molecular drawings are shown in Figures 2 (**L1**), 3 (**3**), and 4 and 5 (**10**). Parameters from the data collection and structure solution and refinement are given in Table 1, and selected bond distances and angles are collected in Tables 2 (**L1**), 3 and 4 (**3**), and 5 and 6 (**10**).

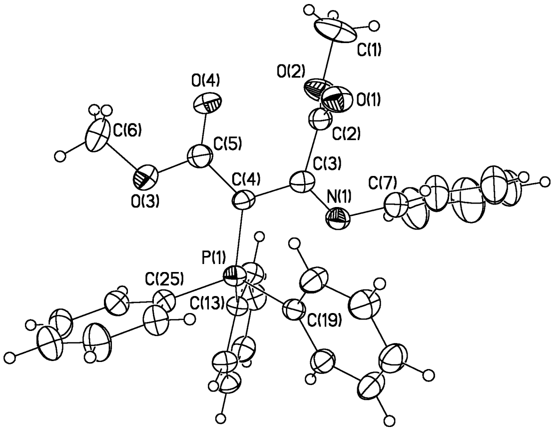

Figure 2. Thermal ellipsoid plot of **L1**. Non-H atoms are drawn at the 50% probability level.

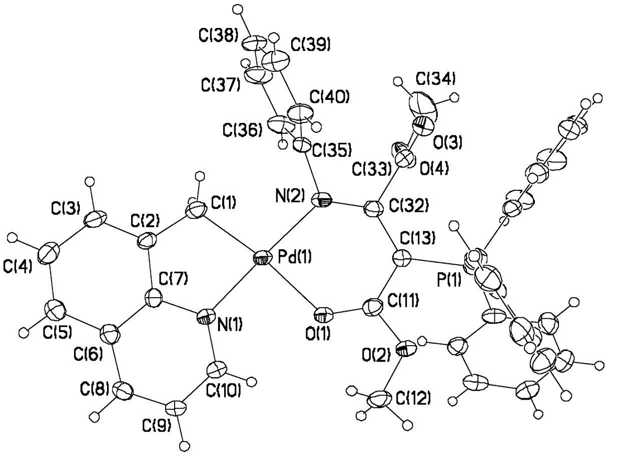

Figure 3. Thermal ellipsoid plot of the cationic part of **3**. Non-H atoms are drawn at the 50% probability level.

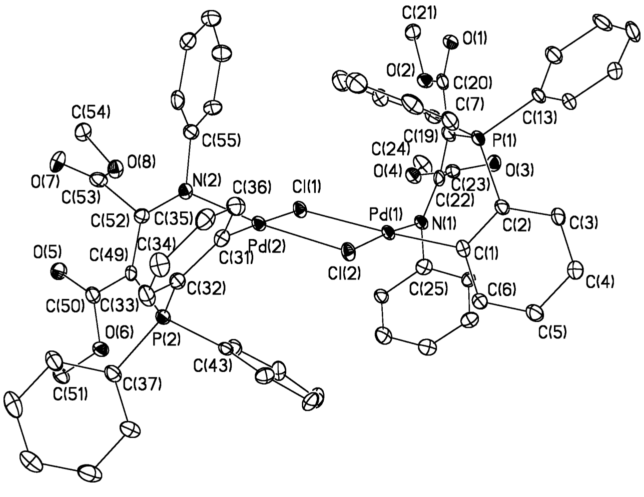

Figure 4. Thermal ellipsoid plot of complex **10**. Non-H atoms are drawn at the 50% probability level.

The molecular skeleton of **L1** is very similar to that reported previously for the closely related ylide $[Ph_3P{=}C(CO_2Me)C({=}NC_6H_4\text{-}p\text{-}Br)CO_2Me]$.[4c] Key features are the cisoid arrangement of the P═C and C═N bonds, also observed in other imine-stabilized ylides,[15] and the transoid arrangement of the P═C and C═O bonds, usually observed in ester-

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(13) For some representative examples, see: (a) Teagle, J. A.; Burmeister, J. L. *Inorg. Chim. Acta* **1986**, *118*, 65. (b) Vicente, J.; Chicote, M. T.; Fernández-Baeza, J. *J. Organomet. Chem.* **1989**, *364*, 407. (c) Falvello, L. R.; Fernández, S.; Navarro, R.; Rueda, A.; Urriolabeitia, E. P. *Organometallics* **1998**, *17*, 5887.

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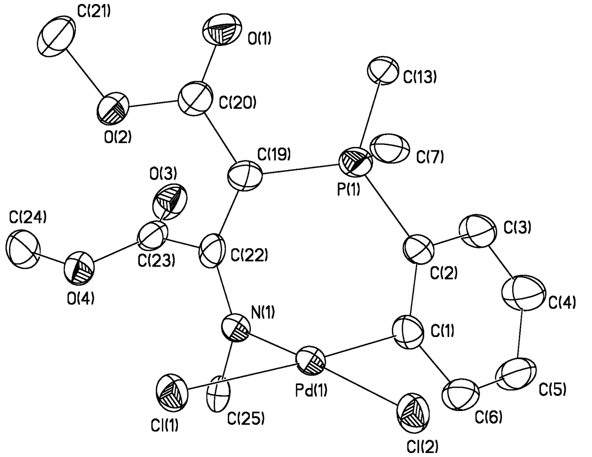

Figure 5. Thermal ellipsoid plot of complex **10**. Detail of the environment of one Pd atom.

stabilized ylides.[2f,16] The atoms P(1), C(4), C(5), O(4), C(3), and N(1) are almost coplanar {maximum deviation 0.10 Å [C(3)]}. The P(1)−C(4) bond distance [1.745(4) Å] is shorter than the P(1)−C(Ph) bond distances, in accord with a partial double-bond character, but is longer than those usually found in stabilized ylides with a single keto stabilizing group [$Ph_3P{=}C(H)C(O)R$, range 1.704−1.711 Å].[2f,17] This signals a higher charge delocalization in **L1**, compared with that found in ylides $Ph_3P{=}C(H)C(O)R$, probably because of the simultaneous presence of two delocalizing groups. This high degree of delocalization is also reflected in the C_α−C bond distances C(4)−C(3) = 1.442(5) Å and C(4)−C(5) = 1.424(5) Å, which are identical within experimental error. These values are shorter than the “standard” value for a C(sp^2)−C(sp^2) single bond (1.478 Å)[18] but are longer than those found in free[2f,17] or O-bonded[9,19] ylides (range 1.366−1.394 Å). The two C═O bond distances are identical, within experimental error [1.196(4) and 1.212(5) Å], while the C(3)−N(1) bond distance [1.287(4) Å] also reflects partial double-bond character.[2f,15] Finally, it is worth noting that the intramolecular distance P(1)−N(1) is 2.841 Å, a value clearly shorter than the sum of the van der Waals radii (3.40 Å),[20] and that the torsion angle P(1)−C(4)−C(3)−N(1) is 14.1°.

Complex **3** (Figure 3) has two independent molecules in the asymmetric unit, although a comparison of the structural parameters of these two molecules reveals quite similar geometric arrangements with minor differences (see Tables 3 and 4). These differences reside mainly in the planarity of the molecule as a whole because in each molecule two different planes can be clearly differentiated: one containing the 8-mq ligand and the other containing the PC(C═N)(C═O) skeleton of the ylide. In one of the organometallic cations (molecule A), the Pd atom lies in the best least-squares plane defined by the atoms N(2), C(32), C(13), P(1), C(11), and O(1) [and, of course, Pd(1); N(2) shows the major deviation from the plane, 0.078 Å], while the 8-mq ligand defines another plane. The dihedral angle between these two planes is 18.2(3)°. In the other cation (molecule B), the Pd atom is best located in the best least-squares plane defined by the 8-mq atoms C(42), C(41), C(47), and N(3) [and Pd(2)], and the angle of this plane with that defined by N(4), C(72), C(53), P(2), C(51), and O(5) [C(72) shows the major deviation from the plane, 0.110 Å] is 25.6(3)°. This means that the planarity of the skeleton of the ylide ligand is preserved after bonding.

In each molecule, the Pd atom is located in a distorted square-planar environment (bond angles around the Pd atom different from 90°, in addition to the loss of planarity), surrounded by the C and N atoms of the metalated 8-mq ligand and the N (imine) and O (carbonyl) atoms of the ylide. This confirms our previous analysis based on NMR data and confirms that the C_α atom of the ylide is not bonded to the Pd atom. The internal structural parameters of the 8-mq ligand are very similar to those described previously[21] and do not merit further comment. The Pd−N bond distances [Pd(1)−N(2) = 2.041(3) Å; Pd(2)−N(4) = 2.033(3) Å] are similar to those found in related N-bonded phenylimines,[22] while the Pd−O bond distances [Pd(1)−O(1) = 2.070(2) Å; Pd(2)−O(5) = 2.103(2) Å] are shorter than those found in other O-bonded ylides trans to a C atom.[19] Moreover, the ligand **L1** has undergone important structural changes during the coordination process. The most relevant of them is that the C═N bond, which initially was cisoid with respect to the P═C bond in **L1**, is now in a transoid arrangement [dihedral angle P(1)−C(13)−C(32)−N(2) = −170.7(4)°]. This rearrangement and the coordination to the metal should be reflected in changes in the internal bond distances and angles, in addition to those reported for the dihedral angles. However, the changes in bond distances, even between atoms directly involved in bonding to the metal, are not as pronounced as expected, as can be inferred from Tables 2−4 and 7, and almost all distances are identical within experimental error. This fact probably means that there is extensive charge delocalization.

The molecule of complex **10**·0.5$CHCl_3$ shows a dimeric structure (Figure 4) in which the two Pd atoms are bridged by two Cl atoms, and each Pd atom is also bonded to the palladated [C_6H_4-2-$PPh_2{=}C(CO_2Me)C(CO_2Me){=}NPh$] unit. The two metalated seven-membered boatlike rings are folded to opposite sides of the molecular plane and have their two aryl groups in a syn arrangement. As a whole, the molecule shows pseudo-C_2 symmetry. Each Pd atom is located in a

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Table 1. Crystal Data and Structure Refinement for **L1**, **3**, and **10**·$0.5CHCl_3$

	L1	**3**	**10**·$0.5CHCl_3$
empirical formula	$C_{30}H_{26}NO_4P$	$C_{40}H_{34}ClN_2O_8PPd$	$C_{60.5}H_{50}Cl_{3.5}N_2O_8P_2Pd_2$
fw	495.49	843.51	1331.84
temp (K)	294(2)	123(1)	100(2)
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	11.194(5)	24.3083(5)	11.8913(11)
b (Å)	13.585(6)	14.5144(2)	32.154(3)
c (Å)	17.625(8)	23.1589(4)	15.7008(15)
β (deg)	90.583(9)	115.874(3)	90.432(2)
V (Å^3)	2680(2)	7351.8(2)	6003.1(10)
Z	4	8	4
D_{calcd} (Mg/m^3)	1.228	1.524	1.474
μ (mm^{-1})	0.137	0.678	0.862
GOF on F^2	0.966	1.006	0.991
final R indices [$I > 2\sigma(I)$]	R1 = 0.0656 wR2 = 0.1166	R1 = 0.0376 wR2 = 0.0699	R1 = 0.0575 wR2 = 0.1367
R indices (all data)	R1 = 0.1666 wR2 = 0.1506	R1 = 0.1076 wR2 = 0.1005	R1 = 0.0850 wR2 = 0.1454
largest diff peak, hole (e Å^{-3})	0.196, −0.206	0.881, −0.426	1.696, −0.628

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **L1**

P(1)−C(4)	1.745(4)	P(1)−C(13)	1.805(4)
P(1)−C(19)	1.806(4)	P(1)−C(25)	1.807(4)
N(1)−C(3)	1.287(4)	N(1)−C(7)	1.426(5)
O(1)−C(2)	1.196(4)	C(2)−C(3)	1.516(5)
C(3)−C(4)	1.442(5)	O(4)−C(5)	1.212(5)
C(4)−C(5)	1.424(5)		
C(3)−N(1)−C(7)	122.0(4)	O(2)−C(2)−O(1)	124.9(4)
O(2)−C(2)−C(3)	123.7(4)	O(1)−C(2)−C(3)	111.2(4)
C(5)−O(3)−C(6)	117.9(4)	N(1)−C(3)−C(4)	119.8(4)
N(1)−C(3)−C(2)	121.5(4)	C(4)−C(3)−C(2)	118.7(4)
C(5)−C(4)−C(3)	119.2(4)	C(5)−C(4)−P(1)	127.2(3)
C(3)−C(4)−P(1)	113.6(3)	O(4)−C(5)−O(3)	119.4(4)
O(4)−C(5)−C(4)	126.0(4)	O(3)−C(5)−C(4)	114.6(4)

Table 3. Selected Bond Lengths (Å) for **3**

molecule A		molecule B	
Pd(1)−N(1)	2.006(3)	Pd(2)−N(3)	2.002(3)
Pd(1)−C(1)	2.028(3)	Pd(2)−C(41)	2.006(3)
Pd(1)−N(2)	2.041(3)	Pd(2)−N(4)	2.033(3)
Pd(1)−O(1)	2.070(2)	Pd(2)−O(5)	2.103(2)
O(1)−C(11)	1.217(4)	O(5)−C(51)	1.237(4)
C(11)−C(13)	1.443(5)	C(51)−C(53)	1.448(5)
C(13)−C(32)	1.413(5)	C(53)−C(72)	1.431(4)
C(13)−P(1)	1.772(4)	C(53)−P(2)	1.767(4)
C(32)−N(2)	1.306(4)	C(72)−N(4)	1.327(4)
C(32)−C(33)	1.528(5)	C(72)−C(73)	1.527(5)
C(33)−O(3)	1.198(4)	C(73)−O(7)	1.181(4)
C(33)−O(4)	1.322(5)	C(73)−O(8)	1.326(5)
O(4)−C(34)	1.436(4)	O(8)−C(74)	1.438(4)
N(2)−C(35)	1.445(4)	N(4)−C(75)	1.450(4)

Table 4. Selected Bond Angles (deg) for **3**

molecule A		molecule B	
N(1)−Pd(1)−C(1)	82.64(13)	N(3)−Pd(2)−C(41)	83.34(12)
C(1)−Pd(1)−N(2)	99.49(13)	C(41)−Pd(2)−N(4)	96.83(12)
N(1)−Pd(1)−O(1)	89.32(10)	N(3)−Pd(2)−O(5)	92.71(10)
N(2)−Pd(1)−O(1)	88.38(10)	N(4)−Pd(2)−O(5)	87.26(10)
C(11)−O(1)−Pd(1)	127.5(2)	C(51)−O(5)−Pd(2)	124.6(2)
O(1)−C(11)−C(13)	128.1(3)	O(5)−C(51)−C(53)	127.3(3)
C(32)−C(13)−C(11)	120.5(3)	C(72)−C(53)−C(51)	119.7(3)
C(32)−C(13)−P(1)	126.2(3)	C(72)−C(53)−P(2)	124.0(3)
C(11)−C(13)−P(1)	112.4(3)	C(51)−C(53)−P(2)	115.3(2)
N(2)−C(32)−C(13)	128.0(3)	N(4)−C(72)−C(53)	125.9(3)
C(32)−N(2)−Pd(1)	125.8(2)	C(72)−N(4)−Pd(2)	124.7(2)

Table 5. Selected Bond Lengths (Å) for **10**·$0.5CHCl_3$

Pd(1)−C(1)	1.960(6)	Pd(1)−N(1)	2.035(5)
Pd(1)−Cl(2)	2.3314(17)	Pd(1)−Cl(1)	2.4437(15)
Pd(2)−C(31)	1.937(7)	Pd(2)−N(2)	2.017(5)
Pd(2)−Cl(2)	2.3377(15)	Pd(2)−Cl(1)	2.4590(17)
P(1)−C(19)	1.757(7)	P(1)−C(7)	1.806(7)
P(1)−C(13)	1.807(6)	P(1)−C(2)	1.822(6)
P(2)−C(49)	1.753(6)	P(2)−C(43)	1.791(7)
P(2)−C(32)	1.798(7)	P(2)−C(37)	1.798(6)
O(1)−C(20)	1.201(8)	O(3)−C(23)	1.196(8)
O(5)−C(50)	1.211(8)	O(7)−C(53)	1.192(9)
N(1)−C(22)	1.307(8)	N(1)−C(25)	1.433(9)
N(2)−C(52)	1.301(8)	N(2)−C(55)	1.443(8)
C(1)−C(2)	1.377(9)	C(1)−C(6)	1.379(9)
C(2)−C(3)	1.395(9)	C(3)−C(4)	1.373(10)
C(4)−C(5)	1.406(10)	C(5)−C(6)	1.359(10)
C(19)−C(20)	1.430(9)	C(19)−C(22)	1.431(10)
C(22)−C(23)	1.518(10)	C(31)−C(32)	1.406(9)
C(31)−C(36)	1.418(9)	C(32)−C(33)	1.400(10)
C(33)−C(34)	1.365(10)	C(34)−C(35)	1.372(10)
C(35)−C(36)	1.373(10)	C(49)−C(52)	1.423(9)
C(49)−C(50)	1.441(9)	C(52)−C(53)	1.536(9)

distorted square-planar environment, surrounded by the metalated aryl C atom and the N atom of the [C_6H_4-2-$PPh_2{=}C(CO_2Me)C(CO_2Me){=}NPh$] ligand and the two bridging Cl atoms (Figure 5). The Pd−Cl bond distances fall in the usual range of distances found for this type of bond,[23] and the observed differences [for instance, Pd(1)−Cl(1) = 2.4437(15) Å; Pd(1)−Cl(2) = 2.3314(17) Å] can be related to their positions trans to atoms with very different trans influences [Cl(1) trans to C(1) and Cl(2) trans to N(1)]. The Pd(1)−C(1) bond distance [1.960(6) Å] is typical for orthopalladated aryl groups of ylide ligands,[13c] and the Pd(1)−N(1) bond distance [2.035(5) Å] is also typical for this type of bond.[12] Within the seven-membered metallacycle, the most relevant facts are as follows: (i) the P(1)−C(19) bond distance [1.757(7) Å] is shorter than the other P−C distances and is identical (within experimental error) to that found in **L1** [1.745(4) Å]; (ii) the C(19)−C(20) [1.430(9) Å] and C(19)−C(22) [1.431(10) Å] bond distances are identical with each other (within experimental error) and to the respective distances in **L1** [1.442(5) and 1.424(5) Å]; (iii) the C(22)−C(23) bond distance [1.518(10) Å] indicates clear single-bond character; (iv) the C(22)−N(1) bond

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[23] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

Table 6. Selected Bond Angles (deg) for **10**·0.5$CHCl_3$

C(1)−Pd(1)−N(1)	85.9(2)	C(1)−Pd(1)−Cl(2)	92.71(19)
N(1)−Pd(1)−Cl(1)	92.81(15)	Cl(2)−Pd(1)−Cl(1)	88.73(6)
C(31)−Pd(2)−N(2)	86.3(2)	C(31)−Pd(2)−Cl(2)	92.33(19)
N(2)−Pd(2)−Cl(1)	93.36(15)	Cl(2)−Pd(2)−Cl(1)	88.23(5)
Pd(1)−Cl(2)−Pd(2)	94.29(5)	Pd(1)−Cl(1)−Pd(2)	88.56(5)
C(22)−N(1)−Pd(1)	122.0(5)	C(52)−N(2)−Pd(2)	129.8(4)
C(2)−C(1)−C(6)	118.7(6)	C(2)−C(1)−Pd(1)	119.4(5)
C(6)−C(1)−Pd(1)	121.8(5)	C(22)−C(19)−P(1)	122.8(5)
C(20)−C(19)−C(22)	123.4(6)	C(20)−C(19)−P(1)	113.3(5)
O(1)−C(20)−C(19)	124.7(6)	O(2)−C(20)−C(19)	112.9(6)
N(1)−C(22)−C(19)	123.3(6)	N(1)−C(22)−C(23)	120.9(6)
C(19)−C(22)−C(23)	115.8(5)	C(32)−C(31)−C(36)	117.6(6)
C(32)−C(31)−Pd(2)	119.4(5)	C(36)−C(31)−Pd(2)	122.9(5)
C(52)−C(49)−P(2)	122.1(5)	C(50)−C(49)−P(2)	120.3(5)
O(5)−C(50)−O(6)	121.5(6)	O(5)−C(50)−C(49)	127.3(6)
O(6)−C(50)−C(49)	111.1(5)	N(2)−C(52)−C(49)	124.9(5)
N(2)−C(52)−C(53)	116.5(5)	C(49)−C(52)−C(53)	118.5(6)

distance [1.307(8) Å] shows that this bond still preserves double-bond character, although it is slightly longer than its analogue in **L1** [1.287(4) Å] because of N coordination to the Pd^{II} atom. All of these facts mean that there is still delocalization of the charge density in the P(1)−C(19)[−C(20)]−C(22)−N(1) chain. Similar results hold for the environment of Pd(2) because the halves of the molecule are identical within experimental error.

3. DFT Studies. The reluctance of **L1** to coordinate to the M^{II} center (M = Pd, Pt) using the ylidic C_α atom, in either its neutral (**1**−**9**) or anionic (**10** and **11**) forms, is quite noteworthy. Two different bonding modes have been characterized (N,O and C_{aryl},N bonding) without the participation of the ylidic C_α. Also relevant is the presence in **10** of a seven-membered ring, which should not be energetically favorable when compared with the, in principle, more stable five-membered ring, which would be formed after hypothetical C_α−Pd bonding. The X-ray structures of **L1**, **3**, and **10** show a high delocalization of the charge density, greater than that observed in the ylides [$R_3P{=}C(H)C(O)R'$], but we think that this isolated fact does not itself seem to offer a reasonable explanation for the lack of reactivity of this atom. In addition to this, as stated in the Introduction, other examples of metal complexes with doubly stabilized ylides are known.[7,24,25]

To shed some light about these questions, the bonding modes of the ylide ligand **L1** to a M^{II} metal fragment have been studied by means of DFT calculations (B3LYP functional)[26] on the ligand **L1** and the metal fragment $PdCl_2$ (complex **9**) (see the Supporting Information for figures of the optimized complexes and other tabular material). The computed geometry for ligand **L1** is in generally good agreement with that experimentally determined for **L1**. A relevant fact in the structure **L1** is the cisoid arrangement of the P═C and C═N bonds. This may suggest that an intramolecular interaction between the positively charged phosphonium P atom and the negatively charged N atom is responsible for this conformation, and this interaction could be similar to the 1,4-P···O interaction described in keto-stabilized phosphorus ylides.[16] We used the topological analysis of the electron density (Bader's atoms in molecules theory)[27] in order to determine and characterize the possible 1,4-P···N contact. Despite many efforts, we were not able to find a bond critical point (cp) between the P and N atoms, which would have confirmed the existence of the P···N interaction. Furthermore, the topological analysis of the Laplacian of the charge density [*L*(r)] provides information about the spatial localization of the electronic charge, showing a remarkable correspondence with the valance-shell electron pair repulsion (VSEPR) model. The local maxima or (3, −3) cp's, whose presence denotes a charge concentration, can be used to locate the lone pairs of the atoms. For the **L1** structure, the (3, −3) cp corresponding to the N lone pair was localized. The angle formed between the N atom, its lone pair, and the P atom is 119.4°. This value is significantly smaller than that found for the O−cp−P angle (162.3°) on $H_3P{=}C(H)C(O)C(H){=}PH_3$ ylide, for which a 1,4-P···O interaction could be characterized.[16] Thus, in the case of the imide-stabilized ylides, the orientation of the N lone pair is not suitable for establishing an electrostatic interaction with the positively charged P atom. This emphasizes the relevance of the spatial arrangement of the charge density in the determination of these nonbonded intramolecular interactions. Thus, the preference of the conformation with a cisoid arrangement of C═P and C═N bonds cannot be attributed to the 1,4-P···N intramolecular contact.

We have computed the energy value for the cisoid (**L1**) and transoid (**L1rot**) arrangements of the C═P and C═N bonds, with the latter conformation being the one found in the X-ray structure of complex **3**. In agreement with the experimental findings for the free ligand, the cisoid conformation gives a slightly lower value of the energy than the transoid one, ΔE(**L1rot**−**L1**) = 30 kJ mol^{-1}. If one analyzes the geometry of the rotated structure **L1rot** (vide infra), important structural changes can be observed. The P═C−C═N skeleton loses its planarity [dihedral angle P(1)−C(4)−C(3)−N(1) = 144.7°], which is probably a consequence of the electrostatic repulsion between the N of the imide moiety and the carbonyl O of the ester-stabilizing moiety (see Scheme 1). Another relevant observation is that the possible 1,5-P···O interaction between the phosphorus ylide and one of the O atoms of the ester group bound to the C_β can be precluded. The P−O distances (P−O = 3.498 and 4.243 Å for carbonylic and methoxy O atoms, respectively) are significantly longer than those previously characterized for 1,4-P···O interaction described in keto-stabilized bis-ylide $H_3P{=}C(H)C(O)C(H){=}PH_3$ (P−O = 2.288 Å).[16] These features are responsible for the higher stability of the conformation with a cisoid arrangement of the P═C and C═N bonds. However, the absence of 1,4-P···N intramolecular interactions explains the modest energy difference between the two conformers, favoring that the cisoid arrangement is not transferred to the metallic fragment, as it was transferred in the case of keto-stabilized phosphorus ylides.[16b]

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Scheme 1

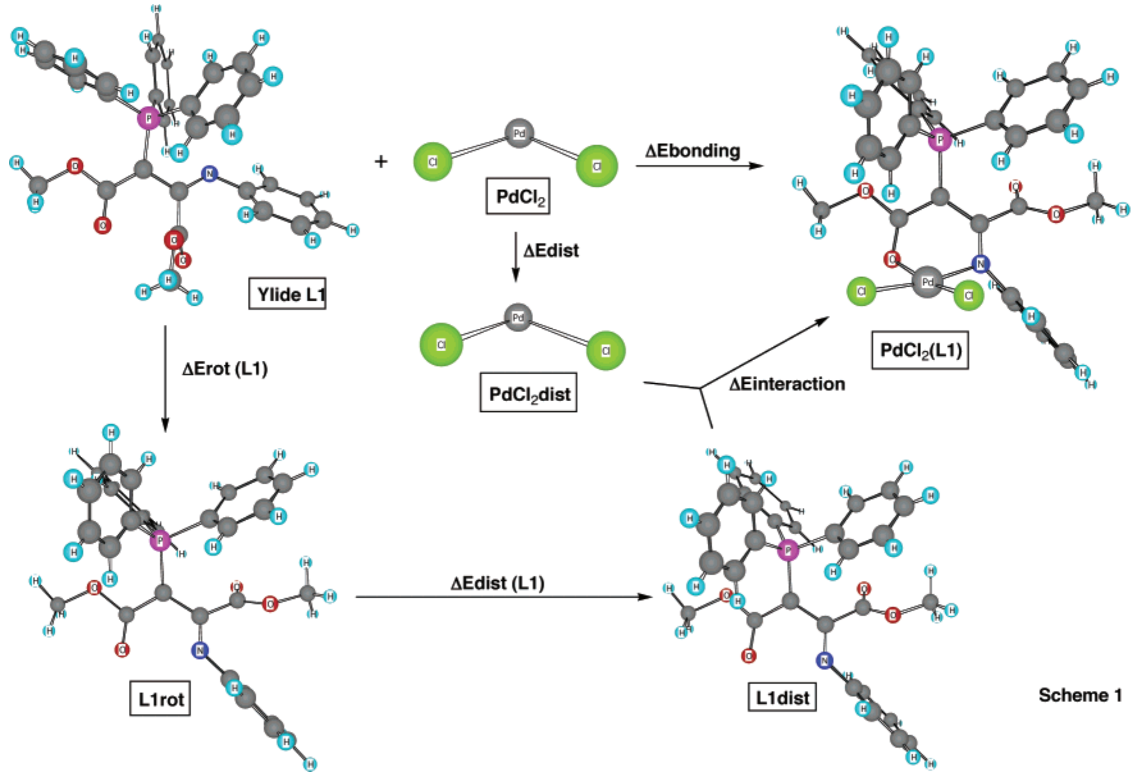

Table 7. Relative Energies (kJ mol^{-1}) of the Different Isomers of **L1** and Energy Decomposition for the Ylide Bonding to PdCl$_2$, Calculated Following Scheme 1

	N,O-chelate six-membered ring **9**	C,N-chelate four-membered ring **9cn**	C,O-chelate five-membered ring **9co**
E_{rel}(complex)	0.0	+12.4	+37.9
E_{rel}(PdCl$_2$dist)	0.0	+2.1	−0.6
E_{rel}(**L1dist**)	0.0	−3.3	+5.9
ΔE_{rot}(**L1**)	+30.0		
ΔE_{dist}(**L1**)	+23.9	+50.6	+59.8
$\Delta E_{rot+dist}$(**L1**)	+53.9		
ΔE_{dist}(Pd)	+10.9	+13.0	+10.3
$\Delta E_{interaction}$	−299.7	−286.1	−267.1
$\Delta E_{bonding}$	−234.9	−222.5	−197.0

The coordination of the ylide **L1** to the PdCl$_2$ fragment gives complex **9**, if the bonding is produced through the N and O atoms, but it could also give other isomeric complexes, namely, all possible chelating modes shown in Chart 1 (structures V−IX). To study the bonding of C$_\alpha$ to the Pd^{II} atom, we have selected, from all of these structures, those in which the C$_\alpha$ atom is coordinated; thus, we have discarded structures VII−IX, and from the two possible structures V, we have only optimized the five-membered ring shown in Chart 1 (see the Supporting Information for figures). As can be seen from Table 7, the most stable structure is that corresponding to the six-membered ring (**9**), with energy differences of +12.4 kJ mol^{-1} (**9cn**) and +37.9 kJ mol^{-1} (**9co**) with respect to **9**. While the lowest energy of isomer **9** is in keeping with experimental facts, the small energy difference between **9cn** and **9** is remarkable, as is the fact that the four-membered ring **9cn** is notably more stable than the five-membered ring **9co**. Thus, subtle effects may be responsible of the relative stabilities of the different coordination modes. The analysis of the bonding energy and its different components has shed some light on this aspect.

We can consider the formation of Cl$_2$Pd(**L1**) (**9**, **9cn**, and **9co**) from the PdCl$_2$ and **L1** fragments, at their optimized geometries when infinitely apart (see Scheme 1). The ΔE of this reaction is the bonding energy of the ylide to the PdCl$_2$ fragment ($\Delta E_{bonding}$). This ΔE can be decomposed into two terms: one accounting for the distortions of the **L1** and PdCl$_2$ fragments from their isolated optimized geometries to the final geometries in the complex (ΔE_{dist}) and the other one for the interaction energy of the distorted fragments to give the complex ($\Delta E_{interaction}$). The distortion energies can be further divided into the distortion of the PdCl$_2$ group and that of the **L1** ylide ligand. In the case of the formation of complex **9**, the distortion of **L1** can be decomposed into two additional terms: the optimized rotation of **L1** to give **L1rot** and the distortion of **L1rot** to give **L1dist**. The structures of **L1**, **L1rot**, PdCl$_2$, and PdCl$_2$(**L1**) for each of the possible cycles (six, five, and four members) have been optimized, while the fragments **L1dist** and PdCl$_2$dist were calculated as single points, using the geometrical parameters of the optimized **9**, **9cn**, or **9co**.

The data presented in Table 7 reveal that the energies of distortion of the PdCl$_2$ unit are similar (ranging from 10.3 to 13.0 kJ mol^{-1}), as are those of the distortion of the ligands (ranging from 50.6 to 59.8 kJ mol^{-1}), despite the very different distortions undergone by **L1** to achieve the final arrangements shown in **9**, **9co**, or **9cn**. The changes from **L1** to **L1dist** in complexes **9co** or **9cn** do not seem to imply large distortions because the cisoid conformations of the P═C and C═O or C═N bonds are retained, and the distortion energies amount to 50.6 kJ mol^{-1} (**9cn**) or 59.8 kJ mol^{-1}

(**9co**). On the other hand, the change from **L1** to **L1dist** in complex **9** through **L1rot** implies a complete rotation around the $C_\alpha-C(N)$ bond, from the cisoid to the transoid form. We have stated that the rotation process from **L1** to **L1rot** has an energy cost of about 30 kJ mol^{-1}. However, this additional energy is compensated for with the lower distortion energy required in the six-membered-ring coordination of the rotated ligand **L1rot** than in the five- and four-membered-ring coordinations of the nonrotated ligand. The computed energy for the distortion from **L1rot** to **L1dist** in **9** is 23.9 kJ mol^{-1}. It is interesting to point out that, because of the absence of stabilizing 1,4-P···N intramolecular interactions, the ligand distortion energy in N,O-bonding remains relatively low, favoring the formation of the complex with a transoid arrangement of the P=C and C=O bonds. Finally, we have similar distortion energies, although the nature, magnitude, and types of bonds implied in the distortions are different.

When the relative energies of the distorted fragments are considered, small differences were found (see Table 7), and in any case, these differences can justify the relative stabilization of the metallic complexes. On the other hand, there is a clear correlation between the relative energy of the complexes (0.0, +12.4, and +37.9 kJ mol^{-1} for **9**, **9cn**, and **9co**, respectively) and their corresponding relative interaction energies (0.0, +13.6, and +32.6 kJ mol^{-1} for **9**, **9cn**, and **9co**, respectively). This should be directly related to the nature of the formed bonds Pd−C, Pd−N, and Pd−O. Unfortunately, the estimation of the interaction energy of one arm of a bindentate ligand on a given environment is a difficult task, and only indirect evidences can be handled. On going from **9cn** to **9**, the Pd−Cl distance trans to the N atom remains virtually the same (2.333 and 2.339 Å, respectively). This suggests that the Pd−C interaction is more or less similar in the two N-bonded complexes and that the energy gap of 13.6 kJ mol^{-1} between **9cn** and **9** comes from the stabilization produced by the change from the ylidic C donor to a better donor, the carbonyl O. The low affinity of the Pd atom for the carbonyl O of a stabilized ylide is well documented.[1,19] However, in this case the presence of two stabilizing substituents at the ylidic C seems to weaken its donor capability, making it a worse donor than the carbonyl O. The final evidence is the very long Pd−C bond distance found in **9co** (2.278 Å) and **9cn** (2.219 Å), compared with those calculated and reported for similar structural environments (range 2.100−2.151 Å for the C-trans-Cl arrangement),[16b] Thus, the concomitant presence of two weak donors at the Pd^{II} center (C and O) in **9co** gives the less stable complex. The substitution of one of the weak donors by a better donor (the N atom) results in a notable stabilization of the resulting complex (**9cn** or **9**) and, in this delicate balance, the N,O bonding gives the most stable arrangement. Thus, the formation of the Pd−C bond seems to be the less favored process, compared with the Pd−O and Pd−N bonds. This particular weakness of the Pd−C bond (in this case) could be related to the low value of the natural population analysis (NPA) charge of the C_α atom (−0.69), while that of the P atom is +0.86 (see the Supporting Information). The values in the closely related stabilized ylide CMPPY [$H_3P=C(H)CO_2Me$][16] are −0.98 and +0.86. While the charges at the P atom are identical in **L1** and CMPPY, there is a notable decrease (0.29e) in the NPA charge at the C_α atom going from CMPPY to **L1**, reflecting the higher delocalization of the charge density in the latter. It is then sensible to assume that this decrease of the charge density at C_α is responsible for the lack of reactivity observed. Even in the case of the CMPPY ylide [$q(C_\alpha) = -0.98$; $q(O) = -0.62$], its behavior toward Pd^{II} has been reported as "ambidentate"; that is, it can competitively coordinate through the O or C_α atoms. A decrease in the charge of the C_α atom breaks this competitive situation, making the ylidic C_α atom unavailable for bonding to the Pd^{II} atom. This fact could be the clue for the understanding of the observed reactivity.

Conclusions. The ylide **L1**, which contains two stabilizing groups at the ylidic C_α atom, coordinates to organometallic Pd^{II} and Pt^{II} moieties through the iminic N atom and through the resonance-stabilized carbonyl O. The X-ray structures of **L1** and complex **3** have been determined, showing extensive delocalization of the ylidic charge density. The orthometalation of **L1** can easily be achieved, with the formation of an unusual C_{aryl},N seven-membered ring. Despite the presumed nucleophilic properties of the ylidic carbon C_α, this atom does not coordinate to the metal center in any of the cases studied. The DFT studies performed on ligand **L1** and complex **9** show that the N,O bonding of ylide **L1** forming a six-membered metallacycle is the most stable situation. These studies also show a notable decrease in the charge density at the C_α atom, compared with the situation found in singly stabilized keto ylides, which seems to be responsible for the lack of reactivity of the C_α.

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.* See: *J. Chem. Educ.* **1973**, *50*, A335−A337.

General Methods. Solvents were dried and distilled under Ar using standard procedures before use. Elemental analyses were carried out on a Perkin-Elmer 2400-B microanalyzer. IR spectra (4000−200 cm^{-1}) were recorded on a Perkin-Elmer 883 IR spectrophotometer from Nujol mulls between polyethylene sheets. ^{1}H (300.13 or 400.13 MHz), ^{19}F (282.41 MHz), $^{13}C\{^1H\}$ (75.47 MHz), and $^{31}P\{^1H\}$ (121.49 MHz) NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, or DMSO-d_6 solutions at room temperature (other temperatures were specified) on Bruker ARX-300 or Avance-400 spectrometers (δ in ppm and J in Hz); ^{1}H and $^{13}C\{^1H\}$ NMR were referenced using the solvent signal as the internal standard, while ^{19}F and $^{31}P\{^1H\}$ NMR were externally referenced to $CFCl_3$ and H_3PO_4 (85%), respectively. The ^{1}H SELNO-1D and SELRO-1D NMR experiments were performed with optimized mixing times (D8), depending on the irradiated signal. The $^{19}F-^1H$ HOESY experiment on complex **8** was carried out on a Bruker Avance-400 spectrometer equipped with a QNP probe. A mixing time (D8) of 600 ms was used. The T_1 values for ^{19}F were calculated using Bruker XwinNMR software, and D_1 was set to $5T_1$ accordingly. Mass spectra (FAB$^+$) were recorded from CH_2Cl_2 solutions on a VG Autospec spectrometer. The starting compounds **L1**,[4] [Pd(μ-

$Cl)(C_6H_4CH_2NMe_2\text{-}C^2,N)]_2$,[28] $[Pd(\mu\text{-}Cl)(S\text{-}C_6H_4C(H)MeNMe_2\text{-}C^2,N)]_2$,[28] $[Pd(\mu\text{-}Cl)(NC_{13}H_8\text{-}C^{10},N)]_2$,[29] $[Pd(\mu\text{-}Cl)(CH_2NC_9H_6\text{-}C^8,N)]_2$,[30] $[Pd(\mu\text{-}Cl)(C_6H_4\text{-}2\text{-}NC_5H_4\text{-}C^2,N)]$,[31] $[M(\mu\text{-}Cl)(o\text{-}CH_2C_6H_4)P(o\text{-}tol)_2]_2$ (M = Pd,[32] Pt[33]), $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$,[34] $[Pd(\mu\text{-}Cl)(C_6F_5)(tht)]_2$,[35] and the ylide $Ph_3P{=}C(H)CO_2Me$[36] were prepared according to reported methods. Other reagents such as $Ph_3P{=}NPh$ and DMAD ($MeO_2C{-}C{\equiv}C{-}CO_2Me$) were purchased from commercial sources (Aldrich) and were used without further purification.

Synthesis of $Ph_3P{=}C(CO_2Me)C({=}NPh)CO_2Me$ (L1). To a solution of $Ph_3P{=}NPh$ (1.00 g, 0.283 mmol) in dry CH_2Cl_2 (20 mL) under an Ar atmosphere was added DMAD (0.35 mL, 0.285 mmol). The yellow solution was stirred at 25 °C for 24 h, and then the solvent was evaporated to dryness. Treatment of the oily residue with Et_2O (20 mL) gave **L1** as a pale-yellow solid. Obtained: 1.20 g (85.6% yield). IR (ν, cm^{-1}): 1571 (ν_{CN}), 1647 (ν_{CO} conjug), 1734 (ν_{CO} nonconjug). ^{1}H NMR (CD_2Cl_2, δ): 3.22 (s, 3H, OMe), 3.54 (s, 3H, OMe), 6.24 (dd, 2H, H_o, NPh, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.2$), 6.81 (tt, 1H, H_p, NPh), 6.99 (t, 2H, H_m, NPh), 7.61−7.46 (m, 9H, PPh_3), 7.85−7.77 (m, 6H, PPh_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 17.37. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 49.83 (OMe), 51.38 (OMe), 59.19 (d, P=C, $^1J_{PC} = 119.6$), 120.28 (C_{meta}, NPh), 122.30 (C_{para}, NPh), 125.93 (d, C_{ipso}, PPh_3, $^1J_{PC} = 94.1$), 127.97 (C_{ortho}, NPh), 128.41 (d, C_{ortho}, PPh_3, $^2J_{PC} = 12.6$), 131.87 (s, C_{para}, PPh_3), 133.77 (d, C_{meta}, PPh_3, $^3J_{PC} = 9.8$), 150.47 (C_{ipso}, NPh), 160.33 (d, C=N, $^2J_{PC} = 6.8$), 166.56 (d, CO nonconjug, $^3J_{PC} = 12.7$), 168.47 (d, CO conjug, $^2J_{PC} = 15.1$).

Synthesis of 1. To a suspension of $[Pd(\mu\text{-}Cl)(C_6H_4CH_2NMe_2\text{-}C^2,N)]_2$ (0.182 g, 0.33 mmol) in dry THF (20 mL) under an Ar atmosphere was added $AgClO_4$ (0.137 g, 0.66 mmol). The resulting suspension was stirred for 20 min at room temperature with exclusion of light and then filtered over a Celite pad in order to remove AgCl. To the freshly prepared solution of the solvate derivative was added the ylide **L1** (0.327 g, 0.66 mmol). The resulting solution was stirred for 1 h at room temperature and then the solvent evaporated to dryness. Treatment of the residue with Et_2O (25 mL) and vigorous stirring gave **1** as a yellow solid, which was filtered, washed with Et_2O (10 mL), and air-dried. Obtained: 0.4474 g (81.0% yield). Anal. Calcd for $C_{39}H_{38}ClN_2O_8PPd$: C, 56.06; H, 4.58; N, 3.35. Found: C, 55.86; H, 4.39; N, 3.44. MS (FAB$^+$, *m/z*, %): 735 [$(M - ClO_4)^+$, 80%]. IR (ν, cm^{-1}): 1590 (br, $\nu_{CN} + \nu_{CO}$ conjug), 1731 (ν_{CO} nonconjug). ^{1}H NMR (CD_2Cl_2, δ): 2.64 (s, 3H, OMe), 2.73 (s, 6H, NMe_2), 3.28 (s, 3H, OMe), 4.00 (s, 2H, CH_2N), 6.93−7.19 (m, 9H, NPh + C_6H_4), 7.62−7.69 (m, 6H, H_m, PPh_3), 7.73−7.79 (m, 3H, H_p, PPh_3), 7.89−7.97 (m, 6H, H_o, PPh_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 19.60. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 52.96 (NMe_2), 54.38 (OMe), 54.77 (OMe), 72.30 (d, P=C, $^1J_{PC} = 117.3$), 74.30 (CH_2N), 124.23 (d, C_{ipso}, PPh_3, $^1J_{PC} = 92.9$), 124.47, 127.03, 127.11, 136.05, 144.59, 151.31 (C_6H_4), 126.37 (C_{meta}), 128.82 (C_{para}), 130.50 (C_{ortho}), 149.65 (C_{ipso}, NPh), 131.48 (d, C_{ortho}, $^2J_{PC} = 12.7$), 135.27 (d, C_{meta}, $^3J_{PC} = 11.3$), 135.80 (C_{para}, PPh_3), 165.43 (CO nonconjug), 167.07 (d, C=N, $^2J_{PC} = 16.4$), 174.47 (d, CO conjug, $^2J_{PC} = 9.4$).

Synthesis of 2. Complex **2** was obtained following the same synthetic method as that described for **1**. $[Pd(\mu\text{-}Cl)(S\text{-}C_6H_4CH(Me)\text{-}NMe_2\text{-}C^2,N)]_2$ (0.116 g, 0.20 mmol) was reacted with $AgClO_4$ (0.083 g, 0.40 mmol) and ylide **L1** (0.198 g, 0.40 mmol) in dry THF at room temperature to give **2** as an orange solid. The yield was quantitative. Anal. Calcd for $C_{40}H_{40}ClN_2O_8PPd$: C, 56.55; H, 4.74; N, 3.30. Found: C, 56.53; H, 4.48; N, 3.22. MS (FAB$^+$, *m/z*, %): 749 [$(M - ClO_4)^+$, 100%]. IR (ν, cm^{-1}): 1590 (br, $\nu_{CN} + \nu_{CO}$ conjug), 1731 (ν_{CO} nonconjug). ^{1}H NMR (CD_2Cl_2, δ): 1.59 (d, 3H, Me, $^3J_{HH} = 6.6$), 2.53 (s, 3H, NMe_2), 2.65 (s, 3H, OMe), 2.79 (s, 3H, NMe_2), 3.28 (s, 3H, OMe), 4.05 (q, 1H, CH), 6.92−7.18 (m, 9H, NPh + C_6H_4), 7.62−7.68 (m, 6H, H_m, PPh_3), 7.74−7.80 (m, 3H, H_p, PPh_3), 7.90−7.97 (m, 6H, H_o, PPh_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 19.62. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 17.91 (Me), 45.41 (NMe_2), 50.78 (NMe_2), 52.62 (OMe), 53.18 (OMe), 70.92 (d, P=C, $^1J_{PC} = 117.2$), 74.57 (CH), 122.23 (d, C_{ipso}, PPh_3, $^1J_{PC} = 93$), 122.76, 125.17, 125.32, 134.08, 143.04, 152.81 (C_6H_4), 124.34 (C_{meta}), 126.85 (C_{para}), 128.70 (C_{ortho}), 149.42 (C_{ipso}) (NPh), 129.67 (d, C_{ortho}, $^2J_{PC} = 12.7$), 133.77 (d, C_{meta}, $^3J_{PC} = 10.0$), 134.04 (C_{para}, PPh_3), 163.90 (CO nonconjug), 164.79 (d, C=N, $^2J_{PC} = 16.5$), 172.52 (d, CO conjug, $^2J_{PC} = 9.4$).

Synthesis of 3. Complex **3** was obtained following the same synthetic method as that reported for **1**, except that **3** precipitated in THF. $[Pd(\mu\text{-}Cl)(CH_2NC_9H_6\text{-}C^8,N)]_2$ (0.114 g, 0.20 mmol) was reacted with $AgClO_4$ (0.083 g, 0.40 mmol) and ylide **L1** (0.198 g, 0.40 mmol) in dry THF to give **3** as a white solid. Obtained: 0.150 g (44.3% yield). Anal. Calcd for $C_{40}H_{34}ClN_2O_8PPd$: C, 56.95; H, 4.06; N, 3.32. Found: C, 56.71; H, 3.81; N, 3.53. MS (FAB$^+$, *m/z*, %): 743 [$(M - ClO_4)^+$, 100%]. IR (ν, cm^{-1}): 1616 (br, $\nu_{CN} + \nu_{CO}$ conjug), 1734 (ν_{CO} nonconjug). ^{1}H NMR (CD_2Cl_2, δ): 2.31 (s, 3H, OMe), 2.94 (s, 2H, $PdCH_2$), 3.39 (s, 3H, OMe), 6.94 (dd, 2H, H_o, NPh, $^3J_{HH} = 7.2$, $^4J_{HH} = 1.2$), 7.13 (tt, 1H, H_p, NPh, $^3J_{HH} = 7.5$), 7.31 (pseudot, 2H, H_m, NPh), 7.40 (dd, 1H, H_7, NC_9H_6, $^3J_{HH} = 7.2$, $^4J_{HH} = 1.2$), 7.48 (t, 1H, H_6, NC_9H_6, $^3J_{HH} = 7.5$), 7.55 (dd, 1H, H_3, NC_9H_6, $^3J_{HH} = 8.4$, $^3J_{HH} = 5.1$), 7.59−7.69 (m, 7H, PPh_3 + H_5), 7.70−7.76 (m, 3H, PPh_3), 7.78−7.85 (m, 6H, PPh_3), 8.38 (dd, 1H, H_4, NC_9H_6, $^3J_{HH} = 8.4$, $^4J_{HH} = 1.5$), 8.76 (dd, 1H, H_2, NC_9H_6, $^3J_{HH} = 5.1$, $^4J_{HH} = 1.5$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 21.74. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 31.38 ($PdCH_2$), 52.03 (OMe), 53.02 (OMe), 65.58 (d, P=C, $^1J_{PC} = 116.6$), 122.28, 123.88, 128.20, 128.37, 128.99, 138.46, 146.89, 148.31, 152.69 (NC_9H_6), 122.72 (d, C_{ipso}, PPh_3, $^1J_{PC} = 93$), 124.21 (C_{meta}), 125.87 (C_{para}), 128.00 (C_{ortho}), 149.45 (C_{ipso}, NPh), 129.58 (d, C_{ortho}, $^2J_{PC} = 12.9$), 133.80 (C_{para}), 133.87 (d, C_{meta}, $^3J_{PC} = 10.2$, PPh_3), 163.06 (CO nonconjug), 165.15 (d, C=N, $^2J_{PC} = 18.3$), 169.67 (d, CO conjug, $^2J_{PC} = 8.4$).

Synthesis of 4. Complex **4** was obtained following the same synthetic method as that reported for **1**, except that **4** precipitated in THF. $[Pd(\mu\text{-}Cl)(C_6H_4\text{-}2\text{-}NC_5H_4\text{-}C^2,N)]_2$ (0.118 g, 0.20 mmol) was reacted with $AgClO_4$ (0.083 g, 0.40 mmol) and **L1** (0.198 g, 0.40 mmol) in dry THF to give **4** as a yellow solid. Obtained: 0.193 g (56.4% yield). Anal. Calcd for $C_{41}H_{34}ClN_2O_8PPd$: C, 57.56; H, 4.00; N, 3.27. Found: C, 57.67; H, 3.85; N, 3.50. MS (FAB$^+$, *m/z*, %): 755 [$(M - ClO_4)^+$, 85%]. IR (ν, cm^{-1}): 1575, 1593 ($\nu_{CN} + \nu_{CO}$ conjug), 1733 (ν_{CO} nonconjug). ^{1}H NMR (CD_2Cl_2, δ): 2.74 (s, 3H, OMe), 3.39 (s, 3H, OMe), 6.80 (dd, 1H, H_6', C_6H_4-phpy, $^3J_{HH} = 7.8$, $^4J_{HH} = 0.9$), 6.97 (td, 1H, H_5', C_6H_4-phpy, $^3J_{HH} = 7.8$, $^4J_{HH} = 1.5$), 7.13 (td, 1H, H_4', C_6H_4-phpy, $^3J_{HH} = 7.5$, $^4J_{HH} = 0.9$),

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7.17−7.38 (m, 6H, NPh + H_5), 7.47 (dd, 1H, $H_{3'}$, C_6H_4-phpy, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.5), 7.59−7.65 (m, 6H, PPh_3), 7.71−7.78 (m, 4H, PPh_3 + H_3), 7.81−7.88 (m, 6H, PPh_3), 7.98 (td, 1H, H_4, NC_5H_4-phpy, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.5), 8.43 (dd, 1H, H_6, NC_5H_4-phpy, $^3J_{HH}$ = 5.7, $^4J_{HH}$ = 1.5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 19.20. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 52.59 (OMe), 53.64 (OMe), 67.15 (d, P═C, $^1J_{PC}$ = 116.6), 119.16, 123.41, 123.82, 125.62, 129.22, 133.93, 140.33, 145.64, 148.29, 148.58, 163.34 (C_6H_4-2-NC_5H_4), 122.72 (d, C_{ipso}, PPh_3, $^1J_{PC}$ = 93), 124.85 (C_{meta}), 127.33 (C_{para}), 128.64 (C_{ortho}), 148.59 (C_{ipso}, NPh), 129.65 (d, C_{ortho}, $^2J_{PC}$ = 12.9), 133.61 (d, C_{meta}, $^3J_{PC}$ = 10.1), 133.95 (d, C_{para}, $^4J_{PC}$ =2.6, PPh_3), 164.53 (CO nonconjug), 165.78 (d, C═N, $^2J_{PC}$ = 16.1), 172.31 (d, CO conjug, $^2J_{PC}$ = 9.1).

Synthesis of 5. Complex **5** was obtained following the same synthetic method as that reported for **1**. $[Pt(\mu\text{-}Cl)(o\text{-}CH_2C_6H_4P(o\text{-}tol)_2)]_2$ (0.195 g, 0.18 mmol) was reacted with $AgClO_4$ (0.076 g, 0.36 mmol) and ylide **L1** (0.181 g, 0.36 mmol) in dry THF to give **5** as a white solid. Obtained: 0.361 g (91.0% yield). Anal. Calcd for $C_{51}H_{46}ClNO_8P_2Pt$: C, 56.02; H, 4.24; N, 1.28. Found: C, 55.63; H, 4.57; N, 1.25. MS (FAB$^+$, m/z, %): 993 [(M − ClO_4)$^+$, 65%]. IR (ν, cm^{-1}): 1591 (br, $\nu_{CN} + \nu_{CO}$ conjug), 1732 (ν_{CO} nonconjug). ^1H NMR (CD_2Cl_2, δ): 2.38 (s, 3H, OMe), 2.62 (s, 3H, OMe), 2.69 (s, br, 6H, Me-tol), 2.89 (s, br, 2H, $PtCH_2$), 6.95−7.42 (m, 17H, NPh + C_6H_4-tol), 7.61−7.81 (m, 15H, PPh_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 16.46 (s, Pt−P, $^1J_{PtP}$ = 4212), 20.85 (P═C). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 11.26 (s, $PtCH_2$, $^1J_{PtC}$ = 835), 22.42 (Me-tol), 22.58 (Me-tol), 52.25 (OMe), 52.42 (OMe), 66.24 (d, P═C, $^1J_{PC}$ = 116.6), 121.83 (d, C_{ipso}, PPh_3, $^1J_{PC}$ = 93), 124.84 (C_{meta}), 126.40 (C_{para}), 127.88 (C_{ortho}), 147.32 (C_{ipso}, NPh), 125.82 (d, C_6H_4-tol, J_{PC} = 8.8), 126.21 (d, C_6H_4-tol, J_{PC} = 9), 128.10 (C_6H_4-tol), 129.64 (d, C_{ortho}, PPh_3, $^2J_{PC}$ = 12.9), 131.29−131.91 (several m, C_6H_4-tol), 132.91 (d, C_6H_4-tol, J_{PC} = 6.7), 132.99 (d, C_6H_4-tol, J_{PC} = 8), 133.85 (d, C_{meta}, PPh_3, $^3J_{PC}$ = 10), 134.11 (d, C_{para}, PPh_3, $^4J_{PC}$ = 2.4), 142.08 (d, C_6H_4-tol, J_{PC} = 11.4), 158.42 (d, C_6H_4-tol, J_{PC} = 27), 163.01 (d, C═N, $^2J_{PC}$ = 17.1), 163.31 (d, CO nonconjug, $J_{P'C}$ = 2.1), 169.04 (d, CO conjug, $^2J_{PC}$ = 8.3).

Synthesis of 6. Complex **6** was obtained following the same synthetic method as that reported for **1**. $[Pd(\mu\text{-}Cl)(o\text{-}CH_2C_6H_4P(o\text{-}tol)_2)]_2$ (0.178 g, 0.20 mmol) was reacted with $AgClO_4$ (0.083 g, 0.40 mmol) and ylide **L1** (0.198 g, 0.40 mmol) in dry THF to give **6** as a white solid. Obtained: 0.312 g (77.7% yield). Anal. Calcd for $C_{51}H_{46}ClNO_8P_2Pd$: C, 60.96; H, 4.61; N, 1.39. Found: C, 60.93; H, 4.88; N, 1.45. MS (FAB$^+$, m/z, %): 904 [(M − ClO_4)$^+$, 100%]. IR (ν, cm^{-1}): 1598 (br, $\nu_{CN} + \nu_{CO}$ conjug), 1731 (ν_{CO} nonconjug). ^1H NMR ($CDCl_3$, δ): 2.34 (s, 3H, OMe), 2.54 (s, 3H, OMe), 2.65 (s, br, 6H, Me-tol), 2.80 (s, br, 2H, $PdCH_2$), 6.87−7.41 (m, 17H, NPh + C_6H_4-tol), 7.58−7.76 (m, 15H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 20.86 (P═C), 35.42 (s, Pd−P). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 22.82 (Me-tol), 22.87 (Me-tol), 32.08 (s, $PdCH_2$), 51.55 (OMe), 52.08 (OMe), 64.76 (d, P═C, $^1J_{PC}$ = 117.1), 122.16 (d, C_{ipso}, PPh_3, $^1J_{PC}$ = 92), 123.85 (C_{meta}), 125.75 (C_{para}), 128.09 (C_{ortho}), 148.32 (C_{ipso}, NPh), 126.25 (d, C_6H_4-tol, J_{PC} = 8.3), 126.31 (s, br, C_6H_4-tol), 128.20 (d, C_6H_4-tol, J_{PC} = 10.8), 129.52 (d, C_{ortho}, PPh_3, $^2J_{PC}$ = 12.8), 131.51−132.48 (m, C_6H_4-tol), 132.88 (d, C_6H_4-tol, J_{PC} = 6.4), 133.89 (C_{para}, PPh_3), 133.90 (d, C_{meta}, PPh_3, $^3J_{PC}$ = 9.8), 141.90 (d, C_6H_4-tol, J_{PC} = 10.2), 156.56 (d, C_6H_4-tol, J_{PC} = 31), 163.37 (d, CO nonconjug, $J_{P'C}$ = 1.6), 164.23 (d, C═N, $^2J_{PC}$ = 17.7), 169.95 (d, CO conjug, $^2J_{PC}$ = 8.7).

Synthesis of 7. Complex **7** was obtained following the same synthetic method as that reported for **1**. $[Pd(\mu\text{-}Br)(\eta^3\text{-}C_3H_5)]_2$ (0.091 g, 0.20 mmol) was reacted with $AgClO_4$ (0.083 g, 0.40 mmol) and ylide **L1** (0.198 g, 0.40 mmol) in dry THF to give **7** as an orange solid. Obtained: 0.261 g (87.8% yield). Anal. Calcd for $C_{33}H_{31}ClNO_8PPd$: C, 53.38; H, 4.21; N, 1.89. Found: C, 52.72; H, 4.03; N, 1.90. MS (FAB$^+$, m/z, %): 642 [(M − ClO_4)$^+$, 40%]. IR (ν, cm^{-1}): 1607 (br, $\nu_{CN} + \nu_{CO}$ conjug), 1751 (ν_{CO} nonconjug). ^1H NMR ($CDCl_3$, δ): 2.23 (s, 3H, OMe), 3.04 (d, 2H, C_3H_5 anti, $^3J_{HH}$ = 12), 3.16 (s, 3H, OMe), 3.57 (s, br, 2H, C_3H_5 syn), 5.77 (tt, 1H, H_c, C_3H_5, $^3J_{HH}$ = 6.9), 6.90 (d, 2H, H_o, NPh, $^3J_{HH}$ = 7.5), 6.98 (t, 1H, H_p, NPh, $^3J_{HH}$ = 7.5), 7.18 (t, 2H, H_m, NPh), 7.57−7.67 (m, 9H, PPh_3), 7.77−7.85 (m, 6H, H_o, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 21.76. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 51.89 (OMe), 52.56 (OMe), 62.50 (CH_2, C_3H_5), 65.49 (d, P═C, $^1J_{PC}$ = 118.2), 117.03 (CH, C_3H_5), 122.36 (C_{meta}), 125.37 (C_{para}), 128.38 (C_{ortho}), 153.14 (C_{ipso}, NPh), 122.49 (d, C_{ipso}, PPh_3, $^1J_{PC}$ = 93), 129.40 (d, C_{ortho}, PPh_3, $^2J_{PC}$ = 12.7), 133.56 (d, C_{para}, PPh_3, $^4J_{PC}$ = 2.5), 133.99 (d, C_{meta}, PPh_3, $^3J_{PC}$ = 10.0), 163.20 (d, C═N, $^2J_{PC}$ = 17.7), 163.66 (d, CO nonconjug, J_{PC} = 2.0), 170.24 (d, CO conjug, $^2J_{PC}$ = 8.6).

Synthesis of 8. Complex **8** was obtained following the same synthetic method as that reported for **1**. $[Pd(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ (0.159 g, 0.20 mmol) was reacted with $AgClO_4$ (0.083 g, 0.40 mmol) and ylide **L1** (0.198 g, 0.40 mmol) in dry THF to give **8** as a white solid. Obtained: 0.208 g (54.0% yield). Anal. Calcd for $C_{40}H_{34}ClF_5NO_8PPdS$: C, 50.22; H, 3.58; N, 1.46; S, 3.35. Found: C, 50.51; H, 3.39; N, 1.32; S, 3.33. MS (FAB$^+$, m/z, %): 856 [(M − ClO_4)$^+$, 85%]. IR (ν, cm^{-1}): 798, 959, 1502 (C_6F_5), 1603 (br, $\nu_{CN} + \nu_{CO}$ conjug), 1732 (ν_{CO} nonconjug). ^1H NMR ($CDCl_3$, δ): 2.07 (s, br, 4H, H_β, SC_4H_8), 2.17 (s, 3H, OMe), 2.96 (s, br, 4H, H_α, SC_4H_8), 3.32 (s, 3H, OMe), 6.52 (m, 2H, H_o), 6.82−6.87 (m, 3H, H_p + H_m, NPh), 7.61−7.77 (m, 15H, PPh_3). ^{19}F NMR ($CDCl_3$, δ): −121.33 (pseudod, 2F_o, $^3J_{FF}$ = 23), −158.91 (t, 1F, F_p, $^3J_{FF}$ = 20), −162.07 (pseudot, 2F, F_m). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 21.45. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 30.02 (C_β, SC_4H_8), 36.49 (SC_α, SC_4H_8), 52.08 (OMe), 53.75 (OMe), 67.12 (d, P═C, $^1J_{PC}$ = 115.6), 110.45 (tm, C_{ipso}, C_6F_5, J_{CF} = 39.7), 121.84 (d, C_{ipso}, PPh_3, $^1J_{PC}$ = 93), 123.82 (C_{meta}), 125.97 (C_{para}), 127.17 (C_{ortho}), 148.94 (C_{ipso}) (NPh), 129.70 (d, C_{ortho}, PPh_3, $^2J_{PC}$ = 12.9), 133.89 (d, C_{meta}, PPh_3, $^3J_{PC}$ = 10.1), 134.08 (d, C_{para}, PPh_3, $^4J_{PC}$ = 2.6), 137.40 (dm, C_6F_5, J_{CF} = 241), 138.38 (dm, C_6F_5, J_{CF} = 247), 146.54 (dm, C_6F_5, J_{CF} = 230), 162.08 (d, CO nonconjug, J_{PC} = 2.2), 164.72 (d, C═N, $^2J_{PC}$ = 17.6), 169.87 (d, CO conjug, $^2J_{PC}$ = 8.3).

Synthesis of 9. $PdCl_2$ (0.071 g, 0.40 mmol) and LiCl (0.034 g, 0.80 mmol) were refluxed in 15 mL of methanol until complete dissolution of the palladium salt (30 min). After cooling, the deep-red solution was filtered over Celite to remove insoluble impurities (mainly Pd^0). To this methanolic solution of $Li_2[PdCl_4]$ (0.40 mmol) was added ligand **L1** (0.198 g, 0.40 mmol). A deep-red solid (**9**) precipitated almost instantaneously. The solid was filtered, washed with additional methanol (10 mL) and ethanol (30 mL), and dried by suction. Obtained: 0.111 g (41.2% yield). Anal. Calcd for $C_{30}H_{26}Cl_2NO_4PPd$: C, 53.55; H, 3.89; N, 2.08. Found: C, 53.81; H, 3.95; N, 2.01. MS (FAB$^+$, m/z, %): 600 [(M − 2Cl − H)$^+$, 25%]. IR (ν, cm^{-1}): 1569, 1581 (br, $\nu_{CN} + \nu_{CO}$ conjug), 1739 (ν_{CO} nonconjug). ^1H NMR ($CDCl_3$, δ): 2.20 (s, 3H, OMe), 2.89 (s, 3H, OMe), 7.05 (m, 3H, H_p + H_m, NPh), 7.33 (d, 2H, H_o, NPh, $^3J_{HH}$ = 7.8), 7.74 (m, 3H, H_p, PPh_3), 8.00 (m, 6H, H_m, PPh_3), 8.26 (m, 6H, H_o, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 20.27. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 52.59 (OMe), 55.38 (OMe), 70.46 (d, P═C, $^1J_{PC}$ = 117.3), 121.62 (d, C_{ipso}, PPh_3, $^1J_{PC}$ = 92), 127.40 (C_{meta}), 128.29 (C_{ortho}), 130.20 (C_{para}), 145.27 (C_{ipso}, NPh), 130.39 (d, C_{ortho}, PPh_3, $^2J_{PC}$ = 12.9), 134.38 (C_{para}, PPh_3), 134.99 (d, C_{meta}, PPh_3, $^3J_{PC}$ = 10.3), 161.62 (CO nonconjug), 164.33 (d, C═N, $^2J_{PC}$ = 17.9), 171.29 (d, CO conjug, $^2J_{PC}$ = 8.1).

Synthesis of 10. A suspension of $Pd(OAc)_2$ (0.200 g, 0.891 mmol) and ylide **L1** (0.442 g, 0.891 mmol) in methanol (15 mL) was refluxed for 30 min. At this point, some decomposition is evident. After cooling, Pd^0 was eliminated by filtration over Celite, and to the resulting clear yellow solution was added LiCl (0.151 g, 3.56 mmol). After 18 h of stirring (25 °C), **10** precipitated as a pale-yellow solid, which was filtered, washed with methanol (2 mL) and ethanol (25 mL), and air-dried. Obtained: 0.241 g (42.5% yield). Anal. Calcd for $C_{60}H_{50}Cl_2N_2O_8P_2Pd_2$: C, 56.62; H, 3.96; N, 2.20. Found: C, 56.39; H, 3.85; N, 2.00. IR (ν, cm^{-1}): 1534 (ν_{CN}), 1647 (ν_{CO} conjug), 1734 (ν_{CO} nonconjug). ^{1}H NMR (CDCl$_3$, δ): 3.09 (s, 3H, OMe), 3.38 (s, 3H, OMe), 6.57 (ddd, 1H, H$_3$, C$_6$H$_4$, $^3J_{PH} = 12.3$, $^3J_{HH} = 7.8$, $^4J_{HH} = 1.5$), 6.72 (ddd, 1H, H$_6$, C$_6$H$_4$, $^3J_{HH} = 7.8$, $^4J_{PH} = 2.4$, $^4J_{HH} = 1.2$), 6.77 (ddd, 1H, H$_4$, C$_6$H$_4$, $^3J_{HH} = 7.5$, $^4J_{PH} = 3.9$, $^4J_{HH} = 1.2$), 6.84 (d, 2H, H$_o$, NPh, $^3J_{HH} = 6.6$), 6.93 (tt, 1H, H$_5$, $^3J_{HH} = 7.5$, $^4J_{HH} = {}^5J_{PH} = 1.2$), 7.19−7.42 (m, 9H, H$_m$ + H$_p$, PPh$_2$ + NPh), 7.48−7.56 (m, 2H, H$_o$, PPh$_2$), 7.83−7.90 (m, 2H, H$_o$, PPh$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$, δ): 9.56. ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 50.00 (OMe), 51.88 (OMe), 61.35 (d, P═C, $^1J_{PC} = 125.1$), 123.45 (d, C$_3$, C$_6$H$_4$, $J_{PC} = 13.0$), 125.19 (C$_{meta}$, NPh), 125.84 (C$_{ortho}$, NPh), 126.65 (d, C$_2$, C$_6$H$_4$, $^1J_{PC} = 23.5$), 127.82−128.10 (br, C$_{para}$ (NPh) + C$_4$, C$_5$ (C$_6$H$_4$)), 128.90 (d, C$_{meta}$, PPh$_2$, $^3J_{PC} = 12.1$), 129.26 (d, C$_{meta}$, PPh$_2$, $^3J_{PC} = 13.6$), 130.30 (d, C$_6$, C$_6$H$_4$, $J_{PC} = 3.1$), 130.56 (d, C$_{ipso}$, PPh$_2$, $^1J_{PC} = 103.6$), 131.95 (C$_{para}$, PPh$_2$), 132.32 (d, C$_{para}$, PPh$_2$, $^4J_{PC} = 2.3$), 132.53 (d, C$_{ortho}$, PPh$_2$, $^2J_{PC} = 14.1$), 135.00 (d, C$_{ortho}$, PPh$_2$, $^2J_{PC} = 12.9$), 148.70 (C$_{ipso}$, NPh), 153.01 (d, C$_1$, C$_6$H$_4$, $^2J_{PC} = 10.8$), 164.56 (d, C═N, $^2J_{PC} = 10.1$), 167.52 (d, CO nonconjug, $^3J_{PC} = 4.9$), 168.16 (d, CO conjug, $^2J_{PC} = 11.2$).

Reactivity of 10 with PPh$_3$. A suspension of **10** (25 mg, 0.019 mmol) in CD$_2$Cl$_2$ (0.5 mL) was treated with PPh$_3$ (10.3 mg, 0.039 mmol). A clear yellow solution of **11** was obtained instantaneously. The NMR spectra were recorded immediately and showed 100% spectroscopic yield of **11** as a single isomer. ^{1}H NMR (CD$_2$Cl$_2$, δ): 3.20 (s, 3H, OMe), 3.39 (s, 3H, OMe), 6.22 (m, 1H, C$_6$H$_4$), 6.41 (m, 1H, C$_6$H$_4$), 6.65−6.75 (m, 2H, C$_6$H$_4$), 7.01−7.93 (m, 30H, PPh$_3$ + PPh$_2$ + NPh). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 13.79 (s, 1P, PPh$_2$), 28.13 (s, 1P, Pd−PPh$_3$).

Computational Details. Calculations were performed using the *Gaussian98* series of programs.[37] The DFT was used, with the B3LYP functional.[26] Effective core potentials and their associate double-ζ LANL2DZ basis set were used for the Pd atom.[37,38] The N, O, P, and Cl atoms, as well as the ylide C$_\alpha$ and iminic and carbonyl C atoms, were represented by means of the 6-31G(d) basis set. The H and C atoms of the methyl and phenyl substituents were represented by means of the 6-31G basis set.[39] All geometry optimizations were full with no restrictions. For the six-membered-ring structure optimization in **9**, the conformation of the X-ray structure of **3** was used as a starting point for geometry optimization. For the four- and five-membered-ring structures, systematic conformational searches were performed at the ONIOM (B3LYP:UFF) level. Then, the most stable conformers were used as starting points for full quantum mechanics calculations. The topological properties of the electron density and Laplacian maps were investigated using the XAIM 1.0 program,[40] whereas the topology of the negative of the Laplacian of the charge density [$L(r)$] was analyzed by means of the AIMPAC series of programs.[41]

Crystal Structure Determination of Ligand L1 and Complexes 3 and 10·0.5CHCl$_3$. Crystals of adequate quality for X-ray measurements were grown by slow vapor diffusion of ethanol into a CH$_2$Cl$_2$ (**L1** and **3**) or CHCl$_3$ (**10**) solution of the corresponding crude compound. A single crystal (dimensions specified in Supporting Information) was mounted at the end of a quartz fiber in a random orientation and covered with epoxy.

Data Collection. Data collection was performed at room temperature (**L1**) or at 100 K (**3** and **10**) on Bruker Smart CCD or Oxford Diffraction Xcalibur2 diffractometers using graphite-monocromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). In all cases, a hemisphere of data was collected based on three ω-scan or ϕ-scan runs. The diffraction frames were integrated using the programs *SAINT*[42] or *CrysAlis RED*,[43] and the integrated intensities were corrected for absorption with *SADABS*.[44]

Structure Solution and Refinement. The structures were solved by direct or Patterson methods.[45] All non-H atoms were refined with anisotropic displacement parameters. The H atoms were placed at idealized positions and treated as riding atoms. Each H atom was assigend 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.[46]

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Supporting Information Available: Tables giving data collection parameters, atomic coordinates, complete bond distances and angles, and thermal parameters for the X-ray crystal structure determination of **L1**, **3**, and **10**·0.5CHCl$_3$; tables giving calculated Cartesian geometries and energies of **L1** and **9**, **9co**, and **9cn**, with their corresponding figures (**6**−**9**); and tables of comparisons of structural parameters and NPA atomic charges. This material is available free of charge via the Internet at http://pubs.acs.org.

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