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Regioselective CH Bond Activation on Stabilized Nitrogen Ylides Promoted by Pd(II) Complexes: Scope and Limitations

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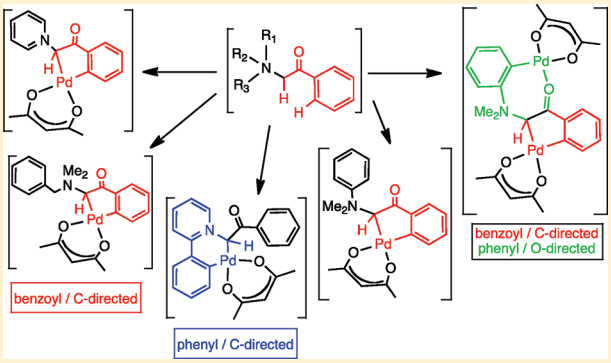
Supporting Information

ABSTRACT: The orthopalladation of N-ylides [H_xC_yN−CHC(O)Ar] (H_xC_yN = pyridine, benzylamine, imidazole, aniline, and phenylpyridine; Ar = aryl) has been studied. The incorporation of the Pd atom to these substrates is regioselective, since the orthopalladation is produced, in most of the cases, only at the aryl ring of the benzoyl group with concomitant C-bonding of the N-ylide. The X-ray structure of one representative example is reported. Factors governing the observed orientation are discussed, because this regioselectivity is worthy of note, considering the deactivating nature of the carbonyl group. Two exceptions to the general trend have been observed. The first one is the double metalation of the ylide [$PhMe_2NCHC(O)Ph$], which incorporates one Pd at each Ph. The second one is the palladation of the phenylpyridine derivative, which occurs at the pyridinic 2-phenyl ring and produces a six-membered palladacycle.



INTRODUCTION

The functionalization of organic molecules through a CH bond activation process promoted by transition metals is, at present, one of the most active research areas in chemistry.[1] This strategy provides alternative methodologies and improved tools to develop more concise and straightforward synthetic routes when compared with the conventional preparative organic procedures.[1] The advantages of the CH activation methodology are evident in terms of economy and waste reduction. However, because of the ubiquity of the C−H bond in organic substrates, the selectivity of the activation process is a critical point, and synthetic strategies must be developed to obtain the best performance in this challenging task. One of the most successful solutions is the ortho functionalization, which is easily achieved in aromatic substrates through the introduction of a directing group on the starting substrate.[2] This strategy results in the formation of orthometalated complexes, which are valuable tools in stoichiometric and/or catalytic processes.[1,3−17] Among different metals, palladium and, therefore, cyclopalladated complexes,[4] have proved to be highly efficient reagents in metal-mediated organic synthesis.[3−17] The versatility of this methodology is clearly reflected by the large variety of molecules that have been functionalized at the ortho position of the directing group, and by the wide scope of functional groups that can be introduced regiospecifically into a given substrate, resulting in the formation of C−C, C−O, C−N, C−S, C−P, or C−X (X = halogen) bonds.[5−17] The combination of the regioselective metalation by the directing group effect, the wide scope of substrates, and the plethora of functional groups available confers a really great synthetic potential to this methodology.

On the other hand, the chemistry of ylides is still a fascinating research field, since they are versatile ligands toward transition metals and show exciting properties and applications.[18−25] We are interested in the chemical behavior of ylides and related species, such as iminophosphoranes, and a significant part of our recent research work has been centered on these substrates,[26] including specific studies on CH bond activations and functionalization processes.[27] One of our most significant results is the regioselective palladation of keto-stabilized iminophosphoranes [$R_3P{=}NC(O)Ar$], that is, those containing an arylamide group.[27d,e,i,j] The incorporation of the Pd is produced exclusively at the ortho position of the arylamide ring, as it is shown in Figure 1 (left). DFT calculations performed on this system showed that the reaction is kinetically controlled[27i] and that the presence of the carbonyl group is critical since, in its absence, the regioselectivity is reversed (Figure 1 right). Obviously, the regioselective palladation of an aromatic ring when several options are possible is of considerable interest, since it would allow for the selective incorporation of a given functional group.[27j]

On the other hand, the comparison of keto-stabilized iminophosphoranes with the homologous keto-stabilized P-ylides reflects a divergent behavior of the two substrates, as shown in Figure 2: whereas the orthopalladation of the iminophosphoranes is produced at the benzamide ring, that of

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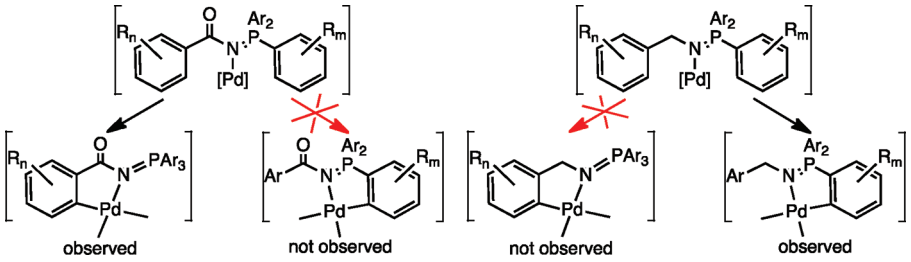


Figure 1. Iminophosphoranes and observed regioselective orthopalladations.[27d,e,i,j]

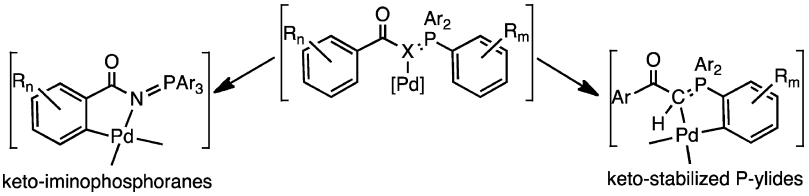


Figure 2. Divergent behavior of iminophosphoranes and ylides toward orthopalladation.[27d]

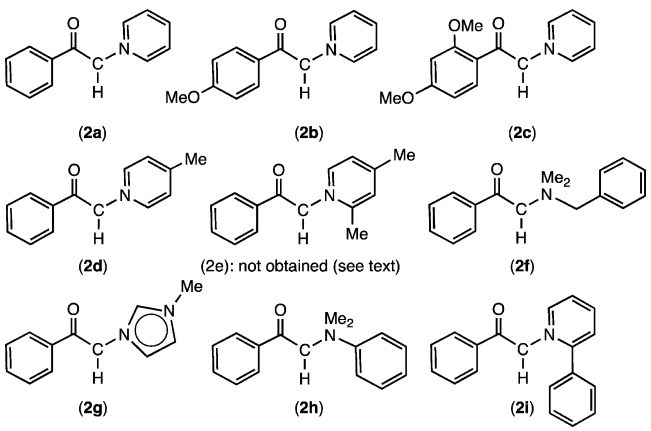
the P-ylides is produced at the P-aryl ring, with full regioselectivity.[27d]

Therefore, it is clear that not only is the carbonyl group important (stabilized vs nonstabilized substrates) but also the nature of the donor group (N vs CH) seems to be critical. Now we want to check if it is possible to extend these observations to other competitive carbonylic substrates, aiming to achieve regioselective functionalizations. In particular, this contribution is focused on the regioselective cyclopalladation of N-ylides derived from pyridine, benzylamine, imidazole, aniline, and phenylpyridine. We have studied N-ylides with benzoyl stabilizing substituents (*N*-phenacylpyridinium ylides), since they have attracted recently a renewed interest as starting materials of high-added-value products.[28] Gratifyingly, we found that N-ylides, such as $[H_xC_yN{-}CHC(O)Ar]$, where H_xC_yN represents one amine or one heterocycle and Ar is an aryl group, can be palladated regioselectively at the benzoyl ring ortho to the carbonyl group, almost regardless of the nature of the amine, the heterocycle, and/or the aryl group. Here, we report the results obtained on this type of chemistry.

RESULTS AND DISCUSSION

Synthesis of the N-Ylides. We have performed the synthesis of five families of N-ylides (Chart 1), namely, derivatives of pyridine (labeled **a**–**e**), *N*,*N*-dimethylbenzylamine (**f**), *N*-methylimidazole (**g**), *N*,*N*-dimethylaniline (**h**), and 2-phenylpyridine (**i**).

Chart 1. *N*-Phenacyl Ylides Studied in This Work



The N-ylides have been synthesized in two steps, as a general procedure. The first one involves the synthesis of the "-onium" salts (**1**) by reaction of the corresponding bromoketone with the appropriate amine[29a] or, alternatively, following the method of King.[29b] In the second step, the ylides are prepared (except **2e**) by deprotonation of the corresponding "onium" salts, using K_2CO_3 or NaOH as a base, in water at 0 °C.[29c,d] In some cases, the ylides are generated and reacted "in situ", because they could not be isolated. All ylides examined in this work have been prepared previously,[29] and we have employed known or slightly modified procedures for their preparation.

Orthopalladation of Pyridinium N-Ylides. The N-ylides were reacted with a classical palladating reagent as $Pd(OAc)_2$, and the outcome of the reaction was examined in detail for each case. The reaction conditions were optimized for each substrate analyzed. For the sake of simplicity and convenience, instead of fully characterizing the complexes with presumably acetate bridges, the resulting orthopalladated complexes were isolated and characterized as dimeric structures with chloride bridges (**4a**–**4i**), and/or as monomeric complexes containing an acac ligand (**5a**–**5i**).

The first set of compounds studied were N-ylides derived of pyridine (**2a**–**2d**). The orthometalation step was carried out by reaction of the ylide with $Pd(OAc)_2$ in dry toluene at temperatures in the range of 25–60 °C (see the Experimental Section), followed by acetate/chloride metathesis by reaction with LiCl in methanol. In this way, the complexes **4a**–**4d** were isolated in good yield as air-stable, yellow solids and characterized as binuclear species with the classical chloride bridging structure (Scheme 1). In some cases, the solubility of **4a**–**4d** avoids proper ^{13}C NMR measurements. Therefore, complexes **4a**–**4d** have been transformed into the more soluble acac derivatives **5a**–**5d** by metathesis of the chloride bridges by the chelate acac ligand. **4a**–**4d** were reacted with Tl(acac) (molar ratio of 1:2) in CH_2Cl_2 at 25 °C (Scheme 1), affording **5a**–**5d** as yellow or pale yellow solids, which were fully characterized by NMR, mass spectrometry, IR, and microanalysis.

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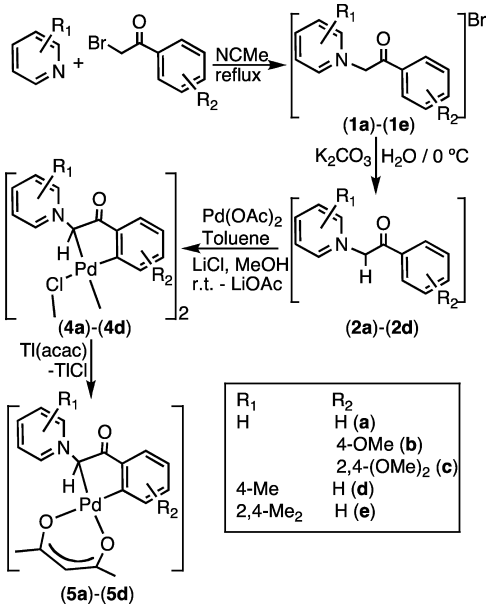
Scheme 1. Synthesis of Complexes 4a−4d and 5a−5d



The analysis of the IR spectra is a very practical tool to evaluate the outcome of these reactions; in particular, the shifts observed for the carbonyl groups are very good indications of the reaction pattern of these systems. In the ylides used as starting materials (**2a−2d**),[29] the IR spectra display a very strong absorption in the range of 1559−1599 cm^{-1} assigned to the carbonyl group, whose positions reflect the presence of electronic conjugation of the negative charge into the ketonic double bond. In the resulting orthopalladated complexes (**4a−4d**), the bands due to the CO moiety moved to 1647−1668 cm^{-1}, indicating that the conjugation with the carbonyl group has been broken, and, therefore, suggesting that the ylidic carbon is coordinated to the palladium. This kind of coordination is expected to drive the C−H activation process to the benzoyl ring, a regiochemistry that is clearly confirmed by the analysis of the NMR data.

In the ^1H NMR spectra of **4a−4d** are observed the disappearances of one of the aromatic protons of the benzoyl group, while the pyridine set of signals remains virtually unaltered. The NMR data also confirmed the σ coordination of the ylidic carbon, which is reflected in the significant upfield shift showed by the signal of the carbon of the ylide unit (for example, from 98.48 to 81.69 ppm for ylide **d**), reflecting the change in the hybridization of sp^2 to sp^3 upon coordination to the Pd center. Complexes **5a−5d** were also characterized by NMR, mass spectrometry, IR, and microanalysis. All data indicate that the ylide remains cyclopalladated after the chloride/acac metathesis, confirming the stability of the five-membered metallacyclic ring. In addition, the structure of **5c** was analyzed by X-ray diffraction studies (see below).

These results show that the palladation of the benzoyl ring is totally regioselective, since we have not detected signals due to other isomers in the NMR spectra. To achieve this metalation, it is very likely that the ylidic Cα atom acts as a directing group with concomitant formation of a five-membered ring. However, in principle, there is a second option (not observed in our case), namely, the cyclometalation of the ortho positions of the pyridine ring, which seems to be directed by interaction of the Pd with the carbonyl oxygen,[28] and formation of a six-membered ring. The coordination of the carbonyl oxygen to the Pd center is well documented for P-ylides,[20,26a,b] but it has been very rarely characterized for N-ylides,[18l,m,30] probably due to the higher nucleophilic character of the Cα atom in these N-ylides, compared with that of the oxygen. The incorporation of the Pd center to the pyridine ring, directed by the N-ylidic moiety, has recently been invoked by Hu et al. in order to explain the catalytic arylation on *N*-phenacylpyridinium derivatives.[28d] These authors provide an explanation based on the HOMO location on the ylide species, which resides on the *ortho*- and *para*-carbons of the pyridine group, and suggest that the ylides are the true reactive species. Surprisingly, our starting materials are *N*-phenacylpyridinium ylides too, and, in our hands, we have detected incorporation of the Pd atom only at the benzoyl ring. This different reactivity is really similar to that found in closely related species, such as *N*-iminopyridinium ylides [H_5C_5N-NC(O)Ph]. The contribution of Dias et al.[28g,h] about the orthopalladation of these ligands reports the regioselective incorporation of the Pd center to the ortho positions of the benzamide fragment, directed by its N-bonding to the iminic nitrogen. However, recent work of Charette et al. describes with great detail the catalytic arylation[28a] and alkenylation[28e] of the ortho positions of the pyridine moiety of the same *N*-iminopyridinium ylides, where the authors suggest that the O-bonding of the carbonyl oxygen assists the orientation. Therefore, we have examples of the two orientations in two different scenarios.

Probably, the different reaction conditions (in our case, there is not an excess of K_2CO_3 during the reaction, nor presence of phosphine or aryl bromide)[28d] and, therefore, the different reaction mechanisms could account for this opposite regioselectivity. In the catalytic process, it is reasonable to assume[28e] that the reaction starts with the reduction of the Pd salt [$Pd(OAc)_2$] to a Pd(0) species due to the action of the phosphine and that this intermediate adds oxidatively the aryl bromide, giving an (aryl)(bromide)−Pd(II) complex, presumably stabilized by additional coordination of the phosphine. This complex could be responsible for the interaction with the *N*-phenacylpyridinium derivatives, and it is, at this point, where the CH bond activation should be produced. The Pd-containing species that interacts with the ylide in that case[28e] (an electron-rich aryl-Pd species) and in our case (the very electrophilic $Pd(OAc)_2$ complex) are clearly quite different, probably this difference accounting for the different reaction outcomes. Additionally, in our case, the observed selectivity can be explained attending to geometrical factors. The higher affinity of the electrophilic Pd center for the ylidic carbon atom over the carbonylic oxygen governs the coordination step. Upon the formation of the intermediary species by palladium coordination to the ylidic carbon, it is obvious that the activation of the ortho proton of the benzoyl group is favored geometrically, because it would drive the formation of a five-membered metallacycle, whereas the C−H activation over the pyridine ring would form a highly unstable cycle of four members.

Although the deprotonation of the pyridinium salts **1a−1d** has been an efficient and practical method for the synthesis of the ylides **2a−2d**, it resulted to be not viable for the derivative **1e**, which contains a methyl group ortho to the quaternary nitrogen of the pyridinium ring. Apparently, the base employed can abstract one of these relatively acidic methyl protons, generating a carbanion able to attack the ketonic carbon, and leading to the formation of the indolizine **3** by means of an intramolecular aldol condensation (see Scheme 2). Although

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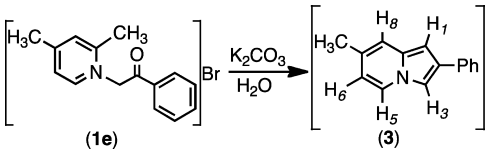
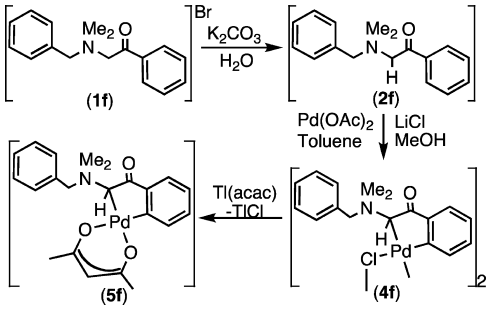
Scheme 2. Unexpected Synthesis of Indolizine 3[29n]



unexpected, this synthesis displays considerable interest due to the multiple applications presented by this kind of molecule,[29n] for example, in medicinal chemistry or in material science. However, and despite this potential interest, we considered that the synthesis of novel indolizines is not the topic of this article, and we have not continued with this type of reaction.

Orthopalladation of N-Ylides Derived from other N Sources. The next ligand studied was the ylide **2f**, which is analogous to the derivatives **2a**−**2d** but contains a *N*,*N*-dimethylbenzylamine group instead of the pyridine moiety. The reaction of the ylide **2f** with $Pd(OAc)_2$ in toluene at 60 °C during 2 h yielded the presumably orthometalated complex with acetate bridges, which is treated with LiCl in methanol, affording complex **4f** (Scheme 3). Although the elemental

Scheme 3. Synthesis of Complexes 4f and 5f

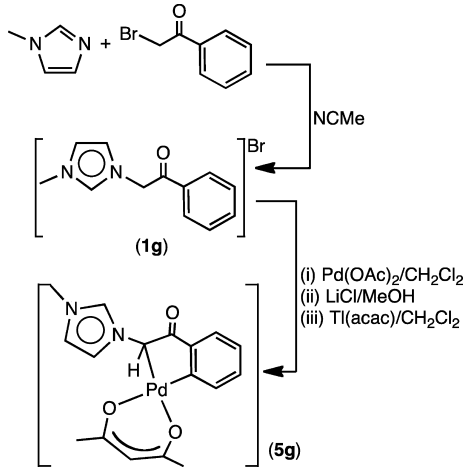


analysis and mass spectrometry of **4f** clearly indicated the formation of a typical structure of an orthometalated complex with chloride bridging ligands, this complex resulted to be poorly soluble in all the common organic solvents, precluding a total characterization. A simple derivatization to the mononuclear species **5f** by treatment with Tl(acac) allowed for a complete analysis of its structure.

The IR band assigned to the carbonyl group of the ylide unit appears at 1647 cm^{-1}, in the range expected for a complex with the ylidic carbon σ-coordinated to palladium and with the CO group nonbonded to the metallic fragment. In the ^1H NMR, the ylidic proton and the NMe_2 group undergo a considerable shift to lower fields (from 4.24 and 2.34 ppm in **2f**, to 5.21 ppm and 3.26 ppm in **5f**, respectively), and the initially equivalent protons of the CH_2N group are now diastereotopic and appear as a well-resolved AB spin system. Both facts are a consequence of the C coordination to the metallic center. A singlet at 3.26 ppm show that the two *N*-methyl groups behave as equivalent in the NMR time scale. The Cα-bonding displays two potential sites for the posterior orthometalation, one is the CH bond activation of the benzoyl ring to afford a metallacycle of five members, and the other is the cyclometalation of the phenyl ring of the dimethylbenzylamine moiety generating a six-membered cycle. If palladation were produced at the benzylic moiety, the two *N*-methyl groups would be located on a six-membered metallacycle, adjacent to the asymmetric ylidic carbon, and a large difference in the chemical environment of the two groups would be expected. This difference has to be reflected in very different chemical shifts, and we have not observed this difference in the ^1H, nor in the ^{13}C, NMR spectra. In fact, the ^1H NMR spectrum shows accidentally isochronous *N*-methyl groups, whereas the $^{13}C\{^1H\}$ NMR spectrum shows very similar chemical shifts for the two *N*-methyl groups (50.23 and 50.49 ppm). These facts strongly suggest that the palladation has been produced at the benzoyl ring. Probably, the different sizes of the resulting palladacycles (five- vs six-membered) are critical in order to achieve a given orientation.

The following substrate evaluated was a derivative of *N*-methylimidazole (**1g**). The reactions of the imidazolium salt **1g** with diverse bases at different temperatures always yielded decomposition products, without traces of the ylide species. In this case, the ylide seems to be too reactive, precluding its isolation and characterization. However, the imidazolium salt **1g** reacts cleanly with $Pd(OAc)_2$ at 25 °C during 2 h in CH_2Cl_2, affording the desired orthopalladated complex **4g** (Scheme 4).

Scheme 4. Synthesis of Complex 5g



In this reaction, probably, the ylide is generated "in situ" by intermediacy of the acetates present in the reaction media, which likely are capable of playing the role of the base. The intermediate with chloride bridges **4g** was poorly soluble in the common organic solvents, avoiding its full characterization. Therefore, **4g** was transformed by the typical strategy into the mononuclear complex **5g**, containing an acac ligand, whose structure was inferred from the NMR data. In the ^1H NMR spectrum, the most informative signals are two different sets of signals for the aromatic fragments, where three aromatic protons are easily assigned to the *N*-methyl imidazole aromatic ring, and only four protons, all of them nonequivalent, are attributed to the benzoyl ring. These data clearly indicate that the benzoyl ring has been cyclometalated, the heterocyclic unit remaining unaltered. It is also remarkable in this spectrum that the initial CH_2N group of the ammonium salt has been transformed into a CHN unit, evidenced by the presence of a singlet at 6.18 ppm in the ^1H NMR, which integrates by only one proton, indicating a σ coordination of the ylidic carbon to the metallic center. This kind of coordination is supported by the fact that, in the ^{13}C NMR, the signal assigned to the ylidic carbon (64.50 ppm) resonates within the typical range of this kind of system. In the IR spectrum, the CO group appears at

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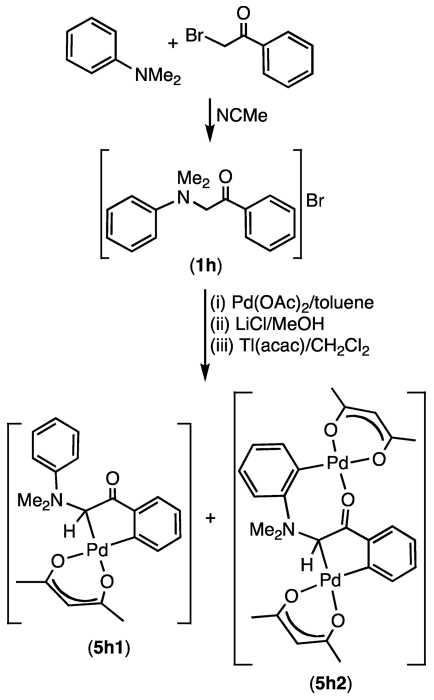
1662 cm^{-1}, in the expected region for C-bonded keto-stabilized ylides.

Considering that coordination through the ylidic carbon seems to be preferred, the regiochemistry observed is predictable. The palladation of the imidazolium ring directed by the C-bonding of the ylide, either at C2 or at C4, seems complicated since it will lead to a cycle of four members. However, the incorporation of the Pd center to the imidazolium ring could be achieved, in principle, in the case of the O-bonding of the ylide since a six-membered palladacycle would be formed, as it has been postulated in the case of the pyridinium salts. We have not detected the presence of other isomers so, once again, it seems that the O-bonding of the ylide is not favored in these reaction conditions and that the C-bonding is the effective directing group of the ylide unit.

The behavior of the ylide derived from *N,N*-dimethylaniline **h** has also been examined. Analogously to what is observed in the case of the *N*-methylimidazole **g**, all efforts to isolate the ylide failed, and orthopalladation was achieved by "in situ" generation of the ylide. The reaction between the anilinium salt **1h** with $Pd(OAc)_2$ in toluene at 65 °C resulted to be an efficient strategy for the synthesis of orthometalated N-ylides (Scheme 5). In this case, the expected chloride-bridging

Scheme 5. Synthesis of Complexes 5h1 and 5h2



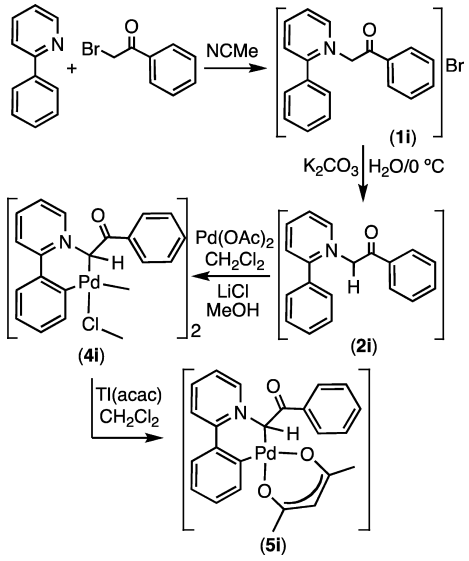
complex **4h** could not be isolated, although one-pot derivatization to the respective mononuclear species containing acac ligands allowed for the synthesis of well-defined species **5h** and a full understanding of the outcome of the reaction.

Conversely to the other examples described above, this reaction was not totally selective and afforded a mixture of the cyclopalladated complexes **5h1** and **5h2** in a molar ratio of 1:5 in the aforementioned conditions. The minor compound (**5h1**) displays a structure similar to the other examples described up to here, in which a palladacycle of five members has been formed by palladation of the benzoyl ring directed by the ylidic unit. However, the major compound (**5h2**) is a bimetallic complex, which is the result of two independent orthopalladations. In **5h2**, in addition to the cyclometalated benzoyl ring, there is another metallacycle of seven members, resulting from the C−H activation of the aromatic ring of the *N,N*-dimethylaniline. This second orthometalation process is assisted by the carbonyl group, which behaves as a directing group, coordinating a second palladium atom and directing the C−H activation process to the *N,N*-dimethylamine moiety. This is the only case we have found where the carbonyl group behaves as a directing group. A similar bis-orthopalladated dinuclear complex has been characterized in P-ylides.[27d] It seems reasonable to propose that **5h2** is formed from **5h1**, which is the species initially generated. This idea is supported by the fact that reactions carried out at room temperature in CH_2Cl_2 afforded mixtures in which **5h1** is the major compound. For example, after 1.5 h of reaction time, the obtained molar ratio of **5h1**/**5h2** is 1.7/1. However, analogous reactions carried out in toluene, but with longer reaction times or higher temperatures, did not show a full conversion to the derivative **5h2**, and severe decomposition was observed instead.

The structures depicted for **5h1** and **5h2** in Scheme 5 are based on the NMR data. The unusual double metalation undergone by **5h2** is inferred from the ^1H NMR spectrum, where the lack of one proton on each aromatic ring is clearly observed. The ^{13}C NMR displays, in addition to the σ-bonded ylidic carbon, signals attributable to two different σ Pd−C bonds, confirming the presence of two cyclopalladated arene rings. On the other hand, the O-bonding of the ylide can be easily inferred from the shift to low energies of the IR absorption due to the ν_{CO} stretch (1555 cm^{-1}), and from the observation of the deshielding of the signal due to the carbonyl group, now appearing at 207.06 ppm. The existence of two nonequivalent acac ligands, as judged from the NMR and IR data, is another evidence of the formation of the bimetallic complex.

Finally, we examined the reactivity of the N-ylide **2i**, which contains a phenylpyridine group. In this case, the stable ylide **2i** was isolated and fully characterized. The reaction of **2i** with $Pd(OAc)_2$ in CH_2Cl_2 at 25 °C for 4 h afforded a new cyclopalladated complex **4i** (Scheme 6), which showed a

Scheme 6. Synthesis of Complexes 4i and 5i



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correct elemental analysis and a very low solubility in common organic solvents. Compound **4i** was derivatized to the species **5i**, containing a chelate acac ligand, to perform the appropriate characterization (Scheme 6).

In this system, there are three potential positions for orthometalation: if the ylidic carbon behaves as a directing group, both the benzoyl ring and the phenyl ring are accessible, and also the pyridine is able to being activated if the carbonyl group orientates the orthometalation. The analysis of the NMR data revealed that only one of the three aromatic rings has been activated selectively, as judged by the lack of only one aromatic proton. The IR indicates that the ketone group was not bonded to the Pd center, since the ν_{CO} absorption appears at 1650 cm^{-1}. This fact suggests that the ylidic carbon is playing the role of a directing group and, therefore, causing the activation of the benzoyl group or the phenyl ring. The $^{1}H-^{13}C$ HMBC spectrum clearly revealed that the benzoyl ring was not activated, because the carbonyl carbon shows a clear correlation with the two equivalent ortho protons of the C_6H_5 moiety nonmetalated. This observation indicates that the C−H activation has taken place over the phenyl ring of the phenylpyridine unit, leading to the formation of the complex **5i**. A full assignation of the structure was achieved by a combination of COSY, 1D-NOESY, HSQC, and HMBC spectra, confirming the connectivity inferred previously and depicted in Scheme 6.

Conversely to all the syntheses discussed up to here, the benzoyl ring remains intact, the orthometalation taking place over the phenyl group of the phenylpyridine moiety selectively. This regioselective C−H activation led to the formation of a six-membered ring, instead of the anticipated formation of a palladacycle of five members resulting from the activation of the benzoyl group. In this particular case, the interpretation of the regiochemistry observed is a challenging task, and probably a delicate balance between electronic and geometric factors seems to be operative. One key to understanding this unexpected reactivity could be the enhanced acidity of the phenyl protons due to the strong electron-withdrawing ability of the quaternary pyridinium salt, in similar way as observed with the dimethylaniline system. Also, geometrical factors can be important, because it is interesting to note that the metallacycle formed is immersed into a tricyclic system, which makes the evaluation of its relative stability difficult.

X-ray Crystal Structure of 5c. A molecular drawing of compound **5c** is shown in Figure 3. The structure shows clearly that the Pd atom has been incorporated to the benzoyl fragment and that the ylide fragment is C-bonded. Therefore, the Pd atom lies in a slightly distorted square-planar environment and is surrounded, additionally, by the oxygen atoms of the chelating acac ligand. The Pd−C(6) bond distance [1.964(2) Å] is identical, within experimental error, to those found in related benzoyl or benzamide systems,[27d] and the Pd−C(13) bond distance [2.022(3) Å] falls in the usual range of distances found for this type of bonds.[26,27] Interestingly, the bond distance of Pd(1)−O(3) [2.076(2) Å] is slightly longer than the bond distance of Pd(1)−O(2) [2.060(2) Å], reflecting the higher trans influence of the orthometalated carbon versus the ylidic carbon. Other internal parameters are as expected.

CONCLUSION

In summary, we have described the syntheses of several orthometalated complexes derived from N-ylides, in particular, derivatives of pyridine, benzylamine, imidazole, aniline, and

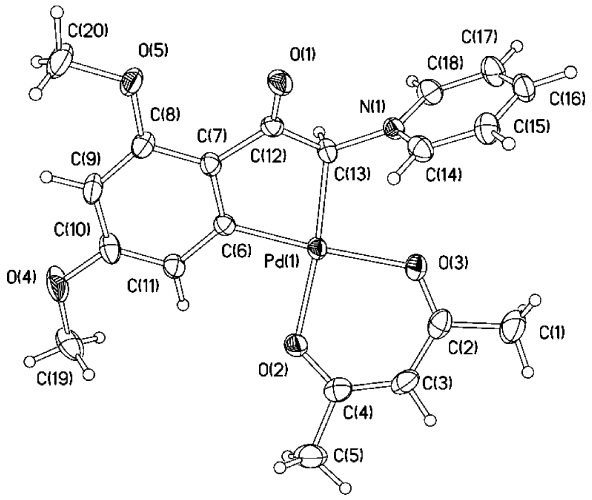

Figure 3. Molecular structure of complex **5c**. Ellipsoids of non-hydrogen atoms have been drawn at 50% probability. Selected bond distances (Å) and angles (deg): Pd(1)−C(6) 1.964(2), Pd(1)−C(13) 2.022(3), Pd(1)−O(2) 2.060(2), Pd(1)−O(3) 2.076(2), N(1)−C(13) 1.476(3), C(12)−C(13) 1.509(3), O(1)−C(12) 1.222(3), C(7)−C(12) 1.480(3); C(6)−Pd(1)−C(13) 80.92(10), C(6)−Pd(1)−O(2) 92.53(8), C(13)−Pd(1)−O(2) 173.17(8), C(6)−Pd(1)−O(3) 174.94(9), C(13)−Pd(1)−O(3) 95.17(8), O(2)−Pd(1)−O(3) 91.25(7), O(1)−C(12)−C(7) 126.8(2), O(1)−C(12)−C(13) 123.6(2), C(7)−C(12)−C(13) 109.4(2), N(1)−C(13)−C(12) 111.9(2), N(1)−C(13)−Pd(1) 114.27(17), C(12)−C(13)−Pd(1) 106.46(15).

phenylpyridine. The incorporation of the Pd atom to these substrates is, in most of the cases, regioselective, since the orthopalladation is produced only at the aryl ring of the benzoyl group, directed by the coordination of the ylidic Cα carbon, and favoring the formation of five-membered rings over other ring sizes. Two exceptions to the general trend have been observed. One is the double metalation of the ylide [$PhNMe_2CHC(O)Ph$], being the first metalation C-directed and the second one directed by the carbonyl oxygen. The second one is more intriguing, because the palladation of the phenylpyridine derivative occurs at the pyridinic 2-phenyl ring and produces selectively a six-membered palladacycle. These results show that the nucleophilicity of the ylidic Cα and the ring size are not the only parameters governing the selectivity and that other geometric, steric, and electronic factors have to be taken into account.

EXPERIMENTAL SECTION

General Methods. Solvents were dried and distilled using standard procedures before use. Elemental analyses (CHN) were carried out on a PerkinElmer 2400-B microanalyser. Infrared spectra (4000−380 cm^{-1}) were recorded on a PerkinElmer Spectrum One IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, DMSO-d_6, or CD_2Cl_2 solutions at 25 °C on Bruker AV300 and AV400 spectrometers (δ in parts per million, J in hertz) at ^{1}H operating frequencies of 300.13 and 400.13 MHz, respectively. ^{1}H and ^{13}C spectra were referenced using the solvent signal as an internal standard. ESI^+ mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonic GmbH) equipped with a standard ESI/APCI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served as both the nebulizer gas and the dry gas. The mass spectra ($MALDI^+$) were recorded from $CHCl_3$ solutions on a MALDI-TOF Microflex (Bruker) spectrometer (DCTB as matrix). Ylides **2a**,[29d,e] **2b**,[29f] **2c**,[29g,h] **2d**,[29a] **2f**,[29i,j] **2g**,[29k,l] **2h**,[29i] and **2i**[28e,29m] were synthesized according to published methods.

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Synthesis of 7-Methyl-2-phenylindolicine (3).[29n] **1e** (0.602 g, 1.96 mmol) was reacted with K_2CO_3 (1.05 g, 8.3 mmol) in H_2O (5 mL) to give **3** as an orange oil in 96% yield. MS (ESI+) [*m*/*z*, (%)]: 207.8 (100%) $[M]^+$. ^1H NMR ($CDCl_3$): δ 3.75 (s, 3H, CH_3), 6.20 (dd, 1H, H_6, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.6), 6.46 (s, 1H, H_1), 7.00 (s, 1H, H_8), 7.17 (t, 1H, H_p, Ph, $^3J_{HH}$ = 7.6), 7.27 (t, 2H, H_m, Ph, $^3J_{HH}$ = 7.6), 7.40 (d, 1H, H_3, $^4J_{HH}$ = 1.2), 7.56 (dd, 2H, H_o, $^4J_{HH}$ = 1.6), 7.69 (d, 1H, H_5).

Synthesis of 4a. A solution of **2a** (0.120 g, 0.659 mmol) and $Pd(OAc)_2$ (0.147 g, 0.659 mmol) in dry toluene (15 mL) was stirred at 60 °C for 2 h. After the reaction time, the resulting suspension was cooled, and the precipitated solid was filtered and washed with toluene (5 mL). This solid was suspended in MeOH and allowed to react with excess LiCl (0.055 g, 1.318 mmol) at 25 °C for 30 min. The color of the suspension evolved, and a yellow solid was finally obtained. The suspension was filtered, and the yellow solid **4a** was washed with MeOH (5 mL) and Et_2O (25 mL) and dried in vacuo. Obtained: 0.19 g (85% yield). Anal. Calcd for $C_{26}H_{20}Cl_2N_2O_2Pd_2$ (676.2): C, 46.18; H, 2.98; N, 4.14. Found: C, 45.92; H, 3.18; N, 3.92. MS (MALDI+) [*m*/*z*, (%)]: 641 (10%) $[M - Cl]^+$. IR: ν = 1668 (ν_{CO}) cm^{-1}. ^1H NMR (dmso-d^6): δ 6.82 (s, 1H, C(H)N), 7.16 (s, br, 2H, H_4 + H_5), 7.42 (s, v br, 1H, H_6), 7.98 (t, 2H, H_m, py, $^3J_{HH}$ = 6.4), 8.21 (s, v br, 1H, H_3), 8.38 (t, br, 1H, H_p, py), 8.82 (s, br, 2H, H_o, py).

Synthesis of 4b. Complex **4b** was obtained following the same method than that described for **4a** with slight modifications. Therefore, **2b** (0.06 g, 0.264 mmol) was reacted with $Pd(OAc)_2$ (0.059 g, 0.264 mmol) in dry toluene (15 mL) at 25 °C for 15 h, and with LiCl (0.023 g, 0.542 mmol) in MeOH (10 mL), giving **4b** as a yellow solid. Obtained: 0.049 g (50% yield). Anal. Calcd for $C_{28}H_{24}Cl_2N_2O_4Pd_2$ (736.25): C, 45.68; H, 3.29; N, 3.80. Found: C, 45.65; H, 3.61; N, 3.68. MS (MALDI+) [*m*/*z*, (%)]: 736 (10%) $[M]^+$. IR: ν = 1647 (ν_{CO}) cm^{-1}. ^1H NMR (dmso-d^6): δ 3.68 (s, 3H, OMe), 6.66 (d, 1H, H_4, $^3J_{HH}$ = 7.6), 6.70 (s, 1H, CHN), 7.33 (d, 1H, H_3), 7.83 (s, 1H, H_6), 7.89 (m, 2H, H_m, py), 8.30 (t, 1H, H_p, py, $^3J_{HH}$ = 7.6), 8.73 (s, br, 2H, H_o, py).

Synthesis of 4c. Complex **4c** was obtained following the same method than that described for **4a** with slight modifications. Therefore, **2c** (0.128 g, 0.499 mmol) was reacted with $Pd(OAc)_2$ (0.112 g, 0.499 mmol) in dry toluene (15 mL) at 40 °C for 2 h, and with LiCl (0.042 g, 1.00 mmol) in MeOH (20 mL), giving **4c** as a yellow solid. Obtained: 0.134 g (68% yield). Anal. Calcd for $C_{30}H_{28}Cl_2N_2O_6Pd_2$ (796.3): C, 45.25; H, 3.54; N, 3.52. Found: C, 45.06; H, 3.99; N, 3.91. MS (MALDI+) [*m*/*z*, (%)]: 761 (60.6%) $[M - Cl]^+$. IR: ν = 1648 (ν_{CO}) cm^{-1}. ^1H NMR (dmso-d^6): δ 3.68 (s, 3H, MeO), 3.75 (s, 3H, MeO), 6.27 (s, 1H, C(H)N), 6.55 (s, 1H, H_4), 7.47 (s, br, 1H, H_6), 7.94 (t, 2H, H_m, py, $^3J_{HH}$ = 6.3), 8.35 (t, 1H, H_p, py), 8.75 (d, 2H, H_o, py). $^{13}C\{^1H\}$ NMR (dmso-d^6): δ 55.01 (CH_3O), 55.06 (CH_3O), 82.13 (C(H)N), 95.75 (C_4), 109.78 (C_6), 122.03 (C_2), 126.09 (C_m, py), 142.22 (C_p, py), 145.40 (C_o, py), 155.87 (C-O), 158.54 (C-O), 160.37 (C_1), 194.05 (CO).

Synthesis of 4d. Complex **4d** was obtained following the same method than that described for **4a** with slight modifications. Therefore, **2d** (0.15 g, 0.71 mmol) was reacted with $Pd(OAc)_2$ (0.16 g, 0.71 mmol) in dry toluene (15 mL) at 60 °C for 1 h, and with LiCl (0.060 g, 1.42 mmol) in MeOH (15 mL), giving **4d** as a yellow solid. Obtained: 0.147 g (78% yield). Anal. Calcd for $C_{28}H_{24}Cl_2N_2O_2Pd_2$ (704.25): C, 47.75; H, 3.43; N, 3.98. Found: C, 47.92; H, 3.68; N, 3.74. MS (MALDI) [*m*/*z*, (%)]: 669 (34.8%) $[M - Cl]^+$. IR: ν = 1655 (ν_{CO}) cm^{-1}. ^1H NMR (dmso-d^6): δ 2.54 (s, 3H, CH_3), 6.74 (s, br, 1H, C(H)N), 7.15 (s, br, 2H, H_4 + H_5), 7.41 (s, br, 1H, H_6), 7.79 (s, br, 2H, H_m, py), 8.21 (s, br, 1H, H_3), 8.65 (s, br, 2H, H_o, py). $^{13}C\{^1H\}$ NMR (dmso-d^6): δ 21.19 (CH_3), 81.69 (C(H)N), 124.34 (C_6), 124.66 (C_5), 126.67 (C_m, py), 129.39 (C_4), 133.88 (C_3), 144.48 (C_p, py), 150.24 (C_o, py), 152.21 (C_2), 155.34 (C_1), 197.73 (CO).

Synthesis of 4f. Complex **4f** was obtained following the same method than that described for **4a** with some modifications. Therefore, **2f** (0.250 g, 0.987 mmol) was reacted with $Pd(OAc)_2$ (0.213 g, 0.951 mmol) in dry toluene (15 mL) at 60 °C for 1.5 h. The resulting suspension was evaporated to dryness and the residue dissolved in MeOH (20 mL) and treated with LiCl (0.084 g, 1.97 mmol). The resulting mixture was stirred at room temperature, and after some minutes, **4f** precipitated as a yellow solid. Obtained: 0.213 g (55% yield). Anal. Calcd for $C_{34}H_{36}Cl_2N_2O_2Pd_2$ (788.41): C, 51.80; H, 4.60; N, 3.55. Found: C, 51.40; H, 4.94; N, 4.02. MS (MALDI+) [*m*/*z*, (%)]: 753.1 (45%) $[M - Cl]^+$. IR: ν = 1648 (ν_{CO}) cm^{-1}. NMR: **4f** could not be fully characterized due to its insolubility in common organic solvents.

Synthesis of 4g. Complex **4g** was obtained following the same method than that described for **4a**, except that the reaction starts from the imidazolium salt instead of the ylide. Therefore, **1g** (0.267 g, 0.951 mmol) was reacted with $Pd(OAc)_2$ (0.213 g, 0.951 mmol) in dry CH_2Cl_2 (15 mL) at 25 °C for 2 h. The resulting suspension was evaporated to dryness and the residue dissolved in MeOH (20 mL) and treated with LiCl (0.084 g, 1.97 mmol). The resulting mixture was stirred at room temperature, and after some minutes, **4g** precipitated as a yellow solid. Obtained: 0.190 g (58.6% yield). Anal. Calcd for $C_{24}H_{22}Cl_2N_4O_2Pd_2$ (682.17): C, 42.26; H, 3.25; N, 8.21. Found: C, 42.09; H, 3.11; N, 7.96. NMR: **4g** could not be fully characterized due to its insolubility in common organic solvents.

Synthesis of 4i. Complex **4i** was obtained following the same method than that described for **4f**. Therefore, **2i** (0.100 g, 0.366 mmol) was reacted with $Pd(OAc)_2$ (0.083 g, 0.366 mmol) in dry CH_2Cl_2 (15 mL) at 38 °C for 4 h, and with LiCl (0.084 g, 1.97 mmol) in MeOH (20 mL), giving **4i** as a yellow solid. Obtained: 0.13 g (85.8% yield). Anal. Calcd for $C_{38}H_{28}Cl_2N_2O_2Pd_2$ (828.36): C, 55.10; H, 3.41; N, 3.38. Found: C, 54.93; H, 3.44; N, 3.12. IR: ν = 1651 (ν_{CO}) cm^{-1}. NMR: **4i** could not be fully characterized due to its insolubility in common organic solvents.

Synthesis of 5a. Complexes **5a**−**5i** were prepared using the same experimental method. Only the representative synthesis of **5a** is detailed here. To a suspension of **4a** (0.101 g, 0.148 mmol) in CH_2Cl_2 (10 mL) was added Tl(acac) (0.089 g, 0.296 mmol). The appearance of the suspension changed, and a white precipitate was obtained after 30 min of stirring at 25 °C. This suspension was filtered through a Celite pad, and the resulting solution was evaporated to dryness. The treatment of the residue with cold *n*-pentane (15 mL) and stirring gave complex **5a** as a pale yellow solid. Obtained: 0.089 g (75.2% yield). Anal. Calcd for $C_{18}H_{17}NO_3Pd$ (401.75 g/mol): C, 53.81; H, 4.27; N, 3.49. Found: C, 53.46; H, 4.01; N, 3.27. IR: ν = 1664 (ν_{CO}, ylide), 1578, 1505 (ν_{CO}, acac) cm^{-1}. MS: (ESI+) [*m*/*z*, (%)]: 301.9 (100%) $[M - acac]^+$. ^1H NMR ($CDCl_3$): δ 1.38 (s, 3H, CH_3, acac), 1.94 (s, 3H, CH_3, acac), 5.11 (s, 1H, CH-acac), 6.54 (s, 1H, C(H)N), 7.03 (td, 1H, H_5, $^3J_{H5-H4} \approx {}^3J_{H5-H6}$ = 7.4, $^4J_{H5-H3}$ = 1.0), 7.16 (td, 1H, H_4, $^3J_{H4-H3}$ = 7.4, $^4J_{H4-H6}$ = 1.4), 7.44 (dd, 1H, H_6), 7.64 (t, 2H, H_m, py, $^3J_{HH}$ = 7.3), 7.86 (d, 1H, H_3), 8.06 (t, 1H, H_p, py), 8.71 (d, 2H, H_o, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 27.57 (CH_3, acac), 28.20 (CH_3, acac), 79.33 (CHN), 99.96 (CH, acac), 124.40 (C_4, C_6H_4), 124.72 (C_3, C_6H_4), 126.07 (C_m, py), 130.21 (C_5, C_6H_4), 132.17 (C_6, C_6H_4), 140.84 (C_p, py), 142.87 (C_2, C_6H_4), 145.17 (C_o, py), 152.20 (C_1, C_6H_4), 186.70 (CO, acac), 187.49 (CO, acac), 200.62 (CO, ylide).

Synthesis of 5b. **4b** (0.030 g, 0.041 mmol) was reacted with Tl(acac) (0.024 g, 0.081 mmol) in CH_2Cl_2 (10 mL), giving **5b** as a yellow solid. Obtained: 0.016 g (90% yield). Anal. Calcd. for $C_{19}H_{19}NO_4Pd$ (431.78): C, 52.85; H, 4.44; N, 3.24. Found: C, 52.74; H, 4.67; N, 3.59. MS (MALDI) [*m*/*z*, (%)]: 331.6 (24.4%) $[M - acac]^+$. IR: ν = 1641 (ν_{CO}, ylide), 1567, 1505 (ν_{CO}, acac) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.41 (s, 3H, CH_3, acac), 1.94 (s, 3H, CH_3, acac), 3.82 (s, 3H, CH_3O), 5.12 (s, 1H, CH, acac), 6.46 (s, 1H, C(H)N), 6.61 (dd, 1H, H_4, $^3J_{H4-H3}$ = 8.4, $^4J_{H4-H6}$ = 2.5), 7.39 (d, 1H, H_6), 7.43 (d, 1H, H_3), 7.64 (t, 2H, H_m, py, $^3J_{HH}$ = 7.8), 8.06 (t, 1H, H_p, py), 8.68 (d, 2H, H_o, py).

Synthesis of 5c. **4c** (0.020 g, 0.025 mmol) was reacted with Tl(acac) (0.015 g, 0.050 mmol) in CH_2Cl_2 (10 mL), giving **5c** as a yellow solid. Obtained: 0.010 g (93% yield). Anal. Calcd for $C_{20}H_{21}NO_5Pd$ (461.8): C, 52.02; H, 4.58; N, 3.03. Found: C, 51.83; H, 4.55; N, 3.26. MS (MALDI+) [*m*/*z*, (%)]: 363 (15.3%) $[M - acac]^+$. IR: ν = 1644 (ν_{CO}, ylide), 1574, 1553, 1511 (ν_{CO}, acac) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.43 (s, 3H, CH_3, acac), 1.94 (s, 3H, CH_3, acac), 3.74 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O), 5.13 (s, 1H, CH, acac), 6.09

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(d, 1H, H_4, $^4J_{H4-H6}$ = 2.1), 6.33 (s, 1H, C(H)N), 7.05 (d, 1H, H_6), 7.64 (t, 2H, H_m, py, $^3J_{HH}$ = 7.8), 8.07 (t, 1H, H_p, py), 8.67 (d, 2H, H_o, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.57 (CH_3, acac), 27.23 (CH_3, acac), 54.25 (OMe), 54.32 (OMe), 78.25 (CHN), 94.92 (C_4, C_6H_4), 98.85 (CH, acac), 105.43 (C_6, C_6H_4), 122.64 (C_2, C_6H_4), 124.79 (C_m, py), 139.77 (C_p, py), 144.32 (C_o, py), 157.37 (C_3, C_6H_4), 158.36 (C_5, C_6H_4), 160.52 (C_1, C_6H_4), 185.59 (CO, acac), 186.56 (CO, acac), 196.96 (CO, ylide).

Synthesis of 5d. **4d** (0.097 g, 0.14 mmol) was reacted with Tl(acac) (0.086 g, 0.28 mmol) in CH_2Cl_2 (10 mL), giving **5d** as a yellow solid. Obtained: 0.030 g (51% yield). Anal. Calcd for $C_{19}H_{19}NO_3Pd$ (415.78): C, 54.89; H, 4.61; N, 3.37. Found: C, 54.91; H, 4.92; N, 3.53. MS (ESI+) [*m*/*z*, (%)]: 314.9 (87.5%) [M − acac]$^+$. IR: ν = 1649, 1636 (ν_{CO}, ylide), 1571, 1509(ν_{CO}, acac) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.43 (s, 3H, CH_3, acac), 1.94 (s, 3H, CH_3, acac), 2.49 (s, 3H, CH_3), 5.12 (s, 1H, CH, acac), 6.46 (s, 1H, C(H)N), 7.03 (t, 1H, H_5, $^3J_{H5-H4} \approx {}^3J_{H5-H6}$ = 7.1), 7.17 (m, 1H, H_4), 7.40−7.50 (m, 3H, H_3 + H_m (pic)), 7.86 (d, 1H, H_6, $^3J_{H6-H5}$ = 7.4), 8.50 (d, 2H, H_o, pic, $^3J_{HH}$ = 5.9). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.87 (CH_3, pic), 27.71 (CH_3, acac), 28.20 (CH_3, acac), 78.56 (CHN), 99.87 (CH, acac), 124.31 (C_5, C_6H_4), 124.61 (C_3, C_6H_4), 126.61 (C_m, pic), 130.11 (C_4, C_6H_4), 132.16 (C_6, C_6H_4), 142.73 (C_p, pic), 144.59 (C_o, pic), 152.26 (C_2, C_6H_4), 154.49 (C_1, C_6H_4), 186.58 (CO, acac), 187.51 (CO, acac), 201.21 (CO, ylide).

Synthesis of 5f. **4f** (0.120 g, 0.152 mmol) was reacted with Tl(acac) (0.092 g, 0.304 mmol) in CH_2Cl_2 (10 mL), giving **5f** as a yellow solid. Obtained: 0.097 g (70% yield). Anal. Calcd for $C_{22}H_{25}NO_3Pd$ (457.86): C, 57.71; H, 5.50; N, 3.06. Found: C, 57.60; H, 5.91; N, 3.19. IR: ν = 1647 (ν_{CO}, ylide), 1574, 1515 (ν_{CO}, acac) cm^{-1}. MS: (MALDI+) [*m*/*z*, (%)]: 357.8 (14%) [M − acac]$^+$. ^1H NMR ($CDCl_3$): δ 1.89 (s, 3H, CH_3, acac), 1.97 (s, 3H, CH_3, acac), 3.26 (s, 6H, Me_2N), 4.89 (d, 1H, CH_2N, $^2J_{HH}$ = 12.6), 5.04 (d, 1H, CH_2N), 5.21 (s, 1H, C(H)N), 5.28 (s, 1H, CH, acac), 7.02 (td, 1H, H_5, $^3J_{H5H4} \approx {}^3J_{H5H6} \approx$ 7.2, $^4J_{H5H3}$ = 1.1), 7.05 (td, 1H, H_4, $^3J_{H4H5} \approx {}^3J_{H4H3} \approx$ 7.2, $^4J_{H4H6}$ = 1.6), 7.33 (dd, 1H, H_6), 7.36−7.39 (m, 3H, H_m + H_p, Ph), 8.71 (dd, 2H, H_o, Ph, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 2.1), 7.80 (d, 1H, H_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 28.29 (CH_3, acac), 28.44 (CH_3, acac), 50.23 (Me_2N), 50.49 (Me_2N), 66.81 (CH_2N), 80.82 (C(H)N), 99.72 (CH, acac), 123.26 (C_3), 124.33 (C_5), 128.70 (C_4), 128.97 (C_m, py), 129.27 (s, C_{ipso}, Ph), 130.12 (C_p, Ph), 130.77 (C_6), 133.01 (C_o, Ph), 141.96 (C_2), 146.87 (C_1), 185.77 (CO, acac), 188.37 (CO, acac), 197.77 (CO, ylide).

Synthesis of 5g. **4g** (0.100 g, 0.146 mmol) was reacted with Tl(acac) (0.087 g, 0.293 mmol) in CH_2Cl_2 (15 mL), giving **5g** as a yellow solid. Obtained: 0.072 g (60.5% yield). Anal. Calcd for $C_{17}H_{18}N_2O_3Pd$ (404.74): C, 50.45; H, 4.48; N, 6.92. Found: C, 50.23; H, 4.17; N, 7.01. IR: ν = 1662 (ν_{CO}, ylide), 1583, 1510 (ν_{CO}, acac) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.62 (s, 3H, CH_3, acac), 1.96 (s, 3H, CH_3, acac), 3.74 (s, 3H, NMe), 5.19 (s, 1H, CH, acac), 6.18 (s, 1H, CHN), 6.92 (s, 1H, H_4, imid), 7.02 (t, 1H, H_4, C_6H_4, $^3J_{HH}$ = 7.3), 7.14 (td, 1H, H_5, C_6H_4, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.1), 7.32 (s, 1H, H_5, imid), 7.40 (d, 1H, H_3, C_6H_4), 7.57 (d, 1H, H_6, C_6H_4), 8.62 (s, 1H, H_2, imid). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 28.18 (CH_3, acac), 28.34 (CH_3, acac), 35.84 (NCH_3, imid), 64.50 (CHN), 99.85 (CH, acac), 120.12 (C_4, imid), 124.21 (C_3, C_6H_4), 125.85 (C_4, C_6H_4), 125.87 (C_5, imid), 129.82 (C_5, C_6H_4), 131.96 (C_6, C_6H_4), 142.04 (C_2, C_6H_4), 151.42 (C_1, C_6H_4), 186.12 (CO, acac), 188.02 (CO, acac), 202.52 (CO, ylide). The signal corresponding to the C_2 (imid) carbon was not observed.

Synthesis of 5h. To a suspension of **1h** (0.174 g, 0.545 mmol) in toluene (15 mL) was added $Pd(OAc)_2$ (0.122 g, 0.545 mmol). This mixture was stirred at 60 °C for 2 h, then the resulting solid was separated by centrifugation. This solid was dissolved in MeOH (10 mL) and was reacted with an excess of LiCl (0.086 g, 2.02 mmol) for 2 h. After the reaction time, the solvent was evaporated in vacuo and the residue redissolved in CH_2Cl_2 (20 mL), giving a yellow solution. This solution was treated with Tl(acac) (0.330 g, 1.09 mmol) and stirred for 25 min at 25 °C. After filtration of all insoluble solids (TlCl and LiCl), the resulting solution was evaporated to dryness and the residue treated with cold *n*-pentane (20 mL). Further stirring gave **5h** as a yellow solid. Obtained: 0.166 g (34.3% yield). Complex **5h** was characterized spectroscopically as the mixture of the mononuclear **5h1** and the dinuclear **5h2** complexes in a 1:5 molar ratio. IR: ν = 1555 (ν_{CO}, ylide), 1573, 1512 (ν_{CO}, acac) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.72 (s, CH_3, acac, **5h1**), 1.80 (s, CH_3, acac, **5h2**), 1.89 (s, CH_3, acac, **5h2**), 1.99 (s, CH_3, acac, **5h1**), 2.02 (s, CH_3, acac, **5h2**), 2.03 (s, CH_3, acac, **5h2**), 3.69 (s, NCH_3, **5h1**), 3.74 (s, NCH_3, **5h2**), 3.76 (s, NCH_3, **5h2**), 3.78 (s, NCH_3, **5h1**), 5.18 (s, CH, acac, **5h1**), 5.23 (s, CH, acac, **5h2**), 5.29 (s, CH, acac, **5h2**), 6.03 (s, CHN, **5h2**), 6.14 (s, CHN, **5h1**), 6.90 (dd, $H_{3'}$, NC_6H_4, **5h2**, $^3J_{HH}$ = 7.1, $^4J_{HH}$ = 1.9), 6.98 (td, H_5, C_6H_4, **5h2**, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.1), 7.13−7.22 (m, H_4 (C_6H_4) + $H_{4'}$,$H_{5'}$ (NC_6H_4), **5h2**), 7.28−7.29 (m, H_3, C_6H_4, **5h2**), 7.54 (dd, H_6, C_6H_4, **5h2**, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.0), 7.67 (dd, $H_{6'}$, NC_6H_4, **5h2**, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 2.2). In the aromatic region, only the following signals assigned to the minor isomer **5h1** could be identified unambiguously: 7.36 (t, H_m, NPh, $^3J_{HH}$ = 7.8), 7.54 (t, H_p, NPh), 8.02 (d, H_o, NPh). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 27.35, 27.65, 27.71, 27.88 (4CH_3, 2 acac), 51.71 (NCH_3), 63.37 (NCH_3), 85.48 (CHN), 99.69 (CH, acac), 100.33 (CH, acac), 114.55, 122.96, 124.99, 127.77, 128.61, 130.19, 131.69, 134.12 (CH of C_6H_4 and NC_6H_4), 146.59, 156.93, 157.00 (C_q of C_6H_4 and NC_6H_4), 186.13, 186.81, 186.95, 188.51 (4CO, 2 acac), 207.06 (CO, ylide) (one of the Cq atoms was not detected). Only the signals of the major isomer, **5h2**, could be unambiguously identified.

Synthesis of 5i. **4i** (0.084 g, 0.100 mmol) was reacted with Tl(acac) (0.061 g, 0.202 mmol) in CH_2Cl_2 (15 mL), giving **5i** as a yellow solid. Obtained: 0.058 g (63% yield). Anal. Calcd for $C_{24}H_{21}NO_3Pd$ (477.84): C, 60.32; H, 4.43; N, 2.93. Found: C, 59.98; H, 4.12; N, 2.55. IR: ν = 1650 (ν_{CO}, ylide), 1580, 1511 (ν_{CO}, acac) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.89 (s, 3H, CH_3, acac), 1.99 (s, 3H, CH_3, acac), 5.23 (s, 1H, CH, acac), 6.70 (s, 1H, CHN), 7.02−7.08 (m, 2H, $H_{4'}$ + $H_{5'}$, C_6H_4), 7.24−7.30 (m, 3H, H_m (Ph) + H_5 (py)), 7.37 (t, 1H, H_p, Ph, $^3J_{HH}$ = 7.6), 7.54 (m, 1H, $H_{6'}$, C_6H_4), 7.61 (m, 1H, $H_{3'}$, C_6H_4), 7.91−7.98 (m, 2H, H_3 + H_4, py), 8.17−8.21 (m, 3H, H_o (Ph) + H_6 (py)). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 28.34 (CH_3, acac), 28.40 (CH_3, acac), 69.71 (CHN), 99.56 (CH, acac), 122.32 (C_5, py), 124.72, 129.51 ($C_{4'}$ + $C_{5'}$, C_6H_4), 126.72 (two collapsed signals, $C_{3'}$ (C_6H_4) + C_4(py)), 128.10 (C_m, PhCO), 128.80 (C_o, PhCO), 132.08 (C_p, PhCO), 135.34, 136.56 (C_{ipso} (PhCO) + $C_{2'}$ (C_6H_4)), 136.86 ($C_{6'}$, C_6H_4), 140.66 (C_3, py), 141.48 (C_6, py), 154.84 ($C_{1'}$, C_6H_4), 162.67 (C_2, py), 186.59 (CO, acac), 187.92 (CO, acac), 192.45 (CO, ylide).

X-ray Crystallography. Crystals of **5c** of suitable quality for X-ray measurements were grown by diffusion of *n*-hexane into a CH_2Cl_2 solution of the crude product at −15 °C. A single crystal was mounted at the end of a quartz fiber in a random orientation, covered with perfluorinated oil and placed under a cold stream of N_2 gas. Data collection was performed on an Oxford Diffraction Xcalibur2 diffractometer using graphite-monocromated Mo Kα radiation (λ = 0.71073 Å). A hemisphere of data was collected based on ω-scan or φ-scan runs. The diffraction frames were integrated using the program CrysAlis RED,[31] and the integrated intensities were corrected for absorption with SADABS.[32] The structure was solved and developed by Patterson and Fourier methods.[33] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed at idealized positions and treated as riding atoms. Each H 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.[34]

■ ASSOCIATED CONTENT

Supporting Information

CIF of complex **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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