Organometallics **2006,** *25,* 1995−2001

A Comparative Study of the Chelating Ability of the $-N(R)-(CH_2)_n-CO-N(R)_2$ Framework in σ-Aryl Palladium(II) Complexes Derived from 2-Iodoanilines and 2-Iodobenzylamines. Synthesis of New Types of Terdentate [C,N,O] Pd(II) Complexes and C,N-Bridged Binuclear Pd(II) Compounds

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Received November 24, 2005

The reaction of iodo anilines 2-$IC_6H_4-N(Me)-CH_2-CO-N(R)_2$ (R = Me, **1a**; R = Et, **1b**) with $Pd_2(dba)_3$ afforded binuclear Pd(II) complexes $[Pd\{\eta\text{-}(N,C)\text{-}\mu\text{-}N(Me)(C_6H_4\text{-}2)CH_2C(O)N(R)_2\}I]_2$ (R = Me, **2a**; R = Et, **2b**), which by reaction with PPh_3 and Tl(TfO) were transformed into the cationic binuclear Pd(II) complexes $[Pd\{\eta\text{-}(N,C)\text{-}\mu\text{-}N(Me)(C_6H_4\text{-}2)CH_2C(O)N(R)_2\}(PPh_3)]_2 2TfO$ (R = Me, **3a**; R = Et, **3b**). On the contrary, the reaction of aniline 2-I-4-$MeC_6H_3-N(Me)-CH_2CH_2-CO-N(Me)_2$ (**4**) with $Pd_2(dba)_3$ and PPh_3 afforded four-membered azapalladacycle $[Pd\{\kappa^2C,N\text{-}4\text{-}MeC_6H_3\{N(Me)CH_2CH_2C(O)N(Me)_2\}\text{-}2\}I(PPh_3)]$ (**5**), which on treatment with Tl(TfO) did not yield a complex with the ligand in a C,N,O-terdentate fashion, the unstable Pd(II) complex $[Pd\{\kappa^2C,N\text{-}4\text{-}MeC_6H_3\{N(Me)CH_2CH_2C(O)N(Me)_2\}\text{-}2\}OTf(PPh_3)]$ (**6**) being obtained instead. On the other hand, 2-$IC_6H_4-CH_2-N(Bn)-CH_2-CO-N(Me)_2$ (**7**) reacted with $Pd_2(dba)_3$ to give the C,N,O-terdentate complex $[Pd\{\kappa^3C,N,O\text{-}C_6H_4\{CH_2N(Bn)CH_2C(O)N(Me)_2\}\text{-}2\}I]$ (**8**), which by reaction with PPh_3 and Tl(TfO) was transformed into the cationic C,N,O-terdentate complex $[Pd\{\kappa^3C,N,O\text{-}C_6H_4\{CH_2N(Bn)CH_2C(O)N(Me)_2\}\text{-}2\}(PPh_3)]TfO$ (**9**). Similarly, treatment of iodo benzylamines 2-$IC_6H_4-CH_2-N(R)-CH_2CH_2-CO-N(Me)_2$ (R = Bn, **10a**; R = Me, **10b**) with $Pd_2(dba)_3$ and then with PPh_3 and Tl(TfO) afforded cationic C,N,O-terdentate complexes $[Pd\{\kappa^3C,N,O\text{-}C_6H_4\{CH_2N(R)CH_2CH_2C(O)N(Me)_2\}\text{-}2\}(PPh_3)]TfO$ (R = Bn, **12a**; R = Me, **12b**). Solid-state structures of palladium complexes **2a**, **2b**, **3a**·C_6H_6·3THF, and **8** have been determined by X-ray analysis.

Introduction

In recent years, many multidentate ligands have been developed in order to obtain new organopalladium complexes with potential applications in several areas such as organic synthesis, homogeneous catalysis, and the design of new materials with interesting properties.[1] In addition to classical palladacycles with monoanionic bidentate [C,N] ligands, interest has also been focused on cyclometalated palladium compounds containing terdentate [C,N,L] ligands (L = heteroatom), in which the formation of two fused rings imposes an even greater restriction in the coordination sphere of the metal and has important chemical consequences.[2] Within this class of terdentate ligands, the [C,N,N] structural arrangement has been extensively studied. In contrast, relatively few [C,N,O]-cyclometalated ligands have been reported.[3−8]

Our interest in C,N-cyclopalladated systems has been centered mainly on the synthesis and reactivity of four-membered

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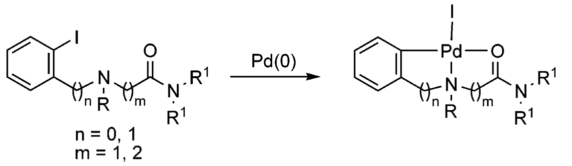
10.1021/om051014m CCC: \$33.50

Scheme 1



azapalladacycles derived from *N*,*N*-dialkyl-2-iodoanilines.[9] In this context, we have shown that the formation of the four-membered [C,N] metallacycle strongly modifies the interaction of the palladium center with potentially chelating pendant groups, such as a distal ketone carbonyl group, resulting in unexpected reaction pathways.[9a] Moreover, we have also reported that the four-membered cyclometalated framework cannot be fit into stable palladium NCN′-pincer complexes since the latter undergo sequential C−H activation and aerobic oxidation to give OCN-pincer complexes.[10]

Continuing our research on this chemistry, we have now focused our attention on C,N-cyclometalated systems with pendant auxiliary fragments, which could in principle act as terdentate [C,N,L] ligands. With this idea in mind we decided to undertake a comparative study of the chemical behavior of the four- and five-membered [C,N] metallacycles when fit in potentially terdentate [C,N,O] ligands in which the O-donor is the carbonyl of an amido group (Scheme 1). It should be noted that although the coordination ability of the carbonyl of the acetamido group[11] and its potential to direct the orthopalladation reaction were recognized a long time ago,[12] the use of the amido framework[13] in terdentate [C,N,O] ligands has scarcely been explored and is in fact limited to a few acylhydrazones.[3a−e,4]

Herein we report the results obtained in the reactions of substrates of the types $2\text{-}IC_6H_4{-}N(R){-}(CH_2)_n{-}CO{-}N(R)_2$ and $2\text{-}IC_6H_4{-}CH_2{-}N(R){-}(CH_2)_n{-}CO{-}N(R)_2$ ($n = 1, 2$) with Pd(0) complexes. Different behavior was observed for each structural type. Thus, we were unable to obtain a terdentate [C,N,O] palladium complex from 2-iodoanilines; instead, the corresponding four-membered azapalladacycle (when $n = 2$) or binuclear palladium complexes (when $n = 1$) were isolated. On the contrary, the reaction of 2-iodobenzylamines with Pd(0) did afford the corresponding terdentate [C,N,O] palladium complexes when either $n = 1$ or $n = 2$. The X-ray crystal structures of four of the new Pd(II) complexes are also reported.

Results and Discussion

The studies were begun with iodoanilines **1a**,**b**, from which we expected to obtain terdentate [C,N,O] palladium complexes containing a four-membered [C,N] metallacycle fused with a five-membered [N,O] chelate ring.[14] The reaction of **1a** with $Pd_2(dba)_3$ (1:0.55 molar ratio) in benzene at room temperature afforded Pd(II) complex **2a** in 71% yield (Scheme 2). Under similar treatment, **1b** gave Pd(II) complex **2b** in 88% yield. Coordination of the amine nitrogen atom to palladium in both complexes was confirmed by the low-field shift of the N-CH_3 (47.4 ppm for **2a** and 47.1 ppm for **2b**) and N-CH_2 resonances (69.8 ppm for **2a** and 69.1 ppm for **2b**) in their ^{13}C NMR spectra. The ^1H NMR spectra showed a singlet resonance at 3.43 ppm assigned to the N-CH_3 protons, shifted to a higher frequency in accordance with coordination of the palladium atom to the amine nitrogen. On the other hand, the lower frequency shift[3,4] of the ν(C═O) band (1608 cm^{-1} for **2a** and 1594 cm^{-1} for **2b**) in the IR spectra and the low-field shift of the C═O resonance (176.6 ppm for **2a** and 175.7 ppm for **2b**) in the ^{13}C NMR spectra were in accordance with coordination of the amide oxygen to the metal center. All these data were in principle compatible with a terdentate Pd(II) complex containing a four-membered [C,N] metallacycle fused with a five-membered [N,O] chelate ring. However, the X-ray diffraction analysis of **2a** and **2b** (vide infra) revealed the real structure of these compounds, which are binuclear palladium species bridged by two $-C_6H_4{-}N(Me){-}CH_2{-}CO{-}NR_2$ ligands, instead of the expected mononuclear complexes with the ligand coordinating one palladium atom in a [C,N,O] terdentate fashion.

The reaction of complexes **2a**,**b** with PPh_3 and Tl(TfO) resulted in the removal of the iodine ligand and coordination by PPh_3 to give cationic binuclear palladium complexes **3a**,**b** in good yields. On the other hand, the reaction of **1a** with $Pd(PPh_3)_4$ (1:1 molar ratio) afforded the corresponding *trans*-bis(triphenylphosphane)palladium(II) complex.[9b] The attempts to purify this complex by either chromatography or crystallization resulted in the formation of an inseparable mixture of two monophosphine complexes of unknown structure. The mixture was converted to the cationic binuclear palladium complex **3a** by treatment with Tl(TfO) (47% overall yield from **1a**).

Iodoaniline **4**, containing two methylene groups between the aniline N and the carbonyl group, behaved differently from **1a**,**b**. Thus, while the reaction of **4** with $Pd_2(dba)_3$ (1:0.55 molar ratio) in benzene at room temperature afforded an untreatable mixture that was not further investigated, when **4** was reacted with both $Pd_2(dba)_3$ and PPh_3 (1:0.55:1.1 molar ratio), four-membered azapalladacycle **5** was obtained in 97% yield (Scheme 3). Palladium complex **5** is a robust compound that can be purified by flash chromatography without decomposition and was characterized by elemental analysis, IR spectrum, and ^1H, ^{13}C, and ^{31}P NMR spectra. The structure of **5** was assigned by comparing its spectroscopic data with those of related azapalladacycles previously reported by us.[9] For **5** the position of the C═O band in the infrared spectrum is essentially identical with that of the starting material **4**, indicating no C═O coordination. It is noteworthy that the terdentate [C,N,O] palladium complex containing a four-membered metallacycle fused with a six-membered chelate ring could not be obtained, not even when **5** was treated with Tl(TfO) to remove the iodo ligand and facilitate the coordination of the carbonyl group, the resulting product instead being palladacycle **6**. Unfortunately, palladium complex **6** is unstable in solution, so it was impossible to obtain analytically pure species and crystals suitable for X-ray studies.

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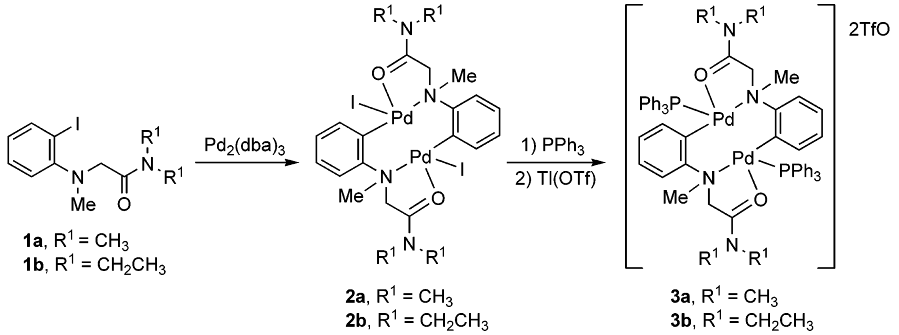
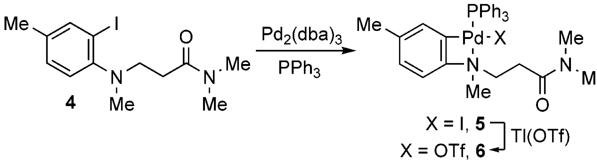
(13) For the preparation of Pd(II) complexes with coordination by one of the carbonyl groups of the phthaloyl moiety, see: Enzmann, A.; Eckert, M.; Ponikwar, W.; Polborn, K.; Schneiderbauer, S.; Beller, M.; Beck, W. *Eur. J. Inorg. Chem.* **2004**, 1330−1340.

(14) The intermediacy of a related palladium(II) complex with a coordinated ketone carbonyl oxygen has been proposed to explain the "anomalous" behavior of some (2-haloanilino) alkanones in their Pd(0)-catalyzed reactions.[9a]

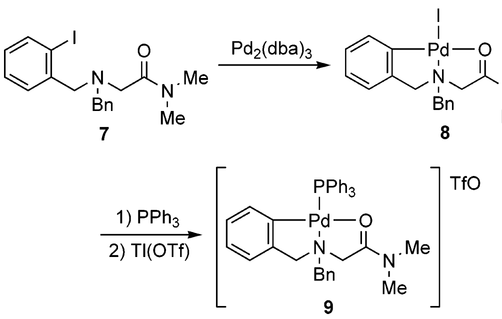
Scheme 2



Scheme 3



Scheme 4

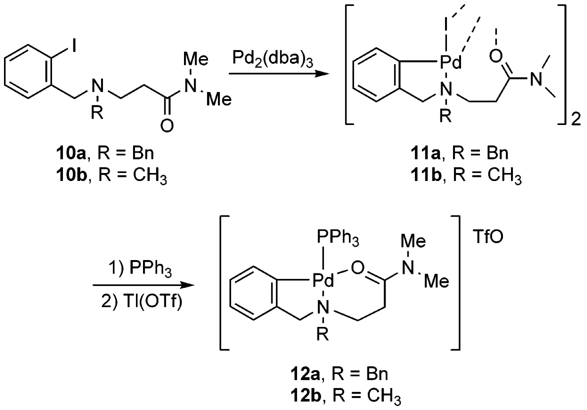


However, the structure of **6** could be unambiguously assigned from its spectroscopic data.

We can conclude that the four-membered [C,N] palladacycle cannot be introduced into terdentate [C,N,O] palladium complexes in which the O-donor is the carbonyl of an amido group. Thus, in the reaction of the 2-IC$_6$H$_4$−N(R)−CH$_2$-CO−N(R)$_2$ substrates (**1a** and **1b**) with Pd(0), the formation of a highly stable five-membered [N,O] chelate ring thwarts the formation of the four-membered [C,N] palladacycle and forces the formation of binuclear bridged Pd(II) complexes (**2a** and **2b**). This might be due to the high strain that would be associated with the generation of a four- and five-membered ring fused together and sharing a palladium atom with square-planar geometry.[15] On the other hand, the four-membered [C,N] palladacycle appears to be more stable than a six-membered [N,O] chelate ring, as demonstrated by the isolation of azapalladacycles **5** and **6**, in which the ligand acts as a two-coordinate, four-electron donor, without closing the [N,O] chelate ring.

At this point, we turned our attention to 2-iodobenzylamine type substrates (**7**, **10a**, and **10b**). The reaction of 2-iodobenzylamine **7**, which bears one carbon atom between the amine N and the carbonyl group, with Pd$_2$(dba)$_3$ (1:0.55 molar ratio) produced the cyclometalated [C,N,O] palladium(II) complex **8** (99%), which simultaneously contains a five-membered palladacycle and a five-membered [N,O] chelate ring (Scheme 4). Both the ν(C=O) stretching frequency in the IR spectrum and the resonances assigned to the N*CH*$_2$ and C=O carbons in the ^{13}C NMR spectrum were in agreement with Pd−O and Pd−N coordination in complex **8**. The [C,N,O] terdentate chelation was confirmed by X-ray crystal structure resolution of **8** (vide infra).

Scheme 5



Complex **8** reacted with PPh$_3$ and Tl(TfO) to give the cationic complex **9** resulting from the substitution of the iodo ligand by PPh$_3$.

Finally, we studied the reactions of 2-iodobenzylamines **10a**,**b**, which have two methylene carbons between the amine N and the carbonyl group. Treatment of 2-iodobenzylamine **10a** with Pd$_2$(dba)$_3$ (1:0.55 molar ratio) afforded a reaction mixture from which a slightly soluble compound (**11a**) was obtained (Scheme 5). The ν(C=O) stretch clearly shows there is coordination of the carbonyl group to the palladium atom. On the other hand, both the ^{1}H NMR and mass spectra point to a dimeric structure for **11a**. A similar reaction was observed starting from **10b**, which on treatment with Pd$_2$(dba)$_3$ afforded the dimeric complex **11b**.[16,17] Unfortunately, as we failed to obtain a single crystal suitable for X-ray studies, the exact coordination mode in these complexes cannot be established. However, treatment of **11a** with PPh$_3$ and Tl(TfO) gave the cationic palladium(II) complex **12a**, which simultaneously contains a five-membered palladacycle and a six-membered [N,O] chelate ring (81% overall yield from benzylamine **10a**). Under similar treatment, **11b** afforded palladium complex **12b** in 62% overall yield from **10b**. Compounds **12a**,**b** are air-stable foams, which were characterized by elemental analysis, high-

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(15) However, it should be noted that the generation of a transient [C,N,O] terdentate [4,5] Pd(II) complex, which then would evolve to the more stable binuclear Pd(II) complex, could not be completely rejected.

(16) The ^{1}H NMR spectra of **11a** and **11b** showed broad signals. If one proton is assigned to the resonance with the least integration in the spectra of **11a** and **11b**, 46 and 38 protons are obtained, respectively, which corresponds at least to a dimeric structure for these complexes (see Experimental Section).

(17) For an example in which the simultaneous coordination of sulfur and oxygen atoms in a multidonor ligand results in the formation of polymeric species, see: Vicente, J.; Chicote, M.-T.; Rubio, C.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1999**, *18*, 2750−2759.

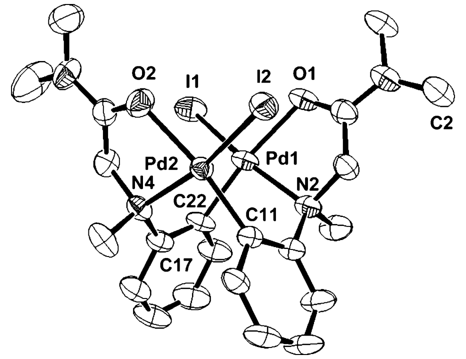

Figure 1. Molecular structure of **2a** (ORTEP view). H atoms are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Pd(1)−Pd(2) = 2.9965(18), Pd(1)−I(1) = 2.5931(15), Pd(1)−O(1) = 2.117(4), Pd(1)−N(2) = 2.165(4), Pd(1)−C(22) = 1.975(5), Pd(2)−I(2) = 2.6074(9), Pd(2)−O(2) = 2.164(4), Pd(2)−N(4) = 2.176(5), Pd(2)−C(11) = 1.979(5), O(1)−Pd(1)−I(1) = 89.32(13), O(1)−Pd(1)−N(2) = 80.46(18), C(22)−Pd(1)−N(2) = 93.7(2), C(22)−Pd(1)−I(1) = 95.62(15), N(2)−Pd(1)−I(1) = 167.60(13), C(22)−Pd(1)−O(1) = 171.6(2), O(2)−Pd(2)−I(2) = 95.99(13), O(2)−Pd(2)−N(4) = 79.20(18), C(11)−Pd(2)−N(4) = 93.5(2), C(11)−Pd(2)−I(2) = 90.21(18), N(4)−Pd(2)−I(2) = 165.51(12), C(11)−Pd(2)−O(2) = 171.9(2).

resolution mass spectrometry, IR spectra, and ^{1}H, ^{13}C, and ^{31}P NMR spectra. The IR spectra showed a shift of the ν(C=O) stretch toward lower numbers compared with the free ligand, due to Pd−O coordination. On the other hand, the ^{31}P{^{1}H} NMR spectra of **12a** and **12b** displayed a phosphorus resonance at δ 38.9 and 41.0 ppm, respectively, and the ^{1}H NMR spectra of **12b** showed resonances due to the NCH_3 and NCH_2Ar protons coupled to the ^{31}P nucleus of the phosphine ligand (ca. 1.5 and 3.6 Hz, respectively); these data are in agreement with a phosphorus *trans* to the coordinated nitrogen arrangement in these complexes.[9] Finally, the ESI-TOF mass spectra of **12a** and **12b** showed a set of peaks, centered at 664 and 588 amu, respectively, which correspond to the $[MH - CF_3SO_3]^+$ ions. These findings are in accordance with a monomeric terdentate [C,N,O]-coordination mode for cationic Pd(II) complexes **12a**,**b**.

In contrast to the failure of iodoanilines **1a**,**b** and **4** to give the terdentate complexes, 2-iodobenzylamines **7** and **10a**,**b** did afford terdentate [C,N,O] mononuclear palladium complexes with either five-membered or six-membered [N,O] chelate rings. Such strikingly different behavior is a consequence of the formation of a highly stable five-membered azapalladacycle,[18] which allows the ligand to act in a terdentate fashion in both [5,5]- and [5,6]-fused ring systems.

X-ray Crystal Structures. The molecular structures of complexes **2a**, **2b**, **3a**·C_6H_6·3THF, and **8** have been determined by X-ray diffraction studies and are shown in Figures 1−4, respectively.

In complexes **2a**, **2b**, and **3a** the two palladium centers are bridged by two $-C_6H_4-N(Me)-CH_2-CO-NR_2$ ligands, each of which is bonded as a η^1-aryl ligand to one palladium atom and acts as a η^2-(N,O) ligand with the second palladium atom. This arrangement leads to a short Pd−Pd contact [2.9965(18) Å for **2a**, 3.026(2) Å for **2b**, and 3.0447(13) Å for **3a**], which is comparable to those found in related binuclear complexes containing monoanionic three-atom bridging ligands.[19] In the three complexes the bridging ligands are *cis* with respect to each other, whereas the ancillary ligands, I in **2a**,**b** or PPh_3 in **3a** and the amide carbonyl group, are *trans* related. This coordination produces a noncrystallographic pseudo-C_2 symmetry axis in the three compounds. In **2a**, **2b**, and **3a** the palladium atom displays a distorted square-planar coordination with the four ligands deviated to the same side of the plane due to the steric hindrance exerted by the second palladium atom. In the three complexes the five-membered [N,O] chelate ring has an envelope form with the nitrogen atom being the out-of-plane atom.

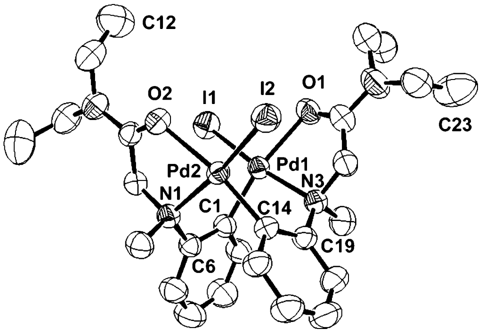

Figure 2. Molecular structure of **2b** (ORTEP view). H atoms are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Pd(1)−Pd(2) = 3.026(2), Pd(1)−I(1) = 2.5867(9), Pd(1)−O(1) = 2.164(3), Pd(1)−N(3) = 2.158(3), Pd(1)−C(1) = 1.968(4), Pd(2)−I(2) = 2.5870(9), Pd(2)−O(2) = 2.164(3), Pd(2)−N(1) = 2.157(3), Pd(2)−C(14) = 1.973(4), O(1)−Pd(1)−I(1) = 93.52(9), O(1)−Pd(1)−N(3) = 79.30(12), C(1)−Pd(1)−N(3) = 93.28(15), C(1)−Pd(1)−I(1) = 92.41(12), N(3)−Pd(1)−I(1) = 169.16(9), C(1)−Pd(1)−O(1) = 168.15(14), O(2)−Pd(2)−I(2) = 94.93(8), O(2)−Pd(2)−N(1) = 79.27(12), C(14)−Pd(2)−N(1) = 93.90(14), C(14)−Pd(2)−I(2) = 90.78(11), N(1)−Pd(2)−I(2) = 167.12(9), C(14)−Pd(2)−O(2) = 171.63(13).

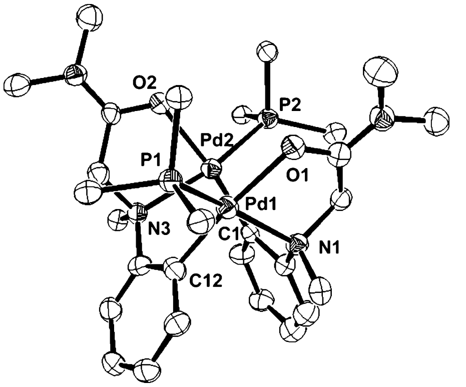

Figure 3. ORTEP view of the cation of **3a**. H atoms and the phenyl groups of the PPh_3 ligands are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Pd(1)−Pd(2) = 3.0447(13), Pd(1)−P(1) = 2.2657(13), Pd(1)−O(1) = 2.101(3), Pd(1)−N(1) = 2.193(3), Pd(1)−C(12) = 1.948(4), Pd(2)−P(2) = 2.2552(12), Pd(2)−O(2) = 2.100(3), Pd(2)−N(3) = 2.192(3), Pd(2)−C(1) = 1.972, O(1)−Pd(1)−P(1) = 92.98(8), O(1)−Pd(1)−N(1) = 80.56(12), C(12)−Pd(1)−N(1) = 92.67(13), C(12)−Pd(1)−P(1) = 92.78(10), N(1)−Pd(1)−P(1) = 159.82(8), C(12)−Pd(1)−O(1) = 172.97(11), O(2)−Pd(2)−P(2) = 91.71(9), O(2)−Pd(2)−N(3) = 81.04(12), C(1)−Pd(2)−N(3) = 93.18(16), C(1)−Pd(2)−P(2) = 92.58(13), N(3)−Pd(2)−P(2) = 158.73(8), C(1)−Pd(2)−O(2) = 173.36(1).

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[18] The formation of the four-membered azapalladacycle has been calculated to be ≈ 10 kcal mol^{-1} less favorable than the corresponding five-membered counterpart. Bosque, R.; Maseras, F. *Eur. J. Inorg. Chem.* **2005**, 4040−4047.

[19] (a) Singhal, A.; Jain, V. K.; Nethaji, M.; Samuelson, A. G.; Jayaprakash, D.; Butcher, R. J. *Polyhedron* **1998**, *17*, 3531−3540. (b) Dupont, J.; Pfeffer, M.; Daran, J. C.; Jeannin, Y. *Organometallics* **1987**, *6*, 899−901, and references therein.

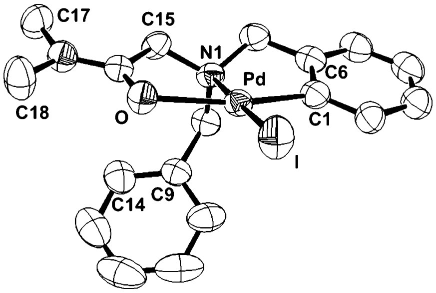

Figure 4. Molecular structure of **8** (ORTEP view). H atoms are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Pd−I = 2.5979(10), Pd−O = 2.1815(19), Pd−N(1) = 2.077(2), Pd−C(1) = 1.973(3), O−Pd−I = 98.11(5), O−Pd−N(1) = 80.40(7), C(1)−Pd−N(1) = 83.39(10), C(1)−Pd−I = 97.90(9).

The main intermolecular interactions in binuclear palladium complexes **2a**, **2b**, and **3b**·C_6H_6·3THF are C−H···*π*-ring interactions. In **2a** intermolecular C−H···*π*-ring interaction between C(2)−H(2B) and the C(17)···C(22) phenyl ring (distance to the aromatic centroid = 2.84 Å) produces a chain of linked molecules along the crystallographic *b*-axis. On the other hand, in **2b** C−H···*π*-ring interactions between C(23)−H(23A) and the C(1)···C(6) phenyl ring (distance to the aromatic centroid = 2.66 Å), and C(12)−H(12C) and the C(14)···C(19) phenyl ring (distance to the aromatic centroid = 3.10 Å), produce layers of linked molecules perpendicular to the crystallographic *c*-axis. Finally, in binuclear cationic complex **3a**·C_6H_6·3THF C−H···*π*-ring interactions between C(24)−H(24) and the C(29)···C(34) phenyl ring (distance to the aromatic centroid = 3.15 Å), and C(31)−H(31) and the C(35)···C(40) phenyl ring (distance to the aromatic centroid = 2.98 Å), produce bimolecular units implying (*x*, *y*, *z*) and (2−*x*, 1−*y*, −*z*) molecules. Moreover, in **3a**·C_6H_6·3THF the benzene solvates act as bridges between different bimolecular units also by means of C−H···*π*-ring interactions [C(32)−H(32)···benzene ring (distance to the aromatic centroid = 2.85 Å) and C(26)−H(26)···benzene ring (distance to the aromatic centroid = 3.04 Å)].

In complex **8** the palladium atom shows a square-planar coordination, the largest deviation from the mean plane being in the N atom [deviation of 0.016(2) Å]. The two fused five-membered rings have an envelope form with the nitrogen atom being in both rings the out-of-plane atom. The main intermolecular interactions in palladium complex **8** are C−H···*π*-ring interactions between C(15)−H(15B) and the C(1)···C(6) phenyl ring (distance to the aromatic centroid = 2.75 Å), C(18)−H(18C) and the C(1)···C(6) phenyl ring (distance to the aromatic centroid = 3.04 Å), and C(17)−H(17B) and the C(9)···C(14) phenyl ring (distance to the aromatic centroid = 3.13 Å), which produce a 3D-net of linked molecules.

In summary, the $-C_6H_4-N(R)-(CH_2)_n-CO-N(R)_2$ (n = 1, 2) and $-C_6H_4-CH_2-N(R)-(CH_2)_n-CO-N(R)_2$ (n = 1, 2) frameworks have been explored for their potential to act as three-coordinate, six-electron-donor ligands. In this study, we have shown that the four-membered [C,N] palladacycle is not compatible with fused five- or six-membered [N,O] chelate rings and that in the reaction of $2-IC_6H_4-N(R)-CH_2-CO-N(R)_2$ substrates with Pd(0) this incompatibility results in the formation of unprecedented C,N-bridged binuclear palladium(II) compounds. On the other hand, the five-membered [C,N] palladacycle fits perfectly into stable terdentate [C,N,O] palladium(II) complexes involving either five-membered or six-membered [N,O] chelate rings. Further investigation to extend this study to related ligands with different donor atoms in the pendant arm and also to examine the chemical behavior and potential application of the new families of palladium(II) complexes are in progress and will be reported in due course.

Experimental Section

General Information. All reactions were performed under an argon atmosphere using dry solvents. THF was distilled under nitrogen from sodium benzophenone ketyl. Benzene was dried over CaH_2 and distilled under nitrogen. Other solvents were used as received. Chemicals were used as received from Aldrich ($Pd_2(dba)_3$), Fluka (PPh_3), and Strem (Tl(TfO)). Chemical shifts are given in parts per million (ppm) relative to Me_4Si for ^1H and ^{13}C NMR. ^{31}P NMR spectra were recorded in $CDCl_3$ with external H_3PO_4 as reference. IR spectra were recorded on a Nicolet 205 FT infrared spectrophotometer, and only noteworthy absorptions are listed. Melting points were determined in a capillary tube and are uncorrected. Chromatography refers to flash chromatography and was carried out on SiO_2 (silica gel 60, 230−400 mesh ASTM). Evaporation of solvents was accomplished with a rotatory evaporator. Microanalyses were performed by Centro de Investigación y Desarrollo (CSIC), Barcelona.

[Pd{*η*-(N,C)-*μ*-N(Me)(C_6H_4-2)CH_2C(O)N(Me)$_2$}I]$_2$ (2a). To a solution of amide **1a** (100 mg, 0.31 mmol) in benzene (15 mL) was added $Pd_2(dba)_3$ (158 mg, 0.17 mmol). The reddish reaction mixture was stirred at room temperature for 3 days. The solvent was evaporated, and the residue was dissolved in dichloromethane (25 mL) and then filtered through Celite. The filtrate was evaporated to dryness and the residue triturated with Et_2O. The resulting solid was filtered, washed with Et_2O, and dried to give **2a** as a brown-orange solid. Yield: 94 mg, 71%. Single crystals of complex **2a** were grown by slowly evaporating a dichloromethane solution. Mp: 160−161 °C. IR (film): ν 1608 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.97 (s, 3H), 3.10 (s, 3H), 3.18 (d, J = 17.1 Hz, 1H), 3.43 (s, 3H), 6.05 (d, J = 17.1 Hz, 1H), 6.34 (dd, J = 7.8 and 1.5 Hz, 1H), 6.50 (ddd, J = 7.8, 7.2, and 1.5 Hz, 1H), 6.63 (ddd, J = 7.8, 7.2, and 1.5 Hz, 1H), 7.65 (dd, J = 7.8 and 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 36.8 (CH_3), 38.2 (CH_3), 47.4 (CH_3), 69.8 (CH_2), 116.2 (CH), 122.8 (CH), 123.9 (CH), 134.9 (C), 138.0 (CH), 154.7 (C), 176.6 (C). Anal. Calcd for $C_{22}H_{30}I_2N_4O_2Pd_2$ (849.15): C, 31.12; H, 3.56; N, 6.60. Found: C, 31.21; H, 3.69; N, 6.64.

[Pd{*η*-(N,C)-*μ*-N(Me)(C_6H_4-2)CH_2C(O)N(Et)$_2$}I]$_2$ (2b). Operating as in the preparation of **2a**, starting from amide **1b** (25 mg, 0.072 mmol) and $Pd_2(dba)_3$ (37 mg, 0.04 mmol), palladium complex **2b** was obtained as a brown-orange solid. Yield: 29 mg, 88%. Single crystals of complex **2b** were grown by slowly evaporating a dichloromethane−Et_2O solution. Mp: 158 °C. IR (film): ν 1594 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.18 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H), 3.08 (d, J = 17.1 Hz, 1H), 3.23 (m, 2H), 3.32 (dq, J = 14.4 and 7.2 Hz, 1H), 3.43 (s, 3H), 3.67 (dq, J = 14.4 and 7.2 Hz, 1H), 6.12 (d, J = 17.1 Hz, 1H), 6.34 (dd, J = 8.1 and 1.5 Hz, 1H), 6.49 (ddd, J = 8.1, 7.5, and 1.5 Hz, 1H), 6.63 (t, J = 7.5 and 1.5 Hz, 1H), 7.66 (dd, J = 7.5 and 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 12.8 (CH_3), 14.0 (CH_3), 41.6 (CH_2), 43.2 (CH_2), 47.1 (CH_3), 69.1 (CH_2), 116.1 (CH), 122.7 (CH), 123.8 (CH), 135.3 (C), 138.0 (CH), 154.7 (C), 175.7 (C). Anal. Calcd for $C_{26}H_{38}I_2N_4O_2Pd_2$ (905.25): C, 34.50; H, 4.23; N, 6.19. Found: C, 34.73; H, 4.24; N, 6.00.

[Pd{*η*-(N,C)-*μ*-N(Me)(C_6H_4-2)CH_2C(O)N(Me)$_2$}(PPh_3)]$_2$ 2TfO (3a). To a solution of complex **2a** (15 mg, 0.018 mmol) in THF (2 mL) was added Tl(TfO) (13 mg, 0.036 mmol). After stirring at room temperature for 10 min, PPh_3 (10 mg, 0.036 mmol) was added. The resulting suspension was stirred at room temperature for 2 h. The mixture was filtered through Celite, washing carefully with

THF. The filtrate was evaporated to dryness, and the residue was triturated with a mixture of THF (2 mL) and benzene (1 mL). The resulting solid was filtered, washed with benzene, and dried to give complex **3a** as a pale yellow solid. Yield: 19 mg, 76%. Single crystals of complex **3a** were grown by slowly evaporating a dichloromethane−benzene−THF solution. Mp: 155−158 °C. IR (film): ν 1613 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.34 (s, 3H), 2.53 (s, 3H), 3.44 (dd, J = 16 and 4 Hz, 1H), 3.53 (s, 3H), 4.22 (d, J = 16 Hz, 1H), 6.58 (t, J = 7.5 Hz, 1H), 6.72 (d, J = 8 Hz, 1H), 6.79 (dd, J = 8 and 7.5 Hz, 1H), 6.92 (dd, J = 7.5 and 4.5 Hz, 1H), 7.30−7.80 (broad band, 15H). ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ 36.3 (CH$_3$), 39.0 (CH$_3$), 48.0 (CH$_3$), 66.5 (CH$_2$), 120.2 (CH), 120.9 (q, J = 320.5 Hz, C), 125.2 (CH), 125.6 (CH), 129.5 (CH), 132.1 (CH), 133.8 (CH), 134.9 (d, J = 5.4 Hz, CH), 139.2 (d, J = 6.1 Hz, C), 153.3 (C), 175.8 (C), one C was not observed. ^{31}P NMR (CDCl$_3$, 121.5 MHz): δ 27.1. Anal. Calcd for $C_{60}H_{60}F_6N_4O_8P_2Pd_2S_2$ (1418.06): C, 50.82; H, 4.26; N, 3.95. Found: C, 50.71; H, 4.35; N, 3.86.

[Pd{η-(N,C)-μ-N(Me)(C$_6$H$_4$-2)CH$_2$C(O)N(Et)$_2$}(PPh$_3$)]$_2$ 2TfO (3b). Operating as in the preparation of **3a**, starting from palladium complex **2b** (22 mg, 0.024 mmol), Tl(TfO) (24 mg, 0.068 mmol), and PPh$_3$ (17 mg, 0.065 mmol), palladium complex **3b** was obtained as a pale yellow solid. Yield: 34 mg, quantitative. IR (film): ν 1595 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 0.73 (t, J = 7.2 Hz, 3H), 0.77 (t, J = 7.2 Hz, 3H), 2.64−2.92 (m, 4H), 3.42 (dd, J = 15.6 and 4.2 Hz, 1H), 3.53 (s, 3H), 4.46 (dd, J = 15.6 and 2.7 Hz, 1H), 6.57 (td, J = 7 and 1.8 Hz, 1H), 6.79−6.93 (m, 3H), 7.30−7.80 (broad band, 15H). ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ 12.8 (CH$_3$), 13.6 (CH$_3$), 42.8 (CH$_2$), 45.2 (CH$_2$), 47.2 (CH$_3$), 65.7 (CH$_2$), 120.8 (CH), 120.8 (q, J = 320.5 Hz, C), 125.4 (CH), 125.8 (CH), 129.6 (d, J = 9.8 Hz, CH), 132.2 (CH), 133.6 (d, J = 9.7 Hz, CH), 134.8 (d, J = 4.6 Hz, CH), 138.3 (d, J = 6.3 Hz, C), 152.4 (C), 174.8 (C), one C was not observed. ^{31}P NMR (CDCl$_3$, 121.5 MHz): δ 27.3. These NMR spectra contain small signals due to the presence of OPPh$_3$, which could not be removed.

[Pd{κ^2*C,N*-4-MeC$_6$H$_3${N(Me)CH$_2$CH$_2$C(O)N(Me)$_2$}-2}I(PPh$_3$)] (5). To a solution of amide **4** (30 mg, 0.087 mmol) in benzene (4 mL) were added Pd$_2$(dba)$_3$ (44 mg, 0.048 mmol) and PPh$_3$ (25 mg, 0.095 mmol). The reddish reaction mixture was stirred at room temperature for 24 h. The mixture was filtered through Celite. The filtrate was evaporated to dryness, and the residue was purified by chromatography. Elution with CH$_2$Cl$_2$−MeOH 1% afforded pure azapalladacycle **5** as a brown foam. Yield: 60 mg, 97%. IR (film): ν 1645 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.89 (s, 3H), 2.56 (m, 1H), 2.87 (s, 3H), 3.01 (s, 3H), 3.16 (s, 3H), 3.33−3.72 (m, 3H), 5.56 (d, J = 0.6 Hz, 1H), 6.77 (d, J = 8.1 Hz, 1H), 6.83 (dd, J = 8.1 and 1.8 Hz, 1H), 7.35−7.50 (m, 9H), 7.67−7.77 (m, 6H). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ 21.9 (CH$_3$), 33.5 (CH$_2$), 35.3 (CH$_3$), 37.7 (CH$_3$), 51.2 (CH$_3$), 56.0 (CH$_2$), 118.8 (CH), 125.5 (d, J = 10.3 Hz, C), 126.3 (CH), 128.1 (d, J = 10.9 Hz, CH), 128.8 (d, J = 7.5 Hz, CH), 130.8 (d, J = 2.3 Hz, CH), 131.6 (d, J = 51.7 Hz, C), 135.0 (d, J = 11.5 Hz, CH), 134.9 (d, J = 2.9 Hz, C), 159.3 (d, J = 4.6 Hz, C), 170.3 (C). ^{31}P NMR (CDCl$_3$, 121.5 MHz): δ 40.9. Anal. Calcd for $C_{31}H_{34}IN_2OPd$ (714.91)·3/4CH$_2$Cl$_2$: C, 48.98; H, 4.60; N, 3.60. Found: C, 49.32; H, 4.56; N, 3.60.

[Pd{κ^2*C,N*-4-MeC$_6$H$_3${N(Me)CH$_2$CH$_2$C(O)N(Me)$_2$}-2}OTf(PPh$_3$)] (6). To a solution of complex **5** (25 mg, 0.035 mmol) in THF (3 mL) was added Tl(TfO) (13 mg, 0.036 mmol), and the mixture was stirred at room temperature for 3 h. The reaction mixture was filtered through Celite, washing carefully with THF. The filtrate was evaporated to dryness to give crude Pd(II) complex **6** (29 mg, quantitative). IR (film): ν 1644 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 1.90 (m, 2H), 1.93 (s, 3H), 2.80 (s, 3H), 3.12 (s, 6H), 3.60−3.80 (m, 2H), 5.60 (s, 1H), 6.89 (s, 2H), 7.36−7.65 (m, 15H). ^{13}C NMR (THF-d_8, 75.4 MHz): δ 22.5 (CH$_3$), 31.3 (CH$_2$), 36.3 (CH$_3$), 38.4 (CH$_3$), 49.8 (CH$_3$), 59.9 (CH$_2$), 119.9 (CH), 126.3 (CH), 127.9 (CH), 129.8 (d, J = 10.8 Hz, CH), 131.7 (d, J = 51.3 Hz, C), 132.4 (CH), 136.1 (d, J = 12.0 Hz, CH), 160.5 (C), 172.0 (C). Only the most significant resonances are reported. Since this compound is unstable, minor resonances were observed in the ^{13}C NMR experiment.

[Pd{κ^3*C,N,O*-C$_6$H$_4${CH$_2$N(CH$_2$C$_6$H$_5$)CH$_2$C(O)N(Me)$_2$}-2}I] (8). To a solution of amide **7** (25 mg, 0.061 mmol) in benzene (4 mL) was added Pd$_2$(dba)$_3$ (31 mg, 0.034 mmol). The reddish reaction mixture was stirred at room temperature for 3 days. The reaction mixture was filtered through Celite, washing carefully with benzene. The benzene filtrate was discarded, and then the washing was continued with dichloromethane. The dichloromethane filtrate was evaporated to dryness to give **8** as a yellow solid. Yield: 31 mg, 99%. Single crystals of complex **8** were grown by slowly evaporating a dichloromethane−benzene solution. Mp: 198 °C. IR (film): ν 1597 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.13 (s, 3H), 2.65 (s, 3H), 3.71 (d, J = 12.4 Hz, 1H), 3.80 (d, J = 16.5 Hz, 1H), 3.98 (d, J = 14.1 Hz, 1H), 4.55 (d, J = 12.4 Hz, 1H), 5.24 (d, J = 14.1 Hz, 1H), 5.87 (d, J = 16.5 Hz, 1H), 6.75 (td, J = 8.1 and 1.8 Hz, 1H), 6.80−6.92 (m, 2H), 7.30−7.42 (m, 3H), 7.77 (dd, J = 8.1 and 1.8 Hz, 2H), 8.02 (d, J = 8.1 Hz, 1H). ^{13}C NMR (CD$_2$Cl$_2$, 75.4 MHz): δ 35.9 (CH$_3$), 38.6 (CH$_3$), 61.8 (CH$_2$), 66.1 (CH$_2$), 70.4 (CH$_2$), 123.1 (CH), 124.3 (CH), 126.6 (CH), 128.8 (CH), 129.8 (CH), 132.3 (CH), 132.4 (C), 142.5 (CH), 143.6 (C), 150.8 (C), 175.9 (C). Anal. Calcd for $C_{18}H_{21}IN_2OPd$ (514.70): C, 42.00; H, 4.11; N, 5.44. Found: C, 41.85; H, 4.09; N, 5.16.

[Pd{κ^3*C,N,O*-C$_6$H$_4${CH$_2$N(CH$_2$C$_6$H$_5$)CH$_2$C(O)N(Me)$_2$}-2}(PPh$_3$)] TfO (9). Operating as in the preparation of **3a**, starting from palladium complex **8** (15 mg, 0.029 mmol), Tl(TfO) (16 mg, 0.045 mmol), and PPh$_3$ (11 mg, 0.042 mmol), palladium complex **9** was obtained as a pale yellow foam. Yield: 20 mg, 87%. IR (film): ν 1609 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.15 (s, 3H), 3.03 (s, 3H), 4.10 (dd, J = 12.3 and 5.4 Hz, 1H), 4.37 (dd, J = 14.4 and 3 Hz, 1H), 4.43 (d, J = 17.4 Hz, 1H), 4.54 (d, J = 12.3 Hz, 1H), 4.70 (dd, J = 17.4 and 3.6 Hz, 1H), 4.98 (dd, J = 14.4 and 2.4 Hz, 1H), 6.36 (dd, J = 7.5 and 4.2 Hz, 1H), 6.55 (td, J = 7.5 and 1.2 Hz, 1H), 6.94 (td, J = 7.5 and 1.2 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 7.20−7.71 (m, 18H), 7.89 (m, 2H). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ 35.6 (CH$_3$), 38.7 (CH$_3$), 61.5 (CH$_2$), 65.3 (CH$_2$), 70.1 (CH$_2$), 120.8 (q, J = 320.5 Hz, C), 124.5 (CH), 125.2 (CH), 126.1 (d, J = 4 Hz, CH), 128.2 (CH), 128.6 (br, CH), 128.7 (CH), 131.4 (CH), 131.8 (CH), 133.2 (C), 134.6 (d, J = 12.1 Hz, CH), 137.6 (d, J = 9.2 Hz, CH), 145.5 (d, J = 4.6 Hz, C), 151.9 (C), 177.0 (C), one C was not observed. ^{31}P NMR (CDCl$_3$, 121.5 MHz): δ 38.3. Anal. Calcd for $C_{37}H_{36}F_3N_2O_4PPdS$ (799.15): C, 55.61; H, 4.54; N, 3.51. Found: C, 55.24; H, 4.99; N, 3.69. HRMS (ESI-TOF): *m/z* 650.1654 ([MH − CF$_3$SO$_3$]$^+$, 650.1673 calcd for $C_{36}H_{37}N_2OPPd$).

[Pd{κ^3*C,N,O*-C$_6$H$_4${CH$_2$N(CH$_2$C$_6$H$_5$)CH$_2$CH$_2$C(O)N(Me)$_2$}-2}(PPh$_3$)] TfO (12a). To a solution of amide **10a** (25 mg, 0.059 mmol) in benzene (4 mL) was added Pd$_2$(dba)$_3$ (30 mg, 0.033 mmol). The reddish reaction mixture was stirred at room temperature for 45 h. The reaction mixture was filtered through Celite, washing carefully with benzene. The benzene filtrate was discarded, and then the washing was continued with dichloromethane. The dichloromethane filtrate was evaporated to dryness to give **11a** as a yellow solid. Yield: 26 mg, 84%. Dimeric palladium complex **11a**: IR (film): ν 1599 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.92 (br, 18H), 3.40 (br, 2H), 3.60−4.20 (br m, 4H), 4.36 (br, 3H), 4.66 (br, 1H), 6.79 (m, 2H), 6.94 (m, 4H), 7.30−7.44 (m, 6H), 7.62 (m, 5H), 8.10 (br, 1H). MS (ESI$^+$): *m/z* 931 (2M$^+$ − I), 401 (M$^+$ − I).

Operating as in the preparation of **3a**, starting from palladium complex **11a** (26 mg, 0.025 mmol), Tl(TfO) (26 mg, 0.075 mmol), and PPh$_3$ (20 mg, 0.075 mmol), palladium complex **12a** was obtained as a pale yellow foam. Yield: 39 mg, 97%. IR (film): ν 1598 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.89 (s, 3H), 2.94 (s,

Table 1. Selected Crystallographic Data of Complexes 2a, 2b, 3a·C_6H_6·3THF, and 8

	2a	**2b**	**3a**·C_6H_6·3THF	**8**
formula	$C_{22}H_{30}I_2N_4O_2Pd_2$	$C_{26}H_{38}I_2N_4O_2Pd_2$	$C_{78}H_{90}F_6N_4O_{11}P_2Pd_2S_2$	$C_{18}H_{21}IN_2OPd$
fw	849.10	905.20	1712.40	514.67
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/a$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a, Å	17.186(12)	16.080(13)	12.637(6)	9.418(4)
b, Å	10.020(3)	11.373(4)	13.777(5)	12.549(4)
c, Å	17.288(8)	17.164(7)	25.508(8)	15.614(5)
α, deg	90	90	76.80(3)	90
β, deg	113.78(4)	91.09(5)	76.80(3)	94.89(4)
γ, deg	90	90	64.27(3)	90
V, Å^3	2724(2)	3138(3)	3852(3)	1838.6(11)
Z	4	4	2	4
D_{calcd}, Mg/m^3	2.070	1.916	1.476	1.859
F(000)	1616	1744	1764	1000
cryst size, mm	0.2 × 0.1 × 0.1	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
θ range, deg	2.38−30.04	2.15−29.96	3.45−31.97	3.50−28.36
no. of rflns collected	8099	9541	28291	3764
no. of indep rflns (R_{int})	7876 (0.0480)	9096 (0.0375)	16 780 (0.0378)	3764 (0.0328)
R1 ($I > 2\sigma(I)$)	0.0581	0.0361	0.0438	0.0420
wR2 ($I > 2\sigma(I)$)	0.1426	0.0940	0.1003	0.0919
goodness of fit on F^2	1.050	1.059	0.893	1.305

3H), 2.88−3.05 (m, 1H), 3.16−3.48 (m, 3H), 3.83 (d, J = 13.5 Hz, 1H), 3.90 (d, J = 13.8 Hz, 1H), 4.24 (d, J = 13.5 Hz, 1H), 4.82 (d, J = 13.8 Hz, 1H), 6.31 (dd, J = 7.8 and 0.9 Hz, 1H), 6.54 (ddd, J = 7.8, 7.5, and 1.2 Hz, 1H), 6.96 (ddd, J = 7.5, 7.2, and 0.9 Hz, 1H), 7.14 (dd, J = 7.2 and 1.2 Hz, 1H), 7.30−7.72 (m, 20H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 31.1 (CH_2), 35.6 (CH_3), 38.7 (CH_3), 52.7 (CH_2), 60.8 (CH_2), 67.3 (CH_2), 120.9 (q, J = 320.4 Hz, C), 124.3 (CH), 125.2 (CH), 125.9 (CH), 128.4 (CH), 128.5 (d, J = 8.6 Hz, CH), 128.7 (CH), 131.3 (CH), 131.9 (CH), 132.6 (C), 134.2 (br, CH), 136.6 (CH), 143.2 (C), 147.3 (C), 173.8 (C), one C was not observed. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 38.9. Anal. Calcd for $C_{38}H_{38}F_3N_2O_4PPdS$ (813.17): C, 56.13; H, 4.71; N, 3.44. Found: C, 56.29; H, 5.11; N, 3.33. HRMS (ESI-TOF): m/z 664.1814 ([MH − CF_3SO_3]$^+$, 664.1829 calcd for $C_{37}H_{39}N_2OPPd$).

[Pd{κ^3*C,N,O*-C_6H_4{$CH_2N(Me)CH_2CH_2C(O)N(Me)_2$}-2}($PPh_3$)]-TfO (12b). To a solution of amide **10b** (25 mg, 0.072 mmol) in benzene (4 mL) was added $Pd_2(dba)_3$ (37 mg, 0.04 mmol). The reddish reaction mixture was stirred at room temperature for 45 h. The reaction mixture was filtered through Celite, washing carefully with benzene. The benzene filtrate was discarded, and then the washing was continued with dichloromethane. The dichloromethane filtrate was evaporated to dryness to give **11b** as a yellow solid. Yield: 25 mg, 75%. Dimeric palladium complex **11b**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.64 (br, 6H), 2.91 (br, 6H), 2.99 (br, 12H), 3.17 (br, 1H), 3.44 (br, 1H), 3.70 (br, 1H), 3.97 (br, 1H), 4.18 (br, 1H), 4.69 (br, 1H), 6.78 (br, 2H), 6.93 (br m, 4H), 7.61 (br m, 1H), 8.04 (br m, 1H).

Operating as in the preparation of **3a**, starting from palladium complex **11b** (25 mg, 0.027 mmol), Tl(TfO) (29 mg, 0.082 mmol), and PPh_3 (22 mg, 0.082 mmol), palladium complex **12b** was obtained as a pale yellow foam. Yield: 33 mg, 83%. IR (film): ν 1598 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.96 (s, 3H), 2.68 (d, J = 1.5 Hz, 3H), 3.04 (s, 3H), 2.94−3.28 (m, 3H), 3.64 (dd, J = 13.2 and 3.6 Hz, 1H), 3.64−3.75 (m, 1H), 4.74 (d, J = 13.2 Hz, 1H), 6.18 (ddd, J = 7.8, 5.4, and 0.9 Hz, 1H), 6.45 (ddd, J = 7.8, 7.5, and 1.2 Hz, 1H), 6.90 (ddd, J = 7.5, 7.2, and 0.9 Hz, 1H), 7.05 (d, J = 7.2 Hz, 1H), 7.38−7.60 (m, 15H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 29.8 (CH_2), 35.6 (CH_3), 38.5 (CH_3), 44.9 (CH_3), 55.5 (CH_2), 70.6 (CH_2), 120.8 (q, J = 320.4 Hz, CF_3), 123.6 (CH), 125.1 (CH), 125.7 (CH), 128.6 (d, J = 9.7 Hz, CH), 130.4 (br, CH), 134.5 (br, CH), 137.1 (CH), 141.4 (C), 148.1 (C), 172.7 (C). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 41.0. Anal. Calcd for $C_{32}H_{34}F_3N_2O_4PPdS$ (737.08): C, 52.14; H, 4.65; N, 3.80. Found: C, 52.08; H, 4.83; N, 3.78. HRMS (ESI-TOF): m/z 588.1505 ([MH − CF_3SO_3]$^+$, 588.1516 calcd for $C_{31}H_{35}N_2OPPd$).

Crystallography. Intensities were collected with an Enraf-Nonius CAD4 four-circle diffractometer for complexes **2a** and **2b** and with a MAR345 diffractometer for complexes **3a**·C_6H_6·3THF and **8**. The structure of complex **2a** was solved by Patterson synthesis, and the structures of complexes **2b**, **3a**·C_6H_6·3THF, and **8** were solved by direct methods, using in all cases the SHELXS97 computer program. The structures were refined by full-matrix least-squares method with the SHELXL97 computer program.[20] Crystal data for complexes **2a**, **2b**, **3a**·C_6H_6·3THF, and **8** are listed in Table 1, and their ORTEP plots are shown in Figures 1-4, respectively (H atoms and solvents are omitted for clarity). Other crystallographic data are deposited as Supporting Information.

Acknowledgment. This work was supported by MEC (Spain)-FEDER (Project CTQ2004-04701/BQU) and DURSI-Catalonia (Grant 2005SGR-00442). D.S. thanks the DURSI for “Distinció per a la Promoció de la Recerca Universitària”.

Supporting Information Available: Crystallographic data of **2a**, **2b**, **3a**·C_6H_6·3THF, and **8** are given in PDF and CIF formats. Characterization data and experimental procedures for the preparation of starting materials are also given. This material is available free of charge via the Internet at http://pubs.acs.org.

OM051014M

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[20] Sheldrick, G. M. *SHELXL97*, computer program for the determination of crystal structure; University of Göttingen: Germany, 1997.