Cyclometalated Compounds. XVI.[1] Double Cyclopalladations of Bis(2-pyridyloxy)naphthalenes. Kinetic versus Thermodynamic Control of Regiospecificity

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A systematic study of the cyclopalladation reactions of bis(2-pyridyloxy)naphthalenes is described. On the basis of a kinetic preference for reaction at the 1-position, over thermodynamically favored reaction in the 3-position, a diverse range of doubly cyclopalladated compounds has been prepared, in a predictable manner, simply by moderating the experimental reaction conditions. Seven isomeric ligands have been employed to prepare many doubly metallated derivatives, all of which have been fully characterized by NMR spectroscopy, and two of which have been the subject of X-ray structure determinations. This study significantly expands the library of doubly cyclopalladated compounds, particularly those involving six-membered metallocycles.

Introduction

Since the first report, in 1965, describing the cyclopalladation of azobenzene,[2] such reactions have attracted enormous interest in a wide variety of contexts.[3] Cyclopalladated compounds have proved useful in organic synthesis,[4] catalysis,[5] and material science[6] and even as bioactive compounds.[7] By varying the donor atoms, ring size, and the nature of the carbon donor, many different types of cyclopalladated compounds have been prepared.[3] In recent years, there has been much interest in multiply cyclopalladated compounds, such as those containing two different metalated phenyl rings.[8] In addition, there have been a number of studies of compounds within which a single benzene ring is doubly cyclopalladated.[1,6c,9,10] In one such study,[10] we described the double cyclopalladations of all three isomers of bis(2-pyridyloxy)benzene, which produced the first examples of doubly cyclopalladated compounds incorporating six-membered metallocycles.

We have also reported[11] a study of the cyclopalladation of 2-(2-pyridyloxy)naphthalene (**1**), in which we showed that under kinetic control the 1-metalated product (**2**) is formed, but under thermodynamic control the 3-substituted analogue (**3**) is produced (Scheme 1). Intriguingly, we also showed that **2** is converted to **3** upon heating and provided experimental evidence that such cyclopalladation reactions are reversible processes.

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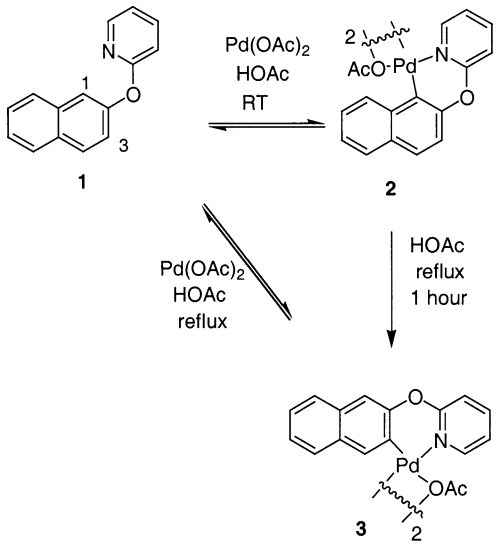
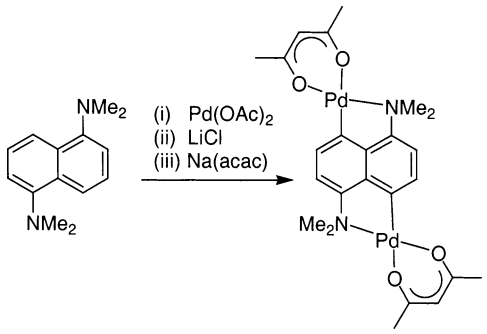
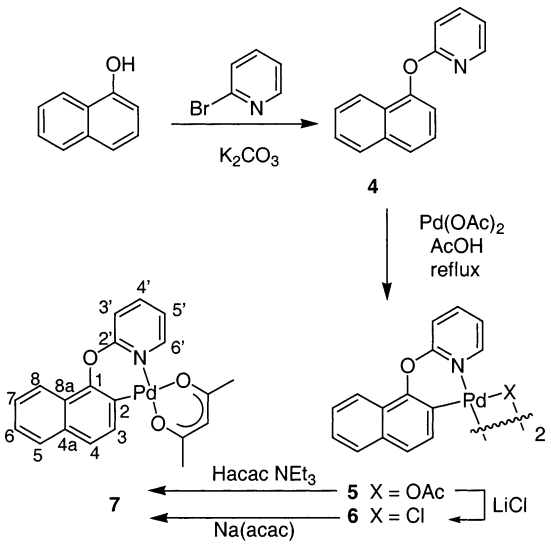
Scheme 1



Scheme 2



Scheme 3



In the present study we extend our work in this area to a study of the double cyclopalladation reactions of bis(2-pyridyloxy)naphthalenes. Whereas disubstitution of a central benzene core offers only three isomeric possibilities (*ortho*, *meta*, and *para*), there are a total of 10 possible isomers for disubstituted naphthalenes. This more diverse range of substitution patterns allows more subtle control over the disposition of the reaction centers and the topology of the resulting metalated adducts. In this context we now describe results of double cyclopalladation reactions for seven of the 10 possible isomers of bis(2-pyridyloxy)naphthalene. A number of naphthalene derivatives have previously been cyclopalladated,[12] but only one has been shown to undergo double metalation of a naphthalene core, namely, the reaction shown in Scheme 2.[13]

Results and Discussion

Before embarking on a study of the reactions of bis(2-pyridyloxy)naphthalenes, it seemed desirable to examine the corresponding reactions of the two possible monosubstituted naphthalenes. We have previously communicated our results (Scheme 1) for the 2-substituted isomer (**1**).[11] The 1-substituted analogue (**4**) was readily prepared (Scheme 3) from 1-naphthol and 2-bromopyridine, in 63% yield, and fully characterized by ^{1}H and ^{13}C NMR, mass spectrometry, and elemental analysis.

Cyclopalladation of 1-(2-Pyridyloxy)naphthalene (4). In contrast to the reaction shown in Scheme 2, reaction of **4** was expected to result in palladation at the 2-position with the formation of a six-membered chelate ring, in preference to reaction at the 8-position, which would require the formation of a less favorable seven-membered chelate ring.[3] In the event, reaction of **4** with palladium acetate in acetic acid gave an acetate-bridged dimeric complex (**5**) (Scheme 3), which was recrystallized from acetone to give a yellow crystalline material that elemental analysis showed to have the formulation $[(\mathbf{4}-H)Pd(OAc)]_2$. The FAB mass spectrum of **5** contains a cluster of peaks centered around 772 amu that shows the correct isotope distribution for the given formula. The ^{1}H NMR spectrum of **5** was completely assigned by the use of a variety of techniques. A doublet at 8.01 ppm was identified as the pyridyl H6′ proton, and irradiation of this in a 1D TOCSY experiment isolated the complete pyridyl ring spin system. The most downfield doublet at 8.12 ppm was assigned as H8 of the naphthalene, and irradiation of this proton isolated the three remaining protons of that ring. Palladation at the 2-position was confirmed by the observation of an AB quartet for the two remaining naphthalene protons, H3 and H4. Irradiation of H5 in a difference NOE experiment resulted in the observation of an NOE enhancement for H4, thus confirming the assignment of H3 and H4, and also the identity of H5 to H8. A singlet for the acetate group appears at 2.16 ppm. The 2D GHSQC and GHMBC experiments allowed the

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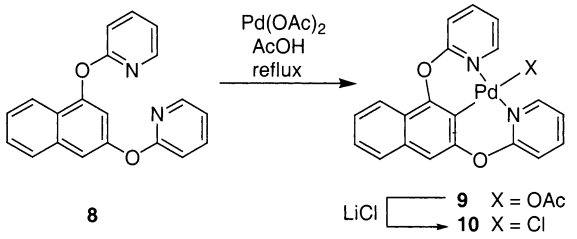
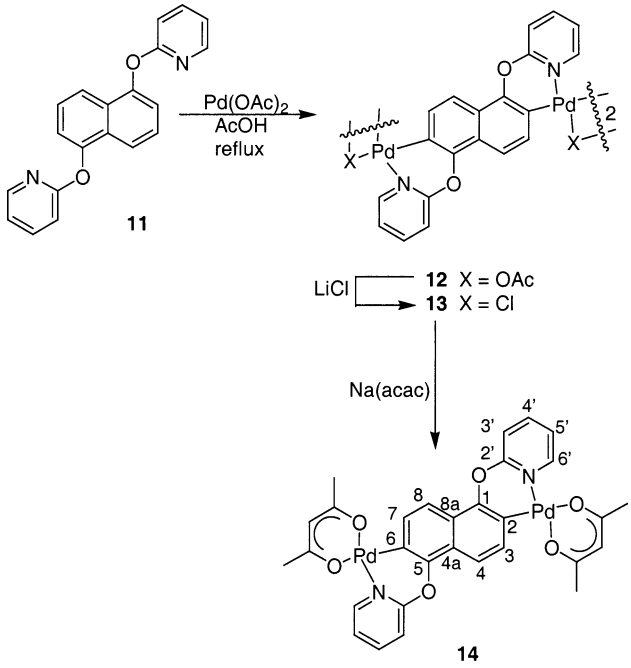
Scheme 4



Scheme 5



complete assignment of the ^{13}C NMR spectrum, with the exception of C2, for which a peak was not observed.

Reaction of **5** with an excess of lithium chloride gave the chloro-bridged complex, **6**, as a violet solid, in 83% yield (Scheme 3). This was then reacted with sodium acac to give the mononuclear acac complex, **7**, as a crimson solid, in 58% yield. Alternatively, reaction of the acetato complex, **5**, with acetylacetone in the presence of triethylamine gave analytically pure **7**, directly, in 70% yield. This complex was found by elemental analysis to have the composition [(**4**−H)Pd(acac)], which was also confirmed by FAB mass spectrometry, by the observation of a cluster of peaks centered about 425 amu. The ^1H and ^{13}C NMR spectra of **7** were assigned using techniques similar to those described above.

Thus, in contrast to the 2-substituted isomer (**1**), which reacts in either the 1- or 3-positions, depending on reaction conditions, the 1-substitited isomer undergoes palladation exclusively in the 2-position. These results are important as models for understanding the more complicated pathways available for cyclopalladation of the disubstituted compounds described below.

In the course of other work centered around the study of the metallosupramolecular chemistry of a diverse range of ligands containing various N-hetererocycles linked to a central arene core by flexible spacer groups, we have previously prepared seven of the 10 possible isomers of bis(2-pyridyloxy)naphthalene.[14] Of the missing members of this series, we have found the 1,4-isomer to be intractably insoluble in common solvents and the 1,2- and 1,8-isomers to be, thus far, synthetically inaccessible. The remaining seven isomers were available from reactions of the corresponding dihydroxynaphthalenes with 2-bromopyridine.[14]

Cyclopalladation of 1,3-Bis(2-pyridyloxy)naphthalene (8). The ligand **8** can potentially react in two modes: either single metalation in the 2-position, with coordination by the two pyridine rings, or double metalation in the 2- and 4-positions. Reaction of **8** with 2 equiv of palladium acetate in refluxing acetic acid gave a product that was identified by ^1H NMR as being monopalladated at the 2-position, by the appearance of only one singlet (2.10 ppm) in the acetate region of the spectrum, and a singlet (7.42 ppm) for H4. Accordingly, the reaction was repeated with 1 equiv of palladium acetate, and the monomeric acetato complex, **9**, was obtained as a brown solid (Scheme 4). The FAB mass spectrum of **9** shows a cluster of peaks centered about 419 amu, corresponding to the loss of acetate from **9**. The ^1H NMR spectrum of **9** was assigned by use of 1D TOCSY and difference NOE experiments.

Reaction of **9** with excess lithium chloride gave the monomeric chloro complex, **10**, in 58% yield, as an off-white solid. A sample was recrystallized by vapor diffusion of pentane into a chloroform solution of **10**, and this was found to analyze as [(**8**−H)PdCl]. FAB mass spectrometry identified the ion $[(\mathbf{8}-H)Pd]^{+\bullet}$, as observed for **9**, which is consistent with the loss of chloride from **10**. The assigned NMR spectra are given in the Supporting Information.

Thus, for this specific isomer, the combined forces of the two pyridyloxy substituents act to direct the metal specifically into the 2-position to produce monopalladated products with so-called pincer-like structures.[15]

Cyclopalladation of 1,5-Bis(2-pyridyloxy)naphthalene (11). On the basis of the observed results for the two model compounds **1** and **4**, the ligand **11** would be expected to only undergo palladation at the 2- and 6-positions to give symmetrical doubly palladated complexes. Reaction of **11** with 2 equiv of palladium acetate in refluxing benzene gave the acetato complex **12** as an olive solid, in 99% yield, which was used without further purification (Scheme 5). The IR spectrum of **12** contains bands at 1566 and 1416 cm^{-1}, which are typical of bridging acetates. The ^1H NMR spectrum of **12** is consistent with a symmetrical doubly palladated complex, as there are just six aromatic peaks, four due to the two pyridines and two doublets (6.79, 7.24 ppm) that are assigned to H3/7 and H4/8, respectively. There are two singlets (2.11, 2.32 ppm) due to acetates. By analogy to the doubly palladated acetate-bridged dimers observed for the benzene-containing ligands,[1,10] **12** is proposed to have a dimeric tetranuclear structure consisting of two doubly palladated units with the four palladium atoms bridged by four acetates. This proposal was further supported by mass spectrometry.[16]

Reaction of the acetato complex, **12**, with excess lithium chloride gave the chloro complex, **13**, as an olive

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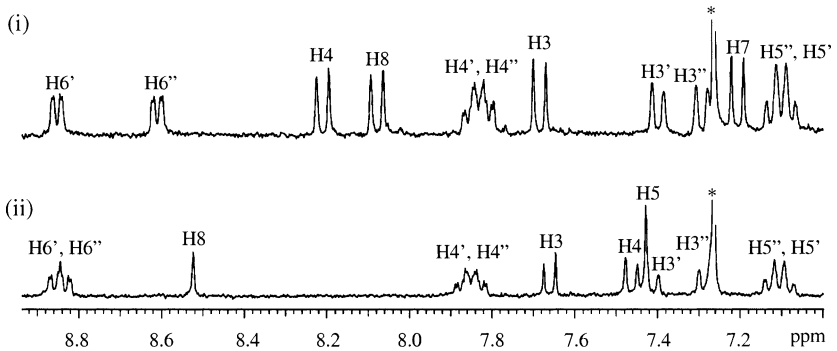


Figure 1. Aromatic region of the ^{1}H NMR spectra of (i) **17** and (ii) **19**. Peaks marked with an asterisk are due to the solvent.

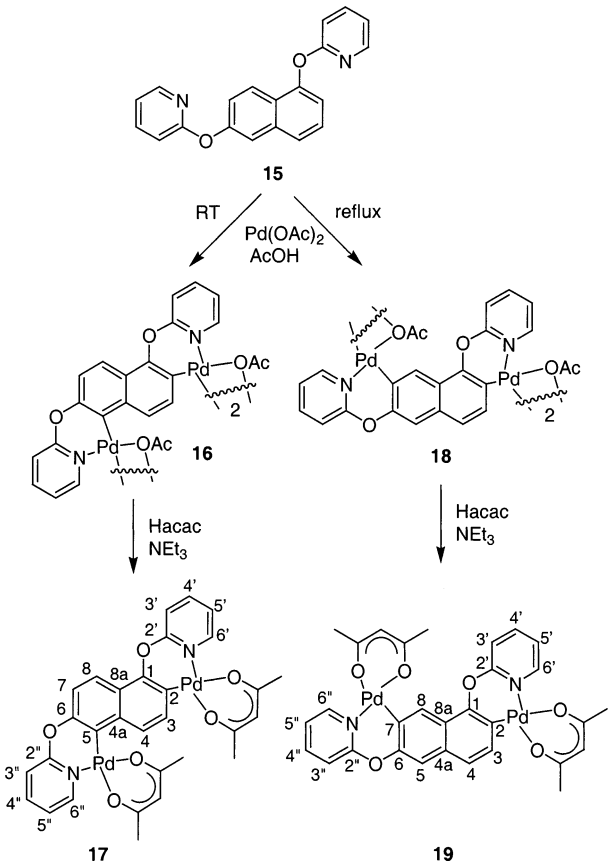
solid, in 91% yield (Scheme 5). This was then reacted with sodium acac to give the monomeric doubly palladated acac derivative, **14**, as a gray solid in 46% yield. This structure was supported by elemental analysis and FAB mass spectrometry.[16] The ^{1}H NMR spectrum of **14** has the expected six resonances in the aromatic region, with two doublets (7.78, 8.04 ppm) due to H3/7 and H4/8, respectively, and four peaks due to the pyridine rings. In addition, there are two singlets (2.06, 2.13 ppm) due to the four acac methyl groups, and a singlet (5.45 ppm) due to the two acac methine protons. Thus, in accord with the results obtained for the monosubstituted model compound **4**, the disubstituted isomer **11** undergoes double metalation in the expected 2- and 6-positions.

Cyclopalladation of 1,6-Bis(2-pyridyloxy)naphthalene (15). The ligand 1,6-bis(2-pyridyloxy)naphthalene (**15**) can potentially undergo double-metalation via either 2,5- or 2,7-double palladation. Given the results of the cyclopalladation of 2-(2-naphthyloxy)pyridine (**1**),[11] the former mode of reaction might be expected to be favored by reaction under kinetic control, while the latter mode should be favored when the reaction proceeds under thermodynamic control. Accordingly, reactions were performed under different conditions (Scheme 6).

Reaction of **15** with palladium acetate in acetic acid at room temperature gave the acetato complex (**16**) as a brown solid, in quantitative yield. The IR and mass spectra[16] supported this structure, which once again is proposed to have a dimeric tetranuclear structure consisting of two doubly palladated ligand units with the four palladiums bridged by four acetates. We have previously structurally characterized two related tetranuclear species.[1,9j]

On reaction with acetylacetone and triethylamine, **16** was converted to the acac derivative, **17**, as a brown solid, in 92% yield. Recrystallization, by vapor diffusion of pentane into a chloroform solution of **17**, gave a pure sample that was identified as a dipalladated compound by elemental analysis and FAB mass spectrometry.[16] The substitution pattern was deduced from the ^{1}H NMR spectrum of **17**, which reveals that the complex is the

Scheme 6



2,5-dipalladated regioisomer, by the presence of four doublets due to the protons H3, H4, H7, and H8, as shown in Figure 1(i). Irradiation of the isolated doublets in 1D TOCSY experiments established the two pairs of doublets belonging to each of the two spin systems, and the peaks were then assigned by comparison with the monopalladated model compounds **7** and the previously reported[11] acac adduct of **2**. The doublets due to the H6 protons of the two pyridine rings (H6′ and H6″) do not overlap with any other signals; thus irradiation of these two protons in 1D TOCSY experiments established the assignments of the two pyridine spin systems. Comparison of the chemical shifts of H6′ and H6″ with those for the mononuclear model compounds allowed assignment of the individual pyridine rings. The presence of two acac ligands is confirmed by two singlets for the two methine protons and four singlets due to the four methyl groups.

(16) The structures of the doubly cyclopalladated compounds were supported by their FAB mass spectra, which for the acac complexes showed a cluster of peaks centered around 724 amu with the isotopic distribution expected for $[(L\text{-}2H)Pd_2(acac)_2]$. The tetranuclear acetate complexes showed peaks centred around 1286 amu, corresponding to $[(L\text{-}2H)Pd_2(OAc)_2]_2$, usually accompanied by peaks at 1227, 1168, and 1109 corresponding to the sequential loss of three acetates. The infrared spectra of the acetate-bridged complexes showed absorptions near 1570 and 1420 cm^{-1}.

Having successfully prepared the 2,5-dipalladated regioisomer under kinetic control, the preparation of the 2,7-dipalladated regioisomer was attempted by reaction under thermodynamically controlled conditions. Thus, **15** was reacted with palladium acetate in refluxing acetic acid to give **18**, as a brown solid, in 70% yield. Again, the IR and FAB mass spectra supported a dimeric tetranuclear structure.[16] This structure is supported by the ^{1}H NMR spectrum of **18**, which contains three singlets in the acetate region (2.08, 2.22, 2.47 ppm), one of which has an integral twice that of the other two. The aromatic region of the spectrum confirms the double palladation of the ligand in the 2- and 7-positions by the presence of two singlets (6.74, 7.78 ppm) for H5 and H8, respectively, and two doublets (6.76, 6.91 ppm) for H4 and H3, respectively. The doublets due to the H6 protons of the two pyridines are isolated, and subsequent 1D TOCSY experiments allow the identification of the two pyridyl ring systems.

Reaction of **18** with acetylacetone and triethylamine gave the acac derivative **19**, as a brown solid, in 94% yield. A sample was recrystallized by vapor diffusion of pentane into a chloroform solution of **19** and was shown to be a monomeric dipalladated compound by elemental analysis and FAB mass spectrometry.[16] Again, double palladation in the 2- and 7-positions is confirmed in the ^{1}H NMR spectrum of **19** by the presence of two singlets (7.43, 8.52 ppm) for H5 and H8, respectively, and two doublets (7.46, 7.66 ppm) for H4 and H3, respectively (Figure 1(ii)). The spin systems of the two pyridine rings were identified by irradiation of the two well-separated doublets for H3′ and H3″ in 1D TOCSY experiments and assigned to the specific pyridine rings by comparison with the monopalladated model compounds.

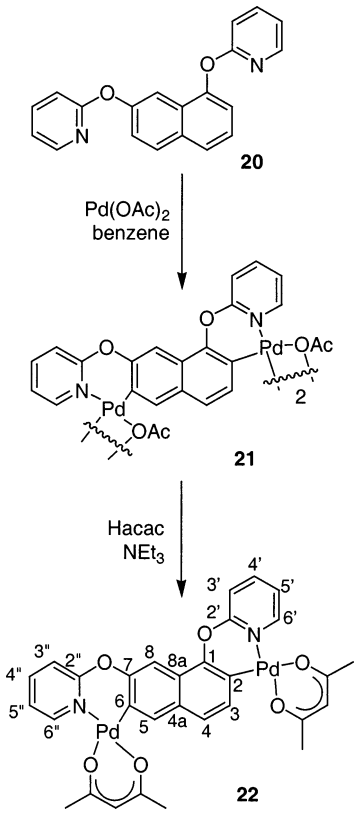
Thus, the ligand 1,6-bis(2-pyridyloxy)naphthalene (**15**) has been shown to undergo regiospecific double cyclopalladation to give either the 2,5- or 2,7-dipalladated isomers, depending on the reaction temperature, by performing the palladation reactions under kinetic or thermodynamic control (Scheme 6).

Cyclopalladation of 1,7-Bis(2-pyridyloxy)naphthalene (20). The 1,7-disubstituted isomer (**20**) can also potentially undergo metalation via two modes: double palladation either at the 2- and 6-positions or at the 2- and 8-positions. Given the results described above, the former mode of reaction should be favored by reaction under thermodynamic control, while the latter mode should be favored when the reaction occurs under kinetic control.

However, reaction of **20** with palladium acetate at room temperature in acetic acid failed to give a cyclopalladated complex. The ^{1}H NMR spectrum of the isolated product shows a species with 14 proton resonances in the aromatic region, with shifts different from those of the starting ligand. The individual spin systems of the naphthalene and pyridine rings were isolated by 1D TOCSY experiments. We believe that this compound is simply a coordination complex of **20**.

To enforce cyclopalladation of **20**, it was reacted with palladium acetate in refluxing benzene, conditions that we[10] and others[17] have previously used to prepare cyclopalladated complexes. This method gave the acetato complex (**21**), as a pale brown solid, in 94% yield (Scheme 7), for which a dimeric doubly palladated structure is proposed, on the basis of the IR and mass spectra.[16]

Scheme 7

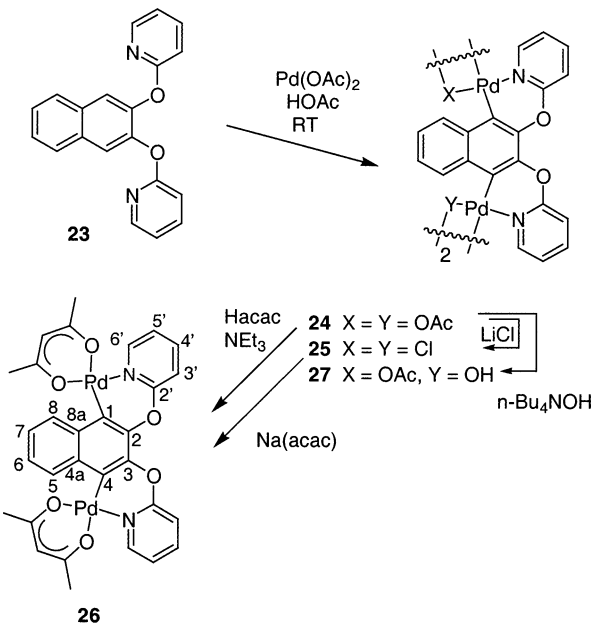


Reaction of **21** with acetylacetone and triethylamine gave the acac complex (**22**), as a light brown solid, in 86% yield. A sample was recrystallized by vapor diffusion of pentane into a chloroform solution of **22**, and this was characterized by elemental analysis and mass spectrometry.[16] The aromatic region of the ^{1}H NMR spectrum establishes that the complex is the 2,6-dipalladated regioisomer by the presence of two singlets (7.87, 8.00 ppm) for H8 and H5, respectively, and two doublets (7.53, 7.64 ppm) for H4 and H3, respectively. The assignments of these peaks were confirmed by the observation of NOE enhancements between H4 and H5. The doublets due to the H3 protons of the two pyridine rings are isolated, so they were irradiated in 1D TOCSY experiments to isolate the individual spin systems, which were assigned to specific rings by comparison with the model monopalladated compounds. Thus, the ligand 1,7-bis(2-pyridyloxy)naphthalene (**20**) has been cyclopalladated to give the thermodynamically favored 2,6-dipalladated complexes only.

Cyclopalladation of 2,3-Bis(2-pyridyloxy)naphthalene (23). The ligand 2,3-bis(2-pyridyloxy)naphthalene (**23**) can undergo double metalation only in the 1- and 4-positions. Reaction of **23** with palladium acetate in acetic acid at room temperature gave the acetato complex (**24**), as a brown solid, in 54% yield (Scheme 8). The dimeric structure is supported by its IR and mass spectra.[16] The ^{1}H NMR spectrum of **24** contains six aromatic proton peaks with four due to the pyridine rings, and two multiplets at 7.01 and 8.40 ppm due to H6/7 and H5/8, respectively. This is consistent with the

(17) Fuchita, Y.; Tsuchiya, A.; Miyafuji, A. *Inorg. Chim. Acta* **1995**, *233*, 91.

Scheme 8



ligand being doubly metalated in the 1- and 4-positions. Two singlets are observed for the bridging acetates.

Reaction of the acetato complex (**24**) with excess lithium chloride gave the chloro complex, **25**, as a brown solid, in 74% yield. This was then converted to the acac complex (**26**) by reaction with sodium acac. Alternatively, reaction of the acetato complex (**24**) with acetylacetone and triethylamine gave **26** directly, as a yellow-brown solid, in 89% yield. A sample was recrystallized by vapor diffusion of pentane into a chloroform solution of **26**, and the structure was supported by elemental analysis, mass spectrometry,[16] and the ^{1}H NMR spectrum, which contains six aromatic proton signals, with four of them due to the pyridines and the other two due to the symmetrical doubly palladated naphthalene.

From attempts to recrystallize the acetato complex (**24**) evidence for another complex (**27**) was observed in the ^{1}H NMR spectrum. A second set of six aromatic proton peaks was observed that also displayed the characteristic features of the 1,4-dipalladated naphthalene unit, i.e., four pyridyl proton peaks and two naphthyl multiplets. In the acetate region there appeared only one singlet. The structure of this compound remained unknown until a recrystallization involving diffusion of diethyl ether into a DMF solution of **24** furnished crystals of **27** that were suitable for analysis by X-ray crystallography; thus such an analysis was performed.

Crystal Structure of 27. Complex **27** crystallizes in the centrosymmetric monoclinic space group $P2_1/c$. The complex has a dimeric structure consisting of two doubly palladated ligand units that are bridged by two acetates and two hydroxides. One complete dimer and a diethyl ether solvate molecule form the contents of the asymmetric unit. The dimeric structure is shown in Figure 2, with selected atom labeling and bonding geometry.

The ligand acts as a doubly chelating C,N-donor bridging two palladium atoms by forming six-membered chelate rings. Each ligand is dipalladated in the 1- and 4-positions, as suggested by the ^{1}H NMR spectrum of **27**. The two ligand units are bridged to form a tetra-

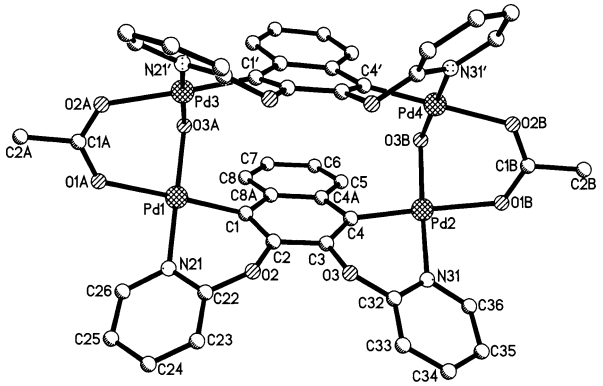


Figure 2. Dimeric structure and selected atom labeling of **27**. Hydrogen atoms and the solvate molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−C1 1.978(3), Pd1−N21 2.009(3), Pd1−O3A 2.034(2), Pd1−O1A 2.136(2), Pd2−C4 1.989(3), Pd2−N31 2.011(3), Pd2−O3B 2.026(2), Pd2−O1B 2.157(2), Pd3−C1′ 1.963(3), Pd3−N21′ 2.025(2), Pd3−O3A 2.036(2), Pd3−O2A 2.131(2), Pd4−C4′ 1.975(3), Pd4−N31′ 2.020(3), Pd4−O3B 2.035(2), Pd4−O2B 2.129(2); C1−Pd1−N21 87.7(1), C1−Pd1−O3A 93.5(1), C1−Pd1−O1A 177.9(1), N21−Pd1−O3A 174.7(1), N21−Pd1−O1A 91.4(1), O3A−Pd1−O1A 87.6(1), C4−Pd2−N31 88.1(1), C4−Pd2−O3B 94.6(1), C4−Pd2−O1B 177.5(1), N31−Pd2−O3B 175.4(1), N31−Pd2−O1B 89.6(1), O3B−Pd2−O1B 87.7(1), C1′−Pd3−N21′ 88.4(1), C1−Pd3−O3A 91.7(1), C1−Pd3−O2A 178.1(1), N21′−Pd3−O3A 172.4(1), N21′−Pd3−O2A 90.5(1), O3A−Pd3−O2A 89.5(1), C4′−Pd4−N31′ 87.3(1), C4′−Pd4−O3B 92.8(1), C4′−Pd4−O2B 176.5(1), N31′−Pd4−O3B 177.6(1), N31′−Pd4−O2B 89.6(1), O3B−Pd4−O2B 90.3(1), Pd1−O3A−Pd3 97.2(1), Pd2−O3B−Pd4 96.7(1).

nuclear dimeric structure with pairs of palladium atoms bridged by one acetate ligand and one hydroxide ligand.

The geometry at each of the palladium atoms is square planar, and the bond lengths are within the range of values observed in related structures,[18] although the bond lengths of the bridging hydroxides are at the short end of the range previously reported for two palladium atoms bridged by a hydroxide.[19] The inter-palladium separations are 3.052(1) and 3.034(1) Å, for Pd1−Pd3 and Pd2−Pd4, respectively, which are considered nonbonding. In two tetranuclear acetate-bridged cyclometalated structures, that we have previously reported,[1,9j] the palladium coordination planes were approximately parallel. However, in **27**, which is bridged by one hydroxide and one acetate, the coordination planes are nearly orthogonal, with the Pd1 and Pd3 coordination planes forming an angle of 85.2(2)° and the Pd2 and Pd4 planes subtending an angle of 96.8(2)°. This is probably because the one-atom hydroxide bridge requires the two planes to twist toward each other, whereas two three-atom acetate bridges allow the

(18) (a) Churchill, M. R.; Wasserman, H. J.; Young, G. J. *Inorg. Chem.* **1980**, *19*, 762. (b) Navarro-Ranninger, C.; Zamora, F.; Martinez-Cruz, L. A.; Isea, R.; Masauger, J. R. *J. Organomet. Chem.* **1996**, *518*, 29.

(19) (a) Pisano, C.; Consiglio, G.; Sironi, A.; Moret, M. *J. Chem. Soc., Chem. Commun.* **1991**, 421. (b) López, G.; Ruiz, J.; García, G.; Vicente, C.; Casabó, J.; Molins, E. *Inorg. Chem.* **1991**, *30*, 2605. (c) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890. (d) Pieri, G.; Pasquali, M.; Leoni, P.; Englert, U. *J. Organomet. Chem.* **1995**, *491*, 27. (e) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 4206. (f) Ruiz, J.; Cutillas, N.; Sampedro, J.; López, G.; Hermoso, J. A.; Martínez-Ripoll, M. *J. Organomet. Chem.* **1996**, *526*, 67. (g) Kuzneetsov, V. F.; Bensimon, C.; Facey, G. A.; Grushin, V. V.; Alper, H. *Organometallics* **1997**, *16*, 97.

planes to be apart and parallel. This further results in the naphthalene ring systems deviating significantly from planarity. The palladated atoms C1 and C4 are pulled up out of the mean-plane of the naphthalene by 0.102(4) and 0.094(4) Å, respectively, while C2 and C3 are below the mean-plane by 0.129(4) and 0.114(4) Å, respectively. Similarly, for the second ligand, C1′ and C4′ are pulled out of the mean-plane by 0.102(4) and 0.064(4) Å, respectively, while C2′ and C3′ lie out of the mean-plane on the opposite side by 0.097(4) and 0.122(4) Å, respectively. The palladium atoms are all significantly pulled out of the naphthalene mean-planes by 0.323(2)−0.601(2) Å. The pyridine rings are inclined to their connecting naphthalenes at angles of 29.0(4)−51.8(4)°. The four six-membered chelate rings all have boat conformations with the palladium and oxygen atoms lying out of the planes of the carbon and nitrogen atoms. The palladium atoms lie out of the planes by 0.789(2)−0.859(2) Å, while the oxygen atoms lie out of the planes by 0.306(4)−0.471(4) Å.

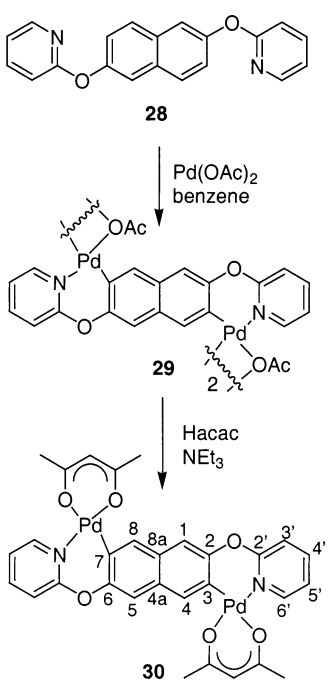
The mean-planes of the two naphthalenes are nearly parallel, being inclined at an angle of only 3.3(4)°, but they are separated by 4.03(1) Å, a distance too great for an attractive $\pi-\pi$ interaction.[20] A number of significant deviations in bond lengths and angles is sufficient to exclude the possibility of any missing crystallographic symmetry from within one dimeric molecule. However, in solution the molecule has sufficient conformational freedom to exhibit higher symmetry, as observed in the ^{1}H NMR spectrum.

The substitution of two acetate ligands from **24** by two hydroxides to give **27** must have occurred due to the presence of water in the solvents used in the recrystallization. The displacement of the acetate appears to occur readily, and this is probably due to the steric strain that would occur between the displaced acetates and the protons in the 5- and 8-positions of the naphthalenes. This strain is relieved on substitution by the hydroxide.

Rather than relying on adventitious incorporation of water from the recrystallization solvent to prepare the mixed acetato/hydroxo-bridged dimer, an attempt was made to prepare **27** directly from the acetato complex (**24**). A mixture of **24** and tetrabutylammonium hydroxide (2 equiv per dimer) was stirred in acetone and water. The resulting precipitate was filtered off to give **27** as a brown solid, in 80% yield. A sample was recrystallized by diffusion of diethyl ether into a chloroform solution of **27** to give pale yellow crystals. The IR spectrum of **27** shows a peak at 3549 cm^{-1} that is assigned to the bridging hydroxide. The FAB mass spectrum confirms the structure by the appearance of a cluster of peaks centered about 1202 amu that is consistent with the formulation [(**23**-2H)Pd$_2$(OAc)(OH)]$_2$. Closer inspection of the ^{1}H NMR spectrum revealed the presence of a singlet at −0.67 ppm due to the bridging hydroxide ligand. Such an upfield chemical shift is typical for a hydroxide bridging two palladium atoms.[18] The ^{13}C NMR spectrum was assigned with the assistance of the GHSQC experiment.

(20) Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. *J. Chem. Soc., Perkin Trans. 2* **2001**, 651.

Scheme 9



Thus, 2,3-bis(2-pyridyloxy)naphthalene (**23**) undergoes cyclopalladation exclusively in the 1- and 4-positions.

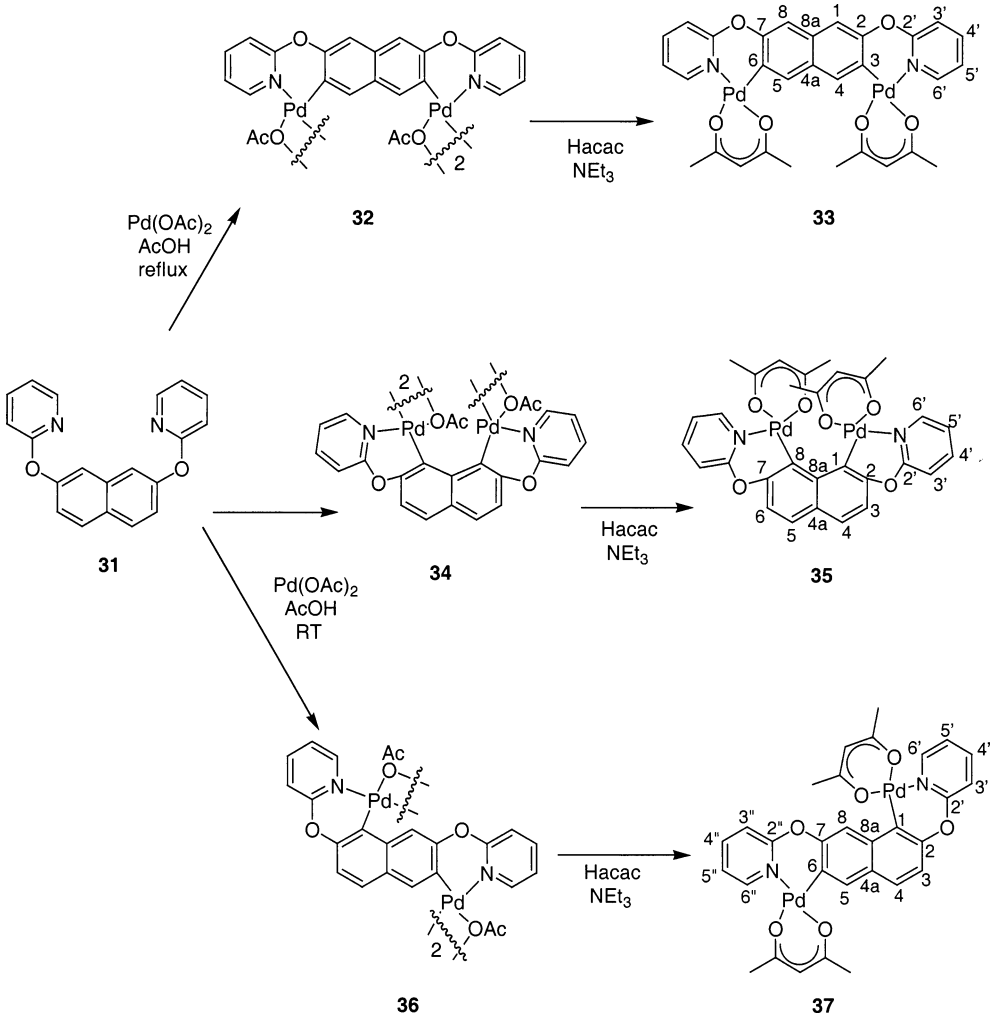
Cyclopalladation of 2,6-Bis(2-pyridyloxy)naphthalene (28). The ligand 2,6-bis(2-pyridyloxy)naphthalene (**28**) can potentially undergo double metalation in three ways: double palladation either at the 1- and 5-positions or at the 3- and 7-positions to give symmetrical regioisomers, or at the 1- and 7- positions to give an unsymmetrical regioisomer. Again, these isomers should be readily distinguished by ^{1}H NMR.

Reaction of **28** with palladium acetate in acetic acid at room temperature, followed by conversion to the acac derivative, via the chloro intermediate, gave a mixture of products on analysis by ^{1}H NMR. The mixture included unreacted ligand and possibly some monomeric species; however, none of the expected three doubly palladated derivatives could be identified.

Instead, **28** was reacted with palladium acetate in refluxing benzene to give **29**, as a yellow solid, in a poor yield of 25% (Scheme 9). The IR spectrum of **29** contains bands at 1570 and 1416 cm^{-1} that are typical of bridging acetates. The complex is not sufficiently soluble for analysis by NMR spectroscopy; however, on the basis of the previous cyclopalladated complexes, a doubly palladated tetranuclear dimeric structure is proposed for **29**.

Reaction of **29** with acetylacetone and triethylamine gave the acac derivative, **30**, as a gray solid, in 98% crude yield. A sample was purified by Soxhlet extraction with chloroform and washing with acetone and characterized by elemental analysis and mass spectrometry.[16] The aromatic region of the ^{1}H NMR spectrum contains six peaks due to the symmetrical double cyclopalladation of the ligand. Four of these peaks are due to the pyridine rings, and the remaining two are singlets (7.44, 7.91 ppm) due to H1/5 and H4/8, respectively, which identifies the 3- and 7-positions as the sites of palladation. The two singlets were assigned by comparison with

Scheme 10



the corresponding monopalladated model compound.[11] The ^{13}C NMR spectrum of **30** was assigned by comparison with the model compound and by GHSQC and GHMBC experiments.

Thus, the symmetrical 3,7-dipalladated regioisomer has been prepared by the reaction being performed under thermodynamic control.

Cyclopalladation of 2,7-Bis(2-pyridyloxy)naphthalene (31). The ligand 2,7-bis(2-pyridyloxy)naphthalene (**31**) can also potentially undergo double metalation in three ways: double palladation either at the 1- and 8-positions or at the 3- and 6-positions to give symmetrical regioisomers, or at the 1- and 6-positions to give an unsymmetrical regioisomer. Once again, these isomers should be readily distinguishable by ^1H NMR. Therefore, reactions were performed under different conditions in attempts to control the regiochemistry of the product.

Reaction of **31** with palladium acetate in refluxing acetic acid gave the acetato complex, **32**, as a brown solid, in 69% yield (Scheme 10). A sample was recrystallized from a mixture of dichloromethane and acetone and characterized by elemental analysis and mass spectrometry.[16] The ^1H NMR spectrum of **32** displays two acetate singlets and six peaks in the aromatic region, which suggests that the ligand is symmetrically dipalladated, and the presence of two singlets (6.66, 6.85 ppm) due to H1/8 and H4/5, respectively, confirms that metalation has occurred in the 3- and 6-positions. Thus, the proposed structure for **32** is dimeric, consisting of two 3,6-dipalladated ligand units with the four palladium atoms being bridged by four acetate ligands.

On reaction with acetylacetone and triethylamine, **32** was converted to the monomeric acac derivative (**33**), in 78% yield, and this was supported by elemental analysis and mass spectrometry.[16] The ^1H NMR spectrum of **33** also contains six peaks in the aromatic region, and the presence of two singlets (7.34, 7.97 ppm) due to H1/8 and H4/5, respectively, again confirms double palladation in the 3- and 6-positions.

Having demonstrated that reaction of **31** with palladium acetate in refluxing acetic acid occurs under thermodynamic control leading to the 3,6-dipalladated derivatives, we also performed reactions under other conditions in attempts to prepare the other two possible regioisomers. On one occasion reaction of palladium acetate and **31** in acetic acid at room temperature gave a product that was identified by ^1H NMR to be the 1,8-dipalladated regioisomer (**34**). This was established by the presence of six peaks in the aromatic region of the spectrum, four of which are due to the pyridines, with the remaining two doublets (7.02, 7.36 ppm) being due to H3/6 and H4/5. However, this proved to be an isolated occurrence, as the reaction at room temperature generally produced a mixture of the three regioisomers **32**, **34**, and **36**, which are all proposed to have dimeric

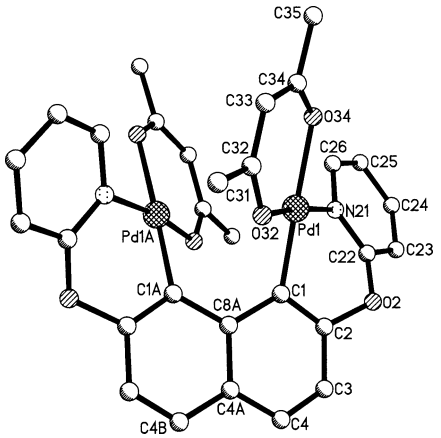


Figure 3. Molecular structure of **35**. Hydrogen atoms and the chloroform solvate molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−C1 1.961(4), Pd1−N21 2.023(2), Pd1−O32 2.029(2), Pd1−O34 2.090(2); C1−Pd1−N21 87.2(1), C1−Pd1−O32 89.6(1), C1−Pd1−O34 178.6(1), N21−Pd1−O32 171.4(1), N21−Pd1−O34 91.5(1), O32−Pd1−O34 91.5(1).

tetranuclear structures. Reaction of **31** with palladium acetate in refluxing chloroform produced a similar mixture of the three species.

This mixture of three acetato complexes was reacted with acetylacetone and triethylamine to give a mixture of the corresponding three acac regioisomers **33**, **35**, and **37**, as a brown solid, in a combined yield of 85%. The isomers were determined by ^{1}H NMR to be present in the approximate ratio 1:4:2, respectively. Recrystallization of the crude mixture from chloroform selectively separated the 1,8-dipalladated regioisomer (**35**), as yellow crystals that were initially characterized by elemental analysis and mass spectrometry.[16] The ^{1}H NMR spectrum of **35** contains six peaks in the aromatic region, with four due to the pyridine rings and two doublets (7.05, 7.39 ppm) due to H3/6 and H4/5, respectively, thus confirming the 1- and 8-positions as the sites of palladation. The acac methine proton has an unusually high-field chemical shift of 5.26 ppm, and one acac methyl group also has an unusual upfield shift of 0.96 ppm. We surmised that these upfield shifts were due to the shielding effect of the adjacent pyridine rings, as a consequence of the crowded environment that results from the double palladation in the 1- and 8-positions. In view of the unusual chemical shifts observed and to determine unambiguously the exact structure of this complex, a single-crystal X-ray structure determination was performed.

Crystal Structure of 35. The complex crystallizes in the noncentrosymmetric orthorhombic space group *Fdd*2 and has a monomeric dipalladated structure. The asymmetric unit consists of half of a palladated ligand unit and a disordered chloroform solvate molecule. Two half-molecules are related by a 2-fold rotation axis that passes through C4A and C8A, to give the full molecular structure shown in Figure 3. The ligand **31** acts as a doubly chelating C,N-donor bridging two palladium atoms by forming two six-membered chelate rings. Each molecule of **31** is doubly palladated in the 1- and 8-positions (i.e., at C1 and C1A in Figure 3), as suggested by the ^{1}H NMR spectrum of **35**. Each palladium atom is also coordinated to two oxygen atoms of an acac ligand, which also forms a six-membered chelate ring. The palladium geometry is approximately square planar, and the palladium−donor bond lengths are similar to those in related compounds in the literature.[8c,d,13]

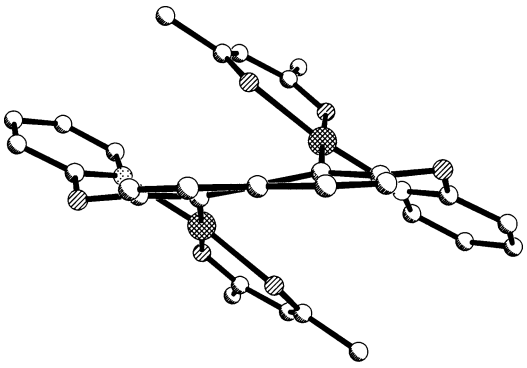


Figure 4. View down the C4A−C8A bond (the 2-fold rotational axis) of **35**.

To accommodate the two palladium atoms and the acac ligands, the naphthalene core is substantially twisted so that C1 and C1A each lie out of the naphthalene mean-plane, in opposite directions, by 0.168(5) Å, and the palladium atoms, Pd1 and Pd1A, each lie out of the mean-plane by 0.813(3) Å. These deviations can be seen in the view down the C4A−C8A bond, shown in Figure 4. The coordination planes are twisted out of the mean-plane of the naphthalene by 43.9(2)°, while the pyridine rings are inclined to the naphthalene at an angle of 31.9(2)°. This twisting results in a palladium−palladium separation of 3.152(1) Å, a distance too great for a bonding interaction. The twisting of the molecule also results in the methine hydrogen and one methyl group of an acac ligand sitting over the face of a pyridine ring, thereby explaining the upfield shifts observed in the ^{1}H NMR spectrum.

The C,N-donor six-membered chelate ring exists in a boat conformation with Pd1 and O2 sitting out of the plane of the nitrogen and carbon atoms by 0.799(3) and 0.361(5) Å, respectively. Meanwhile, the acac chelate ring is approximately planar [mean deviation 0.043(5) Å]. The twisting of the molecule results in it being chiral; however, the crystal itself contains a racemic mixture of molecules of opposite chirality related by glide planes. The correct absolute configuration of the molecule shown is confirmed by the Flack parameter that refines to −0.02(0.03).[21]

Following fractional recrystallization of **35** a mixture of the remaining two regioisomers, **33** and **37**, was obtained by vapor diffusion of pentane into a chloroform solution of the residue. After identifying the peaks due to **33**, the unsymmetrical 1,6-dipalladated regioisomer (**37**) was also identified in the ^{1}H NMR spectrum of the two compounds. The two pyridine rings were isolated by 1D TOCSY experiments, and H3, which is overlapped by signals from three other protons, was isolated by irradiating H4 in a 1D TOCSY experiment. The singlets due to H5 and H8 and the doublets due to H3 and H4 were assigned by comparison with the spectra of the two symmetrical compounds **33** and **35**.

Thus, the ligand **31** has been shown to undergo double palladation via three modes. The thermodynamically

(21) Flack, H. D.; Bernardinelli, G. *J. Appl. Crystallogr.* **2000**, *33*, 1143.

most stable 3,6-dipalladated regioisomer can be formed selectively by performing the reaction under thermodynamic control, while a mixture of the three regioisomers is produced under milder reaction conditions.

Conclusion

This study represents the first systematic investigation of the cyclopalladation reactions of naphthalene-based ligands. We have shown that the naphthalene ring system provides a fascinating platform about which one can construct a diverse range of doubly cyclopalladated derivatives in a predictable and controlled manner, based on the kinetic preference for reaction in the 1-position over a thermodynamic preference for reaction in the 3-position. The range of compounds prepared in this study represents a significant increase in the number of cyclopalladated naphthalene complexes; in particular the number of doubly palladated naphthalenes has been extensively expanded from the one previous example.[13] As well, this study significantly extends the number of doubly cyclopalladated complexes that contain six-membered chelate rings.

Experimental Section

General Procedures. For general procedures and instrumentation see ref 9j and the Supporting Information. Infrared spectra and fully assigned ^{1}H and ^{13}C NMR spectra of the cyclopalladated compounds are listed in the Supporting Information.

1-(2-Pyridyloxy)naphthalene (4). A mixture of 1-naphthol (1.02 g, 7.07 mmol), 2-bromopyridine (1.69 g, 10.7 mmol), and potassium carbonate (1.96 g, 14.2 mmol) in sulfolane/toluene (2:1) was heated under nitrogen for 40 h. The mixture was added to a solution of aqueous sodium hydroxide (10%), and this was repeatedly extracted with chloroform. The chloroform was removed in vacuo, and the resulting sulfolane solution was added to acetone. This solution was heated, treated with decolorizing charcoal, then filtered. The acetone was removed in vacuo, and water was added to the sulfolane solution to precipitate crude **4** as a brown solid (980 mg, 63%). This was sufficiently pure for the preparation of complexes; however a sample of **4** was recrystallized from ethanol for characterization, mp 88−89 °C (Found: C, 81.56; H, 5.01; N, 6.36. $C_{15}H_{11}NO$ requires: C, 81.43; H, 5.01; N, 6.33. Found: $M^{+\bullet}$, 221.0840. $C_{15}H_{11}NO$ requires: $M^{+\cdot}$, 221.0841). ^{1}H NMR ($CDCl_3$) δ: 6.94, 1H, d, H3′; 7.00, 1H, t, H5′; 7.24, 1H, d, H2; 7.44, 1H, t, H7; 7.50, 1H, t, H6; 7.48, 1H, t, H3; 7.69, 1H, t, H4′; 7.74, 1H, d, H4; 7.89, 1H, d, H5; 8.00, 1H, d, H8; 8.18, 1H, d, H6′. ^{13}C NMR ($CDCl_3$) δ: 110.87, C3′; 117.05, C2; 118.36, C5′; 121.96, C8; 124.92, C4; 125.68, C3; 126.04, C7; 126.33, C6; 127.42, C8a; 127.88, C5; 134.92, C4a; 139.41, C4′; 147.86, C6′; 149.98, C1; 164.23, C2′.

Cyclopalladation of 1-(2-Pyridyloxy)naphthalene (4): (a) Preparation of 5. A solution of **4** (120 mg, 0.54 mmol) and palladium acetate (124 mg, 0.55 mmol) in glacial acetic acid was stirred at room temperature for 44 h. The solvent was removed under reduced pressure. The residue was redissolved in chloroform and filtered. The chloroform solution was reduced to dryness to give the crude acetato-bridged dimer (**5**) as a crimson solid (266 mg). A sample of the crude was recrystallized from acetone to give **5** as yellow crystals (yield >95%), mp 161−166 °C (Found: C, 53.17; H, 3.69; N, 3.60. $C_{34}H_{26}N_2O_6Pd_2$ requires: C, 52.94; H, 3.40; N, 3.63. Found: $M^{+\bullet}$, 771.9859. $C_{34}H_{26}N_2O_6{}^{106}Pd^{108}Pd$ requires: $M^{+\cdot}$, 771.9862).

(b) Preparation of 6. A mixture of the acetato complex **5** (112 mg, 0.15 mmol) and LiCl (55 mg, 1.3 mmol) was stirred in acetone/water (3:2, 5 mL) for 3 days. The precipitate was filtered off and washed with water to give **6** as a violet solid (87 mg, 83%).

(c) Preparation of 7. A mixture of the chloro complex **6** (59 mg) and sodium acac in methanol was stirred for 3 days. The resulting precipitate was filtered off and washed with methanol to give crude **7** as a crimson solid, (40 mg, 58%). Alternatively, the acetato complex **5** (66 mg, 0.086 mmol) was stirred in an acetone solution (7 mL) containing acetylacetone (60 mg, 0.60 mmol) and triethylamine (66 mg, 0.65 mmol) for 2.5 h. The acetone was removed under reduced pressure. The residue was suspended in water, and **7** was filtered off as a crimson solid (51 mg, 70%), mp 158−160 °C (Found: C, 56.33; H, 4.15; N, 3.36. $C_{20}H_{17}NO_3Pd$ requires: C, 56.42; H, 4.02; N, 3.29. Found: $M^{+\bullet}$, 425.0236. $C_{20}H_{17}NO_3{}^{106}Pd$ requires: $M^{+\bullet}$, 425.0240).

Cyclopalladation of 1,3-Bis(2-pyridyloxy)naphthalene (8): (a) Preparation of 9. A mixture of **8** (100 mg, 0.32 mmol) and palladium acetate (79 mg, 0.35 mmol) in benzene was refluxed for 14 h. The solvent was removed under reduced pressure. Soxhlet extraction of the resulting solid with chloroform isolated the crude acetato complex (**9**) as a brown solid (202 mg), which was used without further purification (Found: $M^{+\bullet}$, 419.0020. $C_{20}H_{13}N_2O_2{}^{106}Pd$ requires: $M^{+\bullet}$, 419.0009).

(b) Preparation of 10. A mixture of the acetato complex **9** (98 mg, 0.20 mmol) and LiCl (91 mg, 2.1 mmol) was stirred in acetone/water (3:2, 10 mL) for 3 days. The precipitate was filtered off and washed with water to give **10** as an off-white solid (54 mg, 58%). A sample was recrystallized by vapor diffusion of pentane into a chloroform solution of **10** for further analysis, mp >200 °C (dec) (Found: C, 52.45; H, 2.63; N, 5.91; Cl, 8.17. $C_{20}H_{13}N_2O_2PdCl$ requires: C, 52.77; H, 2.88; N, 6.15; Cl, 7.79. Found: 419.0. $C_{20}H_{13}N_2O_2{}^{106}Pd$ requires $M^{+\bullet}$, 419.0).

Cyclopalladation of 1,5-Bis(2-pyridyloxy)naphthalene (11): (a) Preparation of 12. A mixture of **11** (200 mg, 0.64 mmol) and palladium acetate (297 mg, 1.3 mmol) in benzene was refluxed for 18 h. The precipitated product was filtered off and washed with benzene to give crude **12** as an olive solid (416 mg, 99%), which was used without further purification (Found: $M^{+\bullet}$, 1287. $C_{48}H_{36}N_4O_{12}{}^{105}Pd^{106}Pd^{108}Pd_2$ requires: $M^{+\bullet}$, 1287).

(b) Preparation of 13. A mixture of the acetato complex **12** (342 mg, 0.27 mmol) and LiCl (179 mg, 4.2 mmol) was stirred in acetone/water (3:2, 12 mL) for 3 days. The precipitate was filtered off and washed with water and acetone to give **13** as an olive solid (288 mg, 91%).

(c) Preparation of 14. A mixture of the chloro complex **13** (235 mg) and sodium acac in methanol was stirred for 4 days. The resulting precipitate was filtered off and washed with methanol, then hot acetone to give **14**, as a gray solid, (130 mg, 46%), mp >245 °C (dec) (Found: C, 49.75; H, 3.40; N, 3.96. $C_{30}H_{26}N_2O_6Pd_2$ requires: C, 49.81; H, 3.62; N, 3.87. Found: $M^{+\bullet}$, 723.9840. $C_{30}H_{26}N_2O_6{}^{106}Pd^{108}Pd$ requires: $M^{+\bullet}$, 723.9862).

Cyclopalladation of 1,6-Bis(2-pyridyloxy)naphthalene (15). 2,5-Dipalladated Complexes: (a) Preparation of 16. A mixture of **15** (108 mg, 0.34 mmol) and palladium acetate (157 mg, 0.70 mmol) was stirred in glacial acetic acid (10 mL) at room temperature for 17 h. The reaction mixture was reduced to dryness in vacuo. Soxhlet extraction of the resulting solid with chloroform isolated the crude acetato complex (**16**) as a brown solid (221 mg, 100%), which was used without further purification (Found: $M^{+\bullet}$, 1285.7. $C_{48}H_{36}N_4O_{12}Pd_4$ requires: $M^{+\bullet}$, 1285.7).

(b) Preparation of 17. A mixture of the acetato complex (**16**) (150 mg, 0.12 mmol), acetylacetone (177 mg, 1.8 mmol), and triethylamine (203 mg, 2.09 mmol) was stirred in acetone (8 mL) for 24 h. The solvent was removed in vacuo. The resulting solid was suspended in water, filtered off, and washed with water to give crude **17** as a brown solid (157 mg, 92%). The crude was recrystallized by diffusion of pentane into a chloroform solution of **17** to give the product as a light brown

solid, mp >225 °C (dec) (Found: C, 49.06; H, 3.48; N, 4.06. $C_{30}H_{26}N_2O_6Pd_2 \cdot 1/2(H_2O)$ requires: C, 49.20; H, 3.72; N, 3.83. Found: $M^{+\bullet}$, 723.9876. $C_{30}H_{26}N_2O_6{}^{106}Pd^{108}Pd$ requires: $M^{+\bullet}$, 723.9862).

2,7-Dipalladated Complexes: (a) Preparation of 18. A mixture of **15** (111 mg, 0.35 mmol) and palladium acetate (166 mg, 0.74 mmol) was refluxed in glacial acetic acid (10 mL) for 17 h. The reaction mixture was reduced to dryness in vacuo. Soxhlet extraction of the resulting solid with chloroform isolated the crude acetato complex **18**, as a brown solid (158 mg, 70%), which was used without further purification (Found: $M^{+\bullet}$, 1285.8520. $^{12}C_{47}{}^{13}CH_{36}N_4O_{12}{}^{106}Pd_2{}^{108}Pd^{105}Pd$ requires: $M^{+\bullet}$, 1285.8512).

(b) Preparation of 19. A mixture of the acetato complex **18** (59 mg, 0.046 mmol), acetylacetone (71 mg, 0.71 mmol), and triethylamine (75 mg, 0.74 mmol) was stirred in acetone (8 mL) for 24 h. The solvent was removed in vacuo. The resulting solid was suspended in water, filtered off, and washed with water to give crude **19** as a brown solid (63 mg, 94%). Diffusion of pentane into a chloroform solution of the crude product gave **19** as a light brown solid, mp >240 °C (dec) (Found: C, 49.22; H, 3.62; N, 3.92. $C_{30}H_{26}N_2O_6Pd_2 \cdot 1/2(H_2O)$ requires: C, 49.20; H, 3.72; N, 3.83. Found: $M^{+\bullet}$, 723.9881. $C_{30}H_{26}N_2O_6{}^{106}Pd^{108}Pd$ requires: $M^{+\bullet}$, 723.9862).

Cyclopalladation of 1,7-Bis(2-pyridyloxy)naphthalene (20): (a) Preparation of 21. A mixture of **20** (147 mg, 0.47 mmol) and palladium acetate (211 mg, 0.94 mmol) was refluxed in benzene (10 mL) for 16 h. The reaction mixture was reduced to dryness in vacuo. Soxhlet extraction of the resulting solid with chloroform isolated the crude acetato complex **21**, as a pale brown solid (282 mg, 94%), which was used without further purification (Found: $M^{+\bullet}$, 1285.8497. $C_{48}H_{36}N_4O_{12}{}^{106}Pd_2{}^{108}Pd_2$ requires: $M^{+\bullet}$, 1285.8500).

(b) Preparation of 22. A mixture of the acetato complex **21** (157 mg, 0.12 mmol), acetylacetone (180 mg, 1.8 mmol), and triethylamine (228 mg, 2.25 mmol) was stirred in acetone (10 mL) for 16 h. The solvent was removed in vacuo. The resulting solid was suspended in water, filtered off, and washed with water to give crude **22** as a light brown solid (153 mg, 86%). The crude was recrystallized by diffusion of pentane into a chloroform solution of **22** to give yellow crystals of **22**, mp >195 °C (dec) (Found: C, 48.95; H, 3.58; N, 3.77. $C_{30}H_{26}N_2O_6Pd_2 \cdot 1/2(H_2O)$ requires: C, 49.20; H, 3.72; N, 3.83. Found: $M^{+\bullet}$, 723.9841. $C_{30}H_{26}N_2O_6{}^{106}Pd^{108}Pd$ requires: $M^{+\bullet}$, 723.9862).

Cyclopalladation of 2,3-Bis(2-pyridyloxy)naphthalene (23): (a) Preparation of 24. A mixture of **23** (67 mg, 0.21 mmol) and palladium acetate (99 mg, 0.44 mmol) was stirred in glacial acetic acid (8 mL) at room temperature for 64 h. The reaction mixture was reduced to dryness in vacuo. Soxhlet extraction of the resulting solid with chloroform isolated the crude acetato complex **24**, as a brown solid (148 mg, 54%), which was used without further purification (Found: $M^{+\bullet}$, 1285.8512. $^{12}C_{47}{}^{13}CH_{36}N_4O_{12}{}^{106}Pd_2{}^{108}Pd^{105}Pd$ requires: $M^{+\bullet}$, 1285.8513).

(b) Preparation of 25. A mixture of the acetato complex **24** (223 mg, 0.17 mmol) and LiCl (151 mg, 3.6 mmol) was stirred in acetone/water (3:2, 8 mL) for 3 days. The precipitate was filtered off and washed with water and acetone to give **25** as a brown solid (153 mg, 74%).

(c) Preparation of 26. A mixture of the chloro complex **25** (100 mg) and sodium acac in methanol was stirred for 4 days. The resulting precipitate was filtered off and washed with methanol to give a black solid. Soxhlet extraction of this solid with chloroform gave crude **26** as a yellow solid (60 mg, 49%). Alternatively, a mixture of the acetato complex **25** (156 mg, 0.12 mmol), acetylacetone (189 mg, 1.9 mmol), and triethylamine (257 mg, 2.54 mmol) was stirred in acetone (10 mL) for 40 h. The solvent was removed in vacuo. The resulting solid was suspended in water, filtered off, and washed with water to give crude **26** as a yellow-brown solid (155 mg, 89%), which was recrystallized by diffusion of pentane into a chloroform solution of the crude to provide **26** as a light brown solid, mp >165 °C (dec) (Found: C, 49.89; H, 3.56; N, 3.87. $C_{30}H_{26}N_2O_6Pd_2$ requires: C, 49.81; H, 3.62; N, 3.87. Found: $M^{+\bullet}$, 723.9888. $C_{30}H_{26}N_2O_6{}^{106}Pd^{108}Pd$ requires: $M^{+\bullet}$, 723.9862).

(d) Preparation of 27. Vapor diffusion of diethyl ether into a DMF solution of the acetato complex **24** yielded pale yellow crystals of **27** suitable for single-crystal X-ray structure determination. Alternatively, a mixture of the acetato complex **24** (150 mg, 0.12 mmol) and tetrabutylammonium hydroxide (60 mg, 0.23 mmol) in acetone/water (5:1, 12 mL) was stirred for 18 h. The reaction mixture was reduced to dryness under reduced pressure, and the residue was suspended in water. The precipitate was filtered off and washed with water to give crude **27** as a brown solid (113 mg, 80%). A sample was recrystallized by diffusion of diethyl ether into a chloroform solution of **27** to give pale yellow crystals, mp >190 °C (dec) (Found: C, 43.67; H, 2.93; N, 4.15. $C_{44}H_{32}N_4O_{10}Pd_4 \cdot (H_2O) \cdot 1/2(C_4H_{10}O)$ requires: C, 43.94; H, 3.13; N, 4.46. Found: $M^{+\bullet}$, 1201.8282. $C_{44}H_{32}N_4O_{10}{}^{105}Pd_2{}^{108}Pd_2$ requires: $M^{+\bullet}$, 1201.8288).

Cyclopalladation of 2,6-Bis(2-pyridyloxy)naphthalene (28): (a) Preparation of 29. A mixture of **28** (105 mg, 0.33 mmol) and palladium acetate (166 mg, 0.74 mmol) was refluxed in benzene (8 mL) for 16 h. The reaction mixture was reduced to dryness in vacuo. Soxhlet extraction of the resulting solid with chloroform isolated the crude acetato complex **29**, as a yellow solid (54 mg, 25%), which was used without further purification.

(b) Preparation of 30. A mixture of the acetato complex **29** (157 mg, 0.12 mmol), acetylacetone (200 mg, 2.0 mmol), and triethylamine (209 mg, 2.1 mmol) was stirred in acetone (10 mL) for 36 h. The solvent was removed in vacuo. The resulting solid was suspended in water, filtered off, and washed with water to give crude **30** as a gray solid (175 mg, 98%). A sample of the crude was further purified by Soxhlet extraction with chloroform to give a pale yellow solid. This solid was suspended in hot acetone and was filtered off to give **30** as an off-white solid, mp >210 °C (dec) (Found: C, 49.16; H, 3.64; N, 3.84. $C_{30}H_{26}N_2O_6Pd_2 \cdot 1/2(H_2O)$ requires: C, 49.20; H, 3.72; N, 3.83. Found: $M^{+\bullet}$, 723.9843. $C_{30}H_{26}N_2O_6{}^{106}Pd^{108}Pd$ requires: $M^{+\bullet}$, 723.9862).

Cyclopalladation of 2,7-Bis(2-pyridyloxy)naphthalene (31). 3,6-Dipalladated Complexes: (a) Preparation of 32. A mixture of **31** (64 mg, 0.20 mmol) and palladium acetate (104 mg, 0.46 mmol) was refluxed in glacial acetic acid (8 mL) for 16 h. The reaction mixture was reduced to dryness in vacuo. Soxhlet extraction of the resulting solid with chloroform isolated the crude acetato complex **32**, as a brown solid (90 mg, 69%), which was used without further purification. A sample was recrystallized from a dichloromethane/acetone solution to give **32** as a pale brown solid, mp >230 °C (dec) (Found: C, 44.92; H, 2.94; N, 4.24. $C_{48}H_{36}N_4O_{12}Pd_4$ requires: C, 44.82; H, 2.82; N, 4.36. Found: $M^{+\bullet}$, 1286. $C_{48}H_{36}N_4O_{12}Pd_4$ requires: $M^{+\bullet}$, 1286).

(b) Preparation of 33. A mixture of the acetato complex **32** (109 mg, 0.12 mmol), acetylacetone (121 mg, 1.2 mmol), and triethylamine (144 mg, 1.4 mmol) was stirred in acetone (12 mL) for 1 h. The solvent was removed in vacuo. The resulting solid was suspended in water, filtered off, and washed with water to give crude **33** as a light brown solid (95 mg, 78%). A sample was recrystallized, by diffusion of pentane into a chloroform solution of the crude, to give **33** as yellow crystals, mp >220 °C (dec) (Found: C, 49.56; H, 3.51; N, 4.00. $C_{30}H_{26}N_2O_6Pd_2$ requires: C, 49.81; H, 3.62; N, 3.87. Found: $M^{+\bullet}$, 723.9858. $C_{30}H_{26}N_2O_6{}^{106}Pd^{108}Pd$ requires: $M^{+\bullet}$, 723.9862).

1,8-Dipalladated Complexes: (a) Preparation of 34. A mixture of **30** (102 mg, 0.32 mmol) and palladium acetate (151 mg, 0.67 mmol) was stirred in glacial acetic acid (10 mL) at room temperature for 72 h. The reaction mixture was reduced to dryness in vacuo. Soxhlet extraction of the resulting solid with chloroform isolated a mixture of the acetato complexes

32, **34**, and **36** as a brown solid (201 mg, 96%), which was used without further purification. This reaction was carried out several times, and on one fortuitous occasion, **34** alone was isolated.

(b) Preparation of 35. A mixture of the acetato complexes **32**, **34**, and **36** (170 mg, 0.13 mmol), acetylacetone (183 mg, 1.8 mmol), and triethylamine (190 mg, 1.9 mmol) was stirred in acetone (12 mL) for 16 h. The solvent was removed in vacuo. The resulting solid was suspended in water, filtered off, and washed with water to give a mixture of **33**, **35**, and **37**, in the approximate ratio 1:4:2, as a light brown solid (163 mg, 85%). Recrystallization of the crude product from chloroform gave **35**, as yellow crystals suitable for single-crystal X-ray structure determination, mp >200 °C (dec) (Found: C, 40.15; H, 2.53; N, 2.84. $C_{30}H_{26}N_2O_6Pd_2 \cdot 2(CHCl_3)$ requires: C, 39.95; H, 2.93; N, 2.91. Found: $M^{+\bullet}$, 723.9894. $C_{30}H_{26}N_2O_6{}^{106}Pd^{108}Pd$ requires: $M^{+\bullet}$, 723.9862).

1,6-Dipalladated Complexes: (a) Preparation of 36. This was only obtained as a mixture of **32**, **34**, and **36**, as described above.

(b) Preparation of 37. See above for the preparation of a mixture of **33**, **35**, and **37**. Following fractional recrystallization of **35**, further recrystallization by vapor diffusion of pentane into a chloroform solution of the remaining product gave a mixture of **33** and **37**. ^{1}H NMR allowed the identification of the acac complex **37**.

X-ray Crystallography. The crystal data, data collection, and refinement parameters for the X-ray structures are listed in Table 1. Data were collected with a Siemens SMART CCD area detector, using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS[22] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-97.[23] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier atoms. The functions minimized were $\sum w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + aP^2]^{-1}$, where $P = [\max(F_o)^2 + 2F_c^2]/3$.

Table 1. X-ray Crystal Data and Details of Data Collections and Structure Refinements

	27	**35**
formula	$C_{48}H_{42}N_4O_{11}Pd_4$	$C_{32}H_{28}Cl_6N_2O_6Pd_2$
fw	1276.46	962.06
temp (K)	185(2)	168(2)
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	$Fdd2$
a (Å)	12.284(3)	38.876(13)
b (Å)	25.345(6)	12.434(4)
c (Å)	14.741(3)	15.099(5)
β (deg)	92.012(3)	90
V (Å^3)	4587(2)	7299(4)
Z	4	8
D_c (Mg m^{-3})	1.849	1.751
μ (mm^{-1})	1.609	1.470
F(000)	2520	3808
cryst size (mm)	0.67 × 0.19 × 0.19	0.59 × 0.38 × 0.17
θ range (deg)	2.12 to 26.47	2.19 to 26.47
data collected	57 126	22 907
unique data [R_{int}]	9321 [0.0343]	3683 [0.0527]
no. of data obsd [$I > 2\sigma(I)$]	7264	3408
params	608	248
GoF on F^2	1.014	1.014
wR^a(all data)	0.0562	0.0556
R^b[$I > 2\sigma(I)$]	0.0245	0.0242

[a] $wR = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$. [b] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$.

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Supporting Information Available: Details of general instrumentation. Infrared spectra and fully assigned ^{1}H and ^{13}C NMR spectra of all new cyclopalladated compounds. Figure showing the aromatic regions of the ^{1}H NMR spectra of **33**, **35**, and **37**. Details of the X-ray crystal structures of **27** and **35**. This information is available free of charge via the Internet at http://pubs.acs.org.

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