Doubly Cyclometalated Pyridazines: Contrasting Behavior with Palladium and Platinum

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Received May 29, 2001

The cyclometalation of 3,6-diphenylpyridazines with palladium and platinum has been studied. When palladium acetate is used as the metal source, two sequential cyclometalations are observed, with the first cyclometalation deactivating the system toward a second cyclometalation. Both monocyclopalladated and dicyclopalladated species have been isolated and characterized as their acetylacetonate derivatives. When potassium tetrachloroplatinate is used as the metal source, only double cycloplatination is observed: the first cycloplatination activates the system toward a second cycloplatination through a combination of nitrogen coordination and a chloride bridging two platinums. A doubly cycloplatinated compound has been isolated as its triphenylphosphine derivative, which has been fully characterized: the single-crystal X-ray structure shows that the two platinums are bridged by a chloride.

Introduction

Cyclometalation has conventionally involved one ligating group holding a metal center close to a C−H bond and the subsequent closure of the ring via the formation of a carbon to metal bond.[1] While some have adapted this reaction to activate bonds other than C−H (for example, C−Si[2] or C−C bonds[3]), we have been investigating bringing about double cyclometalations with a single metal (generating C∧N∧C tridentate complexes).[4,5] Others have followed Trofimenko's pioneering work of 30 years ago[6,7] using two ligating groups to hold two metal centers close to a single benzene ring, thus forming two metal to carbon bonds on the same aromatic ring. Trofimenko's original work concerned systems where the two metals on the metalated ring are ortho, meta, and para to each other, while we[8] and others[9−12] have largely restricted our investigations to systems where the two metals are opposite (para) across a phenyl ring, though other arrangements have been studied.[13−16] Another variant on the cyclometalation reaction has been to use a central ring incorporating two ligating groups and to use this to bring about two cyclometalations on separate ring systems.[15] It is in this last area that we have recently made considerable progress, and we present the results of those investigations here.

Suitable ligands for bringing about two cyclometalations on adjacent aromatic rings include 2,5-diphenylpyrazines and 3,6-diphenylpyridazines. 3,6-Diphenylpyridazines (**1**) are conveniently prepared by the coupling of 2 equiv of an aryl methyl ketone, as outlined in Scheme 1,[17] and it is these ligands that we concern ourselves with in this paper.

Results and Discussion

Cyclopalladation. Pyridazines **1** react cleanly with 1 equiv of palladium acetate at 60 °C in acetic acid to yield a cyclopalladated species in high yield (Scheme 2). We presume this species is the dimer **2**, as all the characterization (NMR, mass spectrometry, elemental analysis) we have is consistent with this formulation, and an acetate-bridged dimer is a very common feature of similar palladium complexes.[18] We can then react this dimer with sodium acetylacetonate (Na(acac)) to yield the monomeric species **3**. While we lack a single-crystal X-ray structure of **3**, all other data are consistent with this formulation. The proton NMR of **3** is particularly useful, indicating the inequivalence of the two protons in the pyridazine ring, the presence of one metalated

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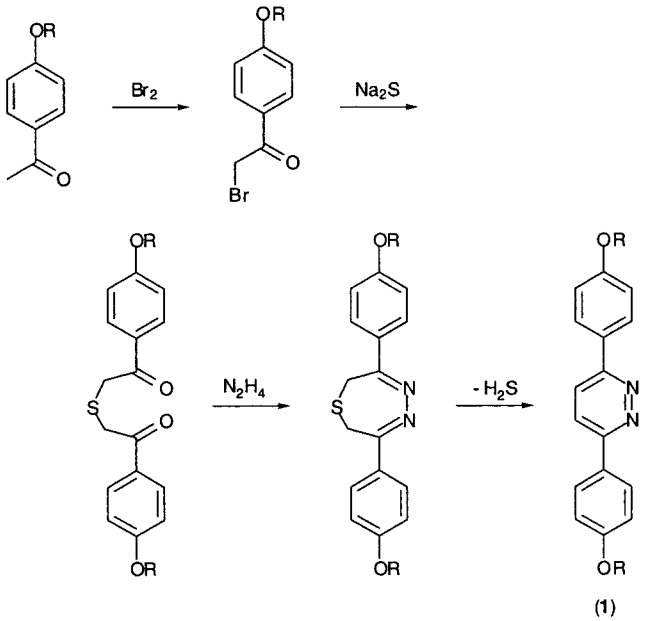
10.1021/om010449g CCC: $20.00
Publication on Web 09/11/2001

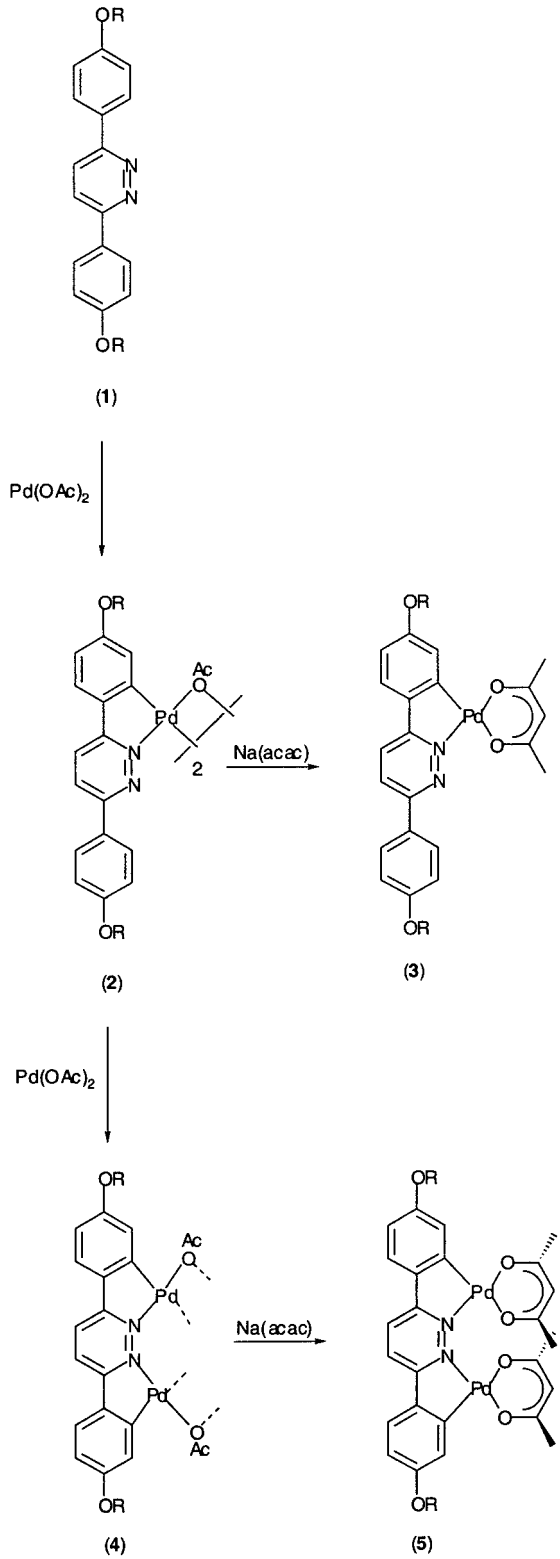
Scheme 1



and one nonmetalated phenyl ring, and one acac per pyridazine core. If we use 2 equiv of palladium acetate (or indeed, react our monometalated species **2** with a second equivalent) and an extended reaction time, we can bring about a second cyclometalation to give a new species (**4**). We have been unable to characterize compound **4** in detail—solution NMR spectra are too broad to interpret—but we believe the compound to be doubly cyclopalladated. Whether **4** is polymeric with bridging acetate groups or, by analogy with other work,[10,19] a simple dimer is of little relevance here. Subsequent reaction of **4** with sodium acac yields a well-characterized compound (**5**) with the formulation depicted in Scheme 2. In particular, the proton NMR of **5** is very informative: the aromatic region shows only four resonances of equal intensity (one singlet for the central pyridazine ring and three multiplets for the metalated ring, one a doublet of 8.5 Hz, one a doublet of 3 Hz, and one a double doublet of 8.5 and 3 Hz), there is a singlet for the central acac proton of the same intensity as the aromatic resonances, and the resonances for the methyl groups of the acacs are 6 times this intensity. While we were unable to grow a crystal of **5** suitable for X-ray diffraction, all other data fit with this formulation.

While we are confident that this is the correct formulation for **5**, it does raise the issue of the arrangement of the acac groups. Simple modeling demonstrates the impossibility of achieving the preferred planar arrangement of the pyridazine core, both cyclometalated rings, and both acac groups—indeed, this is one of the reasons we wanted to make these compounds. Hence, we suggest the helical twist on the structure of **5** shown in Scheme 2. The practical effect of this twist is to reduce the symmetry of the compound, leaving a C_2 axis as the only symmetry element—hence, the molecule must be chiral. It follows that, if these molecules are chiral, we must have a racemic mixture, as no attempt was made to control any stereochemistry in the reaction. The solution state proton and carbon NMRs of **5** do not show any unusual features: the chemical shifts of neither the aromatic nor acac resonances are much different from those in the monocyclopalladated **3**. The only potentially significant feature of the solution NMR is the equivalence of the chemical shifts of the methyl groups of the acac—both ends of the acac resonate as singlets at 2.08 ppm in the proton NMR and at 27.4 ppm in the carbon NMR. This equivalence might at first suggest that the correct structure is one in which the palladiums are tetrahedral (with the acac groups per-

Scheme 2



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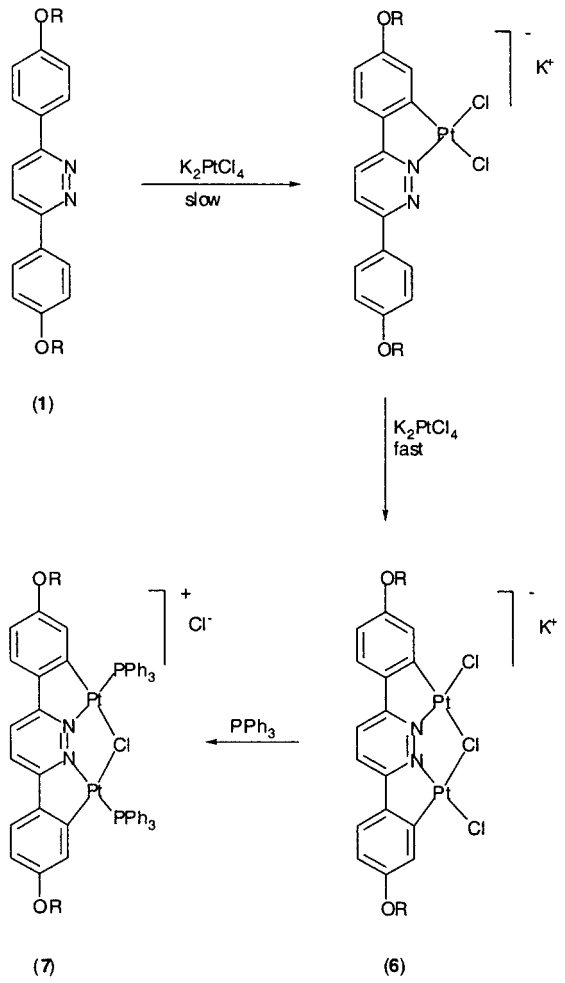
pendicular to the pyridazine core), but this would require the palladiums to be paramagnetic, and the sharp NMR precludes this possibility. Another interpretation of the solution NMR data is that the molecule is fluxional and the ends of the acacs are interchanging rapidly on the NMR time scale, but cooling the sample to −80 °C did not reveal any significant changes in the NMR. Thus, we conclude that there is an accidental equivalence of the methyl groups in the NMR and the structure is indeed the helically twisted one depicted in Scheme 2. Platinum derivatives of diphenylpyridine with a similar sterically imposed helical twist have been isolated in good yields,[20−24] indicating that our proposed structure is not unprecedented. It is not obvious whether the enantiomers of our doubly cyclometalated acac compound will be sufficiently configurationally stable to ever allow their separation.

In any event, the situation we observe with pyridazines and palladium is that a first cyclometalation is facile and a subsequent cyclometalation less so. Whether this is due to the steric hindrance presented by the first metal or an electronic effect due to the nature of the second pyridazine nitrogen has been touched upon,[15] and we will return to this issue later in this paper. One other point to note is the liquid crystallinity of compound **3** (R = Bu), where a smectic A phase was unambiguously identified on the basis of its optical texture when observed through the crossed polarizers of a hot-stage microscope: this aspect of the behavior of compounds **3** will be discussed in a later paper.[25]

Cycloplatination. Pyridazines **1** react cleanly with either 1 or 2 equiv of potassium tetrachloroplatinate in acetic acid to yield a single dimetalated species (leaving unreacted ligand if only 1 equiv of platinum is used). We believe the product to be **6**, as depicted in Scheme 3, since all the data we have are consistent with this formulation. ^{1}H NMR data show the molecule to be symmetric in solution (only four aromatic resonances); elemental analysis and mass spectrometry are consistent with three chlorides, two platinums, and one potassium per pyridazine unit. Cycloplatinated compounds do not react with sodium acetylacetonate in the same way as cyclopalladated compounds; therefore, we were unable to prepare the platinum analogue of the helically twisted compound **5**. However, subsequent reaction of **6** with triphenylphosphine cleanly gave compound **7**, to which we can unambiguously assign the illustrated structure. Solution NMR indicates only one type of phosphine in **7** (the presence of satellites in the ^{31}P NMR clearly showing the phosphine is bound to platinum), and the symmetric nature of the molecule is confirmed by the uncomplicated proton NMR, which is qualitatively similar to that of **6**. Both elemental analysis and mass spectrometry are consistent with the proposed formulation, which was confirmed by the single-crystal X-ray structure.

Scheme 3



Both compounds **6** and **7** are salts, but with a fundamental difference between them. In compound **6** the large organometallic species is the anion with the counterion being potassium, whereas in **7** the large organometallic species is the cation, with the counterion being chloride. This difference manifests itself as very different solubilities for the two compounds: compound **6** is very soluble in acetone but insoluble in chloroform, whereas **7** is insoluble in acetone but readily soluble in chloroform. Acetone is well-known to be able to solubilize smaller cations such as potassium, whereas chloroform is equally well able to solubilize smaller anions such as chloride through hydrogen bonding.

The chloride bridge between the two cyclometalated platinums is clearly a key feature of compounds **6** and **7**. We believe it to be part of the driving force of the second cyclometalation: if we react pyridazine with only 1 equiv of K_2PtCl_4 or use short reaction times, we only isolate unreacted pyridazine and doubly metalated **6**. If we follow the reaction in deuterated acetic acid by NMR, we do not see any indication of the monocyclometalated species that must exist as an intermediate (Scheme 3). One can therefore imagine a second platinum being held in close proximity to the relevant C−H bond by a combination of nitrogen coordination and a chloride bridge and this species reacting faster than free pyridazine. Thus, the first cyclometalation activates the

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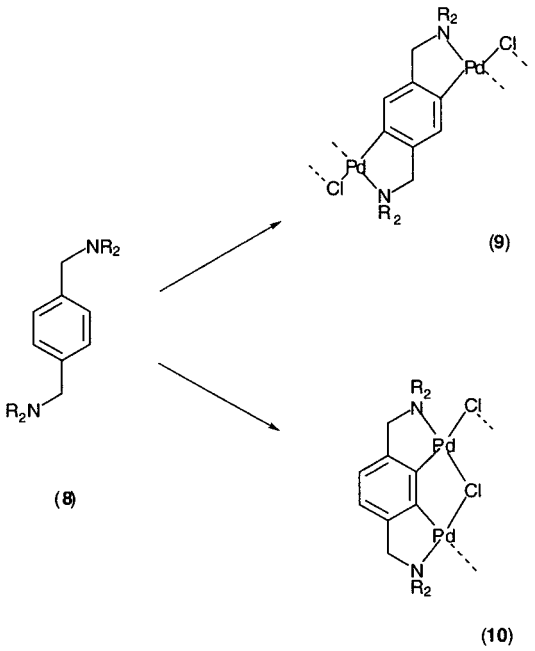
Scheme 4



system to a second cyclometalation, in contrast to that which we ourselves observe with palladium and in complete contrast to all comparable systems reported to date. For example, when Steel attempted to doubly cyclopalladate a pyridazine he was only able to induce a single cyclometalation, with the failure to bring about the second cyclopalladation being ascribed to the steric encumbrance of the second nitrogen donor on the pyridazine.[15]

The activation of a pyridazine system toward a second cyclometalation that we observe has parallels in Trofimenko's original work: diamines **8** could doubly metalate to give either trans isomers **9** or cis isomers **10** (Scheme 4).[7] The driving force for the formation of the sterically more crowded cis isomer must be the presence of the intramolecular chloride bridge. It perhaps should be noted that both we[26] and others[27] have reported systems where a platinum(II) salt brings about a C−H activation without the prior coordination of a ligating group.

NMR Studies. We have attempted to follow the course of both the cyclopalladation and the cycloplatination of pyridazines by NMR. Thus, solutions of pyridazine in deuterated acetic acid were treated with palladium acetate or potassium tetrachloroplatinate and proton NMR spectra recorded at regular intervals. The experiment with palladium acetate at 60 °C proved to be of little use: while the 2 equiv of palladium acetate was soluble in the solvent, as were all products, neither a resonance for the palladium acetate nor any resonances for the acetate of any products could be distinguished (presumably the nondeuterated starting material exchanged acetate groups with vast excess of deuterated acetate groups from the solvent). In addition, the aromatic resonances for the pyridazine quickly disappeared (gone within 2−3 h), to be replaced by a number of broad humps from which no useful information could be inferred. Subsequent workup of the experiment with sodium acetylacetonate showed that both monocyclometalation and dicyclometalation had occurred. The experiment with platinum was slightly more illuminating. The 2 equiv of potassium tetrachloroplatinate used was not soluble in the reaction solvent at 70 °C, and neither was the yellow precipitate of the doubly cycloplatinated **6** that formed (subsequently identified by NMR in acetone after filtration). The only resonances observed were those of the unreacted pyridazine, and at no point did we see any signals in the baseline that might have risen from our postulated intermediate, any other intermediate, or the final product **6**. Thus, we conclude that any intermediate that does form must react on to form **6** more quickly that the starting pyridazine. We did, however, observe a progressive deuteration of the diphenylpyridazine at the 2′-position of the phenyl rings (i.e., the position where the platinum would be attached in a cyclometalated compound). After about 1 day at 70 °C, when approximately one-third of the platinum source appeared to have been consumed, the signal for the 2′-protons of the phenyl rings was down to about half the intensity of the 3′-protons. This clearly indicates the reversible nature of the initial steps of the cycloplatination reaction under the conditions we are using.

Crystal Structure. The single-crystal X-ray structure of the triphenylphosphine platinum compound **7** has been determined. It consists of the diplatinum cation (Figure 1) and chloride anions solvated by chloroform molecules via hydrogen bonds. A certain amount of disorder exists in the solvated anions and in the extended hydrocarbon chains attached to the pyridazine, but the core of the molecule (the three aromatic rings of the diphenylpyridazine, the two platinums, the two triphenylphosphine ligands, and the bridging chloride) is clearly defined.

The coordination geometry of each platinum is a slightly distorted square plane: the N−Pt−C angles are 81.3(4) and 81.4(4)°, the P−Pt−C angles are 96.0(3) and 95.1(3)°, the P−Pt−Cl angles are 91.3(2) and 91.4(2)°, and the Cl−Pt−N angles are 91.9(1) and 92.1(1)°. Each plane is flat to within an rms deviation of 0.1 Å with the two planes inclined at 8.6° to each other. The angle that the two Pt−Cl bonds make at the chloride is 105.39(11)°, very close to tetrahedral. The Pt−Cl bond lengths at 2.388(3) and 2.371(3) Å are slightly longer than those of 2.339(7) and 2.312(6) Å that we have observed in a cycloplatinated diphenylpyridine with two chlorides bridging two platinums, when the chlorides are trans to the pyridine nitrogen, and somewhat shorter than those of 2.468(8) and 2.460(7) Å observed in the same compound when the chlorides are trans to a cyclometalated carbon.[5] The Pt−C distances at 2.027(10) and 2.023(11) Å are not significantly different from the values of 1.98(3) and 1.96(2) Å observed in that same compound. Overall, the backbone of the three aromatic rings of the diphenylpyridazine is bowed toward the two platinums while the whole core of the molecule is kept effectively flat (Figure 2). The phenyl rings in the diphenylpyridazine are undistorted: all the bond lengths are within 0.03 Å of 1.40 Å and all internal angles within 2° of 120°. The pyridazine ring is largely sym-

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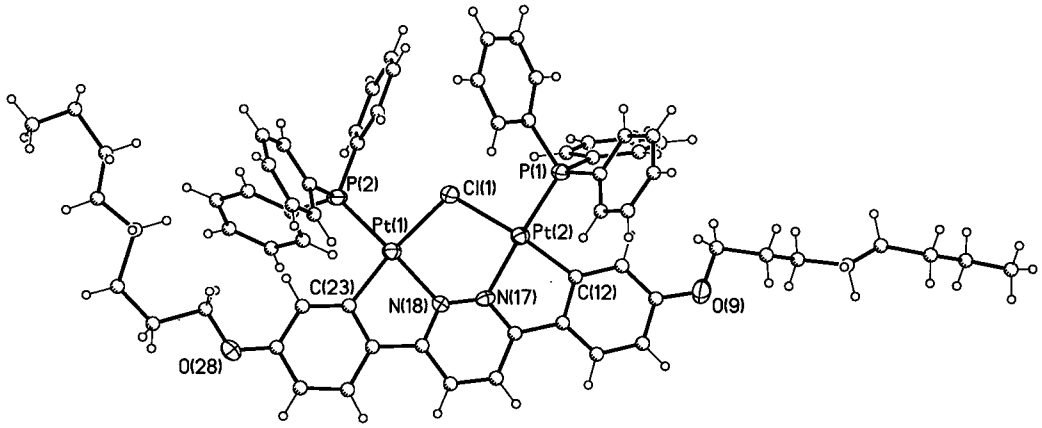

Figure 1. Crystal structure of **7**.

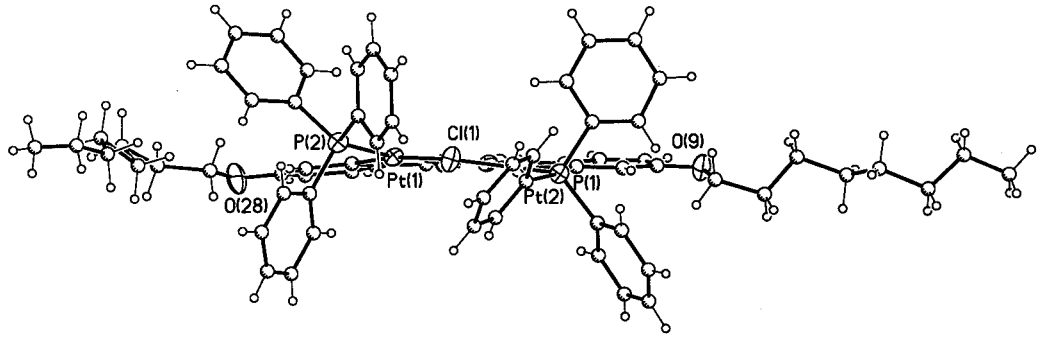

Figure 2. Another view of the crystal structure of **7**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 7

Pt(1)−C(23)	2.027(10)	Pt(2)−N(17)	2.122(8)
Pt(1)−N(18)	2.101(8)	Pt(2)−P(1)	2.249(3)
Pt(1)−P(2)	2.251(3)	Pt(2)−Cl(1)	2.371(3)
Pt(1)−Cl(1)	2.388(3)	N(17)−N(18)	1.314(11)
Pt(2)−C(12)	2.023(11)		
C(23)−Pt(1)−N(18)	81.3(4)	N(17)−Pt(2)−Cl(1)	91.4(2)
C(23)−Pt(1)−P(2)	96.0(3)	P(1)−Pt(2)−Cl(1)	92.11(10)
N(18)−Pt(1)−P(2)	173.1(3)	Pt(2)−Cl(1)−Pt(1)	105.39(11)
C(23)−Pt(1)−Cl(1)	170.3(3)	N(18)−N(17)−C(16)	122.5(9)
N(18)−Pt(1)−Cl(1)	91.3(2)	N(18)−N(17)−Pt(2)	125.1(6)
P(2)−Pt(1)−Cl(1)	91.95(10)	C(16)−N(17)−Pt(2)	112.3(7)
C(12)−Pt(2)−N(17)	81.4(4)	N(17)−N(18)−C(19)	120.8(9)
C(12)−Pt(2)−P(1)	95.1(3)	N(17)−N(18)−Pt(1)	126.1(6)
N(17)−Pt(2)−P(1)	176.5(2)	C(19)−N(18)−Pt(1)	113.0(7)
C(12)−Pt(2)−Cl(1)	170.1(3)		

metric with all internal angles within 1.5° of 120°; bond lengths vary from 1.423(14) Å for the C−C bond opposite the nitrogens through 1.344(12) and 1.342(13) Å for the N−C bonds to 1.314(11) Å for the N−N bond. The phenyl rings of the triphenylphosphine ligands appear to be interleaved with no significant interactions. The chloride counterion is hydrogen-bonded to three chloroform molecules with a linear Cl−H−C arrangement. A pyramidal arrangement of the three chloroforms about the chloride results, with the distance of the chloride to the carbons of the solvating chloroforms being 3.30(1), 3.34(1), and 3.30(1) Å. Selected bond lengths and angles are listed in Table 1, full data are available as Supporting Information.

Conclusions

Palladium acetate and potassium tetrachloroplatinate will both smoothly metalate pyridazines under appropriate conditions and can conveniently be used to bring about two cyclometalations to adjacent phenyl rings. We do, however, observe contrasting behavior with palladium and platinum metal reagents. An initial cyclopalladation deactivates the system toward a second cyclopalladation, an effect we believe to be largely steric in origin. In contrast, an initial cycloplatination activates the system toward a second cycloplatination, so much so in fact that it proved impossible to isolate single cycloplatinated species. We believe this activation to be the results of a combination of nitrogen coordination and the presence of a chloride bridge.

Experimental Section

General Considerations. All chemicals were used as supplied, unless noted otherwise. The pyridazines were synthesized via the published route.[17] All elemental analyses were performed by Warwick Analytical Service.

Preparation of Bis(*μ*-acetato)bis[3,6-bis(4′-(butyloxy)-phenyl)pyridazine]dipalladium (2). Palladium acetate (0.059 g, 2.63×10^{-4} mol) was added to a solution of 3,6-bis(4′-(butyloxy)phenyl) pyridazine (0.100 g, 2.63×10^{-4} mol) in acetic acid (25 mL) and heated (60 °C, 6 h). The solvent removed to yield a yellow solid. Yield 0.142 g (100%, 1.32×10^{-4} mol). ^{1}H NMR (δ_H; 400 MHz, $CDCl_3$): 7.95 (4H, AA′XX′, unmetalated phenyl, ortho to pyridazine), 7.45 (2H, d, $^3J = 8.5$ Hz, pyridazine), 7.05 (2H, d, $^3J = 8.5$ Hz, pyridazine), 7.00 (4H, AA′XX′, unmetalated phenyl, ortho to OCH_2), 6.75 (2H, d, $^3J = 8.5$ Hz, metalated phenyl, meta to Pd), 6.30 (2H, d, $^4J = 2.5$ Hz, metalated phenyl, ortho to Pd), 6.25 (2H, dd, $^3J = 8.5$ Hz, $^4J = 2.5$ Hz, metalated phenyl, para to Pd), 4.00 (8H, t, OCH_2), 2.35 (6H, s, acetate), 1.80 (8H, m, chain), 1.45 (8H, m, chain), 0.95 (12H, m, chain Me).

Preparation of (Acetylacetonate)[3,6-bis(4-(butyloxy)-phenyl)pyridazine)]palladium (3). Sodium acetylacetonate (0.032 g, 2.63×10^{-4} mol) was added to a solution of bis(*μ*-

acetato)bis[3,6-bis(4′-(butyloxy)phenyl)pyridazine]dipalladium (**2**; 0.142 g, 1.32×10^{-4} mol) in acetone (30 mL). The solution was stirred (room temperature, 18 h) and the solvent removed to yield a yellow solid that was purified on a silica column using a 90/10 chloroform/methanol eluent. The solvent was removed to yield a crystalline yellow solid. Yield: 0.111 g (73%, 1.92×10^{-4} mol). Anal. Found (calcd for $C_{29}H_{34}N_2O_4Pd$): C, 63.3 (63.3); H, 6.96 (6.93); N, 3.99 (4.21). ^{1}H NMR (δ_H; 400 MHz, $CDCl_3$): 8.05 (2H, AA′XX′, unmetalated phenyl, ortho to pyridazine), 7.90 (1H, d, $^3J = 9$ Hz, pyridazine), 7.65 (1H, d, $^3J = 9$ Hz, pyridazine), 7.35 (1H, d, $^3J = 8.5$ Hz, metalated phenyl, meta to Pd), 7.25 (1H, d, $^4J = 2.5$ Hz, metalated phenyl, ortho to Pd), 6.95 (2H, AA′XX′, unmetalated phenyl, ortho to OCH_2), 6.65 (1H, dd, $^3J = 8.5$, $^4J = 2.5$ Hz, metalated phenyl, para to Pd), 5.45 (1H, s, central acac), 4.10 (2H, t, $^3J = 6$ Hz, OCH_2), 4.00 (2H, t, $^3J = 6$ Hz, OCH_2), 2.15 (3H, s, acac Me), 2.10 (3H, s, acac Me), 1.75 (4H, m, chain), 1.50 (8H, m, chain), 0.95 (6H, m, chain Me). Melting behavior: crystal → smectic A, 198 °C; smectic A → isotropic, 276 °C. FAB MS (NBA): *m*/*z* 580 (largest, M^+), 481 (M^+ − acac).

Preparation of Bis(*μ*-acetato)[3,6-bis(4′-(butyloxy)phenyl)pyridazine]dipalladium (4). Palladium acetate (0.239 g, 1.06×10^{-3} mol) was added to a solution of 3,6-bis(4-(butyloxy)-phenyl)pyridazine (0.200 g, 5.31×10^{-4} mol) in acetic acid (100 mL). The reaction mixture was stirred (60 °C, 48 h), yielding a dark red-orange solution. The solvent was removed under reduced pressure, the solid dissolved in chloroform, and this solution filtered through Celite to remove traces of palladium black. The chloroform was removed under reduced pressure to yield a dark red solid. Yield: 0.325 g (87%, 4.61×10^{-4} mol). NMR: too broad to interpret.

Preparation of Bis(acetylacetonato)[3,6-bis(4-(butyloxy)phenyl)pyridazine]dipalladium (5). Sodium acetylacetonate (0.112 g, 9.22×10^{-4} mol) was added to a solution of bis(*μ*-acetato)[3,6-bis(4′-butyloxyphenyl)pyridazine]dipalladium (**4**; 0.325 g, 4.61×10^{-4} mol) in THF (125 mL). The solution was stirred (room temperature, 4.5 h) and the solvent removed. The resulting yellow-orange product was washed with hexane (2×10 mL) and diethyl ether (2×10 mL) to yield a yellow solid which was dried under vacuum. Yield: 0.304 g (84%, 3.87×10^{-4} mol). Anal. Found (calcd for $C_{34}H_{40}N_2O_6Pd_2$): C, 51.5 (52.0); H, 4.9 (5.1); N, 3.6 (3.6). ^{1}H NMR (δ_H; 400 MHz, $CDCl_3$): 7.80 (2H, s, pyridazine), 7.25 (2H, d, $^3J = 8.5$ Hz, phenyl, meta to Pd), 7.10 (2H, d, $^4J = 3$ Hz, phenyl, ortho to Pd), 6.65 (2H, dd, $^3J = 8.5$ Hz, $^4J = 3$ Hz, phenyl, para to Pd), 5.35 (2H, s, central acac), 4.00 (4H, t, $^3J = 6$ Hz, OCH_2), 2.08 (12H, s, acac Me), 1.80 (4H, m, chain), 1.30 (8H, m, chain), 0.95 (6H, t, chain Me). ^{13}C NMR (δ_C; 100.6 MHz, $CDCl_3$): 186.5 (acac C−O), 164.2 (phenyl, bonded to pyridazine), 159.4 (phenyl, bonded to OCH_2), 156.8 (pyridazine, bonded to phenyl), 132.8 (phenyl, bonded to Pd), 125.1 (phenyl, meta to Pd, meta to OCH_2), 124.6 (pyridazine), 116.0 (phenyl, ortho to Pd, ortho to OCH_2), 111.8 (phenyl, para to Pd), 99.8 (central acac), 67.8 (OCH_2), 29.3 (chain), 27.4 (acac Me), 22.6 (chain), 14.0 (chain Me).

Preparation of Potassium Trichloro[3,6-bis(4′-(octyloxy)phenyl)pyridazine]diplatinum (6). Potassium tetrachloroplatinate(II) (0.180 g, 4.35×10^{-4} mol) was added to a solution of 3,6-bis(4-(octyloxy)phenyl)pyridazine) (0.100 g, 2.18×10^{-4} mol) in acetic acid (50 mL); the solution was refluxed for 4 days, during which time an orange-brown precipitate formed. The solvent was removed under reduced pressure and the orange product washed with hexane, diethyl ether, and chloroform. The product was then dissolved in acetone and filtered. The solvent was removed under reduced pressure to yield an orange product. Yield: 0.12 g (56%, 1.22×10^{-4} mol). Anal. Found (calcd for $C_{32}H_{42}Cl_3KN_2O_2Pt_2$): C, 37.5 (37.6); H, 4.2 (4.1); N, 2.9 (2.7). ^{1}H NMR (δ_H; 400 MHz, CD_3COCD_3): 8.10 (2H, s, pyridazine ring), 7.58 (2H, d, $^4J = 2.7$ Hz, ^3J(PtH) = 52 Hz, phenyl ring, ortho to Pt), 7.28 (2H, d, $^3J = 9$ Hz, phenyl ring, meta to Pt), 6.52 (2H, dd, $^3J = 9$ Hz, $^4J = 2.7$ Hz, phenyl ring, para to Pt), 3.89 (4H, t, $^3J = 6.4$ Hz, OCH_2), 1.85 (8H, m, chain), 1.25 (16H, m, chain), 0.85 (6H, t, Me). FAB MS (NBA): *m*/*z* 983 (largest, M^+ − K), 1021 (M^+) and 1058 (M^+ + K).

Preparation of Bis(triphenylphosphine)(*μ*-chloro)[3,6-bis(4′-(octyloxy)phenyl)pyridazine]diplatinum Chloride (7). Triphenylphosphine (0.011 g, 4.10×10^{-5} mol) was added to a stirred solution of **6** (0.021 g, 2.05×10^{-5} mol) in acetone (2 mL), and the mixture was stirred for 5 min, whereupon a color change from orange to yellow was observed. The solvent was removed under reduced pressure to yield a yellow solid which was purified by column chromatography using an 80:20 mixture of chloroform and methanol as an eluent. Yield: 0.018 g (82%, 1.68×10^{-5} mol). ^{1}H NMR (δ_H; 400 MHz, $CDCl_3$): 9.05 (2H, s, pyridazine ring), 7.68 (2H, d, $^3J = 8.5$ Hz, metalated ring, meta to Pt), 7.50 (12H, m, PPh_3), 7.35 (6H, tt, PPh_3), 7.28 (12H, m, PPh_3), 6.55 (2H, dd, $^3J = 9$ Hz, $^4J = 3$ Hz, metalated ring, para to Pt), 5.90 (2H, t, $^4J = 3$ Hz, ^4J(PH) = 3 Hz, ^3J(PtH) = 64 Hz, metalated ring, ortho to Pt), 3.80 (4H, t, $^3J = 7$ Hz, OCH_2), 1.25 (4H, m, chain), 1.10 (4H, m, chain), 1.00 (16H, m, chain), 0.80 (6H, t, $^3J = 7$ Hz, methyl). ^{31}P NMR (δ_P; 121.4 MHz, $CDCl_3$): 25.28 ppm (s, ^1J(Pt−P) = 4373 Hz). FAB MS (NBA): *m*/*z* 1436 (M^+ − Cl) and 944 (M^+ − $PtCl_2PPh_3$)

X-ray Crystallographic Study of 7. Crystals suitable for structural analysis were grown from chloroform/ether. An orange prism (dimensions 0.60 × 0.06 × 0.04 mm) was mounted with oil on a thin quartz fiber. Data were collected at 180(2) K using a Siemens SMART CCD area-detector diffractometer. Crystal data for **7**: $C_{68}H_{72}Cl_2O_2N_2Pt_2 \cdot 3.25CHCl_3$, $M_r = 1860.75$, monoclinic, space group $P2_1/c$, $a = 9.8492(5)$ Å, $b = 25.009(1)$ Å, $c = 32.025(2)$ Å, $\beta = 91.263(5)°$, $V = 7886.57(14)$ Å^3, $Z = 4$, D(calcd) = 1.567 Mg/m^3. Refinement was by full-matrix least squares on F^2 for 19 139 reflection positions using SHELXL-96[28] with additional light atoms found by Fourier methods. The asymmetric unit includes three full-occupancy molecules of solvent $CHCl_3$ and one with occupancy estimated at 0.25; the atoms in one of the hydrocarbon chains have very high displacement parameters, probably indicating partial disorder (though it was refined with 100% occupancy); the alternative position lies in the same region as the partial-occupancy solvent, and it could not be fully modeled. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms, apart from the carbon of the partly occupied solvent and the outer atoms of the disordered chain; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H atom is attached. The weighting scheme was calculated using $w = 1/[\sigma^2(F_o^2) + (0.0580P)^2 + 17.000P]$ where $P = (F_o^2 + 2F_c^2)/3$. The goodness of fit on F^2 was 1.016; R1 = 0.0771 for 8813 reflections with $I > 2\sigma(I)$, and wR2 = 0.1741. The number of data/restraints/parameters was 19 139/9/811. The largest difference Fourier peak and hole were 1.103 and −1.308 e Å^{-3}; the only large peaks are in the solvent region and indicate additional disorder that could not be fully modeled. The relatively high R value is to be expected in view of the disorder.

Acknowledgment. We thank Johnson-Matthey for the loan of chemicals.

Supporting Information Available: Tables of positional parameters, bond distances, bond angles, and anisotropic parameters for the structural analysis of **7** as well as crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010449G

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