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C−H Activation Induced by Water. Monocyclometalated to Dicyclometalated: C∧N∧C Tridentate Platinum Complexes

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Metalation of 2,6-diphenylpyridine (**1**) by potassium tetrachloroplatinate in acetic acid gives a monocyclometalated chloride-bridged dimer **4**. This dimer is split with CO to give a kinetic product **9t** with the incoming CO trans to the orthometalated carbon. The kinetic product of cleavage is shown to be 16 kJ mol^{-1} higher in energy than the thermodynamic product **9c**, which has the CO trans to the pyridine nitrogen. The isomerization of **9t** to **9c** is shown not to take place via an associative mechanism and, with analogue **11**, is effectively suppressed when excess chloride is added, implying that it takes place via a chloride dissociation. The monocyclometalated **9** undergoes a second cyclometalation to give the C∧N∧C dicyclometalated complex **15** in high yield. This second cyclometalation is brought about by the simple expedient of adding water to the monocyclometalated precursor. The addition of water is rationalized on the basis of needing to ionize the HCl byproduct of the reaction. Using a substituted pyridine (**5**) analogous chemistry is observed. Single-crystal X-ray structures of one of the intermediates (**6**) and one of the final products (**15**) have been solved. Density functional theory calculations are used to rationalize the isomerizations of the monocyclometalated intermediates and the need to ionize HCl in the second cyclometalation.

Introduction

Cyclometalation, a recent paper begins, “has been so well refined that a new but standard report in this area seems rather ordinary”.[1] Cyclometalation might well have been both widely studied[2,3] and widely used,[4,5] but it is still generating much interest. Our own use of the reaction has been to generate novel cyclopalladated metallomesogens[6−8] and some unusual platinum complexes.[9] Some researchers have returned to the area of double cyclometalation of the same aromatic ring,[7,10−14] as pioneered by Trofimenko[15,16] more than a quarter of a century ago. Another area of research has been the synthesis of tridentate cyclometalated species where two coordinating groups hold a C−H bond close to the metal and this bond is activated. These are relatively common; thus N∧C∧N[17] donor sets,[18,19] P∧C∧P donor sets,[20−23] or S∧C∧S donor sets[24] are well-known. Indeed, some groups have used two ligating groups to induce a C−C[25] or C−Si activation.[26] In addition, the use of a chelating N∧N donor set to yield N∧N∧C tridentate cyclometalated species has been reported.[27]

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[1] Ryabov, A. D.; Panyashkina, I. M.; Polyakov, V. A.; Howard, J. A. K.; Kuz'mina, L. G.; Datt, M. S.; Sacht, C. *Organometallics* **1998**, *17*, 3615.

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[17] The abbreviation N∧C∧N refers to a tridentate ligand bonding through two N donors and one C donor, with the ligand connectivity being N linked to C linked to N. Thus N∧N∧C also represents a tridentate ligand bonding through two N donors and one C donor, but this time the ligand connectivity is N linked to N linked to C.

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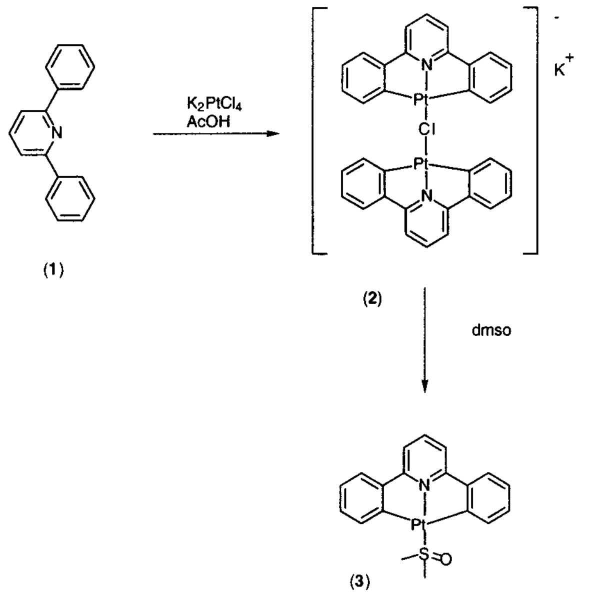
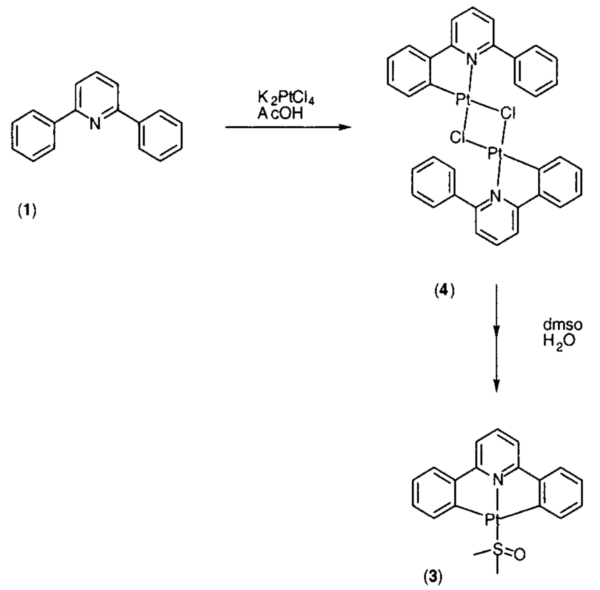
10.1021/om9910423 CCC: $19.00

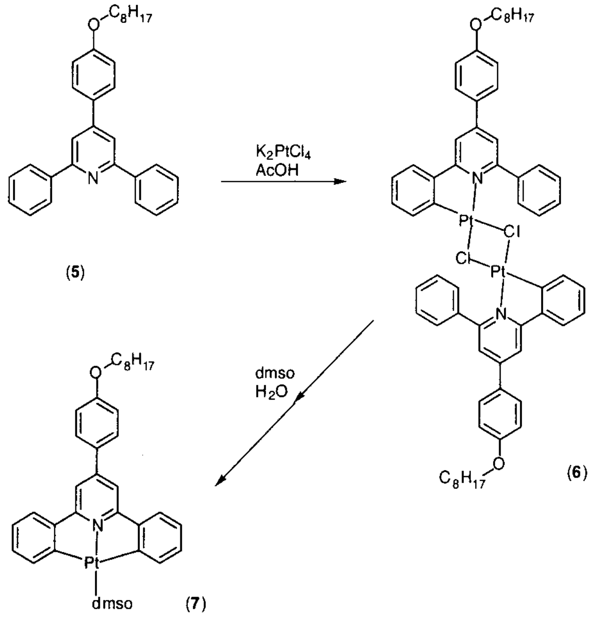
Scheme 1



Scheme 2



Scheme 3



Relatively uncommon are double cyclometalations to give complexes with tridentate C∧N∧C or C∧P∧C donor sets, which arise when two cyclometalated rings have been formed via two C−H activations by the same metal. In a recent paper[28] we reported the first high-yield synthesis of such tridentate C∧N∧C compounds of platinum. Here we present mechanistic details on the crucial second cyclometalation, theoretical studies on the intermediates, and suggestions as to how to generalize the reaction.

Results and Discussion

Monocyclometalated Species: Cis and Trans Intermediates. In our earlier paper[28] we reported that the reaction of potassium tetrachloroplatinate with diphenylpyridine in acetic acid gave a complex we tentatively formulated as **2** in essentially quantitative yield (Scheme 1). While we could get no solution data on **2**, solid-state characterization was consistent with this formulation. On dissolution in hot dimethyl sulfoxide (dmso), followed by precipitation with water, **2** gave dmso complex **3**, which was fully characterized (NMR, elemental analysis, single-crystal X-ray diffraction). Our new data conclusively proves that **2** is not the correct formulation, that the intermediate we isolate is actually only the monocyclometalated chloride bridged dimer **4**, and that the dissolution in dmso followed by precipitation with water is inducing the second cyclometalation to give complex **3** (Scheme 2).

Monometalated halide bridged dimers of type **4** are well-known, and with suitable pyridines, they may be fully characterized. Thus we have used the 4-substituted pyridine **5** and reacted this to form chloride-bridged dimer **6** via a literature route (Scheme 3).[29] Compound **6** is soluble in common organic solvents, unlike **4**, and has been well characterized, including the solving of the single-crystal X-ray structure (Figure 1). Using the same conditions as we used in the isolation of doubly cyclometalated **3** (dissolution in hot dmso, precipitation with water) we can bring about a second cyclometalation to give analogue **7** (Scheme 3), which we use as a convenient source of the C∧N∧C tridentate Pt moiety (dmso can be readily displaced).

In addition to this indirect evidence for the formulation of **4** as a chloride-bridged dimer, we now have definitive solution NMR data on **4**. By using deuterated dmf we can clearly see 10 different signals, with appropriate couplings, corresponding to the 12 protons expected for a compound such as **4** (Figure 2). Our earlier assignment of the structure as **2** had been on the basis of elemental analysis, MALDI mass spectrometry, and proton NMR. However, the elemental analysis fits either formulation **2** or **4**, and the peak in MALDI mass spectrum at $m/z = 39$ (which we assigned to K^+) could just as well have come from contamination such as a fingerprint. Our previous attempts to run the NMR

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(29) Ceder, R. M.; Sales, J. *J. Organomet. Chem.* **1985**, *294*, 389.

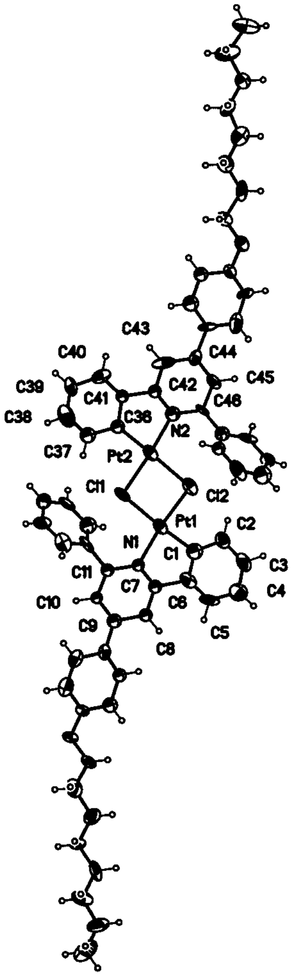


Figure 1. Crystal structure of **6** (50% thermal ellipsoids).

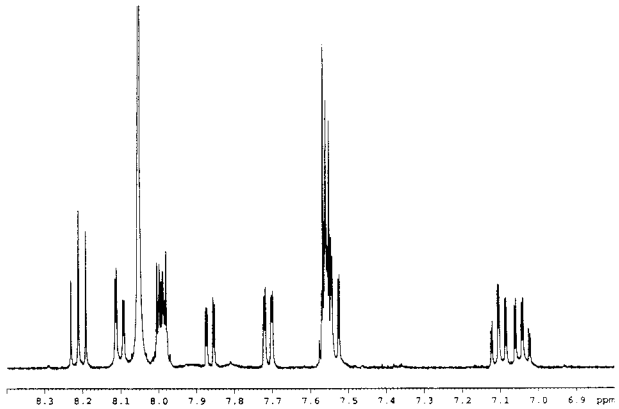
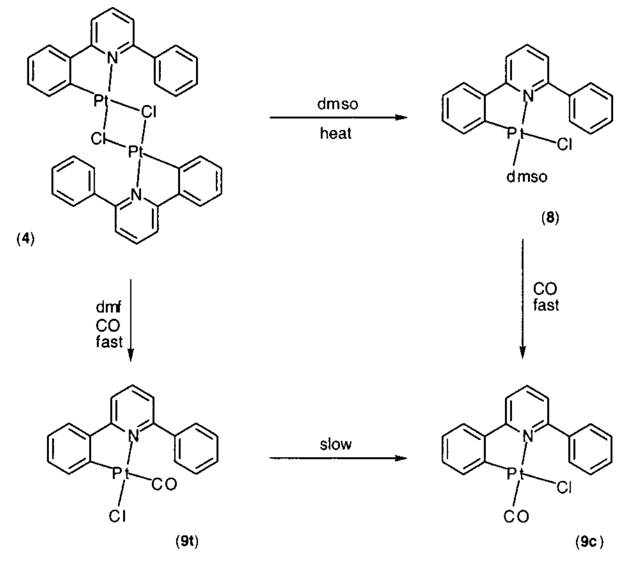


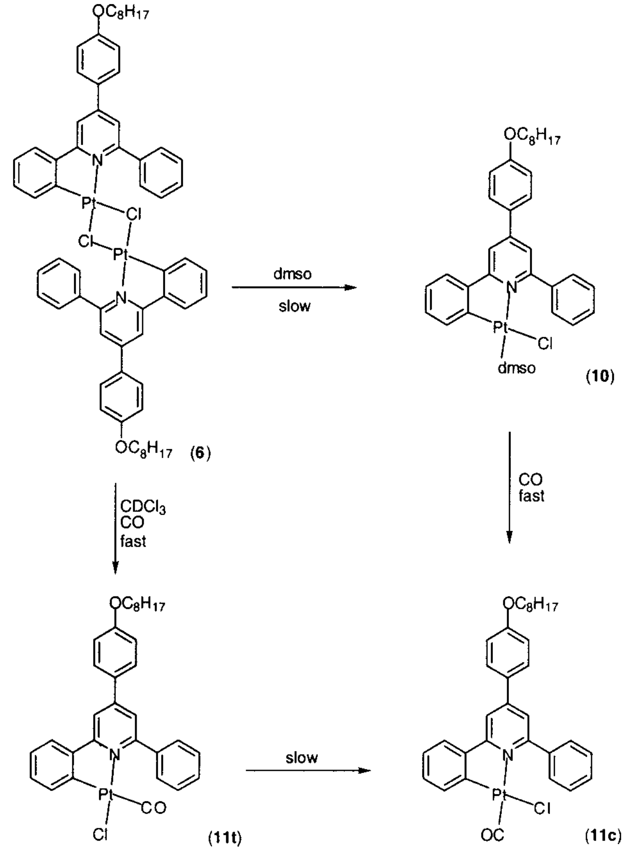
Figure 2. ^{1}H NMR spectrum of **4** in dmf.

of **4** in dmso were hampered by the reaction of **4** with the dmso to give **3**. We have now ascertained that, by using dry dmso and a minimum of heat to assist dissolution, an NMR spectrum, relatively uncontaminated by **3**, can be obtained in dmso. One crucial difference between this spectrum and that of **4** in dmf is the presence of a dmso coordinated to platinum (Pt satellites on the signal), implying that the dmso has split the dimer to give the dmso complex **8** (Scheme 4). Similar behavior is observed when dimer **6** is dissolved in $CDCl_3$ and dmso is added (Scheme 5). The cleavage of **6** to give dmso complex **10** is relatively slow at room temperature (taking about an hour to go to completion).

Scheme 4



Scheme 5



The coordinated dmso molecules in **8** and **10** have similar spectroscopic properties: the chemical shift of the dmso protons in $CDCl_3$ are 3.44 and 3.43 ppm, respectively (both with $^3J(\text{Pt}-\text{H}) = 23$ Hz). These are comparable with the 26 Hz couplings observed in the C∧N∧C compounds **3** and **7**, implying that the dmso is trans to the pyridine: we would expect these values to be on the order of 15 Hz if the dmso were cis to the N (and therefore trans to a C).[30,31] On this basis, together with the modeling studies and the information we can

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(30) Eaborn, C.; Kundu, K.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1981**, 933.

infer from carbonyl complexes **9** and **11** we have assigned the geometry as that with the dmso trans to the pyridine N (thus the chloride is cis to the N). No spectroscopic evidence for the formation of more than one isomer of either of the dmso complexes **8** or **10** was observed by NMR or IR, even when the cleavage was performed at −40 °C.

Different behavior is observed when CO is used as a ligand. If a dmf solution of chloride-bridged dimer **4** is exposed to CO gas, the color of the solution changes rapidly (<5 s) to a much paler yellow, the NMR spectrum changes significantly (but maintains the same number of signals, with the same coupling patterns), and an IR stretching band appears at 2088 cm^{-1}, indicating the formation of a compound consistent with the formulation **9t** (Scheme 4). Compound **9t** isomerizes to another compound, consistent with the formulation **9c** (Scheme 4). This isomerization is very clear by NMR, where signals move by up to 0.8 ppm, but less obvious by IR, where a difference of only 6 cm^{-1} is observed. The isomerization of **9t** to **9c** is apparent after 30 min at room temperature, halfway after 2.5 h, and complete after 15 h. Addition of CO gas to a solution of **8** results in the rapid formation of **9c**: as soon as the spectrum could be run (less than 2 min later), only peaks corresponding to **9c** were seen in the NMR.

Similar behavior is seen when we start with dimer **6**: the reaction of **6** to give **11t** in $CDCl_3$ is very fast, being complete as soon it was possible to obtain an NMR, and the isomerization of **11t** to **11c** in chloroform is obvious by NMR (halfway by about 3 h and complete in less than 16 h) (Scheme 5). The isomerization of **11t** to **11c**, and that of **9t** to **9c**, occurs with solutions that have been purged with nitrogen. Together with the independence of the isomerization rate upon concentration, and the observation of isomerization in CD_2Cl_2 (no HCl present) at a rate similar to that observed in $CDCl_3$ (potential contamination with traces of HCl), we can rule out the associative ligand exchange type of reaction that can occur with platinum being responsible for the isomerization.[32,33] This leaves a dissociative mechanism as the likely route.[34,35] Addition of 4 equivalents of tetrabutylammonim chloride to a chloroform solution of **11t** effectively suppressed the isomerization to **11c**, implying that chloride dissociation is responsible for the isomerization process. Dissolution of dimer **6** in $CDCl_3$, followed by addition of dmso, indicates that the cleavage of **6** to give **10** is relatively slow (taking about an hour to go to completion at room temperature), but the reaction of **10** to give **11c** is very fast, being complete as soon as it was possible to obtain an NMR (less than 2 min later). The slow rate of cleavage by dmso could be due to the sterically larger dmso molecule finding it more difficult to approach the platinum, or it could be due to the dmso complex being less thermodynamically stable than the CO complex, or indeed a combination of both factors.

Conventional arguments based on trans effects would suggest that each of the compounds **8**, **9**, **10**, or **11**, formed by dimer cleavage, should form with the ligand coming in trans to the C and cis to the N (indeed, in the crystal structure of **6** it is very clear that this Pt−Cl bond is significantly longer than the other one).[36] This is what we believe we observe when we use the mild conditions of a CO atmosphere with a room-temperature solution of the chloride-bridged dimers **4** and **6** to form **9t** and **11t**. (Quite how large this trans effect is in cyclometalated complexes has been the subject of some debate recently,[32,37−39] and we do not propose to discuss it further here.) However, it is apparent from our modeling studies (see later) that these isomers (the kinetic products) with the CO cis to the N are unfavorable with respect to those with the chloride cis to the N (the thermodynamic products). Thus we would expect **9t** and **11t** to isomerize to **9c** and **11c**, respectively. When we use dmso as the ligand, we might expect the energy difference between the isomers of **8** and **10** to be even greater than in the analogous CO complexes. Thus the fact that we do not observe the isomer with the dmso cis to the N could be due to the very unfavorable nature of this isomer with respect to the other: as soon as any formed, it could be expected to isomerize and therefore would not be observed by NMR. (Additionally, since the dmso would be less strongly bound than the CO, it would also find it easier to isomerize via a dissociative mechanism.) Alternatively, the steric constraints posed by the noncyclometalated phenyl ring could render bridge cleavage trans to the C so energetically unfavorable that none is ever formed. In any event, once the geometry in **8** and **10** is established with the chloride cis to the N, displacement of dmso with CO gas gives compounds **9c** and **11c** exclusively.

Similar compounds have been reported: thus when the cyclometalated phenyl pyridine compound **12** is reacted with either more phenyl pyridine or CO, the only complexes isolated have the new ligand trans to the N (Scheme 6), evidence being in the form of crystal structures of **13** and **14**.[40]

Dicyclometalation. The reactions of dmso complex **8** to give doubly cyclometalated **3** and of **10** to give **7** are quantitative. The reactions progress slowly in dry dmso at room temperature, but can be brought to completion in less than 5 min by adding water or base (solid Na_2CO_3) to a hot dmso solution of the appropriate starting material (Scheme 7). The reactions of carbonyl compounds **9** to form **15** and of **11** to form **16** also proceed in high yield, in either dmf or dmso solution (Scheme 7). Doubly cyclometalated compound **15** has been fully characterized: the ^1H NMR spectrum is shown (Figure 3), as is the single-crystal X-ray structure (Figure 4). It should be noted that the reactions of **9** and **11** to form **15** and **16** do not need a CO atmosphere.

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[33] Schmülling, M.; Grove, D. M.; van Koten, G.; van Eldik, R.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 1384.

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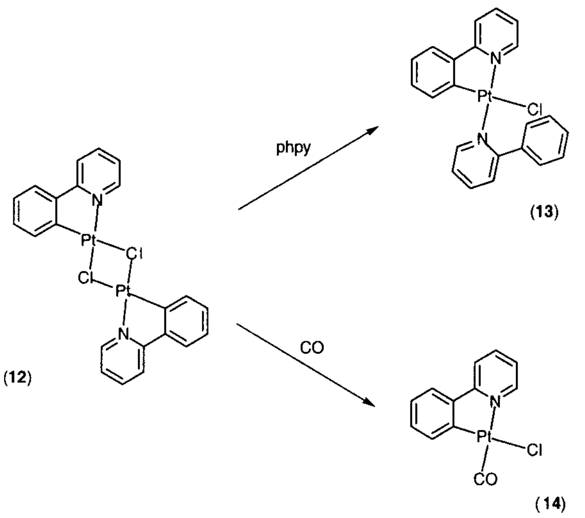
[38] Schmülling, M.; Ryabov, A. D.; van Eldik, R. *J. Chem. Soc., Dalton Trans.* **1996**, 1472.

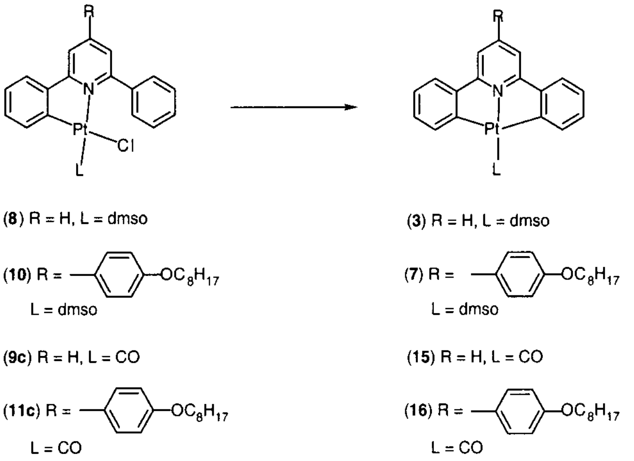
[39] Wendt, O. F.; Oskarsson, Å.; Leipoldt, J. G.; Elding, L. I. *Inorg. Chem.* **1997**, *36*, 4514.

[40] Mdleleni, M. M.; Bridgewater, J. S.; Watts, R. J.; Ford, P. C. *Inorg. Chem.* **1995**, *34*, 2334.

Scheme 6



Scheme 7



Indeed a CO atmosphere results in reduction of some of the species; hence these reactions are purged of CO with either nitrogen or argon.

The question of which isomer of **9** and **11** is reacting arises. The reaction of **9c** to give doubly cyclometalated **15** in dmso is complete in about 3 h at room temperature, but is speeded up dramatically by the addition of base (if solid Na_2CO_3 is added, the reaction is complete in less than 15 min) or by the application of heat (reaction is complete after 20 min at 100 °C). The reaction of **9t** in dmf gives **15** on a similar time scale; again heating and the addition of base increase the rate of reaction. However, since **9t** is isomerising to **9c**, it is impossible to definitively say whether it is **9t** or **9c** that is reacting to form **15**. We know that the isomerization reaction of **11t** to **11c** in $CDCl_3$ is much faster than the reaction of **11c** to give **16** in $CDCl_3$, which appears to be very slow (no observable reaction after one week). Since we can then react pure **11c** to give **16** (by adding base) at a rate comparable to that of mixed isomers of **11**, we would suggest that it is indeed the isomers **9c** and **11c** that react to give **15** and **16**.

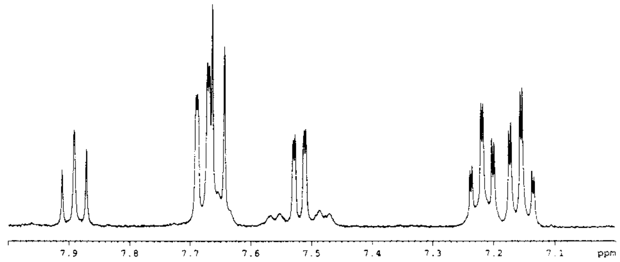


Figure 3. ^{1}H NMR spectrum of **15** in dmso.

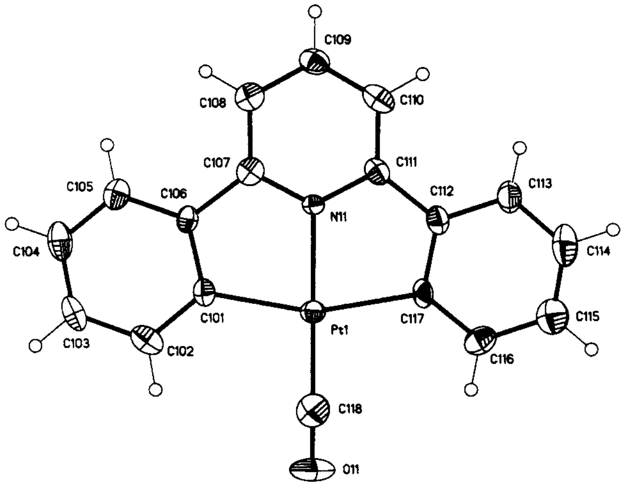


Figure 4. Crystal structure of **15** (50% thermal ellipsoids).

The rate of the second cyclometalation is clearly dependent on solvent and the presence of water and base. There is no observable reaction of **11c** to give C∧N∧C **16** in the nonpolar chloroform, but a relatively fast reaction in the polar solvents dmf and dmso. With all these solvents an increase in the reaction rate is observed with the addition of water and/or base. A dependence of the rate of cycloplatination on solvent has been observed before: when *cis*-$PtCl_2(dmso)_2$ is reacted with tertiary ferrocenylamines in chloroform or acetone, a simple ligand substitution reaction is observed, whereas heating in methanol or water results in high yields of the cycloplatinated product.[41] In this instance a possible reaction route involving the dissociation of chloride was invoked, in contrast to reactions where a formal oxidative addition takes place.[42] Our modeling studies (see later) indicate that a possible driving force for the cycloplatination is the elimination of HCl, which, crucially in our case, must subsequently be ionized. This need for the HCl to be ionized fits with our experimentally observed reaction rates and in particular the dependence on the presence of water.

The rate of reaction of dmso complex **8** to **3** is significantly slower than the rate of reaction of carbonyl **9** to **15** under identical conditions (including using the same batch of dmso as solvent): the first reaction took 5 days to go to completion, whereas the second one took 14 h. Such a variation provides evidence to suggest that the second cyclometalation takes place via an electrophilic attack by the platinum: we would expect the CO ligand to be acting as a much better acceptor than dmso, giving rise to a reduced electron density on the Pt. The dissociation of chloride prior to an electrophilic type mechanism has been postulated[41,43] and would seem to be likely in our case, given our analogous dependence

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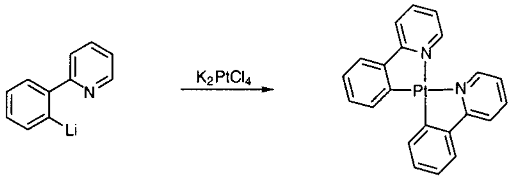
(41) Ranatunge-Bandarage, P. R. R.; Robinson, B. H.; Simpson, J. *Organometallics* **1994**, *13*, 500.

(42) Harper, T. G. P.; Desrosiers, P. J.; Flood, T. C. *Organometallics* **1990**, *9*, 2523.

(43) Bednarski, P. J.; Ehrensperger, E.; Schönenberger, H.; Burgemeister, T. *Inorg. Chem.* **1991**, *30*, 3015.

Scheme 8



(17) (18)

of reaction rate on solvent. Addition of AgBF$_4$ to a solution of **11c** in acetone under conditions that have been used to induce cyclometalations[44] results in the rapid formation of C∧N∧C **16** in good yield, providing further evidence for the elimination of HCl being a driving force for the reaction.

That our second cyclometalation requires different conditions from the first is evident, unlike other examples.[45] Whether our second cyclometalation takes place via a mechanistically different reaction route is less clear. Our first cyclometalation occurs in high yields in acetic acid under conditions that parallel those reported in the synthesis of chloride-bridged dimer **12** (Scheme 2).[40] Prolonged reaction times under these conditions do not result in a second cyclometalation, even when we use 2 equiv of 2-phenylpyridine, where we might have expected to make **18**.[46] The only reported conditions for the synthesis of compounds such as **18** entail the use of 2 equiv of lithiated phenyl pyridine (Scheme 8),[47] and while this method has been used successfully with a variety of pyridine derivatives,[48−51] it resulted in only very poor yields of **3** from **1** (due to the nonregiospecific nature of the second lithiation).[52] Thus it appears that the different reaction conditions that we need for the first and second cyclometalations in the synthesis of compounds such as **3** cannot be attributed to steric crowding or unfavorable distortions within the C∧N∧C platinum moiety: they must be due to either the changed properties of the metal affecting the rate of reaction substantially or the changed nature of the metal, requiring a mechanistically different reaction route. Since we also know that a first cyclometalation will not occur under the conditions required for the second one, this would suggest that the two cyclometalations have different mechanisms. Even though we are presenting evidence here that our second cyclometalation arises through electrophilic attack by platinum, the mechanism of our first cyclometalation is unknown,[2,53] and thus we cannot say for certain that the two metalations take place via mechanistically different routes.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in the Crystal Structure of 6

Pt(1)−C(1)	1.98(3)	Pt(2)−Cl(2)	2.468(8)
Pt(1)−N(1)	2.078(18)	N(1)−C(7)	1.26(3)
Pt(1)−Cl(2)	2.339(7)	N(2)−C(42)	1.32(3)
Pt(1)−Cl(1)	2.460(7)	C(1)−C(6)	1.38(3)
Pt(2)−C(36)	1.96(2)	C(6)−C(7)	1.53(3)
Pt(2)−N(2)	2.07(2)	C(36)−C(41)	1.42(3)
Pt(2)−Cl(1)	2.312(6)	C(41)−C(42)	1.50(3)
C(1)−Pt(1)−N(1)	80.7(10)	Pt(2)−Cl(1)−Pt(1)	99.1(2)
C(1)−Pt(1)−Cl(2)	93.5(9)	C(7)−N(1)−C(11)	119(2)
N(1)−Pt(1)−Cl(2)	173.5(6)	C(7)−N(1)−Pt(1)	113.2(17)
C(1)−Pt(1)−Cl(1)	171.0(9)	C(11)−N(1)−Pt(1)	127.3(15)
N(1)−Pt(1)−Cl(1)	104.4(5)	C(42)−N(2)−C(46)	121(2)
Cl(2)−Pt(1)−Cl(1)	80.9(2)	C(42)−N(2)−Pt(2)	111.9(16)
C(36)−Pt(2)−N(2)	78.9(9)	C(46)−N(2)−Pt(2)	126.1(17)
C(36)−Pt(2)−Cl(1)	97.0(7)	C(6)−C(1)−Pt(1)	116(2)
N(2)−Pt(2)−Cl(1)	174.8(7)	C(1)−C(6)−C(7)	111(3)
C(36)−Pt(2)−Cl(2)	175.4(8)	N(1)−C(7)−C(6)	117(2)
N(2)−Pt(2)−Cl(2)	102.6(6)	C(41)−C(36)−Pt(2)	119.0(17)
Cl(1)−Pt(2)−Cl(2)	81.2(2)	C(36)−C(41)−C(42)	108(2)
Pt(1)−Cl(2)−Pt(2)	98.2(2)	N(2)−C(42)−C(41)	118(2)

Table 2. Selected Bond Lengths (Å) and Angles (deg) in the Crystal Structure of 15

	$n = 1$	$n = 2$
Pt(n)−C(n)18	1.864(11)	1.837(10)
Pt(n)−N(n)1	2.027(7)	2.003(7)
Pt(n)−C(n)01	2.057(9)	2.084(9)
Pt(n)−C(n)17	2.083(8)	2.084(10)
N(n)1−C(n)07	1.329(10)	1.370(10)
N(n)1−C(n)11	1.352(10)	1.361(11)
C(n)01−C(n)06	1.409(12)	1.401(13)
C(n)06−C(n)07	1.491(11)	1.446(13)
C(n)07−C(n)08	1.407(13)	1.419(13)
C(n)08−C(n)09	1.384(12)	1.383(13)
C(n)09−C(n)10	1.381(13)	1.359(12)
C(n)10−C(n)11	1.375(13)	1.398(12)
C(n)11−C(n)12	1.459(13)	1.453(11)
C(n)12−C(n)17	1.421(12)	1.395(12)
C(n)18−Pt(n)−N(n)1	179.4(4)	179.5(4)
C(n)18−Pt(n)−C(n)01	100.4(4)	99.7(4)
N(n)1−Pt(n)−C(n)01	80.2(3)	80.0(3)
C(n)18−Pt(n)−C(n)17	99.4(4)	100.2(4)
N(n)1−Pt(n)−C(n)17	80.0(3)	80.1(3)
C(n)01−Pt(n)−C(n)17	160.2(4)	160.0(4)
C(n)07−N(n)1−C(n)11	124.0(8)	123.5(8)
C(n)07−N(n)1−Pt(n)	117.6(6)	118.5(5)
C(n)11−N(n)1−Pt(n)	118.3(6)	117.9(6)
C(n)06−C(n)01−Pt(n)	113.0(6)	111.6(7)
C(n)01−C(n)06−C(n)07	114.9(8)	116.7(8)
N(n)1−C(n)07−C(n)06	114.2(8)	113.6(8)
N(n)1−C(n)11−C(n)12	112.9(8)	112.1(8)
C(n)17−C(n)12−C(n)11	117.6(7)	118.2(8)
C(n)12−C(n)17−Pt(n)	111.1(6)	111.0(6)

Theoretical Studies. We have performed density functional theory (DFT) calculations on compounds **9c**, **9t**, and **15**, to arrive at relative ground-state energies. A series of unconstrained geometry optimizations were carried out for the C∧N∧C complex **15** to determine the optimal combination of Pt frozen core size and functional. Both Pt[4f] and Pt[5p] were considered in conjunction with the Becke/Perdew (BP) gradient-corrected functional or the local density approximation (LDA). Scalar relativistic corrections were included throughout.

The optimized Pt−L distances are shown in Table 3. The effect of the frozen core and functional on the Pt−CO distance is minimal, but there are significant variations in the calculated Pt−C and Pt−N distances. With the ADF program, the best combination is the simple LDA and the larger Pt frozen core. This result parallels our previous findings[54] inasmuch as the LDA-optimized metal−ligand distances are in better agreement with experiment than those obtained from a

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Table 3. Selected Bond Lengths (Å) in the Structure of 15

method	Pt−CO	Pt−C	Pt−N
Pt[4f]/BP	1.85	2.00	1.95
Pt[5p]/BP	1.88	2.12	2.07
Pt[5p]/LDA	1.86	2.09	2.04
experiment	1.864	2.070	2.027

gradient-corrected functional. However, we have also demonstrated that the LDA gives poorer energies.[55] Thus, the optimal theoretical methodology for the present systems is to optimize the structure at the LDA/Pt[5p] level and to compute the total binding energy at this geometry using the BP functional.

The optimized structures of **9c** and **9t** are shown in Figure 5. In both cases, the uncoordinated phenyl ring is not perpendicular to the coordination plane. The steric interactions between this group and the ligand directed toward it cause the phenyl ring to rotate and the Pt coordination geometry to distort away from strict planarity. The calculated binding energies show that **9c** is 16 kJ mol^{-1} lower in energy than **9t**. This energy difference allows us to rationalize **9t** as the kinetic product and **9c** as the thermodynamic product in Scheme 4 and is in agreement with the experimentally observed isomerization of **9t** to **9c**. We expect the energy difference between **11c** and **11t** to be similar in magnitude and, hence, would expect that **11t** is the kinetic product and **11c** the thermodynamic product in Scheme 5.

The same calculations indicate that **15** is 68 kJ mol^{-1} higher in energy than **9c**, implying that the reactions in Scheme 7 are endothermic. However, it must be noted that the calculations assume that the other product of the reaction (HCl) is free and not solvated or ionized. The ionization of HCl in water is known to be exothermic by 74.8 kJ mol^{-1}, with the neutralization of the liberated proton generating a further 55.8 kJ mol^{-1}.[56] These quantities of energy are more than sufficient to drive the reaction. This result ties in with our experimentally observed dependence of the rate of reaction on solvent polarity: **11c** does not react to form **16** in $CDCl_3$ unless water and/or base is present, and the reactions of **9c** to **15** in either dmf or dmso are speeded up dramatically by the addition of water or base.

Crystal Structures. The single-crystal X-ray structure of dimer **6** and C∧N∧C **15** were solved (Figures 1 and 4). The structure of **6** has a central core consisting of a Pt_2Cl_2 rectangle, with Cl−Pt−Cl angles of 81.2(2)° and 80.9(2)° and Pt−Cl−Pt angles of 99.1(2)° and 98.2(2)°. Within this rectangle the Pt−Cl bonds are 2.460(7) and 2.468(8) Å for the chlorines trans to the cyclometalated carbon and 2.312(6) and 2.339(7) Å for the chlorines trans to the pyridine N. This difference is to be expected on the basis of the relative trans effects of C and N. Of particular interest is the five-membered cyclometalated ring: here there are Pt−N distances of 2.078(18) and 2.07(2) Å, Pt−C distances of 1.96(2) and 1.98(3) Å, and an N−Pt−C angle of 80.7(10)° and 78.9(9)°. Bond lengths and angles of this order are comparable to those observed in the crystal structure of **13**.[40] There are no significant intermolecular interactions in the structure of **6**, and all other bond lengths and angles are normal: selected bond lengths and angles are listed in Table 1.

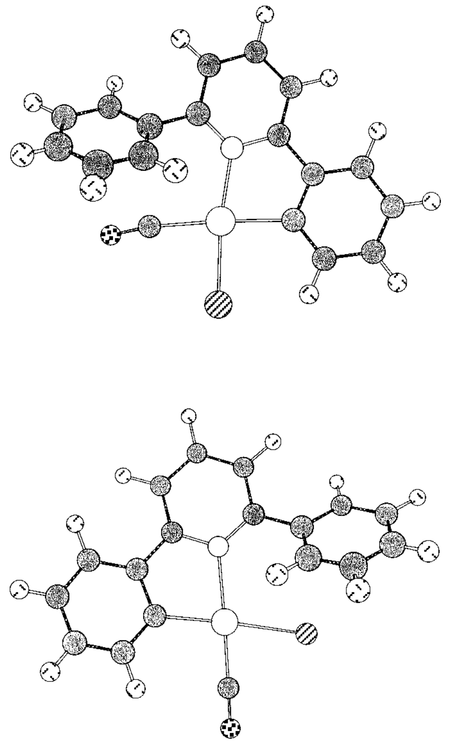

Figure 5. Optimized structures of **9t** and **9c**.

The structure of **15** has two essentially identical molecules in the asymmetric unit. These molecules are flat, with an rms deviation from the plane of 0.0368 and 0.0499 Å, and are inclined at 1.87(8)° to each other with no significant interactions between them. Selected bond lengths and angles are listed in Table 2. The two five-membered cyclometalated rings, fused along the Pt−N bond, have bond lengths similar to those observed in the monocyclometalated compounds **6** and **13**. A significant difference is observed in the angles at the pyridine nitrogen: these are 117.6(6)°, 118.5(5)°, 118.3(6)°, and 117.9(6)° inside the cyclometalated rings and 124.0(8)° and 123.5(8)° inside the pyridine. Thus, whereas in the monocyclometalated compounds **6** and **13** the pyridine ring has been distorted by the cyclometalation with the pyridine being "pulled over" by the five-membered ring, in the dicyclometalated compound **15** the ring has been "pulled" back to a more symmetrical arrangement. All the bond lengths and angles observed in the structure of **15** are similar to those seen in the X-ray structure of **3**.[28] It is salient to note that in both cases it is the more flexible six-membered pyridine ring, rather than the five-membered metalated ring, that is distorted the most. This type of distortion has been noted previously in N∧N∧C complexes of Pd and Pt.[27,57,58]

Conclusions

We have shown that the monocycloplatinated chloride-bridged dimers of diphenylpyridines can be reacted to

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form dicycloplatinated C∧N∧C complexes if they are first cleaved by ligands to give monomeric species. When CO is used as a ligand, the monomeric species formed is a kinetic product with the incoming CO cis to the pyridine N, and this then isomerizes so that the CO is trans to the N. Modeling studies show that the isomer with the CO cis to the N is 16 kJ mol^{-1} less stable than the isomer with the CO trans to the N, fitting in with our observed isomerization. We have ruled out an associative mechanism for this isomerization and have evidence that suggests chloride dissociation is implicated in the isomerization process. When dmso is used to split the dimers, the only product observed is the thermodynamic product with the dmso trans to the N.

The reaction of monocycloplatinated complexes to form the dicycloplatinated complexes is very dependent on solvent and the presence of water and base. Our modeling studies indicate that with the simple 2,6-diphenylpyridine the reaction is endothermic unless the HCl byproduct is ionized. This leads to the situation whereby the second cyclometalation can be induced by the simple expedient of adding water. The dependence of the rate of reaction of the second cyclometalation on solvent and ligand also indicates that it is taking place via an electrophilic attack by platinum on the aromatic ring, in contrast to the first cyclometalation, where the mechanism is unclear. However, we are confident the very different conditions required for the two cyclometalations indicate two mechanistically different steps. Thus we would suggest that other workers trying to synthesize analogous complexes should treat the two cyclometalation steps separately and adjust their conditions accordingly.

Experimental Section

General Considerations. All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on either a Bruker Avance 300 or Avance 400 and are referenced to external TMS, assignments being made with the use of decoupling and the DEPT, COSY, and GOESY pulse sequences. All elemental analyses were performed by Warwick Analytical Service. 2,6-Diphenylpyridine was used as supplied (Lancaster), and 4-(4-octyloxyphenyl)-2,6-diphenylpyridine synthesized via a standard Kröhnke route.[59]

Synthesis of [(2,6-diphpy)Pt(dmso)] (3). The yellow (2,6-diphpyPtCl)$_2$ produced below (407 mg, 0.441 mol) was dissolved in hot dmso (1 mL), allowed to cool, and precipitated with water (1 mL) to give a yellow crystalline product. Yield: 441 mg (99%, 0.880 mmol). Anal. Found (expected): C 45.0 (45.4), H 3.4 (3.4), N 2.8 (2.8). NMR δ_H (400 MHz, CDCl$_3$): 7.80 (2H, dd, $^3J = 7.6$, $^4J = 1.2$, ^3J(Pt−H) 24 Hz, phenyl ortho to Pt), 7.62 (1H, t, $^3J = 7.3$ Hz, central pyridine), 7.47 (2H, dd, $^3J = 7.6$, $^4J = 1.2$ Hz, phenyl ortho to pyridine, meta to Pt), 7.30 (2H, d, $^3J = 7.3$ Hz, pyridine), 7.28 (2H, td, $^3J = 7.6$, $^4J = 1.2$ Hz, phenyl), 7.21 (2H, td, $^3J = 7.6$, $^4J = 1.2$ Hz, phenyl), 3.68 (6H, s, ^3J(Pt−H) = 26.8 Hz, dmso).

Synthesis of [(2,6-diphpyPtCl)$_2$] (4). Potassium tetrachloroplatinate (374 mg, 0.900 mmol) was added to a solution of 2,6-diphenylpyridine (233 mg, 1.00 mmol) in glacial acetic acid (250 mL). The reaction was stirred at 80 °C until the red platinum salt was no longer visible (3 days). The reaction mixture was filtered, yielding the product as a yellow powder, which was washed with water, acetone, and ether. Yield: 407 mg (98%, 0.441 mmol). Anal. Found (expected): C 43.7 (44.2), H 2.6 (2.6), N 3.0 (3.0). NMR δ_H (400 MHz, d_7-dmf) 8.22 (2H, t, $^3J = 7.6$ Hz, central pyridine), 8.10 (2H, dd, $^3J = 7.6$, $^4J = 1.1$ Hz, pyridine, metalated side), 7.95 (4H, m, unmetalated phenyl ring), 7.86 (2H, dd, $^3J = 7.8$, $^4J = 1.2$ Hz, phenyl, ortho to Pt), 7.71 (2H, dd, $^3J = 7.8$, $^4J = 1.2$ Hz, phenyl ortho to pyridine), 7.56 (6H, m, unmetalated phenyl ring), 7.54 (2H, dd, $^3J = 7.6$, $^4J = 1.1$ Hz, pyridine, unmetalated side), 7.11 (2H, dd, $^3J = 7.3$, $^4J = 1.2$ Hz, phenyl para to Pt), 7.05 (2H, dd, $^3J = 7.3$, $^4J = 1.2$ Hz, phenyl meta to Pt).

Synthesis of [(4-(4-Octyloxyphenyl)-2,6-diphpyPtCl)$_2$] (6). Potassium tetrachloroplatinate (187 mg, 0.450 mmol) was added to a solution of 4-(4-octyloxyphenyl)-2,6-diphenylpyridine (218 mg, 0.500 mmol) in glacial acetic acid (250 mL). The reaction was stirred at 80 °C until the red platinum salt was no longer visible (3 days). The reaction mixture was filtered, yielding the product as a yellow powder, which was washed with water, acetone, and ether. Yield: 289 mg (97%, 0.217 mmol). Anal. Found (expected): C 55.6 (56.0), H 5.2 (4.85), N 2.0 (2.1). NMR δ_H (400 MHz, CDCl$_3$): 7.85 (4H, m, unmetalated phenyl), 7.72 (2H, d, $^4J = 2.4$ Hz, pyridine, metalated side), 7.65 (4H, AA′XX′, phenyl, meta to OC$_8$H$_{17}$ chain), 7.51 (6H, m, unmetalated phenyl), 7.41 (2H, dd, $^3J = 7.6$, $^4J = 1.2$ Hz, phenyl meta to Pt, ortho to pyridine), 7.35 (2H, d, $^4J = 2.4$ Hz, pyridine, unmetalated side), 7.06 (2H, dt, $^3J = 7.6$, $^4J = 1.2$ Hz, phenyl para to Pt), 7.0 (6H, m, phenyl meta to Pt, para to pyridine and phenyl ortho to OC$_8$H$_{17}$ chain), 6.93 (2H, dd, $^3J = 7.6$, $^4J = 1.2$, ^3J(Pt−H) = 35.3 Hz, phenyl, ortho to Pt), 4.03 (4H, t, $^3J = 6.4$ Hz, OCH$_2$), 1.80 (4H, m, OCH$_2$CH_2), 1.51 (20H, m, chain), 0.91 (6H, t, $^3J = 7.0$ Hz, CH$_3$). NMR δ_C (75.4 MHz, CDCl$_3$): 178.1, 162.1, 161.3, 150.0, 145.0, 139.9, 132.4, 130.2, 130.0, 129.2, 128.9, 128.7, 124.2, 124.0, 121.3, 115.7, 113.9, 68.7, 32.2, 32.0, 29.8, 29.6, 26.4, 23.1, 14.5.

X-ray Crystallographic Study of 6. Crystals suitable for structural analysis were grown from chloroform. A yellow prism (dimensions 0.26 × 0.04 × 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 **6**: C$_{62}$H$_{64}$N$_2$O$_2$Pt$_2$, $M = 1330.23$, orthorhombic, space group $P2(1)2(1)2$, $a = 20.8902(15)$ Å, $b = 34.532(2)$ Å, $c = 7.5473(6)$ Å, $U = 5444.5(7)$ Å^3, $Z = 4$, D(calcd) = 1.623 Mg/m^3. Refinement was by full-matrix least-squares on F^2 for 7562 reflections using SHELXL-97.[60] 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; 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 $w = 1/[\sigma^2(F_o^2) + (0.0962P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. Goodness-of-fit on F^2 was 1.004, R1[$I > 2\sigma(I)$] = 0.0823, wR2 = 0.2016. Data/restraints/parameters 7562/8/532. Largest difference Fourier peak and hole 2.768 and −2.620 e Å^{-3}; the only large peaks are near the Pt atoms. The Flack parameter was determined as 0.49(2); thus the absolute structure could not be determined reliably. Selected bond lengths and angles are listed in Table 1.

Synthesis of [4-(4-Octyloxyphenyl)-2,6-diphpyPt(dmso)] (7). (4-(4-Octyloxyphenyl)-2,6-diphpyPtCl)$_2$ (120 mg, 0.0902 mol) was dissolved in hot dmso (1 mL), allowed to cool, and precipitated with water (1 mL) to give a yellow crystalline product. Yield: 121 mg (95%, 0.171 mmol). Anal. Found (expected): C 56.3 (56.1), H 5.5 (5.3), N 2.3 (2.0). NMR δ_H (300 MHz, CDCl$_3$): 7.84 (2H, dd, $^3J = 7.8$, $^4J = 1.7$, ^3J(Pt−H) = 34.8 Hz, phenyl ortho to Pt), 7.68 (2H, AA′XX′, phenyl, meta to OC$_8$H$_{17}$ chain), 7.58 (2H, dd, $^3J = 7.8$, $^4J = 1.7$ Hz, phenyl ortho to pyridine, meta to Pt), 7.48 (2H, s, pyridine), 7.31 (2H, dt, $^3J = 7.8$, $^4J = 1.7$ Hz, phenyl meta to Pt), 7.15 (2H, dt, $^3J = 7.8$, $^4J = 1.7$ Hz, phenyl para to Pt), 7.05 (2H, AA′XX′,

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phenyl, ortho to OC_8H_{17} chain), 4.05 (2H, t, $^3J = 7.5$ Hz, OCH_2), 3.61 (6H, s, ^3J(Pt−H) = 26.3 Hz, dmso), 1.84 (2H, m, OCH_2CH_2), 1.32 (10H, m, $(CH_2)_5$), 0.89 (3H, t, $^3J = 7.2$ Hz, CH_3). NMR δ_C (75.4 MHz, $CDCl_3$): 165.6, 165.1, 159.9, 152.1, 148.8, 135.2, 129.6, 128.6, 127.4, 123.8, 123.3, 114.0, 111.6, 67.2, 47.3, 30.8, 28.6, 28.3, 28.2, 25.0, 21.6, 13.1.

Synthesis of [(2,6-diphpy)Pt(Cl)(dmso)] (8). [((2,6-diphpy)PtCl)$_2$] (**4**) was dissolved in dmso. The compound was not isolated. NMR δ_H (400 MHz, d_6-dmso): 8.20 (3H, m, central pyridine, pyridine on metalated side, phenyl ortho to Pt), 7.96 (2H, m, unmetalated phenyl), 7.84 (1H, dd, $^3J = 9.0$, $^4J = 1.4$ Hz, phenyl meta to Pt, ortho to pyridine), 7.72 (1H, dd, $^3J = 6.2$, $^4J = 2.8$ Hz, pyridine, unmetalated side), 7.48 (3H, m, unmetalated phenyl), 7.23 (1H, dt, $^3J = 9.0$, $^4J = 1.4$ Hz, phenyl para to Pt), 7.14 (1H, dt, $^3J = 9.0$, $^4J = 1.4$ Hz, phenyl meta to Pt, para to pyridine). NMR δ_H ($CDCl_3$): 3.38 (6H, s, ^3J(Pt−H) = 24 Hz, dmso, note: from a DMF solution spectrum).

Synthesis of [(2,6-diphpy)Pt(Cl)(CO)] (9). Trans Isomer 9t. Carbon monoxide gas was bubbled through a solution of [((2,6-diphpy)PtCl)$_2$] (**4**) in dmf. The compound was not isolated.

NMR δ_H (400 MHz, d_7-dmf): 8.38 (1H, t, $^3J = 7.4$ Hz, central pyridine), 8.33 (1H, dd, $^3J = 7.4$, $^4J = 2.0$ Hz, pyridine), 8.02 (1H, dd, $^3J = 8.2$, $^4J = 1.3$ Hz, phenyl ortho to Pt), 7.96 (1H, dd, $^3J = 8.2$, $^4J = 1.3$ Hz, phenyl, ortho to pyridine, meta to Pt), 7.85 (2H, m, unmetalated phenyl), 7.72 (4H, m, pyridine, unmetalated phenyl), 7.38 (1H, dt, $^3J = 8.2$, $^4J = 1.3$ Hz, phenyl meta to Pt, para to pyridine), 7.32 (1H, dt, $^3J = 8.2$, $^4J = 1.3$ Hz, phenyl para to Pt). FT-IR: ν(C≡O) 2087 cm^{-1} (dmf).

Cis Isomer 9c. Carbon monoxide gas was bubbled through a solution of [(2,6-diphpy)PtCl(dmso)] (**8**) in dmso. The compound was not isolated. NMR δ_H (400 MHz, d_6-dmso) 8.20 (3H, m, central pyridine, pyridine on metalated side, phenyl ortho to Pt), 7.95 (2H, m, unmetalated phenyl), 7.84 (1H, dd, $^3J = 9.0$, $^4J = 1.4$ Hz, phenyl meta to Pt, ortho to pyridine), 7.72 (1H, dd, $^3J = 6.2$, $^4J = 2.8$ Hz, pyridine, unmetalated side), 7.48 (3H, m, unmetalated phenyl), 7.22 (1H, dt, $^3J = 9.0$, $^4J = 1.4$ Hz, phenyl para to Pt), 7.14 (1H, dt, $^3J = 9.0$, $^4J = 1.4$ Hz, phenyl meta to Pt, para to pyridine). FT-IR: ν(C≡O) 2098 cm^{-1} (dmso).

Synthesis of [(4-(4-Octyloxyphenyl)-2,6-diphpy)Pt(Cl)(dmso)] (10). [((4-(4-Octyloxyphenyl)2,6-diphpy)PtCl)$_2$] (**6**) was dissolved in chloroform and an excess of dmso added. The mixture was shaken for 1 h. The compound was not isolated. NMR δ_H (400 MHz, $CDCl_3$): 8.31 (1H, dd, $^3J = 7.6$, $^4J = 1.2$, ^3J(Pt−H) = 38 Hz, phenyl, ortho to Pt), 7.98 (2H, m, unmetalated phenyl), 7.89 (1H, d, $^4J = 2.4$ Hz, pyridine, metalated side), 7.72 (2H, AA′XX′, phenyl, meta to OC_8H_{17} chain), 7.66 (1H, dd, $^3J = 9.0$, $^4J = 1.4$ Hz, phenyl meta to Pt, ortho to pyridine), 7.59 (1H, d, $^4J = 2.4$ Hz, pyridine, unmetalated side), 7.50 (3H, m, unmetalated phenyl), 7.23 (1H, dt, $^3J = 9.0$, $^4J = 1.4$ Hz, phenyl para to Pt), 7.20 (1H, dt, $^3J = 9.0$, $^4J = 1.4$ Hz, phenyl meta to Pt, para to pyridine), 7.05 (2H, AA′XX′, phenyl ortho to OC_8H_{17} chain), 4.03 (2H, t, $^3J = 6.4$ Hz, OCH_2), 3.43 (6H, s, ^3J(Pt−H) = 23 Hz, dmso), 1.80 (2H, m, OCH_2CH_2), 1.51 (10H, m, chain), 0.91 (3H, t, $^3J = 7.0$ Hz, CH_3).

Synthesis of [(4-(4-Octyloxyphenyl)-2,6-diphpy)Pt(Cl)(CO)] (11). Trans Isomer 11t. Carbon monoxide gas was bubbled through a solution of [((4-(4-octyloxyphenyl)2,6-diphpy)PtCl)$_2$] (**6**) in chloroform. The compound was not isolated. NMR δ_H (400 MHz, $CDCl_3$): 8.06 (1H, dd, $^3J = 7.6$, $^4J = 1.2$, ^3J(Pt−H) = 34 Hz, phenyl, ortho to Pt), 7.93 (1H, d, $^4J = 2.0$ Hz, pyridine), 7.72 (2H, AA′XX′, phenyl, meta to OC_8H_{17} chain), 7.68 (2H, m, unmetalated phenyl), 7.60 (1H, dd, $^3J = 7.6$, $^4J = 1.4$ Hz, phenyl meta to Pt, ortho to pyridine), 7.55 (3H, m, unmetalated phenyl), 7.48 (1H, d, $^4J = 2.0$ Hz, pyridine), 7.26 (1H, dt, $^3J = 7.6$, $^4J = 1.4$ Hz, phenyl meta to Pt, para to pyridine), 7.19 (1H, dt, $^3J = 9.0$, $^4J = 1.4$ Hz, phenyl para to Pt), 7.03 (2H, AA′XX′, phenyl ortho to OC_8H_{17} chain), 4.01 (2H, t, $^3J = 6.4$ Hz, OCH_2), 1.80 (2H, m, OCH_2CH_2), 1.51 (10H, m, chain), 0.91 (3H, t, $^3J = 7.0$ Hz, CH_3). FT-IR: ν(C≡O) 2097 cm^{-1} ($CDCl_3$).

Cis Isomer 11c. Carbon monoxide gas was bubbled through a solution of [(4-(4-octyloxyphenyl)-2,6-diphpy)PtCl(dmso)] (**10**) in either dmso or chloroform. The compound was not isolated. NMR δ_H (400 MHz, $CDCl_3$): 7.97 (1H, d, $^4J = 2.4$ Hz, pyridine), 7.78 (2H, m, unmetalated phenyl), 7.75 (1H, dd, $^3J = 8.0$, $^4J = 1.4$, phenyl, metalated ring), 7.74 (2H, AA′XX′, phenyl, meta to OC_8H_{17} chain), 7.60 (1H, d, $^4J = 2.4$ Hz, pyridine),7.56 (1H, dd, $^3J = 8.0$, $^4J = 1.4$ Hz, phenyl, metalated ring), 7.53 (3H, m, unmetalated phenyl), 7.28 (1H, dt, $^3J = 8.0$, $^4J = 1.4$ Hz, phenyl, metalated ring), 7.17 (1H, dt, $^3J = 8.0$, $^4J = 1.4$ Hz, phenyl, metalated ring), 7.06 (2H, AA′XX′, phenyl ortho to OC_8H_{17} chain), 4.04 (2H, t, $^3J = 6.4$ Hz, OCH_2), 1.80 (2H, m, OCH_2CH_2), 1.51 (10H, m, chain), 0.91 (3H, t, $^3J = 7.0$ Hz, CH_3). FT-IR: ν(C≡O) 2103 cm^{-1} ($CDCl_3$).

Synthesis of [(2,6-diphpy)Pt(CO)] (15). Carbon monoxide gas was bubbled through a solution of [(2,6-diphpy)Pt(dmso)] (**3**) (56 mg, 0.108 mmol) in chloroform (1 mL). All solvents were removed in vacuo to give a red product. Yield: 50 mg (99%, 0.107 mmol). Or, a solution of **9** in either dmf or dmso was left for 6 h at room temperature. Anal. Found (expected): C 47.5 (47.8), H 2.5 (2.4), N 3.3 (3.1). NMR δ_H (400 MHz, d_6-dmso) 7.89 (1H, t, $^3J = 7.8$ Hz, central pyridine), 7.68 (2H, dd, $^3J = 7.6$, $^4J = 1.1$ Hz, phenyl ortho to pyridine), 7.65 (2H, d, $^3J = 7.8$ Hz, pyridine), 7.52 (2H, dd, $^3J = 7.3$, $^4J = 1.2$, ^3J(Pt−H) = 33.1 Hz, phenyl ortho to Pt), 7.22 (2H, dd, $^3J = 7.3$, $^4J = 1.2$ Hz, phenyl meta to Pt), 7.16 (2H, dd, $^3J = 7.3$, $^4J = 1.2$ Hz, phenyl para to Pt). NMR δ_H (400 MHz, d_7-dmf) 7.99 (1H, t, $^3J = 7.8$ Hz, central pyridine), 7.75 (2H, dd, $^3J = 7.6$, $^4J = 1.1$ Hz, phenyl ortho to pyridine), 7.74 (2H, d, $^3J = 7.8$ Hz, pyridine), 7.61 (2H, dd, $^3J = 7.3$, $^4J = 1.2$, ^3J(Pt−H) = 33.1 Hz, phenyl ortho to Pt), 7.28 (2H, dd, $^3J = 7.3$, $^4J = 1.2$ Hz, phenyl meta to Pt), 7.20 (2H, dd, $^3J = 7.3$, $^4J = 1.2$ Hz, phenyl para to Pt). FAB MS (NBA): m/z 452 (M$^+$). FT-IR: ν(C≡O) 2044 cm^{-1} (KBr), 2056 cm^{-1} (dmso), 2055 cm^{-1} (dmf).

X-ray Crystallographic Study of 15. Crystals suitable for structural analysis were grown from chloroform. An orange-red prism (dimensions 0.3 × 0.12 × 0.10 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 **10**: $C_{18}H_{11}NOPt$, $M = 452.37$, orthorhombic, space group $P2(1)2(1)2(1)$ $a = 7.3337(6)$ Å, $b = 19.1794(12)$ Å, $c = 18.9464(12)$ Å, $U = 2664.9(3)$ Å^3, $Z = 8$, D(calcd) = 2.55 Mg/m^3. Refinement was by full-matrix least-squares on F^2 for 6260 reflections using SHELXL-97.[60] Hydrogen atoms were added at calculated positions. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which the H atom is attached. The weighting scheme was calculated using $w = 1/[\sigma^2(F_o^2) + (0.0272P)^2 + 11.62P]$, where $P = (F_o^2 + 2F_c^2)/3$. Goodness-of-fit on F^2 was 1.105, R1[$I > 2\sigma(I)$] = 0.0351, wR2 = 0.0836. Data/parameters 6260/379. Largest difference Fourier peak and hole 1.393 and −1.360 e Å^{-3}; the only large peaks are near the Pt atoms. The Flack parameter was 0.020(14) and confirms that the correct absolute structure has been determined. The asymmetric unit contains two essentially identical molecules. Selected bond lengths and angles are listed in Table 2.

Synthesis of [(4-(4-Octyloxyphenyl)-2,6-diphpy)Pt(CO)] (16). [(4-(4-Octyloxyphenyl)2,6-diphpy)Pt(dmso)] (**7**) (60 mg, 0.085 mmol) was dissolved in chloroform and CO gas bubbled through it. The solvent was removed to yield the orange product. Yield: 55 mg (99%, 0.084 mmol). Anal. Found (expected): C 58.0 (58.5), H 4.4 (4.8), N 2.6 (2.1).

NMR δ_H (400 MHz, $CDCl_3$): 7.57 (2H, AA′XX′, phenyl, meta to OC_8H_{17} chain), 7.50 (2H, dd, $^3J = 7.5$, $^4J = 1.5$, ^3J(Pt−H) = 38 Hz, phenyl, ortho to Pt), 7.39 (2H, dd, $^3J = 7.5$, $^4J = 1.5$ Hz, phenyl meta to Pt, ortho to pyridine), 7.23 (2H, s, pyridine)

Table 4. Relative Binding Energies (kJ mol^{-1})

compound	relative binding energy
9c	0
9t	16
15 + HCl	68

7.14 (2H, dt, $^3J = 7.5$, $^4J = 1.5$ Hz, phenyl meta to Pt, para to pyridine), 7.06 (2H, dt, $^3J = 7.5$, $^4J = 1.5$ Hz, phenyl para to Pt), 6.99 (2H, AA′XX′, phenyl ortho to OC_8H_{17} chain), 4.01 (2H, t, $^3J = 7.0$ Hz, OCH_2), 1.80 (2H, m, OCH_2CH_2), 1.51 (10H, m, chain), 0.89 (3H, t, $^3J = 7.0$ Hz, CH_3). FT-IR: $\nu(C{\equiv}O)$ 2061 cm^{-1} ($CDCl_3$).

Theoretical Studies. The DFT calculations were based on the numerical Amsterdam Density Functional (ADF) program system version 2.3.0.[61] The supplied basis sets IV were used which comprise uncontracted triple-ζ Slater-type-orbital (STO) expansions for the valence orbitals with an additional function (2p for H, 3d for C, N, O, and Cl, and 6p for Pt). Geometry optimizations were generally carried out using the uniform electron gas local density approximation[62] (LDA) and analytical energy gradients.[63] The LDA correlation energy was computed according to Vosko, Wilk, and Nusair's[64] parametrization of electron gas data. Gradient-corrected (GC) functionals for the LDA exchange and correlation terms employed the formulations of Becke[65] and Perdew,[66,67] respectively. Unless otherwise stated, the GC functionals were applied after geometry optimization at the LDA level. The lower core shells on the atoms (1s on O, 1s to 2p on Cl, 1s to 5p or 4f on Pt) were treated by the frozen core approximation.[68] The total molecular electron density was fitted in each SCF cycle by auxiliary s, p, d, f, and g STO functions.[69] Scalar relativistic corrections[70,71] were applied throughout. Table 3 lists selected bond lengths in the structure of **15** and Table 4 the relative binding energies of **9c**, **9t**, and **15**. Coordinates of the optimized structures are available as Supporting Information.

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Supporting Information Available: Tables of positional parameters, bond distances, bond angles, and anisotropic parameters for the structural analysis of **6** and **15** are available free of charge via the Internet at http://pubs.acs.org, as are the coordinates for the optimized structures of **9c**, **9t**, and **15**.

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