2238 *Organometallics* **2008,** *27,* 2238–2245

Reactivity of Low-Valent Iridium, Rhodium, and Platinum Complexes with Di- and Tetrasubstituted Hydrazines

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Three complexes, $IrCl(PEt_3)_3$, Rh(NNN)Cl (NNN = 2,6-$(CyN{=}CH)_2C_5H_3N$), and $(NN)PtMe_2$ [NN = 1,10-phenanthroline (phen) or 2,2′-bipyridine (bpy)], have been investigated for N−N oxidative addition reactivity with di- and tetrasubstituted hydrazines. The reaction of $IrCl(PEt_3)_3$with 1,2-diphenylhydrazine (PhNHNHPh) forms the cyclometalated azobenzene complex $(Et_3P)_2Cl(H)Ir(C_6H_4N{=}NPh)$ (**1**) and the 2:1 complex $[(Et_3P)_2Cl(H)Ir]_2(\mu\text{-}C_6H_4N{=}NC_6H_4)$ (**2**). The Rh(NNN)Cl pincer complex catalyzes the disproportionation of PhNHNHPh to azobenzene and aniline with no change in the Rh complex. The reaction of $(bpy)PtMe_2$ with the hydrazine $AcNHNHC(O)CH_2CH_2CH{=}CH_2$ (**3**) yields the platinum metallacycle $(bpy)Pt(\eta^2\text{-}AcN\text{-}NC(O)(CH_2)_2CHCH_2$ (**4**). Although $IrCl(PEt_3)_3$, Rh(NNN)Cl, and $(NN)PtMe_2$ all undergo facile oxidative addition of other X−Y bonds, such reactivity is not observed for hydrazines; in the Ir and Pt systems there is a clear preference for cleavage of the stronger N−H bond over the N−N bond. The tetrasubstituted hydrazines tetraphenylhydrazine, 1,2-diphenyl-1,2-dimethylhydrazine, bisuccinimide, biphthalimide, and N-dimethylamino phthalimide do not react with $IrCl(PEt_3)_3$, Rh(NNN)Cl, and $(NN)PtMe_2$. This lack of reactivity appears to be due to kinetic rather than thermochemical factors.

Introduction

Oxidative addition reactions are important routes to new metal–ligand σ bonds and are fundamental steps in metal-catalyzed reactions. Early studies of this process focused on the addition of H_2 to metal complexes to give new dihydride species,[1] followed by an interest in C−H,[2] C−X,[3] C−O,[4] and C−S[5] bond activations. There have also been reports of the oxidative addition of S−S,[6] O−O,[7] and even C−C[8]bonds to yield stable high oxidation state thiolate, alkoxide, aryl, or alkyl complexes. C−N oxidative addition reactions have been observed primarily for strained substrates[9] or low-valent early metal systems,[10] although the corresponding reductive elimination reactions can be facile.[11] While oxidative addition processes are common to a variety of bonds, there is little evidence for the simple oxidative addition of the N−N bond of hydrazines.

Hydrazine reactivity with metal complexes has been studied primarily in the context of the cleavage of N−N bonds by nitrogenase enzymes.[12] Our interest in hydrazine oxidative addition derives from its possible application in catalytic olefin diamination. Diamination is an oxidative process that forms two C−N bonds, and there have been recent reports of catalytic diaminations using amines and added oxidants.[13] Diamination using a hydrazine is directly analogous to the hydroamination of olefins with amines, allowing the hydrazine to act as its own oxidant. Such a process could occur by oxidative addition of a hydrazine to a metal center to make an oxidizing bis(amido) complex followed by addition of the amido ligands to an alkene with a two-electron reduction of the metal center. A related reaction is the addition of a diaziridinone to dienes catalyzed

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by Pd^0, which is proposed to proceed through an oxidative addition pathway.[14]

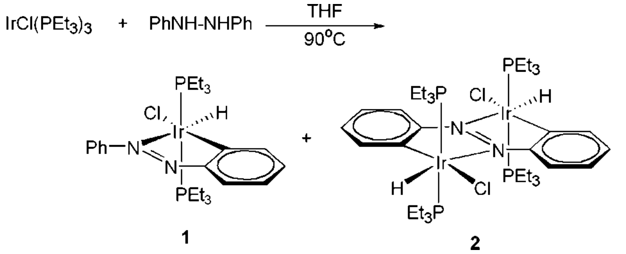
The oxidative addition of an N−N bond to a metal center to yield a bis(amido) complex has not been reported. N−N cleavage has been observed with sulfur- and hydride-ligated metal clusters,[15] low-valent early metal complexes,[16] and Mo and W systems developed by Schrock and co-workers.[17] Reduced iron and ruthenium complexes have been reported to cleave the N−N bond of PhNHNHPh in multistep processes to give amido or imido dimers or oligomers, such as $Cp^*{}_2Fe_2(\mu\text{-}NPh)_2$ from $Cp^*Fe[N(SiMe_3)_2]$,[18] $Fe_4(\mu\text{-}NPh)_4(SAr)_4$ from the *in situ* generated $Fe[N(SiMe_3)_2](SAr)$,[19] and our recent report of $Cp^*{}_2Ru_2(\mu\text{-}NHPh)_2Cl_2$ from $[Cp^*RuCl]_4$.[20] Holland and co-workers have described binding of N_2H_4 to $LFe(\mu\text{-}H)_2BEt_2$ (L = 2,4-bis(2,6-diisopropylphenylimino)pent-2-yl) to give an η^1-hydrazine complex, which upon heating cleaves the N−N bond to form the diaminoborate complex $LFe(\mu\text{-}NH_2)_2BEt_2$ with loss of H_2.[21] The cleavage of azines by a $(PCP)Rh(N_2)$ species (PCP = $2,6\text{-}(CH_2PR_3)_2C_6H_3$) to give the corresponding imine and nitrile complexes has been reported.[22] Imido complexes are formed by N−N cleavage in some systems, such as the cleavage of the N=N bond of azobenzene by a tungsten(II) aryloxide complex to give a bis(imido) monomer[23] and by a chromium(I) complex with β-diketiminate ligands to give the bis(imido)-bridged dimer.[24] The reaction of $ReOCl_3(PPh_3)_2$ with hydrazines forms $Re(NR)Cl_3(PPh_3)_2$.[25] Scission of the N−N bond, however, has not been observed in typical organometallic systems that undergo oxidative addition.

The goal of the present study is to discover N−N oxidative addition processes that form oxidizing bis(amido) complexes, which could be used in catalytic diamination reactions. We report here the reactivity of di- and tetrasubstituted hydrazines with three systems known to undergo facile oxidative addition processes: $IrCl(PEt_3)_3$, Rh(NNN)Cl (NNN = $2,6\text{-}(CH{=}NCy)_2\text{-}C_5H_3N$), and $(NN)PtMe_2$(NN = phenanthroline or 2,2′-bipyridine).

Results

I. Reaction of $IrCl(PEt_3)_3$ with PhNHNHPh. The 16-electron Ir(I) trisphosphine complexes $IrCl(PR_3)_3$ (R = Me, Et) have been shown to oxidatively add B−B,[26] O−H,[27] and C−H[28] bonds, among others.[29] Of particular interest is the addition of the aniline N−H bond to form the stable six-coordinate amido hydride complex $Ir(PEt_3)_3(NHPh)(H)Cl$.[29d] The formation of the stable Ir(III) anilide species suggests that an Ir(III) bis(anilide) complex may also be accessible.

A solution of $IrCl(PEt_3)_3$, generated from $[Ir(COE)_2Cl]_2$ and PEt_3,[30] reacts with excess 1,2-diphenylhydrazine (PhNHNHPh) at 90 °C to give two major iridium-containing products. Both products contain a cyclometalated azobenzene ligand: the 1:1 complex $(Et_3P)_2Cl(H)Ir(C_6H_4N{=}NPh)$ (**1**) and the bimetallic 2:1 complex $[(Et_3P)_2Cl(H)Ir]_2(\mu\text{-}C_6H_4N{=}NC_6H_4)$ (**2**) (eq 1). Complexes **1** and **2** account for ~60% of the starting Ir; their ratio and yields vary depending upon initial reaction conditions. Small amounts (~10–20%) of the dihydride complex $Ir(PEt_3)_3Cl(H)_2$[29b] are formed, in addition to several other hydride-containing products (~10–20%). In sealed NMR tube reactions, H_2 is not observed, but we estimate that even 100% yield of H_2 would have given a concentration barely at our detection limit by ^1H



1 **2**

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NMR spectroscopy.[31] $PhNH_2$ is not observed over the course of the reaction, but azobenzene (PhN=NPh) is observed in small amounts and may be an intermediate in the formation of **1** and **2**. Monitoring the reaction by ^1H NMR spectroscopy indicates that the ratio of $Ir(PEt_3)_3Cl(H)_2$ to all the azobenzene-containing species combined (**1**, **2**, and PhN=NPh) remains constant over the course of the reaction (Supporting Information S1). Treatment of $IrCl(PEt_3)_3$ with PhN=NPh also forms complexes **1** and **2**, without the formation of any other hydride-containing species. Isolated **1** converts to bimetallic **2** upon heating with 2 equiv of $IrCl(PEt_3)_3$ in THF-d_8. Related additions of azobenzene to $IrCl(PR_3)_3$[32] or $IrCl(PR_3)_2CO$[33] to give species analogous to **1** have been previously reported.

Characterization of $(Et_3P)_2Cl(H)Ir(C_6H_4N{=}NPh)$ (1). Complex **1** is pentane-soluble and was isolated by column chromatography in low yield (~20%). The ^1H NMR spectrum of **1** has seven aryl resonances, indicating a cyclometalated ring. A hydride resonance is observed at −17.8 ppm (t, $^2J_{HP} = 17$ Hz), which is consistent with a hydride *cis* to two equivalent phosphines. The methylene protons of the phosphine ethyl groups appear as diastereotopic resonances, but $^{31}P\{^1H\}$ NMR spectroscopy shows only a single resonance ($\delta = -6.40$). These data are consistent with the isomer of **1** as shown in eq 1. These spectroscopic data are in agreement with those of the known triphenylphosphine analogue of **1**.[34] In addition, the isotope pattern observed by ESI/MS confirms **1** as a monomer with $m/z = 647$ $[M + H]^+$.

Characterization of $[(PEt_3)_2Cl(H)Ir]_2(\mu\text{-}C_6H_4N{=}NC_6H_4)$ (2). The 2:1 complex **2** was isolated from the reaction mixture by precipitation with pentane in 20% yield. Precipitation is more selective when **2** is prepared from $IrCl(PEt_3)_3$ with PhN=NPh, since this avoids the coprecipitation of PhNHNHPh. The ^1H NMR spectrum of **2** in THF-d_8 shows only four aryl resonances and a hydride resonance at $\delta = -17.6$ ppm (t, $^2J_{HP} = 18$ Hz) indicating coupling to two equivalent *cis* phosphines. This is confirmed by a single resonance in the $^{31}P\{^1H\}$ NMR spectrum ($\delta = -4.37$ ppm). Complex **2** is bimetallic in solution, as indicated by the isotope pattern observed by ESI/MS ($m/z = 955$, $[M - (Cl + PEt_3)]^+$). Although cyclometalated azobenzene complexes typically contain a single metal center like **1**, a bimetallic structure has been reported for the Cp*Ir system $[Cp^*IrBr]_2(\mu\text{-}C_6H_4N\text{-}NC_6H_4)$.[35]

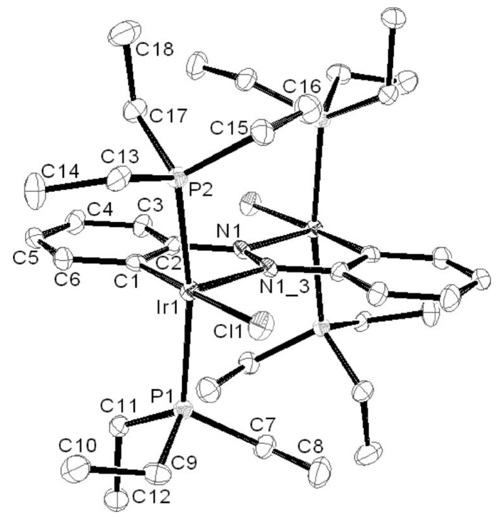

Figure 1. ORTEP of $[(Et_3P)_2Cl(H)Ir]_2(\mu\text{-}C_6H_4N{=}NC_6H_4)$ (**2**) with 50% probability ellipsoids. The hydride ligands were not located in the structure (but presumably occupy the sites *trans* to N1 and N1_3).

Table 1. Selected Bond Distances (Å) and Angles (deg) in 2

Ir1−C1	1.970(5)	C1−Ir1−N1_3	75.83(16)
Ir1−N1_3	2.219(4)	C1−Ir1−Cl1	176.87(12)
Ir1−P1	2.3193(13)	P1−Ir1−P2	163.92(5)
Ir1−P2	2.3224(13)		
Ir1−Cl1	2.5074(11)		
N1−N1_3	1.316(8)		
N1−C2	1.391(6)		

Table 2. Crystallographic Data for 2 and 4

	2	4
formula	$C_{36}H_{68}Cl_2Ir_2N_2P_4$	$C_{17}H_{18}N_4O_2Pt$
fw	1108.14	505.44
space group	$P2_1/c$	$P2_1/c$
cryst syst	monoclinic	monoclinic
cryst color	red	yellow
cryst dimen (mm)	0.50 × 0.40 × 0.2	0.10 × 0.10 × 0.05
a (Å)	12.1403(4)	14.4886(2)
b (Å)	12.0878(3)	22.0667(4)
c (Å)	16.6594(4)	10.2932(3)
α (deg)	90	90
β (deg)	127.4751(12)	105.1153(7)
γ (deg)	90	90
V (Å^3)	2100.64(10)	3177.04(12)
Z	2	8
d_{calc} (mg m^{-3})	1.755	2.113
μ_{calc} (mm^{-1})	6.635	8.851
F(000)	1092	1936
no. of unique rflns	5154	8181
no. of data used	5154	8181
no. of params refined	214	437
R^a	0.0383	0.0497
$R_w{}^b$	0.0991	0.1103
GOF^c	0.990	0.916

[a] $R = \sum||F_o| - |F_c||/\sum F_o$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. [c] $GOF = [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{parms})]^{1/2}$.

Crystals of **2** suitable for X-ray diffraction analysis were grown from vapor diffusion of pentane into a solution of **2** in THF and confirm a bimetallic species in which the two halves are related by an inversion center, as shown in Figure 1 (the metric and crystallographic data are shown in Tables 1 and 2). Each iridium center is octahedral with a hydride ligand, not seen in the structure, occupying the sixth site. The azobenzene has a chelate angle of 75.83(16)° and an N−N distance (1.316(8) Å) longer than that in both the monomeric PPh_3 analogue $(PPh_3)_2Cl(H)\overline{Ir(C_6H_4N{=}N}Ph$ (1.269(20) Å)[34] and a related Cp*Ir dimer $[Cp^*IrBr]_2(\mu C_6H_4N{=}NC_6H_4)$ (1.247(21) Å), but is much shorter than that of the *hydrazido*-bridged dimer $[Cp^*Ir]_2(\mu\text{-}C_6H_4N{-}NC_6H_4)$ (1.419 Å).[35] The small torsion angle (N1_3-

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[31] An NMR tube containing 1 atm of H_2 (1.9 mL, 0.08 mmol) and 500 μL of THF-d_8 was found to have a concentration of 19 mM of H_2 in solution (by NMR integration vs a standard). Our conditions typically include 10–15 μmol of $IrCl(PEt_3)_3$; forming 10–15 μmol of H_2 would mean a soluble concentration of 2.5–3.7 mM. Thus the concentrations of H_2 formed in these reactions would be difficult to observe by ^1H NMR spectroscopy.

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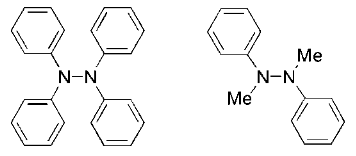
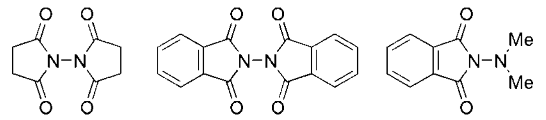
Chart 1. Tetrasubstituted Hydrazines Examined

(a) electron rich R_2N-NR_2



(b) electron deficient R_2N-NR_2



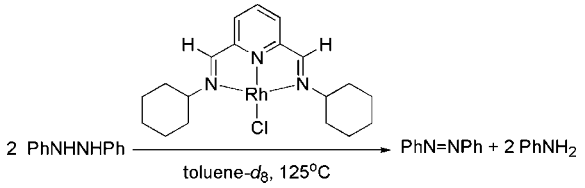
N1-C2−C1 = −2.6(6)°) indicates a planar azobenzene ligand. The Ir−N bond length (2.219(4) Å) is longer than that of both the monomeric PPh_3 complex (2.148(14) Å)[34] and the Cp*-ligated dimer (2.041(10) Å).[35] The Ir−C bond length (1.970(5) Å) is similar to that in both the monomeric PPh_3 analogue (2.002(19) Å)[36] and the $[Cp^*IrBr]_2(\mu\text{-}C_6H_4N{=}NC_6H_4)$ system (2.023(14) Å).[35]

Competition between PhNHNHPh and PhN=NPh in the Formation of 1. The formation of the cyclometalated iridium complexes **1** and **2** as the major products in the reaction of $IrCl(PEt_3)_3$ with PhNHNHPh was unexpected. To determine if PhNHNHPh is oxidized to PhN=NPh before cyclometalation, $IrCl(PEt_3)_3$ was combined with an equimolar mixture of either PhNHNHPh and TolN=NTol, or TolNHNHTol and PhN=NPh, and heated in THF-d_8 at 90 °C. The reactions formed **1** and its tolyl analogue $(Et_3P)_2Cl(H)Ir((CH_3)C_6H_3N{=}NTol)$ (**1-Tol**) in ratios of 1:3.6 and 4.5:1, respectively (Figures S2 and S3). Both reactions formed only minor amounts of the bimetallic products **2** and **2-Tol**$[(Et_3P)_2Cl(H)Ir]_2(\mu\text{-}CH_3C_6H_3N{=}NC_6H_3CH_3)$. In both experiments, the cyclometalated complex derived from the azo compound is formed more rapidly than that from the hydrazine. Thus the azo compound is likely to be an intermediate in the reaction of $IrCl(PEt_3)_3$ with PhNHNHPh.

Reactivity of $IrCl(PEt_3)_3$ with Tetrasubstituted Hydrazines. To avoid the formation of the azo complexes, $IrCl(PEt_3)_3$ was treated with the tetrasubstituted hydrazines shown in Chart 1. Heating a mixture of $IrCl(PEt_3)_3$ with tetraphenylhydrazine (Ph_2NNPh_2) at 70 °C in THF-d_8 leads only to formation of diphenylamine, with no change in the Ir starting material as indicated by ^{31}P NMR spectroscopy. Control experiments show that Ph_2NNPh_2 converts to Ph_2NH under these conditions in the absence of the iridium complex. The source of H is not clear; a Ph_2NH resonance is observed at $\delta = 7.3$ ppm in the ^1H NMR spectra in THF-d_8, and this has likely undergone exchange with the residual H_2O in the solvent. The thermal decomposition of Ph_2NNPh_2 to form Ph_2NH and other rearrangement products is known.[37] Similarly, 1,2-diphenyl-1,2-dimethylhydrazine (PhMeN−NMePh) does not react with $IrCl(PEt_3)_3$ up to 90 °C. The more electron-deficient tetrasubstituted hydrazines bisuccinimide, biphthalimide, and *N*-dimethylaminophthalimide (Chart 1b) also did not react with $IrCl(PEt_3)_3$. In all cases, the $IrCl(PEt_3)_3$ starting material is observed by $^{31}P\{^1H\}$ NMR spectroscopy after ~30 h at 90 °C. Under these conditions ($IrCl(PEt_3)_3$, 70 °C, THF-d_8) oxidative addition of the N−H bond of Ph_2NH is not observed over the course of 2 days or at higher temperatures (90 °C) for a day, although addition of the N−H bond of $PhNH_2$ occurs readily under milder conditions (50 °C).[29d]

II. Reactivity of Rh(NNN)Cl with Hydrazines. Square-planar Rh(I) complexes containing tridentate "pincer" nitrogen donor ligands, $Rh(2,6\text{-}(RN{=}CR')_2C_5H_3N)Cl$, have been described by Vrieze and co-workers.[38] These compounds undergo rapid oxidative addition of a variety of C−Cl bonds under mild conditions. The hemilabile nature of the imine arm provides accessible coordination sites on the Rh(I) complex, while the tridentate binding mode is available to stabilize the Rh(III) product. One derivative (R = *i*-Pr, R′ = Me) has been shown to react with O_2 to form a stable side-on bound peroxo species.[39]

Heating a mixture of 8 equiv of PhNHNHPh and Rh(NNN)Cl (NNN = $2,6\text{-}(CyN{=}CH)_2C_5H_3N$) in toluene-$d_8$ at temperatures up to 125 °C results in no change in the rhodium complex, and only the conversion of PhNHNHPh (2.4 equiv after 8 h) to PhN=NPh and $PhNH_2$ is observed by ^1H NMR spectroscopy (eq 2). Under the same conditions in the absence of the rhodium complex, <5% yields of PhN=NPh and $PhNH_2$ are observed. This is consistent with literature reports that the disproportionation of PhNHNHPh occurs thermally only at higher temperatures.[40] In sum, Rh(NNN)Cl shows limited reactivity with PhNHNHPh and oxidative addition of the N−N bond has not been observed.



(2)

Rh(NNN)Cl is unreactive with both Ph_2NNPh_2 (~3 equiv) and Ph(Me)NN(Me)Ph (~6 equiv) at 50 °C, 80 °C, and even heating at 125 °C in toluene-d_8 for 14 h. Under these conditions, the hydrazine decomposes to the amine (diphenylamine and *N*-methylaniline respectively) and the rhodium starting material remains unchanged. Similarly, after heating an excess of each of the more electron-deficient hydrazines (bisuccinimide, biphthalimide, and *N*-dimethylaminophthalimide) with Rh(NNN)Cl in toluene-d_8 no reaction was observed by ^1H NMR spectroscopy at temperatures up to 125 °C.

III. Reactivity of $(NN)PtMe_2$ with Hydrazines. Dimethylplatinum complexes with nitrogen donor ligands have been shown to oxidatively add a number of species including those with C−X, C−H, C−O, O−H, and Sn−H bonds.[41] Of particular interest are the oxidative additions of O−O, S−S, and Se−Se bonds by the phenanthroline complex $(phen)PtMe_2$ to give the six-coordinate $(phen)Pt(Me)_2(RE)_2$ species.[42] The preference of these systems to react with the O−O bond in H_2O_2 rather than the O−H bond indicates that protonolysis can be slower than

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(39) Haarman, H. F.; Bregman, F. R.; van Leeuwen, P. W. N. M.; Vrieze, K. *Organometallics* **1997**, *16*, 979–985.

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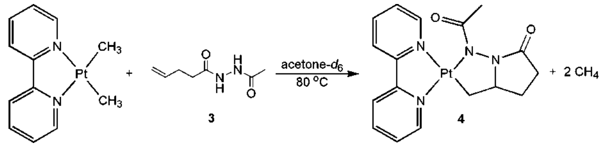
oxidative addition in this system. By analogy, N−N bond activation could be observed instead of N−H cleavage in the analogous reactions with hydrazines.

Addition of PhNHNHPh (∼10 equiv) to a solution of (phen)PtMe$_2$ in acetone-d_6 shows no change in the (phen)PtMe$_2$ resonances of the ^{1}H NMR spectrum after heating at 125 °C for 20 h. In contrast, the 2,2′-bipyridine analogue (bpy)PtMe$_2$ reacts with PhNHNHPh (4 equiv) at 80 °C to form CH$_4$ and an intractable yellow precipitate.

To eliminate the possible N−H addition pathway, the tetrasubstituted hydrazines were studied. Heating a mixture of (bpy)PtMe$_2$ with Ph$_2$NNPh$_2$ in acetone-d_6 to 80 °C leads to the formation of Ph$_2$NH before any change is observed in the Pt species. (bpy)PtMe$_2$ is unreactive toward each of the electron-deficient hydrazines shown in Chart 1b (4 equiv) in DMF-d_7 up to 125 °C; only decomposition of the platinum starting material is observed.

Characterization of (bpy)Pt(η^2-AcN-NC(O)(CH$_2$)$_2$CHCH$_2$ (4). In our efforts to use N−N oxidative addition to develop a catalytic amination reaction, we investigated the reactivity of (bpy)PtMe$_2$ with a hydrazine containing a pendant alkene: AcNHNHC(O)CH$_2$CH$_2$CH=CH$_2$ (**3**). Heating a solution of (bpy)PtMe$_2$ with **3** in acetone at 80 °C for 1 day leads to formation of CH$_4$ and precipitation of a new platinum product (**4**) (eq 3). ESI/MS analysis (m/z = 506) is consistent with the incorporation of a single hydrazine and loss of 2 equiv of CH$_4$. The ^{1}H NMR spectrum of **4** contains eight aryl resonances and seven distinct resonances in the alkyl region due to the hydrazine. This indicates that both the C_{2v} symmetry of the bpy ligand and the C_s symmetry of the hydrazine have been broken. The coupling of the alkyl protons is consistent with cyclization to the metallacycle **4** (eq 3).



(3)

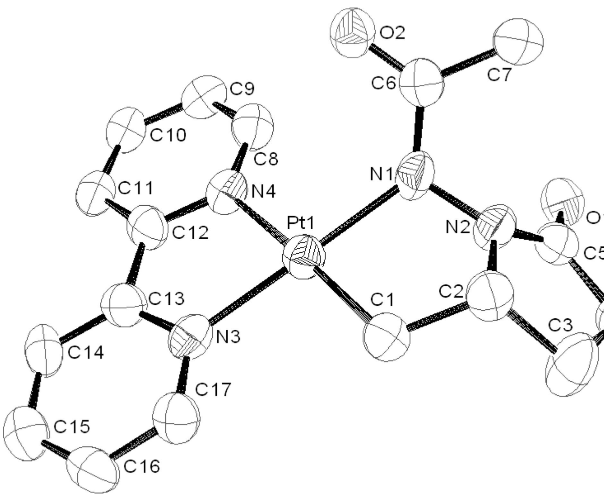


Figure 2. ORTEP of (bpy)Pt(η^2–AcN–NC(O)(CH$_2$)$_2$CHCH$_2$ (**4**) showing one of the two independent molecules in the unit cell with 50% probability ellipsoids.

Table 3. Selected Bond Distances (Å) and Angles (deg) in 4

Pt1−N1	2.007(6)	N1−Pt1−C1	81.8(3)
Pt1−N4	2.085(6)	N1−Pt1−N4	100.7(2)
Pt1−N3	2.022(6)		
Pt1−C1	2.045(7)		
N1−N2	1.394(8)		

The structure of **4** was confirmed by crystallographic structural analysis. X-ray quality crystals of **4** formed in the above reaction mixture after heating at 80 °C. The product crystallized with two independent molecules in the unit cell; one of these is shown in Figure 2 (crystallographic and metric data are shown in Tables 2 and 3). The binding mode of the substrate indicates net cleavage of both N−H bonds and cyclization of the alkene tether to form the five-membered pyrrolidinone, which after protonation would yield the hydrohydrazination product. The platinum center is nearly square planar with chelating bite angles of 81.8° (C1−Pt1−N1) and 79.3° (N3−Pt1−N4). The N−N distance of 1.394(8) Å is consistent with a single bond and is only slightly shorter than those seen in chelating benzoyl- and acyl-hydrazido platinum complexes (1.401(9)[43] and 1.421(6)[44] Å, respectively). The Pt−N(amide) bond distance (Pt1−N1, 2.007(6) Å) is slightly shorter than those reported for the acyl- (2.050(5) Å) and benzoylhydrazido species (2.047(6) Å). The Pt−C bond length (2.045(7) Å) is similar to that in a complex containing a related ring system with a neutral chelating N (2.067(12) Å).[45] The Pt1−N4 distance is 0.063 Å longer than the Pt1−N3 distance, consistent with the stronger *trans* influence of the alkyl ligand compared to the amide ligand.

The metallacycle **4** results from cleavage of both N−H bonds of the hydrazine and addition of one hydrazine nitrogen atom to the alkene to form a new C−N bond. The N−N bond remains intact. A related metallacycle (a fused four- and five-membered ring system) has been isolated by Widenhoefer et al.[46] This complex is derived from an alkene-tethered amine and PtCl$_2$(PPh$_3$)$_2$ and forms through attack of the amine on the coordinated alkene. Widenhoefer's metallacycle involves coordination of a neutral amine, while in **4** the platinum coordinates an anionic amide nitrogen. Further studies of hydrohydrazination by (bpy)PtMe$_2$ are in progress.

Discussion

Overall, the formation of **1** and **2** from IrCl(PEt$_3$)$_3$ and PhNHNHPh (eq 1) involves oxidation of both the hydrazine and the iridium center. This could occur through either initial N−H addition or initial C−H addition. While the data available do not rule out initial C−H activation, the likely intermediacy of PhN=NPh suggests initial N−H addition to give an η^1-hydrazido(1−) complex. This is analogous to the reported oxidative addition of the N−H bond of PhNH$_2$ to IrCl(PEt$_3$)$_3$ which occurs readily under milder conditions (50 °C).[29d] The hydrazido complex can then lose H$_2$ to form azobenzene, followed by cyclometalation to give **1**, which then reacts further with IrCl(PEt$_3$)$_3$ to form **2** (Scheme 1). An alternative pathway involving β-hydride elimination to give IrCl(PEt$_3$)$_3$H$_2$ seems inconsistent with the low yield of this product unless PhN=NPh promotes its reductive elimination of H$_2$.

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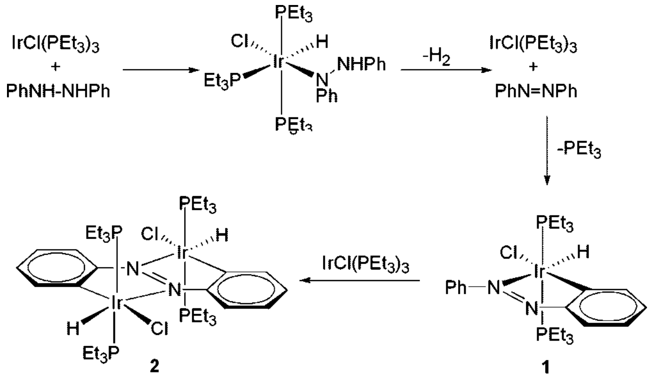
Scheme 1. Plausible Pathway for the Formation of 1 and 2



The Rh(NNN)Cl system reacts with PhNHNHPh to yield only the disproportionation products PhN=NPh and $PhNH_2$. Disproportionation of PhNHNHPh is known to occur at high temperatures (~240–280 °C),[40] and we and others have found this process to be catalyzed by metal complexes under milder conditions,[15a–c] although this catalysis is not well understood.

The reaction of (bpy)$PtMe_2$ with hydrazine **3** led to the isolation of the new Pt metallacycle **4** (eq 3). A plausible mechanism for metallacycle formation begins with the cleavage of the N−H bond and loss of CH_4. $PtCl_2(PR_3)_2$ complexes are known to eliminate both N−H hydrogens of electron-deficient hydrazides (acetyl and benzoyl protected) to give stable square-planar Pt(II) hydrazido(2−) species with loss of HCl.[47] These compounds can also be obtained from reaction of $Pt(PR_3)_2(H_2C{=}CH_2)$ with the corresponding azo compounds.[48] $[Pt(dppp)(OH)]_2$ (dppp = diphenylphosphinopropane) reacts with 1,1- and 1,2-disubstituted hydrazines to give the corresponding hydrazido complexes, where deprotonation of the hydrazine is likely assisted by the basic hydroxo ligands.[49]

Cleavage of N−N vs N−H Bonds. N−N bond cleavage has been observed, as noted above, in strongly reducing early transition metal systems and in a number of multimetallic and metal hydride complexes. In the systems described here, however, which undergo a variety of facile X−Y oxidative addition reactions, N−N bond scission is not favored. Instead, the hydrazines react through different pathways. $IrCl(PEt_3)_3$ reacts with PhNHNHPh to form the cyclometalated azobenzene complexes **1** and **2**. Reaction of (bpy)$PtMe_2$ with the alkene-tethered hydrazide **3** gives an alkyl-amido metallacycle **4**, formed through cleavage of both N−H bonds. The Rh(NNN)Cl complex is unchanged by reaction with PhNHNHPh, although this system promotes the disproportionation of PhNHNHPh into $PhNH_2$ and PhN=NPh via an unknown mechanism. None of these systems react with the tetrasubstituted hydrazines.

Thermodynamic Factors. The inertness of the N−N bond is surprising given the homolytic bond energies. The N−N bond of a hydrazine is by far the weakest bond in the molecule: for H_2NNH_2, $D(N{-}N) = 65$ kcal mol^{-1} and $D(N{-}H) = {\sim}80$ kcal.[50] Although the N−N bond is weak, it is possible that formation of a bis(amido) species is thermodynamically unfavorable. The only example of formation of a hydrazine from a metal amide that we are aware of is the production of Ph_2NNPh_2 upon heating a solution of $Cp^*(PMe_3)_2RuNPh_2$, which likely occurs by homolysis.[51] Polyamido complexes are well known for the early transition metals,[52] but are rare with later metals. Of the late metal amido complexes that are known,[53] a few bis(amido) species have been isolated[54] including an anionic Pd(II) bis(anilide) salt,[55] Ru(IV) and Ru(III) complexes with chelating nitrogen ligands,[56,57] and $Cp^*Ir^{III}(NHTs)_2(PPh_3)$.[58]

If the rarity of higher oxidation state bis(amido) complexes of the late metals is due to their instability, then the difficulty in observing N−N oxidative addition could have a thermochemical origin. An estimate of the thermochemistry of hydrazine oxidative addition can be derived for the $IrCl(PEt_3)_3$ system. We use the relative M−H and M−N bond strengths estimated by Bryndza et al., that M−H are ca. 21 kcal mol^{-1} stronger than M−N, derived from equilibrium exchange experiments of $Cp^*(PMe_3)_2RuX$ (X = OH, H, NHPh).[51] $IrCl(PEt_3)_3$ rapidly oxidatively adds aniline to give the amido hydride complex, cleaving the N−H bond (92 kcal mol^{-1})[50] and forming Ir−NHPh and Ir−H bonds. The oxidative addition of PhHN−NHPh would cleave the *much* weaker N−N bond, only 34 kcal mol^{-1},[59] and form two Ir−NHPh bonds. Based on Bryndza's estimate, the Ir−NHPh bond should be about 21 kcal mol^{-1} weaker than the Ir−H. Overall, however, cleavage of the 58 kcal mol^{-1} weaker bond (N−N vs N−H) is a much larger effect than the formation of the 21 kcal mol^{-1} weaker bond (Ir−NHPh vs Ir−H). Thus PhHN−NHPh oxidative addition is indicated to be more favorable than the facile H−NHPh addition by a remarkable 37 kcal mol^{-1}.[60] Clearly, the inertness of the N−N bond of hydrazines to $IrCl(PEt_3)_3$ does not have a thermodynamic origin.

With (phen)$PtMe_2$, however, the facile addition of HOOH mentioned above does not imply that PhHN−NHPh addition is necessarily favorable. The two Pt−OH bonds should each be ca. 27 kcal mol^{-1} stronger than the Pt−NHR bonds,[61] more than enough to compensate for the stronger O−O bond of HOOH (51 kcal mol^{-1}) relative to PhHN−NHPh (34 kcal mol^{-1}), making N−N addition 37 kcal mol^{-1} less favorable than O−O addition. Still, given the weakness of the hydrazine

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(60) If the linear correlation of M−X and H−X bond strengths is used, the M−H bond is estimated to be 12 kcal mol^{-1} weaker than the M−NHPh. This analysis shows PhHN−NHPh oxidative addition to be 46 kcal mol^{-1} more favorable than H−NHPh addition.

(61) $D(H{-}OH) = 119.2$ kcal mol^{-1}: Reints, W.; Pratt, D. A.; Korth, H.-G.; Mulder, P. *J. Phys. Chem. A* **2000**, *104*, 10713–10720.

N−N bond, with minimal 25 kcal mol^{-1} Pt−NHPh bonds[62] oxidative addition would be exothermic by ca. 16 kcal mol^{-1}.

This analysis suggests that the inability to observe hydrazine oxidative addition does not have a thermochemical origin. While such thermochemical estimates based on bond strength arguments are necessarily approximate, the magnitude of the predicted differences (16 to 37 kcal mol^{-1}) provides a measure of confidence in the conclusions.

Kinetic Factors. The metal complexes examined here are unreactive with the hydrazine N−N bond most likely due to high kinetic barriers. In this respect, N−N oxidative addition may be similar to C−C bond oxidative addition.[63] C−C oxidative addition is typically observed only for highly strained substrates,[8] and one of the few possible examples of hydrazine addition is with a highly strained diaziridinone.[14] In cases where oxidative addition of a nonstrained C−C bond would be thermodynamically favorable, C−H activation usually occurs instead.[64] This is thought to be due at least in part to steric difficulties in bringing the C−C bond to a metal center. Forming monomeric η^2-bound hydrazine complexes appears to be difficult as well, as only a limited number have been isolated These are most commonly obtained by protonation of the corresponding hydrazido species,[65] although a few exceptions include cyclopentadiene-ligated Mo and W complexes,[66] a Co species with a tripod phsophine ligand $[(CH_3C(CH_2PPh_2)_3)Co(\eta^2\text{-}N_2H_4)][BPh_4]$,[67] and the recently reported *cis*-$[Fe(DMeOPrPE)_2(\eta^2\text{-}N_2H_4)][BPh_4]_2$ (DMeOPrPE = 1,2-bis[bis(methoxypropyl)phosphino]ethane).[68] Hydrazine η^1- or bridging η^2-binding modes are more common.[65]

For tetrasubstituted hydrazines, steric factors likely contribute to the difficulty in oxidative addition. While N−H oxidative addition to $IrCl(PEt_3)_3$ is facile for aniline, we observe no reaction with Ph_2NH even at high temperatures. Similarly, the reaction of $(Cp^*RuCl)_4$ with Ph_2NNPh_2 is much slower than the analogous reaction with PhNHNHPh that occurs at room temperature.[69] Thus both the intrinsic inaccessibility of the hydrazine N−N bond and other steric factors seem to contribute to the high-energy transition state for oxidative addition of the nonpolar N−N bond.

Conclusion

The reactivity of hydrazines has been examined with three different low-valent, electron-rich complexes: $IrCl(PEt_3)_3$, Rh(NNN)Cl, and $(NN)PtMe_2$. These systems were chosen because among them they undergo a very wide range of oxidative addition reactions. However, no N−N oxidative addition process has been observed. Disubstituted hydrazines were observed in the Ir and Pt systems to preferentially react via the N−H bond: the iridium complex forming a cyclometalated azo complex and the platinum one a metallahydrazination product. Rh(NNN)Cl promotes the disproportionation of PhNHNHPh into PhN=NPh and $PhNH_2$. No reactivity was observed with any of the systems with tetrasubstituted hydrazines, either electron-rich or electron-deficient derivatives. We conclude that the oxidative addition of the N−N bond of hydrazines is not a facile process and suggest that this has a kinetic and not thermodynamic origin. Oxidative addition of N−N bonds appears to be analogous to C−C oxidative addition, which is also typically kinetically inhibited.

Experimental Section

General Considerations. All manipulations were performed under N_2 using standard high-vacuum-line or inert atmosphere glovebox techniques unless otherwise noted. Solvents were purchased from Fisher and Cambridge (deuterated) and were dried before use (pentane, THF, THF-d_8, toluene-d_8 using sodium/benzophenone; $CHCl_3$ using CaH_2; and acetone, acetone-d_6 using 4 Å mol sieves). DMF-d_7 was used as received. $IrCl_3\cdot 3H_2O$, $RhCl_3\cdot 3H_2O$, and K_2PtCl_4 (Pressure Chemical) were used as received. $IrCl(PEt_3)_3$,[30] $RhCl(2,6\text{-}(CyN{=}CH)_2C_5H_3N)$,[38a] $Pt(bpy)(CH_3)_2$,[70] $Pt(phen)(CH_3)_2$,[71] TolNHNHTol,[72] Ph_2NNPh_2,[73] Ph(Me)NN(Me)Ph,[74] bisuccinimide,[75] biphthalimide,[76] and N-dimethylaminophthalimide[77] were made according to literature procedures. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker Avance 300 (^1H and $^{31}P\{^1H\}$) or 500 (^1H, $^{13}C\{^1H\}$) MHz spectrometers and referenced to the residual solvent signal (^1H and ^{13}C) or an external H_3PO_4 standard (^{31}P); all coupling constants are reported in Hz. Assignments of the $^{13}C\{^1H\}$ NMR resonances were made using a 2D HMQC experiment. Mass spectra were recorded from CH_3CN solutions on a Bruker Esquire ion trap electrospray ionization mass spectrometer (ESI/MS). Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA).

Typical Procedure for NMR Reactions with Hydrazines. All reactions of metal complexes with hydrazines were performed in J. Young NMR tubes under N_2 with dry solvent, heated in an oil bath, and removed to record ^1H and $^{31}P\{^1H\}$ NMR spectra at room temperature.

$(PEt_3)_2Cl(H)Ir(C_6H_4N{=}NPh)$ (1). Compounds **1** and **2** can be prepared from Ir and PhNHNHPh, but purification is easier when azobenzene is used. PEt_3 (175 μL, 1.18 mmol) was added to a solution of $[Ir(COE)_2Cl]_2$ (72.5 mg, 0.081 mmol) in ether (30 mL) at −78 °C. The reaction mixture was allowed to warm to RT and stirred for 1 h. The solvent was removed and the resulting oil was transferred to a sealed tube and combined with PhN=NPh (31.2 mg, 0.17 mmol) and THF (2 mL). After heating at 90 °C for 3 days, the solvent was removed and the crude solids were washed with pentane (3 × 1 mL). The red pentane solution contains mostly

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(62) If Pt^{IV}−NHPh bonds were weaker than 30 kcal mol^{-1}, facile homolysis would be observed, contrary to the behavior of such species (see ref 11c). We estimate that the Pt^{III}−NHPh bond is unlikely to be weaker than 20 kcal mol^{-1}, so the average Pt−N bond strength in the hypothetical $Pt(NHPh)_2$ species is most likely >25 kcal mol^{-1}.

(63) We thank Professor B. Scott Williams for his insightful suggestion.

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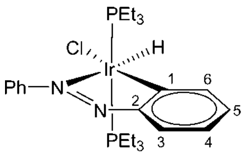
1, which can be purified by silica gel column chromatography (hexanes/CH_2Cl_2, increasing CH_2Cl_2 as each product elutes) to give 20.6 mg of a red solid (0.032 mmol, 20%). ^1H NMR (THF-d_8, 500 MHz): δ 8.76 (d, $J = 7.5$, 2H, *o*), 8.10 (d, $J = 7.5$, 1H, H3), 7.80 (d, $J = 8$, 1H, H6), 7.42 (t, $J = 8$, 2H, *m*), 7.30 (t, $J = 7.5$, 1H, *p*), 7.05 (t, $J = 6.5$, 1H, H4), 6.88 (t, $J = 6.5$, 1H, H5), 1.57 (m, 6H, PCH_2), 1.49 (m, 6H, PCH_2), 0.71 (quint, 18H, CH_3), –17.79 (t, $J = 17.5$, 1H, IrH). $^{31}P\{^1H\}$ NMR (THF-d_8, 121 MHz): δ −6.40 (s). $^{13}C\{^1H\}$ NMR (THF-d_8, 125 MHz): δ 165.1 (C2), 156.8 (t, $J = 6.5$, C1), 141.5 (C6), 132.7 (C5), 131.9 (C3), 130.6 (*p*), 128.9 (*m*), 126.7 (*o*), 122.0 (C4), 16.5 (t, $J = 17.5$, PCH_2), 7.6 (CH_3). ESI/MS (CH_3CN): *m/z* 647 $[M + H]^+$, 611 $[M - Cl]^+$.



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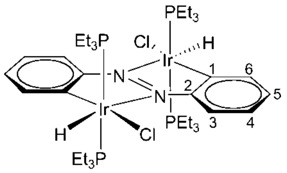

2

$(PEt_3)_2Cl(H)Ir(\mu$-$C_6H_4N{=}NC_6H_4)IrCl(H)(PEt_3)_2$ (2). The dark solids obtained above were recrystallized from THF/pentane at −78 °C to give **2** as a dark purple microcrystalline powder (17.6 mg, 0.032 mmol, 20%). ^1H NMR (THF-d_8, 300 MHz): δ 10.37 (d, $J = 8.4$, 2H, H3), 7.73 (d, $J = 7.5$, 2H, H6), 6.93 (t, 7.5, 2H, H4), 6.74 (t, $J = 6.9$, 2H, H5), −17.64 (t, $J = 18$, 2H, IrH). $^{31}P\{^1H\}$ NMR (THF-d_8, 121 MHz): δ −4.37 (s). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 166.12 (*C*2), 152.85 (C1) 141.25 (C6), 133.54 (C3), 131.36 (C5), 121.33 (C4) 17.35 (t, $J = 17$, PCH_2), 8.25 (CH_3). ESI/MS (CH_3CN): *m/z* 955 ($[Ir_2(PEt_3)_3(PhN{=}NPh)Cl]^+$). Anal. Calcd for $C_{36}H_{70}Cl_2Ir_2N_2P_4$: C, 38.95; H, 6.36; N, 2.52. Found: C, 39.30; H, 6.36; N, 2.46.

Absolute assignments (6 position vs 3 position) were made by analogy to literature.[34]

Pent-4-enoic Acid *N′*-acetyl Hydrazide (3). Pent-4-enoyl chloride (~14.7 mmol) was added dropwise to a solution of acyl hydrazine (from H_2NNH_2 and EtOAc)[78] (1.04 g, 14.0 mmol) and Na_2CO_3 (11 g, 104 mmol) in $CHCl_3$ (20 mL) at 0 °C. The reaction mixture was stirred for 15 min, then warmed slowly to RT for an additional 45 min. The solids were filtered and washed with $CHCl_3$. The solvent was removed from the filtrate to give a white solid (1.95 g, 12.5 mmol, 85% yield). The product was recrystallized from ethyl acetate/hexanes. ^1H NMR (CD_2Cl_2, 300 MHz): δ 8.63 (s, 1H, NH), 8.56 (s, 1H, NH), 5.82 (m, 1H CH), 5.07 (dd, $J = 17{,}1.2$, 1H $=CH_2$), 5.00 (d, $J = 5$, 1H, $=CH_2$), 2.36 (m, 4H, $-CH_2-$), 2.01 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 170.51, 168.18, 137.45, 116.02, 33.85, 29.84, 21.05.

(bpy)Pt(η^2–AcN–NC(O)(CH_2)$_2$CHCH$_2$) (4). Pt(bpy)(CH_3)$_2$ (92.0 mg, 241 mmol) and **3** (83 mg, 530 mmol) were combined in acetone (1 mL) in a sealed tube and heated at 80 °C for 24 h. The resulting yellow precipitate was collected and washed with acetone (0.5 mL) and ether (1 mL) and dried to give 27.7 mg of a yellow solid (54.8 mmol, 23% yield). ^1H NMR (DMF-d_7, 300 MHz): δ 9.98 (d, $J = 3.3$, 1H, bpy H6), 8.92 (d, $J = 3.3$, 1H, bpy H6′), 8.59 (d, $J = 4.5$, 2H, bpy H3 and H3′), 8.38 (t, $J = 5.1$, 1H, bpy H4′), 8.33 (t, $J = 4.5$, 1H, bpy H4), 7.73 (t, $J = 3.9$, 1H, bpy H5), 7.66 (t, $J = 3.6$, 1H, bpy H5′), 3.49 (m, 1H, pyr CH), 2.59 (dd, $J = 6.3$, 4.2, 1H, $PtCH_2$), 2.45 (m, 2H, $Pt-CH_2$, and $PtCH_2CHCH_2$), 2.32 (m, 1H, $PtCH_2CHCH_2CH_2$), 2.18 (m, 1H, $PtCH_2CHCH_2CH_2$), 1.97 (s, 3H, CH_3), 1.78 (m, 1H, $PtCH_2CHCH_2$). $^{13}C\{^1H\}$ NMR (DMF-d_7, 125 MHz): δ 178.28 (*C*O), 172.60 (*C*O), 155.21 (bpy C6), 151.48 (bpy C6′), 139.90 (bpy C4 or C4′), 139.49 (bpy C4 or C4′), 128.79 (bpy C5′), 128.22 (bpy C5), 125.16 (bpy C3 or C3′), 123.57 (bpy C3 or C3′), 60.93 ($PtCH_2CH$), 31.32 ($Pt-CH_2CHCH_2CH_2$), 26.20 ($Pt-CH_2$), 24.90 ($Pt-CH_2CHCH_2$), 22.20 (C(O)H_3). ESI/MS (CH_3CN): *m/z* 506 $[M + H]^+$. Anal. Calcd for **4**·H_2O $C_{17}H_{20}N_4O_3Pt$: C, 39.01; H, 3.85; N, 10.70. Found: C, 39.27; H, 3.46; N, 10.77.

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Supporting Information Available: Figures showing the growth of products in the reactions that yield **1**, **2**, **1-Tol**, and **2-Tol** and CIFs for **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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