Syntheses of Bispyrazolyl Monotriazolyl Heteroscorpionate Platinum(IV) Complexes Including an Unusual Pt-CH₂CH₂-Pt Bridge

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This article is dedicated to the prolific and productive platinum chemist Professor Georgiy B. Shul'pin on the event of his 70th birthday.

Abstract

Scorpionate ligands provide the benefit of hemilability while minimizing complete dissociation of the ligand. Previous investigations into Tp'PtL_nX_m complexes [Tp' = hydridotris(3,5-dimethylpyrazolyl)borate] revealed the importance of hemilability as the Tp' ligand facilitates Pt(II/IV) interconversions. Here we discuss the synthesis and metalation of a series of asymmetric scorpionate ligands bearing two pyrazolyl rings and one triazolyl ring. In addition to utilizing triazole donor arms with differing substituents, we also compare octahedral structures of Pt(IV) complexes with P=O and C-H and B-H caps at the pole of the facial tridentate umbrella. Oxidation from Pt(II) to Pt(IV) with electrophilic reagents, simple acids and acid chlorides, leads to isomers in some cases, and the binding properties of the various donor arms dictate the stereochemistry of the products. Investigations into the reactivity of heteroscorpionate tridentate ligands bound to platinum(II) led to C-Cl activation reactions with methylene chloride and 1,2-dichloroethane. Isolation of a dinuclear platinum complex bridged by an ethylene unit produced

an unusual proton NMR AA'XX' pattern in the ^1H NMR spectrum due to chirality at each platinum center.

1. Introduction

Platinum is known for its paradoxical chemical behaviour, namely its high catalytic activity, which is often easy to probe due to its chemical robustness. More specifically, platinum is able to easily cycle between three different oxidation states, Pt(0)/Pt(II)/Pt(IV), allowing it to catalyse a wide variety of transformations, often involving C-H activation. The homogeneous Shilov system first reported the organometallic transformation of methane to methanol, and the first step is C-H activation of methane.¹ Shul'pin et al. have reported on extensive studies of C_{aryl}-H activation to generate stable Pt(IV) complexes.^{2,3} More recently, investigations into C-H bond activation using Pt centers has focused on hemilabile ligands to help promote formation of stable Pt(IV) complexes that are less prone to reductive elimination.⁴⁻⁷

Hemilabile ligands containing both strong and weak donor arms have been employed in a wide range of metal-mediated processes.^{8,9} Such ligands provide the benefit of opening a coordination site on the metal while preventing complete ligand loss. Bidentate and tridentate hemilabile representations are sketched in Figure 1, where a strong donor ligand (X) remains bound to the metal center while a weaker donor (Y) can bind reversibly, thus creating a vacant coordination site.

Figure 1. Hemilabile representations in(a) bidentate and (b) tridentate ligands.

A plethora of metal-ligand systems have been developed that display reversible binding of one arm, and pincer ligands are an important class of hemilabile ligands. Milstein and co-workers have reported a Ru PNN pincer system that converts alcohols to esters, and the mechanism is believed to involve reversible coordination of a tethered amine.¹⁰ Goldberg et al. have synthesized a PCO tridentate ligand that can adopt κ^1 , κ^2 , and κ^3 coordination modes.¹¹ Van der Vlugt and co-workers have reported a simple synthetic route that generates PNN chelates that reversibly bind to Rh and Ir metal centers.¹² A hemilabile bidentate ligand with an oxygen donor arm bound to Rh(I) developed by Dunbar has been utilized for the reversible uptake of small molecules.^{13,14} A hemilabile Ru(II) system reported by Wolf displays reversible uptake of SMe_2 , DMSO, and acetonitrile.¹⁵ Recently, Miller has synthesized a NCP pincer-crown ether complex that can reversibly bind oxygen from the crown ether to help stabilize the metal center.¹⁶

The past decade has seen significant progress in the development of asymmetrical hemilabile tridentate facial chelates, including contributions from Rominger¹⁷ (NCO, PCO), Zargarian¹⁸ (PCN), Szabó¹⁹ (PCS), and Song²⁰ (PCP). The initial syntheses of asymmetric facially-coordinating ligands suffered from poor yields, especially for tris(3,5-dimethylpyrazolyl)methane (Tpm) derivatives.²¹⁻²⁴ Canty and co-workers developed an improved

synthetic route to asymmetrical Tpm-derived heteroscorpionates containing two pyrazolyl rings and a third, unique donor arm using a cobalt-catalyzed condensation.²⁵⁻³⁰ Deprotonation of free pyrazole followed by the addition of phosgene results in a bispyrazolyl ketone intermediate in this preparative route. Reger³¹ et al. advanced relevant synthetic methodology by using a bispyrazolyl sulfoxide intermediate that was prepared by employing thionyl chloride in place of phosgene, noteworthy since the thionyl chloride is both safer and easier to handle than phosgene (eq 1).

With a goal of facilitating interconversions between Pt(II) and Pt(IV), our lab investigated the synthesis and reactivity of tris(1-R-1H-1,2,3-triazol-4-yl)phosphine oxide (R = phenyl, cyclohexyl) (Tt^{R}).³²⁻³⁴ The Tt^{R} ligand was completely displaced from the Pt(II) center when nucleophilic reagents were introduced to the solution in attempts to attack the carbonyl ligand in the Pt-CO unit at the carbon atom. The inability to add nucleophilic reagents to ligands like CO without displacing the chelating ligand motivated us to synthesize a mixed pyrazolyl/triazolyl ligand. For $\text{Tp}^{\text{P}}\text{Pt}$ derivatives (Tp^{P} = hydridotris(3,5-dimethylpyrazolyl)borate), strong donation from the pyrazolyl nitrogen donors keeps the ligand bound while still allowing the κ^2/κ^3 interconversion.³⁵⁻³⁷

Utilizing Reger's improved method for generating mixed donor ligands, we prepared similar heteroscorpionates with a C-H backbone that incorporates the triazolyl

functionality. Herein, we report the synthesis and metalation of ligands that contain two pyrazolyl rings and one triazolyl ring as well as investigations into their reactivity. Structural data from seven monomeric platinum d⁶ complexes that exhibit octahedral geometries are included here for comparison of Pt(IV) bond distances; four of these structures complement the facial tridentate ligand in the coordination sphere with the PtMe₃ fragment. The second section of our report addresses electrophilic oxidation of Pt(II) isomers to form Pt(IV) products, and the third section probes chloride displacement by Pt(II) as a nucleophile in reactions leading to Pt(IV) alkyl complexes. Both C-13 and ¹H NMR spectra for [(bpztz^{Ph})Me₂PtCH₂CH₂PtMe₂(bpztz^{Ph})] provide definitive data pointing to the dinuclear skeleton due to the presence of Pt-195 coupling in the C-13 spectrum and due to chirality at both platinum centers complicating the ¹H splitting pattern.

2. Results and Discussion

2.1. Scorpionate Ligands: Comparing Tp', Tpm, Tt^R, POPz₃ and Bpztz Geometrical Parameters in Octahedral Pt(IV) Complexes

In the synthetic route to heteroscorpionate ligands reported by Reger,³¹ the final condensation step requires a carbonyl functionality attached to the heterocycle that will ultimately be the unique donor arm of the heteroscorpionate. We synthesized a 1,2,3-triazole with an aldehyde at the 4-position. Employing the same conditions as were used for the copper-catalyzed azide-alkyne cycloaddition “click” reaction that generated Tt^R,^{33,34,38} phenyl azide and propargyl alcohol were combined to produce (1-phenyl-1*H*-1,2,3-triazol-4-yl)methanol **1-L1** in 66% yield (step 1 in eq 2). The analogous cyclohexyl (cy) derivative (**1-L2**) was generated in 69% yield using cyclohexyl azide while the pentafluorophenyl (C₆F₅) derivative was generated in 64% yield. Stahl et al. recently reported selective oxidation of primary alcohols to the corresponding aldehyde using an aerobic Cu(I) triflate/TEMPO

system.³⁹ Utilizing similar reaction conditions here for oxidation of the alcohol produced 1-phenyl-1*H*-1,2,3-triazole-4-carbaldehyde **2-L1** (step 2 in eqn 2).

With the aldehyde compounds in hand, a heteroscorpionate ligand containing two 3,5-dimethyl pyrazolyl donors and a 1,2,3-triazole ring was targeted. Treating a THF solution of 3,5-dimethyl pyrazole with sodium hydride resulted in deprotonation of the pyrazole NH and evolution of hydrogen gas. The addition of thionyl chloride presumably generated the bispyrazolyl sulfonyl intermediate, **3**. Treating **3** with 1,2,3-triazole aldehyde **2-L1** and a catalytic amount of cobalt chloride⁴⁰⁻⁴² while refluxing overnight produced 4-(bis(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)-1-phenyl-1*H*-1,2,3-triazole **4-L1** in 87% yield, which we will abbreviate as bpztz^{Ph} (eq 3). The analogous bpztz^{Cy} ligand **4-L2** was produced in 56% yield while the bpztz^{C6F5} ligand **4-L3** was produced in 72% yield.

Metallation of the bpztz^R ligands was achieved by sequentially treating two equiv of ligand **4** with one equiv of [PtMe₂(SMe₂)]₂ and then an excess of methyl iodide was added (eq 4). The Pt(IV) iodide salt [bpztz^RPtMe₃][I] **5** was isolated as a pale yellow solid. In the ¹H NMR spectrum of **5-L1**, two Pt-Me singlets appear in a 2:1 ratio at 1.4 and 1.3 ppm with platinum satellites (²J_{Pt-H} = 71 Hz and 73 Hz, respectively), reflecting the presence of a molecular mirror plane. The chemical shift values and coupling constants for these Pt-Me signals are typical for Pt(IV)-Me complexes.⁴³⁻⁴⁶ The triazolyl proton in **5-L1** shifts downfield over 2 ppm (to 10.7 ppm) when the triazole ring binds to the metal center, an unusually large shift when compared to ¹H NMR spectra of Tt^R platinum complexes.^{33,38} In the C-13 NMR spectrum, the one-bond platinum-carbon coupling values for the two Pt-Me resonances are 685 Hz (trans to pyrazole) and 706 Hz (trans to triazole) for **5-L3**. These one-bond coupling constants are not good indicators of bond strength; that correlation works well when hydrogen is involved, but for other NMR active nuclei the correlation is far more complex. Coupling constants for Pt-C bonds in **5-L1** and **5-L2** were comparable in magnitude.

As a point of departure before looking at Pt-N bond lengths we note that the pK_a for pyrazole is 19.8 whereas the triazole proton is far more acidic with a pK_a of 13.9. While binding a proton six orders of magnitude more tightly may not map directly to binding a metal center, and occurs at an alternative nitrogen, it's reasonable to keep the proton dissociation properties of pyrazoles and triazoles in mind as we look at structures of Pt(IV) compounds. Figure 2 shows the various ligands that will be discussed throughout this paper.

Figure 2. **a.** hydridotris(3,5-dimethylpyrazolyl)borate. **b.** tris(3,5-dimethylpyrazolyl)phosphine oxide. **c.** tris(3,5-dimethylpyrazolyl)methane. **d.** tris(1-R-1H-1,2,3-triazol-4-yl)phosphine oxide (R = phenyl, cyclohexyl). **e.** 4-(bis(3,5-dimethyl-1H-pyrazol-1-yl)methyl)-1-R-1H-1,2,3-triazole (R = phenyl, cyclohexyl, pentafluorophenyl).

Figure 3 shows the x-ray structure of **5-L2** and selected bond distances and angles are presented in Table 1. The Pt-N bond distance to the triazolyl donor (2.135 Å) is the shortest of the three Pt-N bond lengths. The two pyrazolyl donors, with Pt-N distances of 2.18 and 2.19 Å, appear to be weaker donors to Pt(IV) than the triazole ring. The PtMe₃ unit assures that identical trans influences will impact the three Pt-N bond lengths. The contrast between the pK_a indicators and the observed Pt-N bond distances is striking.

Figure 3. X-ray structure of $[\text{bpztz}^{\text{Cy}}\text{PtMe}_3][\text{I}]$ **5-L2**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and counterion are omitted for clarity. Bond lengths ($\text{\AA}$): Pt-N₁ 2.135(4), Pt-N₄ 2.178(4), Pt-N₆ 2.193(4), Pt-C₁ 2.061(5), Pt-C₂ 2.042(5), Pt-C₃ 2.054(4). Bond angles (deg): N₁-Pt-N₄ 84.85(14), C₁-Pt-N₁ 93.54(17), C₂-Pt-C₁ 84.8(2).

Figure 4 shows the x-ray structure of **5-L3** and selected bond distances and angles are presented in Table 2. The Pt-N(triazole) bond distance of 2.138 $\text{\AA}$ is again shorter than the two Pt-N(pyrazole) distances, both 2.19 $\text{\AA}$, reflecting stronger binding from the triazolyl ring compared to the two pyrazoles. Comparing the Pt-N(triazole) distance to the analogous $[\text{bpztz}^{\text{Cy}}\text{PtMe}_3]^+$ structure reveals that the addition of the pentafluorophenyl substituent did not have a noticeable impact on the donor strength of the triazolyl ring as determined by bond distance measurements.

Figure 4. X-ray structure of $[\text{bpztz}^{\text{C}_6\text{F}_5}\text{PtMe}_3][\text{I}]$ **5-L3**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and the iodide counterion are omitted for clarity. Bond lengths (Å): Pt-N₁ 2.138(3), Pt-N₄ 2.188(3), Pt-N₆ 2.188(3), Pt-C₂₀ 2.042(4), Pt-C₂₁ 2.050(4), Pt-C₂₂ 2.058(4). Bond angles (deg): N₁-Pt-N₄ 84.95(12), C₂₀-Pt-N₁ 91.61(15), C₂₀-Pt-C₂₁ 89.67(18).

While the two $\text{bpztz}^{\text{R}}\text{PtMe}_3^+$ structures were in good agreement with one another, the triazole bond distances were shorter than in the analogous Tt^{R} complex with three triazole arms

for the scorpionate ligand. The average Pt-N bond length for the Tt^R ligand in the $Tt^R PtMe_3^+$ complex³³ was 2.18 Å, longer than the Pt-N bond to the triazole in **5-L2** and **5-L3**.

Since the pentafluorophenyl group on the triazolyl arm had no significant impact on the Pt-N bond length, we turned to an investigation of the influence of the phosphine oxide spine in the Tt^R system. Comparing the new mixed tridentate ligand to the triazole based Tt^R ligand with a P=O spine, it's conceivable that the difference in binding strength of the triazole arm arises from differences in the spine of the umbrella skeletons. Deprotonation of 3,5-dimethylpyrazole with sodium hydride followed by addition of phosphoryl chloride resulted in the desired tris(3,5-dimethylpyrazolyl)phosphine oxide (POPz₃) **6**, in 96% yield. Access to the desired Pt(IV) complex was provided by switching from MeI to a stronger methylating reagent, methyl trifluoromethanesulfonate (MeOTf), and extending the reaction time to form the cationic Pt(IV) complex, [POPz₃PtMe₃][OTf], **7** (eq 7). Complex **7** displayed C_{3v} symmetry in the ¹H NMR spectrum and the pyrazolyl protons showed a small coupling to phosphorus (1 Hz) while the ³¹P NMR signal at -18.3 ppm exhibited 3-bond coupling to platinum (9 Hz).

Figure 5 shows the x-ray structure of **7** and selected bond distances and angles are presented in Table 3. The three pyrazolyl Pt-N bond distances of ca. 2.20 Å are slightly elongated from those of the analogous trimethylPt(IV)Tp' complex, which are near 2.19 Å.⁴⁷ The Pt-N distances for these pyrazolyl donors are also close to the bond lengths observed for the triazole based Tt^R ligand (2.17-2.19 Å).³³

Figure 5. X-ray structure of $[\text{POPz}_3\text{PtMe}_3][\text{OTf}]$ **7**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms, trifluoromethanesulfonate counterion, and benzene molecule are omitted for clarity. Bond lengths (Å): Pt-N₁ 2.201(4), Pt-N₃ 2.199(4), Pt-N₅ 2.185(5), Pt-C₁ 2.041(6), Pt-C₂ 2.047(5), Pt-C₃ 2.052(4). Bond angles (deg): N₁-Pt-N₃ 88.2(2), C₁-Pt-N₃ 92.6(3), C₂-Pt-C₁ 89.0(2).

The phosphine oxide backbone did not significantly change the Pt-N bond lengths so we turned to the C-H backbone in the well-known Tpm ligand, just as the C-H moiety is present in the mixedbpztz^R set of ligands. Employing Tpm³¹ under the same conditions as used for the

preparation of POPz₃ complex **7** generated the desired cationic Pt(IV) complex, [TpmPtMe₃][OTf], **8**, eq 8.

Figure 6 shows the x-ray structure of one of the three independent molecules found in the unit cell, and selected bond distances and angles are presented in Table 4. The Pt-N bond distances in this Tpm complex average 2.18 Å, slightly shorter than those observed in trimethyl Pt(IV) complexes with the other neutral ligands, namely Tt^R and POPz₃, presumably due to the more electron donating C-H backbone. The anionic Tp⁻ ligand leads to a neutral Pt(IV) complex while all the other complexes reported here are cationic Pt(IV) compounds. Despite the slightly shorter bond lengths of the TpmPt complex compared to the mixed ligand system, the Pt-N bonds found in Tpm complex **8** were about 0.02 Å longer than the Pt-N distances for the triazole arm in the bpztz hybrid ligand system.

Figure 6. X-ray structure of [TpmPtMe₃][OTf] **8**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and trifluoromethanesulfonate counterion are omitted for clarity. Bond lengths (Å): Pt-N₂₉ 2.187(6), Pt-N₃₆ 2.189(6), Pt-N₄₃ 2.162(6), Pt-C₂₆ 2.044(7), Pt-C₂₇ 2.072(8), Pt-C₂₈ 2.049(8). Bond angles (deg): N₂₉-Pt-N₃₆ 83.0(2), C₂₆-Pt-N₃₆ 93.3(3), C₂₆-Pt-C₂₇ 88.4(3).

2.2 Electrophilic Addition: Isomer Preferences for d⁸ Pt(II) and d⁶ Pt(IV)

Bidentate binding of the bpztz^{Ph} ligand to form a square planar dimethylPt(II) complex could form two isomers. The ligand could bind either with one free pyrazole arm with both pyrazole rings bound and with the triazole ring free. If these two isomers were energetically equivalent and isomerization were easily accessible, a statistical 1:2 ratio favoring the asymmetrical isomer should result. The addition of two equivalents of bpztz^{Ph} to one equivalent of [PtMe₂(SMe₂)₂] in tetrahydrofuran initially displayed a 1:1 ratio of the symmetric to asymmetric isomers in the ¹H NMR. After 30 minutes a preference (3:1) for the symmetric (κ²-

bpztz^{Ph})Pt(CH₃)₂ isomer with the triazolyl arm free was evident. This ratio increased to 5:1 after 90 minutes. This result implies that in the square planar Pt(II) case, the triazole arm binds less tightly than the pyrazole arms, a different conclusion than was drawn above for Pt(IV) based on solid state Pt-N bond distances. The difference in Pt(II) d⁸ versus Pt(IV) d⁶ binding preferences seemed poised to promote oxidative addition to the metal center: the triazole arm would be non-coordinated in the Pt(II) state then stabilize the high valent Pt(IV) by donating electron density to the metal center and completing a six-coordinate geometry.

Mimicking previous results with Tp' and Tt^R, we synthesized a Pt(IV) hydride complex by protonation of the Pt(II) intermediate. Metalation of the bpztz^{Ph} ligand followed by low temperature addition of tetrafluoroboric acid resulted in the desired complex, [bpztz^{Ph}PtMe₂H][BF₄], **9** (eq 9). The ¹H NMR spectrum of the hydride product displayed two isomers in a 2:3 ratio with the symmetric complex as the major isomer. The major isomer has the hydride trans to the triazole arm and displays ¹J_{Pt-H} = 1424 Hz, while the minor asymmetric isomer has ¹J_{Pt-H} = 1480 Hz. Both ¹J_{Pt-H} values are typical coupling constants for Pt(IV) hydride complexes.^{37,48,49}

The more stable symmetrical isomer of the square planar Pt(II) intermediates with both pyrazole arms bound is presumably trapped by the oxidation of the Pt center as the acid adds to platinum. This places the hydride trans to the triazolyl ligand. However, the hydride is a stronger donating ligand than the methyl groups so it would prefer to bind trans to a pyrazole arm. Isolation of the symmetric Pt(IV) hydride complex demonstrates that once the Pt(IV) complex is formed, the barrier to isomerization increases significantly relative to the Pt(II) barrier. Under the conditions we utilized, isomerization of the mixed ligand only occurs at the Pt(II) d⁸ configuration before the complex is oxidized to Pt(IV).

Similar oxidation of Pt(II) to Pt(IV) addition reactions can be observed with other electrophiles. As shown in equation 10, the addition of acyl chloride to a solution of bpztz^{Ph} and [PtMe₂(SMe₂)]₂ results in a cationic Pt(IV) acyl complex. Anion exchange of chloride to triflate to generate [bpztz^{Ph}PtMe₂(C(O)CH₃)]⁺[OTf]⁻, **10**, was accomplished by addition of MeOTf. Only the symmetric isomer with the triazole donor arm trans to the acyl ligand was observed in the ¹H NMR spectrum. We attribute this to the acyl chloride reacting relatively slowly with the Pt(II) complex. Slow electrophilic addition of the acyl chloride would allow isomerization at the Pt(II) stage and thus the symmetric isomer could be selectively trapped.

An x-ray structure of **10** was obtained to confirm the geometry of the complex. However, due to disorder between the acyl oxygen and methyl group of the acyl ligand the geometrical parameters have been relegated to supporting information.

Comparable acyl chemistry was observed with Tpm as the tridentate ligand. The addition of acyl chloride to a solution of Tpm and [PtMe₂(SMe₂)]₂ followed by exchange of the anion results in the anticipated [TpmPtMe₂(C(O)CH₃)]⁺[OTf]⁻, **11**, (eq 11). The acetyl carbon in the ¹³C

NMR spectrum is seen at 191.5 ppm with 1-bond platinum coupling of 894 Hz, slightly smaller than the coupling seen for complex **10** (ca 912 Hz).

Figure 7 shows the x-ray structure of a monomeric unit of **11** and selected bond distances and angles are presented in Table 5.

Figure 7. X-ray structure of [TpmPtMe₂C(O)CH₃][OTf] **10**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and trifluoromethanesulfonate counterion are omitted for clarity. Bond lengths (Å): Pt-N₆ 2.188(5), Pt-N₁₃ 2.184(4), Pt-N₂₀ 2.170(4), Pt-C₁ 2.047(5), Pt-C₂ 2.024(8), Pt-C₃ 2.075(12), C₃-O 1.197(10). Bond angles (deg): N₆-Pt-N₂₀ 82.52(15), C₁-Pt-N₆ 92.4(2), C₃-Pt-N₂₀ 166.6(5), O-C₃-Pt 130.3(12).

2.3Pt(II) Reactions with alkyl chloride solvents

In the absence of electrophilic reagents, a solution of bpztz^{Ph} and $[\text{PtMe}_2(\text{SMe}_2)]_2$ in dichloromethane results in cleavage of a C-Cl bond of the solvent to form cationic complex $[\text{bpztz}^{\text{Ph}}\text{PtMe}_2(\text{CH}_2\text{Cl})]^+$, **12**, with Cl^- as the leaving group. The addition of tetrafluoroboric acid at low temperature effected anion exchange to produce $[\text{bpztz}^{\text{Ph}}\text{PtMe}_2\text{CH}_2\text{Cl}][\text{BF}_4]$, equation 12. In the ^1H NMR spectrum of **12**, a single resonance for both the Pt- CH_2Cl protons at 4.36 ppm ($^2J_{\text{Pt-H}} = 50$ Hz) along with one resonance for the pyrazolyl-protons at 6.06 ppm, indicate C_s symmetry. A 2D NMR HSQC spectrum displays crosspeaks between the protons at 4.36 ppm and a carbon at 20.3 ppm in the ^{13}C NMR. The peak at 20.3 ppm in the ^{13}C NMR displays 841 Hz coupling to Pt, indicative of a one-bond platinum carbon bond, confirming a direct Pt-C bond as opposed to the solvent binding through a chlorine atom of dichloromethane.⁵⁰⁻⁵²

Figure 8 shows the x-ray structure of a single unit of **12**, and selected bond distances and angles are presented in Table 6. The metal center adopts a slightly distorted octahedral geometry. The $\text{Pt-C}_1\text{-Cl}$ angle through the chloromethyl ligand is 114.8° , surely distorted from the ideal tetrahedral bond angle (109.5°) due to steric effects. The carbon metal bond to the methyl chloride ligand (Pt-C_1) is the shortest of the Pt-C bonds, at $2.026 \text{ \AA}$, consistent with expectations for an electron withdrawing group on the methyl ligand.

Figure 8. X-ray structure of $[\text{bpztz}^{\text{Ph}}\text{PtMe}_2\text{CH}_2\text{Cl}][\text{BF}_4]$ **12**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and counterion are omitted for clarity. Bond lengths ($\text{\AA}$): Pt-N₅ 2.110(4), Pt-N₁₆ 2.196(4), Pt-N₂₃ 2.187(4), Pt-C₁ 2.026(5), Pt-C₂ 2.056(5), Pt-C₃ 2.048(5), C₁-Cl 1.775(6). Bond angles (deg): N₅-Pt-N₁₆ 83.67(13), C₁-Pt-N₁₆ 95.64(19), C₁-Pt-C₂ 87.9(2), Cl-C₁-Pt 114.8(3).

Intrigued by the proclivity of Pt(II) to break C-Cl bonds, we investigated the possibility of the other tridentate ligands facilitating similar reactivity.⁵³⁻⁵⁵ No reactivity was observed with the POPz₃ ligand after a week of stirring in dichloromethane. Due to the low solubility of KTp' in dichloromethane, we first formed the $\kappa^2\text{Pt(II)}$ complex $[\text{K}][\kappa^2\text{Tp}'\text{PtMe}_2]$ in tetrahydrofuran, then added dichloromethane to the reaction mixture. Again, no oxidative addition of methylene chloride was observed. In contrast, the reaction of Tpm and $[\text{PtMe}_2(\text{SMe}_2)]_2$ in dichloromethane resulted in an analogous complex, $[\text{TpmPtMe}_2(\text{CH}_2\text{Cl})][\text{Cl}]$ **13**, after 24 hours, equation 13.

Complex **13** shows a peak in the ^1H NMR spectrum at 4.34 with 49 Hz platinum coupling for the chloromethyl ligand.

Figure 9 shows the x-ray structure of a monomeric unit of **13** and selected bond distances and angles are presented in Table 7. The Pt-CH₂Cl carbon bond length is again shorter than the Pt-C distances to the two methyl ligands, but it is elongated by 0.013 Å compared to the distance in the bpztz^{Ph} complex, **12**.

Figure 9. X-ray structure of [TpmPtMe₂CH₂Cl][Cl] **13**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and counterion are omitted for clarity. Bond lengths (Å): Pt-N₁ 2.147(3), Pt-N₃ 2.109(4), Pt-N₅ 2.208(4), Pt-C₁ 2.039(7), Pt-C₂ 2.046(6), Pt-C₃ 2.060(7), C₁-Cl 1.775(6). Bond angles (deg): N₁-Pt-N₅ 86.23(14), C₁-Pt-N₁ 93.7(2), C₁-Pt-C₂ 88.9(3), Cl-C₁-Pt 114.8(3).

We next attempted the reaction of 1,2-dichloroethane with a Pt(II) precursor. Stirring a solution of bpztz^{Ph} and [PtMe₂(SMe₂)₂] in 1,2-dichloroethane for three days results in the formation of a PtCH₂CH₂Cl entity. Addition of MeOTf to the complex exchanged the anion to the noncoordinating triflate. A secondary anion exchange was accomplished through the addition of sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate (NaB(Ar^F)₄) and led to the isolation of [bpztz^{Ph}PtMe₂CH₂CH₂Cl][B(Ar^F)₄], **14**, (eq 14). In the ¹H NMR spectrum of **14**, the major isomer is the symmetric product, with the triazole donor trans to the chloroethyl ligand. The two protons bound to the carbon alpha to the metal center appear as a distinctive 8-line pattern at 2.81 ppm. Further downfield at 3.38 ppm is a similar splitting pattern corresponding to the protons bound to the beta carbon of the PtCH₂CH₂Cl fragment, reflecting the second order AA'XX' pattern typical of XCH₂CH₂Y entities.

We attempted analogous chemistry with 1,2-dichloroethane and other homoscorpionate ligands to no avail. The ability to activate the C-Cl bond at one end of 1,2-dichloroethane demonstrates the unusual reactivity of this asymmetrical bpztz tridentate ligand.

In an effort to promote elimination from the Pt-CH₂CH₂Cl fragment of complex **14** we added a base, sodium methoxide. We anticipated the methoxide would deprotonate the carbon alpha to Pt and perhaps lead to elimination to form a Pt-vinyl ligand. Alternatively methoxide could simply displace the chloride to form a Pt-CH₂CH₂OCH₃ ligand. The addition of sodium methoxide to cationic complex **14** in THF resulted in the precipitation of a white solid containing platinum. The solid, sparingly soluble in dichloromethane, reacted with NaB(Ar^F)₄ and led to the isolation of a dicationic, dinuclear product,

$[(\text{bpztz}^{\text{Ph}})\text{Me}_2\text{PtCH}_2\text{CH}_2\text{PtMe}_2(\text{bpztz}^{\text{Ph}})][\text{B}(\text{Ar}^{\text{F}})_4]_2$, **15**, eq 15.

The ¹H NMR spectrum of **15** was complex due to second order effects so we begin by describing the definitive C-13 NMR spectrum which led to unambiguous identification of the PtCH₂CH₂Pt unit. The ¹³C NMR spectrum indicates the presence of a dinuclear complex containing a -CH₂CH₂- bridge: a single peak centered at 20 ppm exhibits two sets of Pt satellites, one having ¹J_{Pt-C} = 622 Hz and one having ²J_{Pt-C} = 31 Hz. Note that complex **15** proved challenging to identify by ¹H NMR since “apparent” quartets at 2.92 and 2.06 ppm were misleading. During the formation of **15**, one of the tridentate ligands isomerized, resulting in a pyrazole arm trans to the alkyl bridge, making each of the two Pt centers chiral. The bridging ethylene ligand then becomes an AXA’X’ system, but instead of the AA’ hydrogens residing on the same carbon as in the XCH₂CH₂Y case, the A and A’ hydrogens are on C_α and C_β,

respectively, as are X and X'. These pairwise diastereotopic protons resemble overlapping doublets that are roofed, appearing roughly as quartets. The Pt satellites are an additional complication and there are observable satellite peaks due to the proton seeing a spin active platinum center both 2 and 3 bonds away (although not in the same molecule, figure 10a). Simulations supported our analysis, with a geminal proton coupling of -9.5 Hz and vicinal couplings of 5.0 and 9.0 Hz. We were also able to replicate the platinum satellites through simulations of an AXA'X'M system, calculating $^2J_{\text{Pt-H}}$ and $^3J_{\text{Pt-H}}$ couplings of 70 and 52 Hz respectively. Overlaying the simulated spectrum allows for easy comparison to the NMR spectra (figure 10b).

Figure 10. Observed and simulated spectra of the bridging ligand for complex **15**. Calculated with a geminal coupling constant of -9.5 Hz, vicinal coupling constants of 5.0 and 9.0 Hz, two bond platinum proton coupling constant of 70 Hz and three bond coupling constant of 52 Hz.

Preparation of a complex with two bridging methylene units between platinum centers is rare, and we probed the importance of the base by adding sodium amide to complex **14**. The result was the same product, indicating that the identity of the base is unimportant in forming the dinuclear product. We propose that the base reacts with the Pt(IV) starting material to reductively eliminate the ethylchloride ligand, perhaps by simply attacking the alpha carbon to form $\text{MeOCH}_2\text{CH}_2\text{Cl}$ and the reduced Pt complex. This $\kappa^2\text{-bpztz}^{\text{Ph}}\text{PtMe}_2$ reagent could then react with the C-Cl bond of a second molecule of **15**. Indeed the addition of Pt(IV) complex **14** to a solution of $\kappa^2\text{-bpztz}^{\text{Ph}}\text{Pt(II)Me}_2$ in THF resulted in precipitation of **15**, eq 16.

3. Conclusion

A series of asymmetrical scorpionate ligands bearing two pyrazolyl rings and one triazolyl ring has been synthesized using a cobalt-catalyzed condensation reaction. Metalation of these ligands to generate neutral Pt(II) complexes followed by subsequent methylation results in stable Pt(IV) complexes. Solid-state structural data reveal that the platinum-nitrogen distance to the triazolyl moiety is shorter than the two platinum-nitrogen pyrazolyl distances, indicating that the triazolyl ring is a stronger donor to Pt(IV). An electron withdrawing substituent on the triazole arm does not influence the ligand donor strength as assessed by Pt-N distances. While

Pt(IV) in cationic complexes binds the triazole arm more tightly than the pyrazole arms, the dimethylPt(II) fragment favors binding only the pyrazole arms rather than the triazole arm. The (bpztz^{Ph})PtMe₂d⁸ Pt(II) complex displaces chloride from methylene chloride rather than promoting C-H activation as was reported for various Tp' complexes.⁵⁶ The ability to displace chloride from chlorinated solvents led to the synthesis of an unusual dicationic Pt(IV) dimer bridged by an ethylene ligand.⁵⁷⁻⁵⁹

4. Experimental Section

Materials and Methods. All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk and drybox techniques. Nitrogen was purified by passage through columns of BASF R3-11 catalyst and 4 Å molecule sieves. Dichloromethane, dimethyl ether, tetrahydrofuran (THF), and pentane were purified under an argon atmosphere and passed through a column packed with activated alumina. All other chemicals were used as received without further purification. Silica column chromatography was conducted with 230-400 mesh silica gel and alumina column chromatography was conducted with 80-200 mesh alumina.

¹H, ¹⁹F, ³¹P, and ¹³C NMR spectra were recorded on Bruker DRX400, AVANCE500, or ULTRA SHIELD CRYOQNP600 spectrometers. ¹H NMR and ¹³C NMR chemical shifts were referenced to residual ¹H and ¹³C signals of the deuterated solvents. Elemental analyses were performed by Robertson Microlit Laboratories of Madison, NJ.

[bpztz^{Ph}PtMe₃][I] 5-L1. A 50-mL Schlenk was charged with 0.030 g (0.05 mmol) of [PtMe₂(SMe₂)]₂ and 0.036 g (0.10 mmol) of **4-L1**. The flask was purged with nitrogen and CH₂Cl₂ (10 mL) was added through the septum. The yellow solution was treated with 20 µL (0.30 mmol) of methyl iodide and stirred for 30 min at room temperature. The solvent was removed via rotary evaporation and the resulting oil was triturated with pentane to afford **5-L1** as

a pale yellow solid in quantitative yield. ^1H NMR (δ , CD_2Cl_2 , 298 K): 10.67 (s, 1H, tz H), 8.85 (s, 1H, $\text{HC}(\text{pz})_2(\text{tz})$), 7.84 (d, 2H, *o*-Ph), 7.55 (m, 3H, *m*-Ph and *p*-Ph), 6.00 (s, 2H, pz H), 2.83, 2.32 (s, 3H each, pz CH_3), 1.42 (s, 6H, $^2J_{\text{Pt-H}} = 71$ Hz, Pt- CH_3), 1.32 (s, 3H, $^2J_{\text{Pt-H}} = 73$ Hz, Pt- CH_3). ^{13}C NMR (δ , CD_2Cl_2 , 298 K): 152.8, 142.8 (pz C- CH_3), 139.4 (tz 4-position), 136.4 (ipso-Ph), 130.5, (*p*-Ph), 130.4 (*m*-Ph), 126.2 (tz 5-position), 121.1 (*o*-Ph), 108.8 (pz CH), 61.4 ($\text{HC}(\text{pz})_2(\text{tz})$), 13.2, 13.1 (pz CH_3), -8.0 ($^1J_{\text{Pt-C}} = 688$ Hz, Pt- CH_3), -10.7 ($^1J_{\text{Pt-C}} = 701$ Hz, Pt- CH_3). Anal Calcd for $\text{C}_{22}\text{H}_{30}\text{N}_7\text{IPt}$: C, 36.82; H, 4.23; N, 13.72. Found: C, 35.97; H, 4.50; N, 13.39.

[bpztz^{Cy}PtMe₃][I] 5-L2. A 50-mL Schlenk was charged with 0.030 g (0.05 mmol) of $[\text{PtMe}_2(\text{SMe}_2)]_2$ and 0.037 g (0.10 mmol) of **4-L2**. The flask was purged with nitrogen and CH_2Cl_2 (10 mL) was added through the septum. The yellow solution was treated with 20 μL (0.30 mmol) of methyl iodide and stirred for 30 min at room temperature. The solvent was removed via rotary evaporation and the resulting oil was triturated with pentane to afford **5-L1** as a pale yellow solid in quantitative yield. **Crystal Data.** $\text{C}_{22}\text{H}_{36}\text{IN}_7\text{Pt}$, $M = 720.57$, triclinic, $a = 10.0223(4)$ Å, $b = 10.4114(4)$ Å, $c = 13.6904(5)$ Å, $\alpha = 94.156(2)^\circ$, $\beta = 109.859(2)^\circ$, $\gamma = 107.026(2)^\circ$, $V = 1261.00(8)$ Å³, $T = 100$, space group P-1 (no. 2), $Z = 2$, $\mu(\text{CuK}\alpha) = 20.192$, 21695 reflections measured, 4338 unique ($R_{\text{int}} = 0.0471$) which were used in all calculations. The final wR_2 was 0.0721 (all data) and R_1 was 0.0286 ($I > 2\sigma(I)$). ^1H NMR (δ , CD_2Cl_2 , 298 K): 10.10 (s, 1H, tz H), 8.73 ($\text{HC}(\text{pz})_2(\text{tz})$), 5.98 (s, 2H, pz H), 4.50 (tt, 1H, C_A -H), 2.83, 2.29 (s, 3H each, pz CH_3), 2.33-1.25 (11H, cyclohexyl), 1.34 (s, 6H, $^2J_{\text{Pt-H}} = 72$ Hz, Pt- CH_3), 1.25 (s, 3H, $^2J_{\text{Pt-H}} = 70$ Hz, Pt- CH_3). ^{13}C NMR (δ , CD_2Cl_2 , 298 K): 152.7, 142.6 (pz C- CH_3), 138.6 (tz 4-position), 126.2 (tz 5-position), 108.7 (pz CH), 62.6 (C_A), 61.7 ($\text{HC}(\text{pz})_2(\text{tz})$), 33.4 (C_B), 25.2 (C_C and C_D),

13.4, 13.2 (pz CH₃), -8.3 (¹J_{Pt-C} = 690 Hz, Pt-CH₃), -11.1 (¹J_{Pt-C} = 703 Hz, Pt-CH₃). Anal Calcd for C₂₂H₃₅N₇IPt: C, 36.67; H, 5.04; N, 13.61. Found: C, 36.39; H, 4.91; N, 13.39.

[bpztz^{C6F5}PtMe₃][I] 5-L3. A 50-mL Schlenk was charged with 0.030 g (0.05 mmol) of [PtMe₂(SMe₂)]₂ and 0.041 g (0.10 mmol) of **4-L3**. The flask was purged with nitrogen and CH₂Cl₂ (10 mL) was added through the septum. The yellow solution was treated with 20 μL (0.30 mmol) of methyl iodide and stirred for 30 min at room temperature. The solvent was removed via rotary evaporation and the resulting oil was triturated with pentane to afford **5-L3** as a pale yellow solid in quantitative yield. **Crystal Data.** C₂₂H₂₅F₅IN₇Pt, *M* = 804.48, monoclinic, *a* = 15.1356(5) Å, *b* = 12.7423(5) Å, *c* = 13.9156(6) Å, β = 108.392(2)°, *V* = 2546.71(17) Å³, *T* = 100, space group P2₁/c (no. 14), *Z* = 4, μ(CuKα) = 20.386, 28097 reflections measured, 4714 unique (*R*_{int} = 0.0316) which were used in all calculations. The final *wR*₂ was 0.0658 (all data) and *R*₁ was 0.0257 (*I* > 2σ(*I*)). ¹H NMR (δ, CD₂Cl₂, 298 K): 10.65 (s, 1H, tz H), 8.99 (HC(pz)₂(tz)), 6.03 (s, 2H, pz H), 2.88, 2.32 (s, 3H each, pz CH₃), 1.38 (s, 6H, ²J_{Pt-H} = 72 Hz, Pt-CH₃), 1.36 (s, 3H, ²J_{Pt-H} = 72 Hz, Pt-CH₃). ¹⁹F NMR (δ, CD₂Cl₂, 298 K): -145.0 (d, *o*-F), -147.7 (t, *p*-F), -158.9 (t, *m*-F). ¹³C NMR (δ, CD₂Cl₂, 298 K): 153.2, 143.2 (pz C-CH₃), 140.3 (tz 4-position), 131.0 (tz 5-position), 109.1 (pz CH), 61.4 (HC(pz)₂(tz)), 13.7, 13.3 (pz CH₃), -7.9 (¹J_{Pt-C} = 685 Hz, Pt-CH₃), -10.2 (¹J_{Pt-C} = 706 Hz, Pt-CH₃). Anal Calcd for C₂₂H₃₀N₇F₅IPt: C, 32.64; H, 3.74; N, 12.11. Found: C, 32.01; H, 3.60; N, 12.21.

[POPz₃PtMe₃][OTf] 7. A 50-mL Schlenk was charged with 0.030 g (0.05 mmol) of [PtMe₂(SMe₂)]₂ and 0.035 g (0.10 mmol) of tris(3,5-dimethylpyrazolyl)phosphine oxide). The flask was purged with argon and CH₂Cl₂ (10 mL) was added through the septum. The yellow solution was treated with 34 μL (0.30 mmol) of methyl trifluoromethanesulfonate and stirred for 30 min at room temperature. The solvent was removed under reduced pressure and the resulting

oil was triturated with pentane to afford **7** as white solid in quantitative yield. **Crystal Data** for $C_{31}H_{42}N_6O_4F_3PSPt$ ($M = 877.82$ g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 9.9490(4)$ Å, $b = 17.1179(7)$ Å, $c = 19.9506(8)$ Å, $V = 3397.7(2)$ Å³, $Z = 4$, $T = 100$ K, $\mu(\text{CuK}\alpha) = 9.278$ mm⁻¹, $D_{\text{calc}} = 1.716$ g/cm³, 31914 reflections measured ($6.804^\circ \leq 2\theta \leq 148.884^\circ$), 6861 unique ($R_{\text{int}} = 0.0456$, $R_{\text{sigma}} = 0.0406$) which were used in all calculations. The final R_1 was 0.0241 ($I > 2\sigma(I)$) and wR_2 was 0.0538 (all data). ¹H NMR (δ , CD₂Cl₂, 298 K): 6.31 (d, 3H, ⁴J_{P-H} = 5 Hz, pz H), 2.67, 2.44 (s, 9H each, pz CH₃), 1.51 (s, 9H, ²J_{Pt-H} = 71 Hz, Pt-CH₃), 1.25 (s, 3H, ²J_{Pt-H} = 70 Hz, Pt-CH₃). ¹³C NMR (δ , CD₂Cl₂, 298 K): 159.9, 151.9 (²J_{P-C} = 11 Hz, pz C-CH₃), 114.0 (³J_{P-C} = 10 Hz, pz CH), 14.1, 13.7 (pz CH₃), -6.3 (¹J_{Pt-C} = 693 Hz, Pt-CH₃). ³¹P NMR (externally referenced to 85% H₃PO₄) -18.26 (³J_{Pt-P} = 9 Hz). Anal Calcd for C₁₉H₃₀N₆PtF₃SO₃: C, 33.83; H, 4.48; N, 12.46. Found: C, 33.01; H, 4.50; N, 12.92.

[TpmPtMe₃][OTf] 8. A 50-mL Schlenk was charged with 0.030 g (0.05 mmol) of [PtMe₂(SMe₂)]₂ and 0.031 g (0.10 mmol) of tris(3,5-dimethylpyrazolyl)methane). The flask was purged with argon and CH₂Cl₂ (10 mL) was added through the septum. The yellow solution was treated with 34 μ L (0.30 mmol) of methyl trifluoromethanesulfonate and stirred for 30 min at room temperature. The solvent was removed under reduced pressure and the resulting oil was triturated with pentane to afford **8** as white solid in quantitative yield. **Crystal Data** for $C_{20}H_{31}F_3N_6O_3PtS$ ($M = 687.66$ g/mol): monoclinic, space group $P2_1/n$ (no. 14), $a = 13.6758(9)$ Å, $b = 24.0130(17)$ Å, $c = 23.3289(16)$ Å, $\beta = 98.766(3)^\circ$, $V = 7571.6(9)$ Å³, $Z = 12$, $T = 100$ K, $\mu(\text{CuK}\alpha) = 11.670$ mm⁻¹, $D_{\text{calc}} = 1.810$ g/cm³, 141398 reflections measured ($5.314^\circ \leq 2\theta \leq 133.56^\circ$), 13514 unique ($R_{\text{int}} = 0.0312$, $R_{\text{sigma}} = 0.0143$) which were used in all calculations. The final R_1 was 0.0480 ($I > 2\sigma(I)$) and wR_2 was 0.1165 (all data). ¹H NMR (δ , CD₂Cl₂, 298 K): 7.90 (s, 1H, HC(pz)₃), 6.14 (s, 3H, Pz H), 2.62, 2.35 (s, 9H each, pz CH₃), 1.42 (s, 9H, ²J_{Pt-H} = 70 Hz,

Pt-CH₃). ¹³C NMR (δ, CD₂Cl₂, 298 K): 153.7, 141.6 (pz C-CH₃), 110.0 (pz CH), 70.0 (HC(pz)₃), 13.2, 11.5 (pz CH₃), -8.8 (¹J_{Pt-C} = 693 Hz, Pt-CH₃). Anal Calcd for C₂₀H₃₁N₆F₃SPt: C, 34.93; H, 4.54; N, 12.22. Found: C, 35.01; H, 4.52; N, 12.74.

[bpztz^{Ph}PtMe₂H][BF₄] 9. A 50-mL Schlenk was charged with 0.030 g (0.05 mmol) of [PtMe₂(SMe₂)₂] and 0.036 g (0.10 mmol) of **4-L1**. The flask was purged with argon and CH₂Cl₂ (10 mL) was added through the septum. The solution was cooled to -78°C and 7.8 μl (0.06 mmol) of an 8M solution of tetrafluoroboric acid was added. The solution was warmed to room temperature while stirring for 30 minutes. The solvent was removed under reduced pressure and the resulting oil was triturated with pentane to afford **9** as a pale yellow solid in quantitative yield. Major isomer: ¹H NMR (δ, CD₂Cl₂, 298 K): 9.39 (s, 1H, tz H), 8.26 (s, 1H, HC(pz)₂(tz)), 7.88 (d, 2H, *o*-Ph), 7.59 (m, 3H, *m*-Ph and *p*-Ph), 6.05 (s, 2H, pz H), 2.63, 2.27 (s, 6H each, pz, CH₃), 1.36 (s, 3H, ²J_{Pt-H} = 71 Hz, Pt-CH₃), -19.67 (s, 1H, ¹J_{Pt-H} = 1424 Hz). ¹³C NMR (δ, CD₂Cl₂, 298 K): 152.3, 152.0, 142.9, 142.7 (pz C-CH₃), 139.8 (tz 4-position), 136.0 (ipso-Ph), 130.4 (tz 5-position), 130.2 (*m*-Ph), 124.3, (*p*-Ph), 120.5 (*o*-Ph), 108.8 (pz CH), 60.6 (HC(pz)₂(tz)), 13.9, 13.6, 12.8, 11.1 (pz CH₃), -6.0 (¹J_{Pt-C} = 638 Hz, Pt-CH₃). Minor isomer: ¹H NMR (δ, CD₂Cl₂, 298 K): 9.34 (s, 1H, tz H), 8.20 (s, 1H, HC(pz)₂(tz)), 7.83 (d, 2H, *o*-Ph), 7.59 (m, 3H, *m*-Ph and *p*-Ph), 6.07, 6.05 (s, 1H each, pz H), 2.65, 2.64, 2.35, 2.29 (s, 3H each, pz CH₃), 1.54 (s, 3H, ²J_{Pt-H} = 71 Hz, Pt-CH₃), 1.33 (s, 3H, ²J_{Pt-H} = 70 Hz, Pt-CH₃), -21.01 (s, 1H, ¹J_{Pt-H} = 1450 Hz). ¹³C NMR (δ, CD₂Cl₂, 298 K): 152.3, 152.0, 142.9, 142.7 (pz C-CH₃), 139.8 (tz 4-position), 136.0 (ipso-Ph), 130.4 (tz 5-position), 130.2 (*m*-Ph), 124.3, (*p*-Ph), 120.5 (*o*-Ph), 108.8 (pz CH), 60.6 (HC(pz)₂(tz)), 13.9, 13.6, 12.8, 11.1 (pz CH₃), -6.5 (¹J_{Pt-C} = 709 Hz, Pt-CH₃), -8.3 (¹J_{Pt-C} = 603 Hz, Pt-CH₃).

[bpztz^{Ph}PtMe₂C(O)CH₃][OTf] 10. A 50-mL Schlenk was charged with 0.030 g (0.05 mmol) of [PtMe₂(SMe₂)₂] and 0.036 g (0.10 mmol) of **4-L1**. The flask was purged with argon and CH₂Cl₂ (10 mL) was added through the septum. The solution was treated with 63 μ L (0.06 mmol) of a 1M solution of acetyl chloride and stirred overnight at room temperature. The solvent was removed under reduced pressure to remove any excess acetyl chloride. The resulting oil was dissolved in dichloromethane and 6.2 μ L (0.055 mmol) of methyl trifluoromethanesulfonate was added. The solvent was removed under reduced pressure and the resulting oil was triturated with pentane to afford **10** as a pale yellow solid in quantitative yield. **Crystal Data** for C₂₄H₃₀F₃N₇O₄PtS (*M* = 764.70 g/mol): triclinic, space group P-1 (no. 2), *a* = 9.5435(7) Å, *b* = 10.9989(7) Å, *c* = 13.7606(9) Å, α = 78.506(3)°, β = 77.315(4)°, γ = 85.146(3)°, *V* = 1379.64(16) Å³, *Z* = 2, *T* = 100.15 K, μ (CuK α) = 10.795 mm⁻¹, *D*_{calc} = 1.841 g/cm³, 82587 reflections measured (6.7° ≤ 2 Θ ≤ 140.2°), 5106 unique (*R*_{int} = 0.0394, *R*_{sigma} = 0.0166) which were used in all calculations. The final *R*₁ was 0.0385 (*I* > 2 σ (*I*)) and *wR*₂ was 0.0936 (all data). ¹H NMR (δ , CD₂Cl₂, 298 K): 10.50 (s, 1H, tz H), 9.35 (s, 1H, HC(pz)₂(tz)), 7.95 (d, 2H, *o*-Ph), 7.54 (m, 3H, *m*-Ph and *p*-Ph), 6.10, 6.01 (s, 1H each, pz H), 2.52 (br s, 6H, pz, CH₃), 2.34, 2.18 (s, 3H each, pz CH₃), 2.31 (s, 3H, PtC(O)CH₃), 1.58 (s, 3H, ²*J*_{Pt-H} = 76 Hz, Pt-CH₃), 1.52 (s, 3H, ²*J*_{Pt-H} = 72 Hz, Pt-CH₃). ¹³C NMR (δ , CD₂Cl₂, 298 K): 189.6 (¹*J*_{Pt-C} = 912 Hz, PtCO), 153.1, 152.0, 143.5, 143.3 (pz C-CH₃), 140.6 (tz 4-position), 136.0 (ipso-Ph), 130.3 (*m*-Ph), 130.0, (*p*-Ph), 121.1 (tz 5-position), 121.0 (*o*-Ph), 108.5, 180.4 (pz CH), 61.3 (HC(pz)₂(tz)), 35.8 (²*J*_{Pt-C} = 190 Hz, C(O)CH₃), 13.6, 12.8, 12.1, 11.9 (pz CH₃), -5.9 (¹*J*_{Pt-C} = 691 Hz, Pt-CH₃), -16.3 (¹*J*_{Pt-C} = 685 Hz, Pt-CH₃).

[TpmPtMe₂C(O)CH₃][OTf] 11. A 50-mL Schlenk was charged with 0.030 g (0.05 mmol) of [PtMe₂(SMe₂)₂] and 0.031 g (0.10 mmol) of tris(3,5-dimethylpyrazolyl)methane). The

flask was purged with argon and CH₂Cl₂ (10 mL) was added through the septum. The solution was treated with 63 µL (0.06 mmol) of a 1M solution of acetyl chloride and stirred for 30 minutes at room temperature. The solvent was removed under reduce pressure to remove any excess acyl chloride. The oil was dissolved in dichloromethane and 6.0 µL (0.055 mmol) of methyl trifluoromethanesulfonate was added. The solvent was removed under reduced pressure and the resulting oil was triturated with pentane to afford **11** as a pale yellow solid in quantitative yield. **Crystal Data** for C₂₁H₃₁F₃N₆O₄PtS (*M* = 715.67 g/mol): orthorhombic, space group Pbca (no. 61), *a* = 15.5752(2) Å, *b* = 13.7902(2) Å, *c* = 23.7500(3) Å, *V* = 5101.15(12) Å³, *Z* = 8, *T* = 100 K, $\mu(\text{CuK}\alpha) = 11.609 \text{ mm}^{-1}$, *D*_{calc} = 1.864 g/cm³, 42651 reflections measured (7.444° ≤ 2 Θ ≤ 144.254°), 4988 unique (*R*_{int} = 0.0315, *R*_{sigma} = 0.0171) which were used in all calculations. The final *R*₁ was 0.0381 (*I* > 2 σ (*I*)) and *wR*₂ was 0.0816 (all data). ¹H NMR (δ , CD₂Cl₂, 298 K): 7.96 (s, 1H, HC(pz)₃), 6.20 (s, 2H, pz H), 6.16 (s, 1H, pz H), 2.63, 2.16 (s, 6H each, pz CH₃) 2.99, 2.63 (s, 3H each, pz CH₃), 2.37 (s, 3H, PtC(O)CH₃), 1.64 (s, 3H, ²*J*_{Pt-H} = 72 Hz, Pt-CH₃). ¹³C NMR (δ , CD₂Cl₂, 298 K): 191.5 (¹*J*_{Pt-C} = 894 Hz, PtCO), 154.3, 152.9, 142.0, 141.9 (pz C-CH₃), 121.9 (triflate), 110.4, 109.7 (pz CH), 69.6 (HC(pz)₃), 34.5 (²*J*_{Pt-C} = 202.5 Hz, C(O)CH₃), 13.9, 13.7, 12.8, 12.6 (pz CH₃), -7.4 (¹*J*_{Pt-C} = 717 Hz, Pt-CH₃).

[bpztz^{Ph}PtMe₂CH₂Cl][BF₄] 12. A 50-mL Schlenk was charged with 0.030 g (0.05 mmol) of [PtMe₂(SMe₂)]₂ and 0.037 g (0.10 mmol) of **4-L1**. The flask was purged with argon and CH₂Cl₂ (10 mL) was added through the septum. The yellow solution was stirred overnight at room temperature. The reaction was cooled to -78°C and 7.5 µL (0.06 mmol) of tetrafluoroboric acid was added. The solution was warmed to room temperature while stirring for 30 minutes. The solvent was removed under reduced pressure and the resulting oil was triturated with pentane to afford **12** as a pale yellow solid in quantitative yield. **Crystal Data** for

$\text{C}_{22}\text{H}_{29}\text{BClF}_4\text{N}_7\text{Pt}$ ($M = 708.87$ g/mol): monoclinic, space group $\text{P2}_1/\text{c}$ (no. 14), $a = 21.6316(5)$ Å, $b = 10.1043(2)$ Å, $c = 23.7979(6)$ Å, $\beta = 95.9347(11)^\circ$, $V = 5173.7(2)$ Å³, $Z = 8$, $T = 100$ K, $\mu(\text{CuK}\alpha) = 11.579$ mm⁻¹, $D_{\text{calc}} = 1.820$ g/cm³, 63378 reflections measured ($4.106^\circ \leq 2\theta \leq 133.198^\circ$), 9023 unique ($R_{\text{int}} = 0.0443$, $R_{\text{sigma}} = 0.0268$) which were used in all calculations. The final R_1 was 0.0330 ($I > 2\sigma(I)$) and wR_2 was 0.0875 (all data). ¹H NMR (δ , CD_2Cl_2 , 298 K): 9.41 (s, 1H, tz *H*), 8.23 (s, 1H, *HC*(pz)₂(tz)), 7.84 (d, 2H, *o*-Ph), 7.55 (m, 3H, *m*-Ph and *p*-Ph), 6.06 (s, 2H, pz *H*), 4.36 (2H, ² $J_{\text{Pt-H}} = 50$ Hz, CH_2Cl), 2.634, 2.43 (s, 6H each, pz CH_3), 1.48 (s, 6H, ² $J_{\text{Pt-H}} = 71$ Hz, Pt- CH_3). ¹³C NMR (δ , CD_2Cl_2 , 298 K): 152.7, 142.2 (pz *C-CH*₃), 139.4 (tz 4-position), 136.0 (ipso-Ph), 130.5, (*p*-Ph), 130.3 (*m*-Ph), 124.2 (tz 5-position), 120.6 (*o*-Ph), 108.6 (pz *CH*), 60.6 (*HC*(pz)₂(tz)), 20.3 (¹ $J_{\text{Pt-C}} = 841$ Hz, CH_2Cl), 13.1, 10.8 (pz CH_3), -5.6 (¹ $J_{\text{Pt-C}} = 662$ Hz, Pt- CH_3). Anal Calcd for $\text{C}_{22}\text{H}_{30}\text{N}_7\text{F}_5\text{IPT}$: C, 37.28; H, 4.12; N, 13.83. Found: C, 37.58; H, 3.60; N, 13.51.

[TpmPtMe₂CH₂Cl][Cl] 13. A 50-mL Schlenk was charged with 0.030 g (0.05 mmol) of $[\text{PtMe}_2(\text{SMe}_2)]_2$ and 0.031 g (0.10 mmol) of tris(3,5-dimethylpyrazolyl)methane). The flask was purged with argon and CH_2Cl_2 (10 mL) was added through the septum. The yellow solution was stirred 24 hours at room temperature. The solvent was removed under reduced pressure and the resulting oil was triturated with pentane to afford **13** as white solid in quantitative yield. **Crystal Data** for $\text{C}_{19}\text{H}_{30}\text{Cl}_2\text{N}_6\text{Pt}$ ($M = 608.48$ g/mol): monoclinic, space group $\text{P2}_1/\text{c}$ (no. 14), $a = 13.4026(12)$ Å, $b = 15.9431(14)$ Å, $c = 11.1625(10)$ Å, $\beta = 113.265(2)^\circ$, $V = 2191.2(3)$ Å³, $Z = 4$, $T = 100$ K, $\mu(\text{CuK}\alpha) = 14.356$ mm⁻¹, $D_{\text{calc}} = 1.844$ g/cm³, 26590 reflections measured ($7.18^\circ \leq 2\theta \leq 144.774^\circ$), 4315 unique ($R_{\text{int}} = 0.0288$, $R_{\text{sigma}} = 0.0200$) which were used in all calculations. The final R_1 was 0.0311 ($I > 2\sigma(I)$) and wR_2 was 0.0662 (all data). ¹H NMR (δ , CD_2Cl_2 , 298 K): 7.96 (s, 1H, *HC*(pz)₃), 6.19 (s, 1H, Pz *H*), 6.17 (s, 2H, pz *H*), 4.34 (s, 2H, ² $J_{\text{Pt-H}} = 49$ Hz, CH_2Cl),

2.75, 2.34 (s, 3H each, pz CH₃), 2.72, 2.45 (s, 6H each, pz CH₃), 1.50 (s, 6H, ²J_{Pt-H} = 70 Hz, Pt-CH₃). ¹³C NMR (δ, CD₂Cl₂, 298 K): 153.7, 153.5, 142.4, 141.7 (pz C-CH₃), 110.1, 109.6 (pz CH), 69.7 (HC(pz)₃), 20.9 (¹J_{Pt-C} = 840 Hz, CH₂Cl), 13.2, 13.1, 12.1, 12.0, 11.9 (pz CH₃), -6.6 (¹J_{Pt-C} = 670 Hz, Pt-CH₃). Anal Calcd for C₁₉H₃₀N₆Cl₂Pt: C, 37.50; H, 4.97; N, 13.81. Found: C, 37.21; H, 3.60; N, 12.51.

[bpztz^{Ph}PtMe₂(CH₂CH₂Cl)][BAr^F] 14. In the glove box, a vial was charged with 0.030 g (0.05 mmol) of [PtMe₂(SMe₂)]₂ and 0.037 g (0.10 mmol) of **4-L1**. The solids were dissolved in 1,2-dichloroethane (0.4 ml) and the vial was capped. The yellow solution was stirred 3 days at room temperature. The solvent was removed under reduced pressure and dissolved in dichloromethane. The addition of 6.6 μL (0.06 mmol) methyl trifluoromethanesulfonate followed by solvent removal under reduced pressure gave the triflate anion for the complex. Dissolving the complex in dichloromethane followed by addition of 0.05 g (0.06 mmol) NaB(Ar^F)₄ followed by filtration gave the B(Ar^F)₄ anion for the complex. The solvent was removed under reduced pressure resulting in a clear oil. The resulting oil was triturated with pentane to afford **14** as a white solid in 67% yield (100 mg). ¹H NMR (δ, CD₂Cl₂, 298 K): 8.92 (s, 1H, tz *H*), 7.83 (s, 1H, HC(pz)₂(tz)), 7.75, 7.57 (s, 8H, 4H, B(Ar^F)₄), 7.74 (d, 2H, *o*-Ph), 7.54 (m, 3H, *m*-Ph and *p*-Ph), 6.01 (s, 2H, pz *H*), 3.38 (m, 2H, PtCH₂CH₂Cl), 2.66, 2.40 (s, 6H each, pz CH₃), 2.81 (m, 2H, PtCH₂CH₂Cl), 1.47 (s, 6H, ²J_{Pt-H} = 71 Hz, Pt-CH₃). ¹³C NMR (δ, CD₂Cl₂, 298 K): 162.0 (B(Ar^F)₄), 153.3, 143.0 (pz C-CH₃), 139.5 (tz 4-position), 136.3 (ipso-Ph), 131.0, (*p*-Ph), 130.7 (*m*-Ph), 129.3, 121, 117 (B(Ar^F)₄), 124.2 (tz 5-position), 121.0 (*o*-Ph), 109.4 (pz CH), 60.9 (HC(pz)₂(tz)), 45 (PtCH₂CH₂Cl), 30.1 (PtCH₂CH₂Cl), 13.5, 10.1 (pz CH₃), -6.1 (¹J_{Pt-C} = 675 Hz, Pt-CH₃).

[bpztz^{Ph}Me₂PtCH₂CH₂PtMe₂bpztz^{Ph}][BAr^F]₂ **15** In the glove box, a vial was charged with 0.030 g (0.02 mmol) of **14** and 0.1 mg (0.02 mmol) of NaOMe. The solids were dissolved in THF and the vial was capped overnight. The next morning the solvent was filtered away from the solid. The remaining solid was then washed with dichloromethane and the solution was collected. 0.022 g (0.025 mmol) of NaB(Ar^F)₄ was added to the solution, and the solution was filtered. Removal of the solvent under reduced pressure resulted in a white powder to afford **15** in 41% yield (0.012 g). ¹H NMR (δ, CD₂Cl₂, 298 K): 8.41 (s, 2H, tz *H*), 7.71 (s, 16H, B(Ar^F)₄), 7.54 (s, 8H, B(Ar^F)₄), 7.70 (d, 4H, *o*-Ph), 7.62 (m, 6H, *m*-Ph and *p*-Ph), 7.36 (s, 2H, HC(pz)₂(tz)), 6.10 (s, 2H, pz *H*), 6.00 (s, 2H, pz *H*), 2.92 (sloping doublets, 2H, ²J_{Pt-H} = 71 Hz, ³J_{Pt-H} = 48 Hz, PtCH₂CH₂Pt), 2.51 (s, 12 H, pz CH₃), 2.47, 2.19 (s, 6H each, pz CH₃), 2.06 (sloping doublets, 2H, ²J_{Pt-H} = 44 Hz, ³J_{Pt-H} = 23 Hz, PtCH₂CH₂Pt), 1.36 (s, 6H, ²J_{Pt-H} = 74 Hz, Pt-CH₃), 1.21 (s, 6H, ²J_{Pt-H} = 74 Hz, Pt-CH₃). ¹³C NMR (δ, CD₂Cl₂, 298 K): 152.7, 142.8 (pz C-CH₃), 142.2 (tz 4-position), 140.0 (ipso-Ph), 136.4, (*p*-Ph), 130.7 (*m*-Ph), 122.1 (tz 5-position), 120.1 (*o*-Ph), 109.3, 108.8 (pz CH), 60.9 (HC(pz)₂(tz)), 16.2 (¹J_{Pt-C} = 622 Hz, ²J_{Pt-C} = 31 Hz, PtCH₂CH₂Pt), 14.1, 13.8, 11.5, 11.2 (pz CH₃), -6.7 (¹J_{Pt-C} = 718 Hz, Pt-CH₃), -9.2 (¹J_{Pt-C} = 730 Hz, Pt-CH₃). Anal Calcd for C₇₆H₇₀N₁₄ClF₂₄BPt₂: C, 44.06; H, 3.41; N, 9.47. Found: C, 43.62; H, 3.16; N, 9.51.

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Supporting Information Available: Ligand synthesis, representative ¹H and ¹³C NMR spectra for all complexes and crystallographic data and CIF files for structures **5-L2**, **5-L3**, **7**, **8**, **10**, **11**, **12**, and **13**.

- (1) Goldshle, N. F.; Shteinma, A. A.; Shilov, A. E.; Eskova, V. V. *Russian Journal of Physical Chemistry, Ussr***1972**, 46 (5), 785.
- (2) Shul'pin, G. B.; Shilov, A. E.; Kitaigorodskii, A. N. *J Organomet Chem***1980**, 201 (1), 319.
- (3) Shul'pin, G. B. *J. Organomet. Chem.***1981**, 212 (2), 267.
- (4) Shul'pin, G. B. *Catalysts***2016**, 6, 50.
- (5) West, N. M.; Templeton, J. L. *Can. J. Chem.***2009**, 87 (1), 288.
- (6) Prokopchuk, E. M.; Puddephatt, R. J. *Organometallics***2002**, 22 (3), 563.
- (7) Kloek, S. M.; Goldberg, K. I. *J. Am. Chem. Soc.***2007**, 129 (12), 3460.
- (8) Braunstein, P.; Naud, F. *Angew. Chem. Int. Ed.***2001**, 40 (4), 680.
- (9) Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Progress in Inorganic Chemistry, Vol 48***1999**, 48, 233.
- (10) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.***2005**, 127 (31), 10840.
- (11) Fulmer, G. R.; Kaminsky, W.; Kemp, R. A.; Goldberg, K. I. *Organometallics***2011**, No. 30, 1627.
- (12) Lindner, R.; van den Bosch, B.; Lutz, M.; Reek, J.; van der Vlugt, J. I. *Organometallics***2011**, No. 30, 499.
- (13) Dulebohn, J. I.; Haefner, S. C.; Berglund, K. A.; Dunbar, K. R. *Chemistry of Materials***1992**, 4 (3), 506.
- (14) Dunbar, K. R.; Haefner, S. C. *Inorg. Chem.***1992**, 31 (17), 3676.
- (15) Rogers, C. W.; Wolf, M. O. *Chem. Commun.***1999**, 2297.
- (16) Kita, M. R.; Miller, A. J. M. *J. Am. Chem. Soc.***2014**, 136 (41), 14519.
- (17) Ebeling, G.; Meneghetti, M. R.; Rominger, F. *Organometallics***2002**, No. 21, 3221.
- (18) Spasyuk, D. M.; Zargarian, D.; van der Est, A. *Organometallics***2009**, No. 28, 6531.
- (19) Gagliardo, M.; Selander, N.; Mehendale, N. C.; van Koten, G.; Gebbink, R. J. M. K.; Szabó, K. J. *Chem. Eur. J.* **2008**, No. 14, 4800.
- (20) Niu, J. L.; Chen, Q. T.; Hao, X. Q.; Zhao, Q. X.; Gong, J. F.; Song, M. P. *Organometallics***2010**, No. 29, 2148.
- (21) De Angelis, F.; Gambacorta, A.; Nicoletti, R. *Synthesis***1976**, 798.
- (22) Jameson, D. L.; Castellano, R. K.; Reger, D. L.; Collins, J. E.; Tolman, W. B.; Tokar, C. J. *Inorganic Syntheses*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 1998; Vol. 32, pp 51–63.
- (23) Juliá, S.; del Mazo, J. M.; Avila, L. *Organic Preparations and Procedures Int.***1984**, 5 (16), 299.
- (24) Reger, D. L.; Collins, J. E.; Jameson, D. L. *Inorganic Syntheses*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 1998; Vol. 32.
- (25) Byers, P. K.; Canty, A. J. *Organometallics***1990**, 9 (1), 210.
- (26) Byers, P. K.; Canty, A. J.; Honeyman, R. T. *J. Organomet. Chem.***1990**, 385 (3), 417.
- (27) Byers, P. K.; Canty, A. J.; Honeyman, R. T. *Inorganic Syntheses*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2004; Vol. 34.
- (28) Canty, A. J.; Honeyman, R. T. *J. Organomet. Chem.***1990**, 387 (2), 247.
- (29) Canty, A. J.; Honeyman, R. T.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.***1990**, 389 (2), 277.

- (30) Canty, A. J.; Honeyman, R. T.; Skelton, B. W. *J. Chem. Soc. Dalton Trans.* **1992**, 2663.
- (31) Reger, D. L.; Grattan, T. C.; Brown, K. J.; Little, C. A.; Lamba, J.; Rheingold, A. L.; Sommer, R. D. *J. Organomet. Chem.* **2000**, 607 (1-2), 120.
- (32) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2002**, 41 (14), 2596.
- (33) Frauhiger, B. E.; White, P. S.; Templeton, J. L. *Organometallics* **2011**, 31, 225.
- (34) van Assema, S. G. A.; Tazelaar, C. G. J.; de Jong, G. B.; van Maarseveen, J. H.; Schakel, M.; Lutz, M.; Spek, A. L.; Slootweg, J. C.; Lammertsma, K. *Organometallics* **2008**, 27 (13), 3210.
- (35) West, N. M.; Reinartz, S.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **2006**, 128 (6), 2059.
- (36) MacDonald, M. G.; Kostelansky, C. N.; White, P. S.; Templeton, J. L. *Organometallics* **2006**, No. 25, 4560.
- (37) Jensen, M. P.; Wick, D. D.; Reinartz, S.; White, P. S.; Templeton, J. L.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, 125 (28), 8614.
- (38) Frauhiger, B. E.; Templeton, J. L. *Organometallics* **2012**, 31, 2770.
- (39) Hoover, J. M.; Stahl, S. S. *J. Am. Chem. Soc.* **2011**, 133 (42), 16901.
- (40) Peterson, L. K.; Kiehlmann, E. *Can. J. Chem.* **1974**, 52, 2367.
- (41) The, K. I.; Peterson, L. K. *Can. J. Chem.* **1973**, 51 (3), 422.
- (42) Peterson, L. K.; Kiehlmann, E. *Can. J. Chem.* **1973**, 51, 2448.
- (43) Abo-Amer, A.; Puddephatt, R. J. *Inorganic Chemistry Communications* **2011**, No. 14, 111.
- (44) Engelman, K. L.; White, P. S.; Templeton, J. L. *Organometallics* **2010**, 4943.
- (45) Reinartz, S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2001**, 21 (2), 247.
- (46) Scollard, J. D.; Day, M.; Labinger, J. A.; Bercaw, J. E. *Helvetica Chimica Acta* **2001**, 84 (10), 3247.
- (47) Fekl, U.; van Eldik, R.; Lovell, S.; Goldberg, K. I. *Organometallics* **2000**, 19 (18), 3535.
- (48) O'Reilly, S. A.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, 118 (24), 5684.
- (49) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2000**, 19 (18), 3748.
- (50) Tellers, D. M.; Yung, C. M.; Arndtsen, B. A.; Adamson, D. R.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, 124 (7), 1400.
- (51) Butts, M. D.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1996**, 118 (47), 11831.
- (52) Kulawiec, R. J.; Crabtree, R. H. *Coordination Chemistry Reviews* **1990**, 99, 89.
- (53) Ho, J.; Black, D.; Messerle, B. A.; Clegg, J. K. *Organometallics* **2006**, No. 25, 5800.
- (54) Ito, J.; Miyakawa, T.; Nishiyama, H. *Organometallics* **2006**, No. 25, 5216.
- (55) Tejel, C.; Ciriano, M. A.; López, J. A.; Jiménez, S.; Bordonaba, M.; Oro, L. A. *Chem. Eur. J.* **2007**, 13 (7), 2044.
- (56) Jiao, Y.; Brennessel, W. W.; Jones, W. D. *Organometallics* **2015**, 34 (8), 1552.
- (57) Wei, M. L.; Wayland, B. B. *Organometallics* **1996**, 15 (22), 4681.
- (58) Campazzi, E.; Solari, E.; Scopelliti, R.; Floriani, C. *Chem. Commun.* **1999**, 1617.
- (59) de Bruin, B.; Hetterscheid, D. G. H. *Eur. J. Inorg. Chem.* **2007**, 2007 (2), 211.