Quinone Methide Generation Based on a *cis*-(N,N) Platinum Complex

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Quinone methides (QMs) are highly reactive compounds that play important roles in various chemical and biological processes. In this work, a stable imino-pyridine platinum(IV) complex that bears a silyl-protected oxy-benzyl precursor of the quinone methide BHT−QM, derived from the food preservative 2,6-di-*tert*-butyl-4-methylphenol (BHT), was prepared and fully characterized, including by X-ray structural characterization. De-silylation results in a rarely observed, fully characterized, zwitterionic intermediate η^1-methylene-*p*-phenoxy-Pt(IV), which undergoes de-aromatization to the unstable BHT−QM, which was trapped in solution.

Introduction

Quinone methides (QMs, quinones in which one of the oxygen atoms is replaced by an alkylidene group) are highly reactive compounds that are involved as intermediates in various chemical and biological processes.[1] Transient p-QM intermediates are often utilized in organic synthesis, including in the synthesis of natural products.[2] Biosynthesis of the natural polymers melanin and lignin involves p-QM intermediates.[3] Several drugs, including clinically employed anthracyclins and mitomycin C, are believed to generate a QM moiety as the active form.[4] However, isolation and reactivity studies of simple quinone methides (those not having substituents at the exocyclic methylene group) are difficult, since they are very unstable. They react very rapidly with the medium or polymerize, the driving force behind these rapid reactions being aromatization to the zwitterionic compound, which is capable of reactions with both electrophiles and nucleophiles. Recently, efforts have been directed toward coordination of QMs to metal centers,[5−7] for the purpose of their stabilization, study, and controlled release.[7] The first stable p-QM−metal complex incorporated the QM moiety as part of a bis-chelating PCP ligand framework, and consequently, the QM was very strongly coordinated and was not suitable for release.[6] Later, an approach to form one-site-coordinated QM complexes was developed in our group, leading to $(Ph_2PCH_2CH_2PPh_2)Pd−QM$ complexes with η^2-coordinated

quinone methides.[7] While release of the QM molecule was demonstrated in these systems (by associative displacement), we were interested in a more biologically compatible skeleton than diphosphines and in the use of platinum as an anchor. Such complexes may benefit from possible biological activity of the platinum center[8] and of the released QM moiety, potentially providing enhanced effectiveness and selectivity.[9]

Here we report the preparation of a stable imino-pyridine[10]-based platinum(IV) complex bearing a coordinated benzyl precursor of BHT−QM, the quinone methide derived from the food preservative 2,6-di-*tert*-butyl-4-methylphenol (BHT). This Pt(IV) complex can serve as a QM source, concomitantly generating a *cis*-Pt(II) complex. The generated BHT−QM was directly observed and trapped in solution. The η^1-methylene-*p*-phenoxy intermediate was detected and fully

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Scheme 1
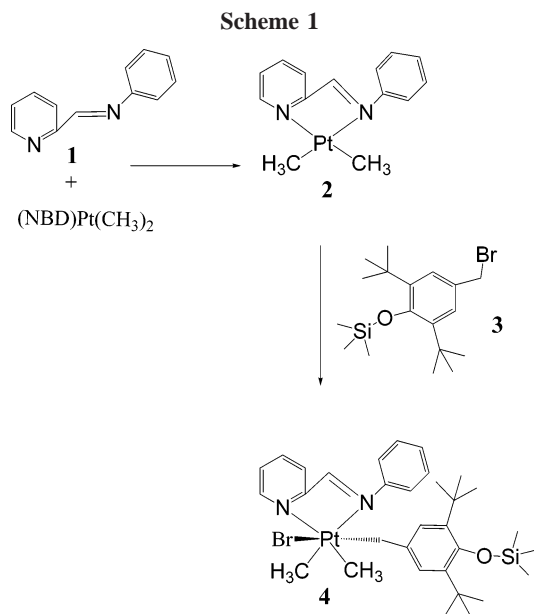
characterized spectroscopically, providing a very rare direct observation of de-aromatization of a zwitterionic oxy-benzyl compound to a quinone methide.

Results and Discussion

Formation of Chelating (N,N)Pt(II) and Pt(IV) Complexes. The imino-pyridine chelating NN ligand **1** was synthesized according to a literature procedure[11] and reacted with (norbornadiene)PtMe$_2$.[12] Upon stirring of the two reagents in benzene at room temperature for 12 h, the violet-purple complex (NN)-PtMe$_2$ (**2**) was formed in 83% yield (Scheme 1). Pure complex **2** was fully characterized by ^{195}Pt, ^{1}H, and ^{13}C NMR spectroscopies, ES/MS, and elemental analysis. It gives rise to a singlet at −3228.00 ppm in the ^{195}Pt{^{1}H} NMR spectrum, while the Pt(Me)$_2$ units are observed as two sets of singlets with Pt satellites at 1.25 (J_{Pt-H} = 87 Hz) and 0.88 ppm (J_{Pt-H} = 89 Hz) in the ^{1}H NMR spectrum and as two singlets with Pt satellites at −14.83 (J_{Pt-C} = 823 Hz) and −15.07 ppm (J_{Pt-C} = 834 Hz) in the ^{13}C{^{1}H} NMR spectrum.

When the benzyl bromide **3**[7b] (the silylated and brominated derivative of BHT) was added to a benzene solution of **2**, oxidative addition to yield the Pt(IV) complex (NN)Pt(Me)$_2$-(BHT)Br (**4**) took place (Scheme 1). Pure complex **4**, obtained in 85% yield, was characterized by multinuclear (^{195}Pt, ^{13}C, ^{1}H) NMR spectroscopies, ES/MS, elemental analysis, and X-ray crystallography. The ^{195}Pt{^{1}H} NMR spectrum of **4** exhibits a singlet at −2474.04 ppm. In the ^{1}H NMR spectrum the two methyl groups of Pt(CH$_3$)$_2$ give rise to signals at 1.51 ppm (s, J_{Pt-H} = 73 Hz) and at 1.12 ppm (s, J_{Pt-H} = 72 Hz), while two doublets are observed for the Pt−CH$_2$−Ar protons at 2.70 ppm (J_{Pt-H} = 94 Hz, J_{H-H} = 10 Hz) and at 2.55 ppm (J_{Pt-H} = 86 Hz, J_{H-H} = 10 Hz). The benzylic protons are not equivalent, due to the lack of a symmetry plane. In the ^{13}C{^{1}H} NMR spectrum the benzyl carbon gives rise to a signal at 23.28 (s, J_{Pt-C} = 632 Hz) and the Pt−Me groups are observed as two singlets at −2.40 (J_{Pt-C} = 706 Hz) and −2.80 (J_{Pt-C} = 690 Hz) ppm. The carbon atom of the ligand C≡N group appears as a singlet at 140.29 (J_{Pt-C} = 16 Hz).

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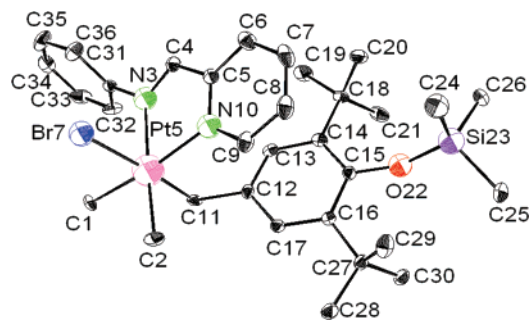

Figure 1. ORTEP view of the crystal structure of **4** with the thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances and Angles of Complex 4

bond length (Å)		angle (deg)	
Pt(5)−C(1)	2.051(3)	C(1)−Pt(5)−C(2)	86.82(14)
Pt(5)−C(2)	2.053(3)	C(1)−Pt(5)−C(11)	87.03(13)
Pt(5)−C(11)	2.13(3)	C(1)−Pt(5)−N(3)	93.2(3)
Pt(5)−N(3)	2.163(2)	C(2)−Pt(5)−N(3)	174.80(11)
Pt(5)−N(10)	2.178(3)	C(11)−Pt(5)−N(3)	93.53(11)
Pt(5)−Br(7)	2.601(7)	N(1)−C(1)−C(2)	173.88(11)
N(3)−C(4)	1.286(4)	C(11)−Pt(5)−N(10)	95.12(11)
C(5)−N(10)	1.369(4)	N(3)−Pt(5)−N(10)	76.22(10)
C(5)−C(4)	1.462(4)	C(1)−Pt(5)−Br(7)	90.10(10)
C(11)−C(12)	1.487(4)	C(11)−Pt(5)−Br(7)	176.99(8)

Orange prisms of **4** suitable for a single-crystal X-ray diffraction study were obtained from a two-phase pentane/benzene solution at room temperature (Figure 1). Complex **4** exhibits a slightly distorted octahedral structure, in which the NN ligand, Pt atom, and two methyl groups are in the same plane, whereas the coordinated benzyl group and the Br atom are *trans* to each other and perpendicular to the plane. The N3−C4 bond length (1.286(4) Å) and the C4−N3−C31 angle (118.8(3)°) correspond to the expected sp^2 configuration of the imine group. The angle between the planes of the aromatic rings of the ligand is 74.4°. Additional bond distances and angles of **4** are listed in Table 1.

Complex **4** is exceptionally stable in various solvents, including protic solvents such as water and MeOH. It is thermally stable, and no reductive elimination or other decomposition modes were observed upon heating to 100 °C in toluene.

Reactivity of Complex 4. The reactivity of **4** with respect to QM formation was investigated. Interestingly, when **4** was treated with 1 equiv of the fluoride salt Bu$_4$NF·3H$_2$O in C$_6$D$_6$, immediate formation of complex **2** accompanied by a color change from orange to violet-purple took place (Scheme 2). ^{1}H NMR measurement of the resulting solution, measured immediately, exhibited formation of free BHT−QM.[7b] Formation and release of the QM molecule in this reaction was also proven by its trapping with methanol. This was possible since BHT−QM can exist for a short time in solution, while the reaction with fluoride is very fast. Thus, when a few drops of MeOH were added following the addition of the fluoride reagent, immediate reaction with free BHT−QM took place to give the expected Michael addition product 2,6-di-*tert*-butyl-4-methoxymethylphenol, which was detected by GC/MS. Corresponding signals in the ^{2}H NMR spectrum and in GC/MS were obtained when the analogous reaction was performed with d_4-MeOH.

Trapping of the Zwitterionic Intermediate. Interestingly, when the reaction of the Pt(IV) complex **4** with Bu$_4$NF·3H$_2$O
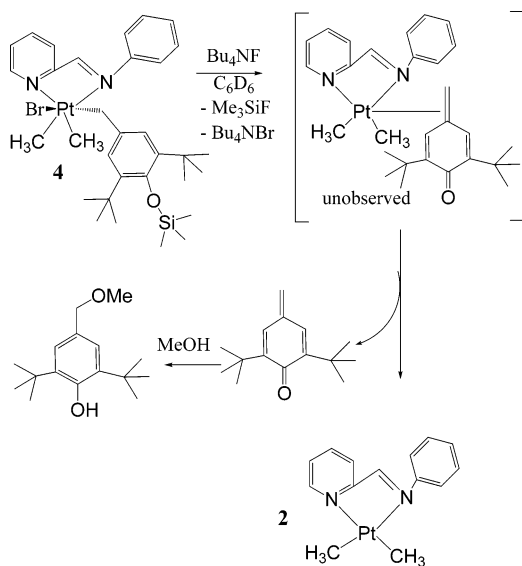
Scheme 2

Scheme 3
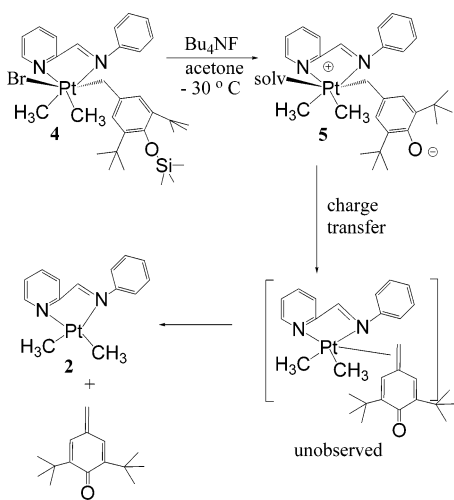
was performed in a more polar (relative to benzene) d_6-acetone medium, the ^{195}Pt{^{1}H} NMR spectrum indicated formation of the new zwitterionic benzyl complex **5** (see below), which gave rise to a signal at −2419.65 ppm, in addition to complex **2**, with a ratio of **5**:**2** = 1:4. Complex **5** was transformed to complex **2** within 2 h, indicating that **5** was an intermediate in the conversion of the neutral benzyl Pt(II) complex **4** to the Pt(II) complex **2** (Scheme 3). Indeed, **5** was the major product when the reaction was performed at low temperature. Thus, when to a d_6-acetone solution of complex **4**, precooled to −30 °C, was added a d_6-acetone solution of Bu$_4$NF·3H$_2$O, precooled to −30 °C, a color change from orange to light purple was observed, and ^{195}Pt NMR (−30 °C) revealed formation of complex **5** in 77% yield, accompanied by only a minor amount of complex **2**.

The zwitterionic complex **5** was characterized at −30 °C. It gives rise to two sets of Pt−Me groups at 1.46 (s, $J_{Pt−H}$ = 69 Hz) and 1.08 (s, $J_{Pt−H}$ = 73 Hz) ppm and two doublets for the Pt−benzyl protons at 2.61 ($J_{Pt−H}$ = 92 Hz, $J_{H−H}$ = 9 Hz) and 2.50 ($J_{Pt−H}$ = 86 Hz, $J_{H−H}$ = 9 Hz) ppm in the ^{1}H NMR spectrum. In the ^{13}C{^{1}H} NMR spectrum, the Pt-coordinated benzyl carbon appears at 22.93 ppm ($J_{Pt−C}$ = 624 Hz), while Pt−Me groups appear at −2.51 (s, $J_{Pt−C}$ = 708 Hz) and −2.86

(s, $J_{Pt−C}$ = 690 Hz) ppm. The signals of the trimethylsilyl protecting group that were present in the spectra of complex **4** (at 0.37 and 4.29 ppm in ^{1}H and ^{13}C NMR, respectively) disappeared and were replaced by signals of the generated Me$_3$-SiF (0.02 ppm in ^{1}H and 1.81 ppm in ^{13}C NMR).[13] A significant downfield shift was observed for the imine group carbon, which gives rise to a singlet at 147.66 with Pt satellites, $J_{Pt−C}$ = 14 Hz. In complex **4** the analogous signal was found at 140.29 ppm with $J_{Pt−C}$ = 16 Hz. The NMR data suggest that the positive charge of the zwitterionic form is mostly localized on the Pt center and on the imine ligand, and not on the benzylic moiety, since the main changes are observed for the (NN)Pt unit, as a result of electron density decrease at the metal center. Upon gradual temperature increase, slow conversion of **5** to **2** took place. When the sample was warmed to room temperature and complexes **5** and **2** were in a 1:2.3 ratio, correspondingly, an ES/MS measurement exhibited the following signals at m/z^+: 626.71 (M + 1 of complex **5**), 430.50 (M + Na$^+$ of complex **2**), and 447.58 (M + K$^+$ of **2**).[14] It is important to note that in the case of complex **4** ES/MS analysis exhibited a signal at 698.81, the difference between **4** and **5** being due to the trimethylsilyl protecting group. This observation confirms that in the case of complex **5** the protecting group was removed from the benzylic ring. Moreover, no additional signals above 626.71 in the ES/MS spectrum were observed (for example, signal of (Bu)$_4$N$^+$ salt of the complex), supporting the assumption of a zwitterion with a naked phenoxy (O$^−$). Further confirmation that there is no bromide coordination to Pt was obtained from parallel experiments with AgBF$_4$ under identical conditions at −30 °C. When AgBF$_4$ was added, the solution in which complex **5** was formed, which contains Bu$_4$Br, immediate precipitation of AgBr was observed, while in the case of complex **4**, in which the bromide is coordinated to the Pt center, no reaction occurred under these conditions. Overall, the multinuclear NMR spectroscopy data, together with the mass spectroscopic data and the observed reactivity, clearly confirm the zwitterionic nature of **5**.[15]

To the best of our knowledge, this is the first direct observation of de-aromatization of a zwitterionic oxy-benzyl compound to a quinone methide. The observation of this η^1-methylene-*p*-phenoxy intermediate (formed by removing the Me$_3$Si unit with fluoride and elimination of Bu$_4$NBr) was probably made possible due to charge stabilization by the polar acetone medium, while in the case of a nonpolar solvent (such as benzene) this intermediate is unstable and undergoes fast charge transfer to give the QM-coordinated form, followed by QM release by the (unobserved) pentacoordinated Pt(II) complex.

Summary

In summary, a stable, chelated imino-pyridine Pt(IV) complex bearing a quinone methide benzylic precursor (complex **4**) was synthesized and fully characterized (including by X-ray structure analysis). Removal of a silyl protecting group by fluoride

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(13) ^{1}H NMR peak integration of the dissolved gaseous Me$_3$SiF was smaller than 9H probably because some of it remained in the gas phase.

(14) Explanation for M + Na$^+$ and M + K$^+$: When ES/MS analysis is performed under regular conditions (regular glass and MeOH solvent), positive ionization may occur from H$^+$ or Na$^+$. In case of Na$^+$ ionization one more experiment with K$^+$ is usually done, in order to confirm that the mass increase by 23 is really due to Na$^+$.

(15) Coordinated acetone is probably too loosely bound to be reflected in the mass of the complex.

attack led to the release and trapping in solution of the quinone methide BHT−QM and formation of the Pt(II) complex *cis*-(NN)PtMe₂. A benzylic zwitterionic intermediate in this process, η^1-methylene-*p*-phenoxy Pt(IV), was characterized and directly observed to release the quinone methide BHT−QM, with concomitant reduction of the Pt(IV) metal center to Pt(II). The high thermal stability of complex **4** and its stability in protic media makes it, as well as analogous complexes, potentially interesting in terms of selective delivery of quinone methides. Further studies of complex **4** that involve its chemical modifications and investigation of its reactivity with biological substrates are in progress.

Experimental Section

General Procedures. All experiments with metal complexes were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with an MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under an argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in a glovebox over 4 Å molecular sieves. Commercially available reagents were used as received. The NMR spectra were recorded at 500 (¹H), 126 (¹³C), and 107 (¹⁹⁵Pt) using a Bruker DPX 500 spectrometer. All spectra were recorded at 23 °C (if not stated otherwise). ¹H NMR and ¹³C{¹H} NMR chemical shifts are reported in ppm downfield from tetramethylsilane. ¹H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvent (2.04 acetone). In ¹³C{¹H} NMR measurements the signal of d_6-acetone (206.0 ppm) was used as a reference. In ¹⁹⁵Pt{¹H} NMR chemical shifts are reported in ppm and referenced to an external solution of K₂PtCl₄. Screw-cap 5 mm NMR tubes were used in the NMR follow-up experiments. Abbreviations used in the description of NMR data are as follows: s, singlet; d, doublet; t, triplet; m, multiplet.

Formation of (NN)PtMe₂ (2). To a benzene solution of (NBD)-PtMe₂ (40 mg, 0.12 mmol) was added a benzene solution of ligand **1** (25 mg, 0.14 mmol), and the reaction mixture was stirred for 12 h at room temperature. The solvent was removed under vacuum, and the violet-purple solid was washed with pentane (10 mL) and ether (7 mL) and dissolved in C₆H₆. Removal of the solvent under vacuum yielded 40 mg (0.10 mmol, 83% yield) of **2**.

¹⁹⁵Pt{¹H} NMR (d_6-acetone): −3228.00 (s). ¹H NMR (d_6-acetone): 9.66 (s, $J_{Pt−H}$ = 32 Hz, 1H, *H*−C=N), 9.29 (d, $J_{H−H}$ = 5 Hz, 1H, pyridine ring), 8.36 (t, $J_{H−H}$ = 7 Hz, 1H, pyridine ring), 8.14 (d, $J_{H−H}$ = 7 Hz, 1H, pyridine ring), 7.85 (t, $J_{H−H}$ = 5 Hz, 1H, pyridine ring), 7.50 (t, $J_{H−H}$ = 8 Hz, 2H, Ar), 7.36 (d, $J_{H−H}$ = 8 Hz, 1H, Ar), 7.32 (dd, $J_{H−H}$ = 8 Hz, 2H, Ar), 1.25 (s, $J_{Pt−H}$ = 87 Hz, 3 H, Pt−C*H₃*), 0.88 (s, $J_{Pt−H}$ = 89 Hz, 3 H, Pt−C*H₃*). ¹³C{¹H} NMR (d_6-acetone): 165.61 (s, pyridine ring), 158.06 (s, pyridine ring), 150.11 (s, pyridine ring), 147.70 (s, $J_{Pt−C}$ = 35 Hz, *C*=N), 138.00 (s, pyridine ring), 129.77 (s, $J_{Pt−C}$ = 14 Hz, pyridine ring), 129.42 (s, Ar), 129.09 (s, $J_{Pt−C}$ = 8 Hz, Ar), 128. 32 (s, Ar), 123.95 (s, $J_{Pt−C}$ = 8 Hz, Ar), −14.83 (s, $J_{Pt−C}$ = 823 Hz, Pt−C*H₃*), −15.07 (s, $J_{Pt−C}$ = 834 Hz, Pt−C*H₃*). ES-MS: m/z^+ 430.50 (M + Na⁺), 447.58 (M + K⁺) [calc 407.24]. Anal. Found (calcd for C₁₄H₁₆N₂Pt): C, 41.08 (41.26); H, 3.90 (3.96); N, 6.80 (6.88).

Formation of (NN)Pt(Me)₂(BHT−OSiMe₃)Br (4). To a benzene solution of complex **2** (30 mg, 0.07 mmol) was added a benzene solution of the bromide **1** (30 mg, 0.08 mmol), and the solution was stirred for12 h at rt. Solvent removal under vacuum yielded complex **3**, which was recrystallized from a mixture of benzene (1 mL) and pentane (10 mL) after 12 h at −20 °C. The orange solid was washed with pentane and dried under vacuum, yielding 46 mg (0.06 mmol, 85% yield) of **4**.

¹⁹⁵Pt{¹H} NMR (d_6-acetone): −2474.04 (s). ¹H NMR (d_6-acetone): 9.23 (s, $J_{Pt−H}$ = 29 Hz, 1H, *H*−C=N), 8.67 (d, $J_{H−H}$ = 5 Hz, 1H, pyridine ring), 8.25 (d, $J_{H−H}$ = 7 Hz, 1H, pyridine ring), 8.21 (td, $J_{H−H}$ = 7 Hz, $J_{H−H}$ = 1 Hz, 1H, pyridine ring), 7.73 (td, $J_{H−H}$ = 5 Hz, $J_{H−H}$ = 1 Hz, 1H, pyridine ring), 7.50 (t, $J_{H−H}$ = 6 Hz, 2H, Ar), 7.49 (d, $J_{H−H}$ = 6 Hz, 1H, Ar), 7.38 (bd, $J_{H−H}$ = 6 Hz, 2H, Ar), 6.62 (s, $J_{Pt−H}$ = 11 Hz, 2H, BHT), 2.70 (d, $J_{Pt−H}$ = 94 Hz, $J_{H−H}$ = 10 Hz, 1H, Pt−C*H₂*), 2.55 (d, $J_{Pt−H}$ = 86 Hz, $J_{H−H}$ = 10 Hz, 1H, Pt−C*H₂*), 1.51 (s, $J_{Pt−H}$ = 73 Hz, 3H, Pt−C*H₃*), 1.25 (s, 18H, t-Bu), 1.12 (s, $J_{Pt−H}$ = 72 Hz, 3H, Pt−C*H₃*), 0.37 (s, 9H, Si(C*H₃*)₃). ¹³C{¹H} NMR (d_6-acetone): 167.65 (s, pyridine ring), 155.20 (s, pyridine ring), 150.75 (s, pyridine ring), 148.25 (s, $J_{Pt−C}$ = 8 Hz, pyridine ring), 140.29 (s, $J_{Pt−C}$ = 16 Hz, *C*=N), 139.93 (s, pyridine ring), 137.84 (s, BHT), 130.59 (s, Ar), 129.77 (s, Ar), 129.71 (s, Ar), 129.15 (s, $J_{Pt−C}$ = 13 Hz, Ar), 128.95 (s, BHT), 125.92 (s, $J_{Pt−C}$ = 21 Hz, BHT), 123.47 (s, BHT), 35.26 (s, *C*(CH₃)₃), 31.51 (s, C(CH₃)₃), 23.28 (s, $J_{Pt−C}$ = 632 Hz, Pt−*C*H₂), 4.29 (s, Me₃Si), −2.40 (s, $J_{Pt−C}$ = 706 Hz, Pt−*C*H₃), −2.80 (s, $J_{Pt−C}$ = 690 Hz, Pt−*C*H₃). (Assignment of ¹³C{¹H} NMR signals was confirmed by ¹³C DEPT). ES-MS: m/z^+ 698.81 (M − Br) [calc 698.81], $m/z^−$ (Br). Anal. Found (calcd for C₃₂H₄₅N₂-PtOSiBr): C, 49.51 (49.35); H, 6.15 (6.08); N, 3.55 (3.60).

X-ray Structural Analysis of 4. Orange crystals of complex **4** were obtained from a benzene solution by layering it with pentane at room temperature.

Crystal Data. C₃₂H₄₀BrN₂OPtSi + 1/2(C₆H₆), prism, orange, 0.4 × 0.3 × 0.2 mm³, triclinic, $P\bar{1}$, a = 10.598(2) Å, b = 12.904-(3) Å, c = 13.385(6) Å, α = 95.03(3)°, β = 105.03(2)°, γ = 91.20-(3)° from 20 degrees of data, T = 120(2) K, V = 1759.2(7) Å³, Z = 2, fw = 810.80, D_c = 1.531, Mg/m³, μ = 5.185 mm⁻¹.

Data Collection and Treatment. Nonius KappaCCD diffractometer, Mo Kα (g = 0.71073 Å), graphite monochromator, 33 673 reflections collected, −13 < h < 13, −16 < k < 16, 0 < l < 17, frame scan width 1.0°, scan speed 1° per 20 s, typical peak mosaicity 0.53°, 8005 independent reflections (R_{int} = 0.047). The data were processed with Denzo-Scalepack.

Solution and Refinement. The structure was solved by direct methods with SHELXS. Full-matrix least-squares refinement based on F^2 with SHELXL-97; 379 parameters with 0 restraints, final R1 = 0.0264 (based on F^2) for data with $I > 2\sigma(I)$ and R1 = 0.0296 on 7996 reflections, goodness-of-fit on F^2 = 1.068, largest electron density peak = 1.348 e/Å³.

Formation of [(NN)Pt(Me)₂(BHT−O⁻)(d_6-acetone)]⁺ (5). To a precooled, −30 °C d_6-acetone solution of complex **4** (25 mg, 0.03 mmol) was added a precooled, −30 °C d_6-acetone solution of Bu₄NF·3H₂O (8.4 mg, 0.03 mmol), resulting in an immediate color change from orange to light purple. The ¹⁹⁵Pt NMR spectrum revealed formation of complex **5** in 77% yield (according to ¹⁹⁵Pt NMR).

Complex **5** was characterized at −30 °C.

¹⁹⁵Pt{¹H} NMR (d_6-acetone): −2419.65 (s). ¹H NMR (d_6-acetone): 9.34 (s, $J_{Pt−H}$ = 29 Hz, 1H, *H*−C=N), 8.67 (d, $J_{H−H}$ = 6 Hz, 1H, pyridine ring), 8.29 (s, 1H, pyridine ring), 8.27 (d, $J_{H−H}$ = 6 Hz, 1H, pyridine ring), 7.90 (m, 1H, pyridine ring), 7.56−7.35 (5H, Ar), 6.41 (s, $J_{Pt−H}$ = 10 Hz, 2H, BHT), 2.61 (d, $J_{Pt−H}$ = 92 Hz, $J_{H−H}$ = 9 Hz, 1H, Pt−C*H₂*), 2.50 (d, $J_{Pt−H}$ = 86 Hz, $J_{H−H}$ = 9 Hz, 1H, Pt−C*H₂*), 1.46 (s, $J_{Pt−H}$ = 69 Hz, 3H, Pt−C*H₃*), 1.08 (s, $J_{Pt−H}$ = 73 Hz, 3 H, Pt−C*H₃*). ¹³C{¹H} NMR (d_6-acetone): 167.71 (s, pyridine ring), 154.75 (s, pyridine ring), 147.98 (s, $J_{Pt−C}$ = 14 Hz, pyridine ring), 147.66 (s, $J_{Pt−C}$ = 14 Hz, *C*=N), 139.98 (s, pyridine ring), 138.74 (s, pyridine ring), 135.88 (s, BHT), 130.51 (s, Ar), 129.71 (s, Ar), 129.27 (s, Ar), 128.94 (s, Ar), 127.06 (s, BHT), 125.47 (s, BHT), 124.35 (s, $J_{Pt−C}$ = 21 Hz, BHT), 34.76 (s, $J_{Pt−C}$ = 32 Hz, *C*(CH₃)₃), 30.50 (s, C(CH₃)₃), 22.93 (s, $J_{Pt−C}$ = 624 Hz, Pt−*C*H₂), −2.51 (s, $J_{Pt−C}$ = 708 Hz, Pt-*C*H₃), −2.86 (s,

J_{Pt-C} = 690 Hz, Pt$-CH_3$). (Assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by ^{13}C DEPT and C$-$H correlation.) ES-MS: m/z^+ 626.71 (M + 1) [calc 626.73].

Supporting Information Available: CIF file for complex **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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