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Dual Role of Acetate as a Nucleophile and as an Internal Base in Cycloplatination Reaction of *sym*-*N*,*N*′,*N*″-Triarylguanidines

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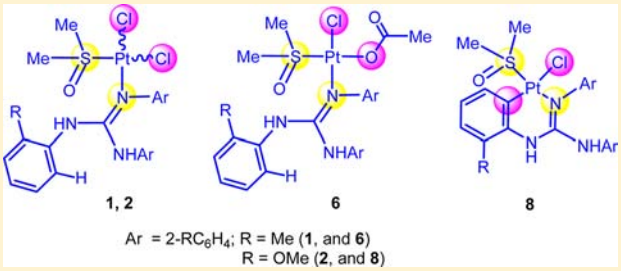
Supporting Information

ABSTRACT: Reaction of *cis*-$[Cl_2Pt(S(O)Me_2)_2]$ with 1 equiv of *sym*-*N*,*N*′,*N*″-triarylguanidines, $ArN{=}C(NHAr)_2$ (*sym* = symmetrical; Ar = 2-MeC_6H_4 ($LH_2^{2\text{-tolyl}}$), 2-$(MeO)C_6H_4$ ($LH_2^{2\text{-anisyl}}$), 4-MeC_6H_4 ($LH_2^{4\text{-tolyl}}$), 2,5-$Me_2C_6H_3$ ($LH_2^{2,5\text{-xylyl}}$), and 2,6-$Me_2C_6H_3$ ($LH_2^{2,6\text{-xylyl}}$)) in toluene under reflux condition for 3 h afforded *cis*- or *trans*-$[Cl_2Pt(S(O)Me_2)(ArN{=}C(NHAr)_2)]$ (Ar = 2-MeC_6H_4 (**1**), 2-$(MeO)C_6H_4$ (**2**), 4-MeC_6H_4 (**3**), 2,5-$Me_2C_6H_3$ (**4**), and 2,6-$Me_2C_6H_3$ (**5**), respectively) in 83−96% yield. Reaction of *cis*-$[Cl_2Pt(S(O)Me_2)_2]$ with 1 equiv of $LH_2^{2\text{-tolyl}}$ and $LH_2^{4\text{-tolyl}}$ in the presence of 1 equiv of NaOAc in methanol under reflux condition for 3 h afforded acetate-substituted products, *cis*-$[(AcO)ClPt(S(O)Me_2)(ArN{=}C(NHAr)_2)]$ (Ar = 2-MeC_6H_4 (**6**) and 4-MeC_6H_4 (**7**)) in 83% and 84% yields, respectively. Reaction of *cis*-$[Cl_2Pt(S(O)Me_2)_2]$ with 1 equiv of $LH_2^{2\text{-anisyl}}$ and $LH_2^{2\text{-tolyl}}$ in the presence of 1 equiv of NaOAc in methanol under reflux condition for 3 and 12 h afforded six-membered [*C*,*N*] platinacycles, $[Pt\{\kappa^2(C,N)\text{-}C_6H_3R\text{-}3(NHC(NHAr)(=NAr))\text{-}2\}Cl(S(O)Me_2)]$ (Ar = 2-RC_6H_4; R = OMe (**8**) and Me (**9**)), in 92% and 79% yields, respectively. The new complexes have been characterized by analytical and spectroscopic techniques, and further the molecular structures of **1**, **2**, **4**, **5**, **6**, and **8** have been determined by single-crystal X-ray diffraction. The platinum atom in **1**, **4**, and **5** exhibited the trans configuration, while that in **2**, **6**, and **8** exhibited the cis configuration. Complex **6** is shown to be the precursor for **9**, and the former is suggested to transform to the latter possibly via an intramolecular C−H activation followed by elimination of AcOH. The solution behavior of new complexes has been studied by multinuclear NMR (^1H, ^{195}Pt, and ^{13}C) spectroscopy. The new complexes exist exclusively as a single isomer (trans (**1** and **5**) and cis (**6** and **7**)), a mixture of cis and trans isomers with the former isomer being predominant in the case of **2** and the latter isomer being predominant in the case of **3**. Complex **5** in the trans form revealed the presence of one isomer at 0.007 mM concentration and two isomers in about 1.00:0.12 ratio at 0.154 mM concentration as revealed by ^1H NMR spectroscopy, and this has been ascribed to the restricted Pt−S bond rotation at higher concentration. Platinacycle **8** exists as one isomer, while **9** exists as a mixture of seven isomers in solution. The influence of steric factor, π-acceptor property of the guanidine, subtle solid-state packing forces upon the configuration of the platinum atom, and the number of isomers in solution have been outlined. Factors that accelerate or slow down the cycloplatination reaction, the role of NaOAc, and a plausible mechanism of this reaction have been discussed.



INTRODUCTION

Platinum(II) imine complexes and imine-derived [*C*,*N*] and [*C*,*N*,*N*′] types of platinacycles have been studied intensively in the past due to their relevance in inorganic and organometallic syntheses, reactivity pattern, and structural aspects.[1−12] Further, these complexes exhibit interesting biological activity,[13,14] materials properties such as mesomorphism, liquid crystalline property,[15,16] and photophysical[17,18] and catalytic properties.[19] *sym*-*N*,*N*′,*N*″-Trisubstituted guanidines $(RNH)_2C{=}NR$ (*sym* = symmetrical; R = alkyl and aryl) are one of the interesting classes of nitrogen donor ligands, capable of binding the metal ion in their (i) neutral form in monodentate (κ^1N) coordination mode, (ii) monoanionic form (i.e., guanidinate(1−)) in chelating (κ^2N,N') and bridging (μ_2-$\kappa^1N;\kappa^1N'$) coordination modes, and (iii) dianionic form (i.e., guanidinate(2−)) in chelating coordination mode (see Chart 1).[20−22] Only two platinum(II) complexes of *sym*-*N*,*N*′,*N*″-triphenylguanidine, $PhN{=}C(NHPh)_2$ (LH_2^{Ph}), have been structurally characterized,[23,24] although synthesis, reactivity studies, and structural aspects of platinum(II) complexes of other classes of guanidines have been steadily increasing since 1988.[25−29]

Steric factor and basicity of primary amines have been shown to promote the cycloplatination reaction.[30] We wanted to study how the subtle variations in steric, basic, and conformational properties of *sym*-*N*,*N*′,*N*″-triarylguanidines, $ArN{=}C(NHAr)_2$ (Ar = 2-MeC_6H_4 ($LH_2^{2\text{-tolyl}}$), 2-$(MeO)C_6H_4$ ($LH_2^{2\text{-anisyl}}$), 4-MeC_6H_4 ($LH_2^{4\text{-tolyl}}$), 2,5-$Me_2C_6H_3$ ($LH_2^{2,5\text{-xylyl}}$), and 2,6-$Me_2C_6H_3$ ($LH_2^{2,6\text{-xylyl}}$)), influence the course of the cycloplatination reaction. The aforementioned properties of *sym*-

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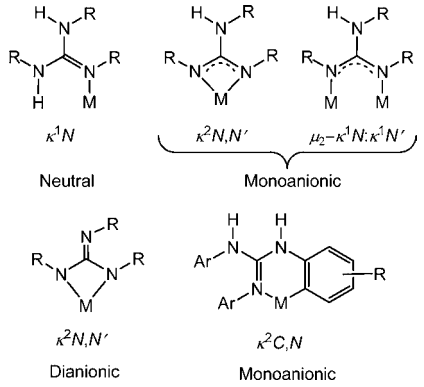
Chart 1



N,N′,N″-triarylguanidines permitted us to incorporate them as κ^2N,N' guanidinate(1−) around the ruthenium(II) atom and as κ^2C,N monoanionic scaffolds around the palladium(II) atom in the past.[31] Further, the substituent(s) on the aryl rings of *sym-N,N′,N″*-triarylguanidine units in palladium(II) and ruthenium(II) complexes have been shown to substantially influence the solid-state structures and solution behavior of these complexes.

Herein, we report the high-yield synthesis and characterization of three classes of platinum(II) guanidine complexes, namely, *cis-* or *trans*-$[Cl_2Pt(S(O)Me_2)(ArN{=}C(NHAr)_2)]$ (Ar = 2-MeC_6H_4 (**1**), 2-$(MeO)C_6H_4$ (**2**), 4-MeC_6H_4 (**3**), 2,5-$Me_2C_6H_3$ (**4**), and 2,6-$Me_2C_6H_3$ (**5**)), acetate-substituted products, *cis*-$[(AcO)ClPt(S(O)Me_2)(ArN{=}C(NHAr)_2)]$ (Ar = 2-MeC_6H_4 (**6**) and 4-MeC_6H_4 (**7**)), and six-membered [*C,N*] platinacycles, *cis*-$[Pt\{\kappa^2(C,N)\text{-}C_6H_3R\text{-}3(NHC(NHAr)(=NAr))\text{-}2\}Cl(S(O)Me_2)]$ (Ar = 2-RC_6H_4; R = OMe (**8**) and Me (**9**)). The molecular structures of seven compounds ($LH_2^{2,5\text{-xylyl}}$, **1**, **2**, **4**, **5**, **6**, and **8**) have been determined by single-crystal X-ray diffraction. Factors that determine the time scale of cycloplatination, the role of NaOAc, and a plausible mechanism of this reaction with *sym-N,N′,N″*-triarylguanidines have been outlined.

EXPERIMENTAL SECTION

Full experimental details pertinent to general considerations may be found in the Supporting Information.

Complex 1. *cis*-$[Cl_2Pt(S(O)Me_2)_2]$ (100 mg, 0.237 mmol) and $LH_2^{2\text{-tolyl}}$ (78.0 mg, 0.237 mmol) were dispersed in toluene (15 mL) in a 50 mL round-bottom flask that was fitted to a water condenser capped with an anhydrous $CaCl_2$ guard tube. The reaction mixture in the flask was simultaneously stirred and refluxed for 3 h. During the course of the reaction, the solid slowly dissolved to afford a clear yellow solution. Subsequently, the reaction mixture was cooled and concentrated under vacuum to about 5 mL. The solution was stored at ambient temperature to afford a solid. The solid was crystallized from $CHCl_3$/toluene mixture at ambient temperature over a period of several hours to afford **1** as pale yellow crystals. Yield: 96% (153 mg, 0.227 mmol). Mp (DSC): 195.8 °C. FT-IR (KBr, cm^{-1}): ν(NH) 3462 (br, m), 3377 (m); ν(C═N) 1620 (vs); ν(S═O) 1142 (m). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.97, 2.34, 2.60 (each s, 3 × 3H, CH_3), 3.31 (s, 6H, $(CH_3)_2S(O)$), 5.62 (s, 1H, N*H*), 6.83−7.21 (m, 11H, Ar*H*), 7.76 (d, $J_{H,H}$ = 7.8 Hz, 1H, Ar*H*), 7.90 (s, 1H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz): δ 17.64, 18.20, 19.39 (CH_3), 43.63 ($(CH_3)_2S(O)$), 124.61, 125.07, 126.19, 126.26, 126.38, 126.44, 126.95, 127.10, 129.16, 130.45, 130.62, 131.63, 131.86, 132.50, 134.36, 135.41, 135.56, 143.01 (ArC and ArCH), 154.54 (*C*═N). $^{195}Pt\{^1H\}$ NMR (85.8 MHz, $CDCl_3$): δ −2967. MS (TOF-ES$^+$), *m/z* (intensity %), [ion]: 674 (37), $[M]^+$; 618 (12), $[M + Na - S(O)Me_2]^+$; 586 (39), $[M - (2HCl, Me)]^+$. Anal. Calcd for $C_{24}H_{29}N_3SOCl_2Pt$ (M_w 673.57): C, 42.80; H, 4.34; N, 6.24; S, 4.76. Found: C, 42.96; H, 4.18; N, 6.12; S, 4.40.

Complex 2. Complex **2** was prepared from *cis*-$[Cl_2Pt(S(O)Me_2)_2]$ (50.0 mg, 0.118 mmol) and $LH_2^{2\text{-anisyl}}$ (45.0 mg, 0.119 mmol) in toluene (15 mL) and purified as described previously for **1**. Yield: 83% (82.0 mg, 0.098 mmol). Mp: 165.0 °C (decomp). FT-IR (KBr, cm^{-1}): ν(NH) 3449 (br, vs); ν(C═N) 1615 (vs); ν(S═O) 1116 (m). Two isomers were observed in about a 1.0:2.1 ratio as estimated from the integrals of OCH_3 and N*H* protons of the guanidine unit. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.23 (br, 6H, $(CH_3)_2S(O)$, major isomer), 3.26 (s, 6H, $(CH_3)_2S(O)$, minor isomer), 3.59 (br, 3H, OCH_3, major isomer), 3.62 (s, 3H, OCH_3, minor isomer), 3.68 (br, 3H, OCH_3, major isomer), 3.71 (s, 3H, OCH_3, minor isomer), 3.82 (s, 3H, OCH_3, minor isomer), 3.86 (br, 3H, OCH_3, major isomer), 6.47−7.19 (m, 24H, Ar*H*), 7.81, 7.84 (each s, 2H, N*H*, minor isomer), 8.04 (s, 2H, N*H*, major isomer). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$, 85.8 MHz): δ −2721 (major isomer), −2771 (minor isomer). MS (TOF-ES$^+$), *m/z* (intensity %), [ion]: 761 (5), $[M + K]^+$; 744 (7), $[M + Na]^+$; 724 (9) [M + K − HCl], 648 (74), $[M - 2HCl]^+$; 378 (30), $[LH_3^{2\text{-anisyl}}]^+$, 377 (100), $[LH_2^{2\text{-anisyl}}]^+$. Anal. Calcd for $C_{24}H_{29}N_3O_4SCl_2Pt\cdot CHCl_3$ (M_w 840.96): C, 35.71; H, 3.60; N, 5.00; S, 3.81. Found: C, 35.68; H, 3.65; N, 4.94; S, 3.92. Pale yellow crystals of **2**·1.5$CHCl_3$ suitable for X-ray diffraction were grown from toluene/$CHCl_3$ mixture in a 5 mm NMR tube at ambient temperature over a period of 1 week.

Complex 3. Complex **3** was prepared from *cis*-$[Cl_2Pt(S(O)Me_2)_2]$ (100 mg, 0.237 mmol) and $LH_2^{4\text{-tolyl}}$ (78.0 mg, 0.237 mmol) in toluene (15 mL) and purified as described previously for **1**. Yield: 93% (158 mg, 0.220 mmol). Mp (DSC): 161.7 °C. FT-IR (KBr, cm^{-1}): ν(NH) 3472 (br), 3402 (br), ν(N−H···Cl) 3262 (m); ν(C═N) 1619 (vs); ν(S═O) 1129 (m). ^1H NMR ($CDCl_3$, 400 MHz): δ 2.15, 2.20 (each br, 2 × 3H, CH_3), 2.30 (s, 3 H, CH_3), 3.27, 3.34 (each s, 2 × 3H, $(CH_3)_2S(O)$), 5.89 (br, 1H, N*H*), 6.72, 6.82, 6.94, 6.97 (each br, 8H, Ar*H*), 7.12, 7.39 (each d, $J_{H,H}$ = 8.0 Hz, 2 × 2H, Ar*H*), 8.00 (br, 1H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz): δ 20.8 (br), 21.1 (CH_3), 43.6 ($(CH_3)_2S(O)$), 122.5, 123.8, 126.7, 129.3, 129.5, 130.2, 134.3, 134.7, 135.2, 136.0, 141.8 (ArC and ArCH), 153.6 (*C*═N). Two carbon resonances were observed for CH_3 carbons and 11 carbon resonances for aryl carbons of the guanidine unit rather than the expected 3 and 12 resonances, respectively, due to overlapping peaks. Two days old $CDCl_3$ solution of **3** revealed the formation of two isomers in about a 1:0.2 ratio as estimated from the integrals of CH_3 and N*H* protons of the guanidine unit. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.14 (br, 3H, CH_3, major isomer), 2.17 (s, 3H, CH_3, minor isomer), 2.20 (br, 3H, CH_3, major isomer), 2.23 (s, 3H, CH_3, minor isomer), 2.27 (s, 3H, CH_3, minor isomer), 2.30 (s, 3H, CH_3, major isomer), 3.28 (s, 3H, $(CH_3)_2S(O)$, major isomer), 3.32 (s, 2 × 3H, $(CH_3)_2S(O)$, minor isomer), 3.34 (s, 3H, $(CH_3)_2S(O)$, major isomer), 5.84 (br, 1H, N*H*, minor isomer), 5.92 (br, 1H, N*H*, major isomer), 6.72, 6.80, 6.82, 6.94, 6.97, 6.99 (each br, 2 × 8H, Ar*H*, major and minor isomers), 7.09 (d, $J_{H,H}$ = 8.0 Hz, 2H, Ar*H*, minor isomer), 7.12 (d, $J_{H,H}$ = 8.4 Hz, 2H, Ar*H*, major isomer), 7.35 (d, $J_{H,H}$ = 8.0 Hz, 2H, Ar*H*, minor isomer), 7.39 (d, $J_{H,H}$ = 8.4 Hz, 2H, Ar*H*, major isomer), 7.86 (br, 1H, N*H*, minor isomer), 8.02 (br, 1H, N*H*, major isomer). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$, 85.8 MHz): δ −2898 (minor isomer), −3009 (major isomer). MS (TOF-ES$^+$), *m/z* (intensity %), [ion]: 661 (8), $[M + Na - Cl]^+$; 639 (18), $[M + H - Cl]^+$; 603 (20), $[M - 2Cl]^+$; 330 (100), $[LH_3^{4\text{-tolyl}}]^+$. Anal. Calcd for $C_{24}H_{29}N_3SOCl_2Pt\cdot 0.5C_7H_8$ (M_w 719.64): C, 45.90; H, 4.62; N, 5.84; S, 4.46. Found: C, 45.80; H, 4.57; N, 5.89; S, 4.46.

Complex 4. Complex **4** was synthesized from *cis*-$[Cl_2Pt(S(O)Me_2)_2]$ (101 mg, 0.239 mmol) and $LH_2^{2,5\text{-xylyl}}$ (89.0 mg, 0.240 mmol) in toluene (15 mL) and purified as described previously for **1**. The sample was crystallized from CH_2Cl_2/toluene mixture at ambient temperature over a period of several hours to afford **4** as pale yellow crystals. Yield: 94% (161 mg, 0.225 mmol). Mp (DSC): 199.6 °C. FT-IR (KBr, cm^{-1}): ν(NH) 3447 (br, m), 3374 (m); ν(C═N) 1602 (vs); ν(S═O) 1139 (m). The number of isomers in solution varied depending upon the concentration of the sample. ^1H NMR ($CDCl_3$, 300 MHz, 0.007 mM): δ 1.94, 2.14, 2.18, 2.30, 2.31, 2.54 (each s, 6 × 3H, CH_3), 3.30, 3.31 (each s, 2 × 3H, $(CH_3)_2S(O)$), 5.61 (s, 1H,

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NH), 6.64 (d, $J_{H,H}$ = 7.8 Hz, 1H, ArH), 6.71−6.75 (m, 2H, ArH), 6.84 (s, 1H, ArH), 6.89−6.93 (m, 2H, ArH), 6.95 (s, 1H, ArH), 7.07 (d, $J_{H,H}$ = 7.5 Hz, 1H, ArH), 7.55 (s, 1H, ArH), 7.69 (s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz, 0.084 mM): δ 17.1, 17.6, 18.9, 20.6, 20.7, 21.0 (CH_3), 43.5 ((CH_3)$_2$S(O)), 125.2, 125.6, 126.7, 126.8, 127.6, 128.4, 129.0, 129.4, 130.0, 130.1, 131.0, 131.2, 135.0, 135.1, 136.0, 136.7, 142.8 (ArC and ArCH), 154.1 (C═N). Note: Only 17 carbon resonances were observed for aryl carbons of the guanidine unit rather than the expected 18 peaks, presumably due to overlapping peaks. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$, 85.8 MHz): δ −2959. Two isomers were observed in about a 1.00:0.12 ratio at 0.154 mM concentration as estimated from the integrals of CH_3 and NH protons of the guanidine unit (see the Supporting Information). ^1H NMR ($CDCl_3$, 400 MHz, 0.154 mM): δ 1.90 (s, 3H, CH_3, minor isomer), 1.94 (s, 3H, CH_3, major isomer), 2.12 (s, 3H, CH_3, minor isomer), 2.14 (s, 2 × 3H, CH_3, major and minor isomers), 2.18 (s, 3 H, CH_3, major isomer), 2.30, 2.31 (each s, 3 × 3H, CH_3, major isomer (6H), minor isomer (3H)), 2.35 (s, 2 × 3H, CH_3, minor isomer), 2.55 (s, 3H, CH_3, major isomer), 3.26, 3.27 (each s, 2 × 3H, (CH_3)$_2$S(O), major isomer), 3.39, 3.45 (each s, 2 × 3H, (CH_3)$_2$S(O), minor isomer), 5.63 (s, 1H, NH, major isomer), 5.74 (s, 1H, NH, minor isomer), 6.57 (d, $J_{H,H}$ = 7.8 Hz, 1H, ArH, minor isomer), 6.64 (d, $J_{H,H}$ = 7.8 Hz, 1H, ArH, major isomer), 6.67−6.75 (m, 2 × 2H, ArH, major and minor isomers), 6.85, 6.90, 6.92, 6.96 (each s, 4H, ArH, major isomer), 7.07 (d, $J_{H,H}$ = 7.8 Hz, 1H, ArH, major isomer), 7.13−7.18 (m, 3H, ArH, minor isomer), 7.24 (d, $J_{H,H}$ = 7.3 Hz, 1H, ArH, minor isomer), 7.43 (s, 1H, ArH, minor isomer), 7.56 (s, 1H, ArH, major isomer), 7.71 (s, 1H, NH, major isomer), 7.94 (s, 1H, NH, minor isomer), 7.97 (s, 1H, ArH, minor isomer). The $^{13}C\{^1H\}$ signals of the minor isomer are indicated by the asterisk (*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz, 0.154 mM): δ 16.8*, 17.0, 17.4*, 17.6, 18.1*, 18.9, 19.0*, 20.6, 20.7, 21.0, 21.1* (CH_3), 43.4, 43.5, 44.5*, 45.4* ((CH_3)$_2$S(O)), 123.8*, 124.3*, 124.8*, 125.2 (CH), 125.5 (CH), 125.8*, 126.4*, 126.7 (CH), 126.8 (CH), 127.1*, 127.6 (CH), 127.8*, 127.9*, 128.1*, 128.4 (C), 128.9 (C), 129.4 (CH), 129.8*, 129.9 (CH), 130.1 (CH), 130.2*, 131.0 (C), 131.2 (CH), 131.4*, 132.0*, 134.7*, 134.9 (C), 135.1 (C), 135.8*, 135.9 (C), 136.0 (C), 136.2*, 136.5*, 136.6 (C), 142.8 (C), 142.9*, 154.0 (C═N), 154.1*. Only 5 resonances were observed for CH_3 carbons of the minor isomer rather than the expected 6 due to overlapping peaks at δ 20.7. MS (TOF-ES$^+$), *m*/*z* (intensity %), [ion]: 834 (12), [M + Cs − Me]$^+$; 679 (5), [M − HCl]$^+$; 565 (9), [M − 2HCl − Me$_2$S(O)]$^+$; 373 (40), [$LH_3^{2,5\text{-xylyl}}$]$^+$; 372 (100), [$LH_2^{2,5\text{-xylyl}}$]$^+$; 370 (35), [$L^{2,5\text{-xylyl}}$]$^+$. Anal. Calcd for $C_{27}H_{35}N_3OSCl_2Pt$ (M_w 715.66): C, 45.31; H, 4.93; N, 5.87; S, 4.48. Found: C, 45.42; H, 4.89; N, 5.59; S, 4.22.

Complex 5. Complex **5** was synthesized from *cis*-[Cl_2Pt(S(O)Me$_2$)$_2$] (50.0 mg, 0.118 mmol) and $LH_2^{2,6\text{-xylyl}}$ (45.0 mg, 0.121 mmol) in toluene (15 mL) and purified as described previously for **1**. The sample was crystallized from $CHCl_3$/toluene mixture at ambient temperature over a period of several hours to afford **5**·C_7H_8 as light brown crystals. Yield: 93% (79.0 mg, 0.110 mmol). Mp (DSC): 191.2 °C. FT-IR (KBr, cm^{-1}): ν(NH) 3442 (br, m), 3341 (m); ν(C═N) 1618 (vs); ν(S═O) 1157 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.06, 2.33, 2.82 (each s, 6 × 3H, CH_3), 3.33 (s, 6H, (CH_3)$_2$S(O)), 5.73 (s, 1H, NH), 6.68, 6.76 (each d, $J_{H,H}$ = 7.4 Hz, 2 × 2H, ArH), 6.80−6.90 (m, 2H, ArH), 7.05−7.23 (m, 3H, ArH), 8.56 (br, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 17.5, 18.1, 19.2 (CH_3), 43.5 ((CH_3)$_2$S(O)), 124.5, 124.9, 126.1, 126.3, 126.8, 127.0, 129.0, 130.3, 130.5, 131.5, 131.7, 132.4, 134.2, 135.3, 135.4, 142.8 (ArC and ArCH), 154.4 (C═N). Note: Only 16 carbon resonances were observed for aryl carbons of the guanidine unit rather than the expected 18 peaks, presumably due to overlapping peaks. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$, 85.8 MHz): δ −2893. MS (TOF-ES$^+$), *m*/*z* (intensity %), [ion]: 1454 (10), [2M + Na]$^+$; 1396 (10), [2M − Cl]$^+$; 776 (7), [M + Cs − 2HCl]$^+$; 739 (8), [M + Na]$^+$; 680 (22), [M − Cl]$^+$; 565 (22), [M − 2HCl − S(O)Me$_2$]$^+$; 372 (100), [$LH_2^{2,6\text{-xylyl}}$]$^+$. Anal. Calcd for $C_{27}H_{35}N_3OSCl_2Pt$ (M_w 715.66): C, 45.31; H, 4.93; N, 5.87; S, 4.48. Found: C, 45.52; H, 4.96; N, 5.85; S, 4.68.

Complex 6. *Method 1*. *cis*-[Cl_2Pt(S(O)Me$_2$)$_2$] (51.0 mg, 0.121 mmol), $LH_2^{2\text{-tolyl}}$ (40.0 mg, 0.121 mmol), and NaOAc (10.0 mg, 0.122 mmol) were charged into a 25 mL round-bottom flask in methanol (10 mL), and the flask was fitted to a water condenser capped with an anhydrous $CaCl_2$ guard tube. The reaction mixture in the flask was simultaneously stirred and refluxed for 3 h and cooled to ambient temperature. The volatiles from the reaction mixture were removed under vacuum to afford a solid. The solid was dissolved in CH_2Cl_2 and filtered. The filtrate was layered with toluene and stored at ambient temperature over a period of several days to afford **6**·S(O)Me$_2$ as pale yellow crystals in 83% (78.0 mg, 0.101 mmol) yield. Mp: 198.6 °C. FT-IR (KBr, cm^{-1}): ν(NH) 3440 (br m), 3384 (m); ν_a(OCO) 1623 (vs); ν(C═N) 1603 (vs); ν_s(OCO) 1384 (m); ν(S═O) 1132 (m). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.96, 2.13, 2.30, 2.52 (each s, 4 × 3H, CH_3), 3.34, 3.53 (each s, 2 × 3H, (CH_3)$_2$S(O)), 5.64 (s, 1H, NH), 6.76 − 6.82 (m, 3H, ArH), 6.87 (t, $J_{H,H}$ = 7.2 Hz, 2H, ArH), 6.98 (d, $J_{H,H}$ = 6.9 Hz, 1H, ArH), 7.05 (d, $J_{H,H}$ = 7.9 Hz, 1H, ArH), 7.16−7.18 (m, 4H, ArH), 7.67 (d, $J_{H,H}$ = 7.8 Hz, 1H, ArH), 10.60 (s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz): δ 17.60, 18.15, 19.35, 20.88 (CH_3), 43.50 ((CH_3)$_2$S(O)), 124.58, 125.07, 126.17, 126.20, 126.33, 126.40, 126.89, 127.04, 129.12, 130.41, 130.57, 131.57, 131.84, 132.52, 134.32, 135.39, 135.54, 142.98 (ArC and ArCH), 154.55 (C═N), 176.80 (OC(O)). $^{195}Pt\{^1H\}$ NMR (85.8 MHz, $CDCl_3$): δ −2718. MS (TOF-ES$^+$), *m*/*z* (intensity %), [ion]: 736 (8), [M + K]$^+$; 698 (25), [M + H]$^+$; 662 (20), [M − Cl]$^+$; 610 (20), [M + Li − (OAc, Cl)]$^+$; 331 (100), [$LH_3^{2\text{-tolyl}}$]$^+$. Anal. Calcd for $C_{26}H_{32}N_3O_3SClPt$·(CH$_3$)$_2$S(O) (M_w 775.34): C, 43.38; H, 4.94; N, 5.42; S, 8.27. Found: C, 43.35; H, 4.91; N, 5.42; S, 8.27. Greenish yellow crystals of **6**·S(O)Me$_2$ for X-ray diffraction were grown from methanol/$CHCl_3$ mixture at ambient temperature over a period of several days.

Method 2. Complex **1** (100 mg, 0.148 mmol) and NaOAc (13.0 mg, 0.158 mmol) were charged into a 25 mL round-bottom flask and dispersed in methanol (10 mL), and the flask was fitted to a water condenser capped with an anhydrous $CaCl_2$ guard tube. The reaction mixture in the flask was simultaneously stirred and refluxed for 3 h and cooled to ambient temperature. Subsequently, the volatiles from the reaction mixture were removed under vacuum to afford a solid. The solid was dissolved in CH_2Cl_2 and filtered. The filtrate was layered with toluene and stored at ambient temperature over a period of several days to afford **6**·S(O)Me$_2$ as pale yellow crystals in 85% (105 mg, 0.135 mmol) yield. The authenticity of **6**·S(O)Me$_2$ prepared by this method was verified by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.

Complex 7. Complex 7 was prepared from *cis*-[Cl_2Pt(S(O)Me$_2$)$_2$] (101 mg, 0.239 mmol), $LH_2^{4\text{-tolyl}}$ (80.0 mg, 0.243 mmol), and NaOAc (20.0 mg, 0.244 mmol) and purified as described previously for **6** (method 1). Yield of **7**·S(O)Me$_2$: 84% (156 mg, 0.201 mmol). Mp: 239.0 °C (decomp). FT-IR (KBr, cm^{-1}): ν(NH) 3381 (m); ν_a(OCO) 1626 (s); ν(C═N) 1604 (vs); ν_s(OCO) 1377 (m); ν(S═O) 1134 (m). ^1H NMR ($CDCl_3$, 400 MHz): δ 2.10 (s, 3H, CH_3), 2.14, 2.20 (each br, 2 × 3H, CH_3), 2.30 (s, 3H, CH_3), 3.27, 3.34 (each s, 2 × 3H, (CH_3)$_2$S(O)), 5.90 (s, 1H, NH), 6.72, 6.80, 6.94, 6.97 (each br, 4 × 2H, ArH), 7.11 (d, $J_{H,H}$ = 8.1 Hz, 2H, ArH), 7.39 (d, $J_{H,H}$ = 8.8 Hz, 2H, ArH), 8.02 (s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz): δ 20.9 (br), 21.1 (CH_3), 43.7 ((CH_3)$_2$S(O)), 122.6, 123.4, 123.6, 123.9, 126.4, 126.7, 128.3, 129.4, 129.6, 130.0, 130.2, 134.3, 134.8, 135.3, 136.1, 136.8, 141.8, 142.1 (ArC and ArCH), 153.7 (C═N), 177.4 (OC(O)). Note: Only two carbon resonances were observed for CH_3 carbons of the guanidine unit rather than the expected three resonances, presumably due to overlapping peaks. $^{195}Pt\{^1H\}$ NMR (85.8 MHz, $CDCl_3$): δ −2891. MS (TOF-ES$^+$), *m*/*z* (intensity %), [ion]: 1312 (10), [2 M + K − 2AcOH]$^+$, 638 (26), [M − OAc]$^+$; 602 (53), [M − Cl − OAc]$^+$; 564 (15), [M + K − Cl − S(O)Me$_2$ − OAc]$^+$, 330 (100), [$LH_2^{4\text{-tolyl}}$]$^+$. Anal. Calcd for $C_{26}H_{32}N_3O_3SClPt$·(CH$_3$)$_2$S(O) (M_w 775.34): C, 43.38; H, 4.94; N, 5.42; S, 8.27. Found: C, 43.40; H, 4.93; N, 5.45; S, 8.29.

Complex 8. *cis*-[Cl_2Pt(S(O)Me$_2$)$_2$] (101 mg, 0.239 mmol), $LH_2^{2\text{-anisyl}}$ (90.1 mg, 0.241 mmol), and NaOAc (20.0 mg, 0.244 mmol) were charged into a 25 mL round-bottom flask in methanol (10 mL), and the flask was fitted to a water condenser capped with an anhydrous $CaCl_2$ guard tube. The reaction mixture in the flask was simultaneously stirred and refluxed for 3 h and subsequently cooled to ambient temperature. The volatiles from the reaction mixture were

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Table 1. Crystallographic Data for 1, 2·1.5CHCl$_3$, and 4

	1	2·1.5CHCl$_3$	4
formula	$C_{24}H_{29}Cl_2N_3OPtS$	$C_{51}H_{61}Cl_{13}N_6O_8Pt_2S_2$	$C_{27}H_{35}Cl_2N_3OPtS$
fw	673.55	1801.21	715.63
temp. (K)	100(2)	120(2)	100(2)
wavelength (λ)	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.504(4)	12.658(5)	10.154(5)
b (Å)	11.299(5)	16.391(5)	11.260(5)
c (Å)	12.294(4)	16.940(4)	12.970(4)
α (deg)	111.917(5)	79.543(5)	106.736(5)
β (deg)	103.026(5)	75.782(5)	99.459(4)
γ (deg)	101.580(4)	76.201(4)	97.130(5)
vol. (Å^3)	1251.7(7)	3280.4(19)	1377.5(11)
Z	2	2	2
ρ_{calcd} (g cm^{-3})	1.787	1.824	1.725
$F(000)$	660	1764	708
μ(Mo Kα) (mm^{-1})	5.924	4.907	5.388
θ range (deg)	1.89−26.00	2.96−26.37	1.68−26.37
no. of reflns collected	7116	48 345	26 064
no. of reflns used	4947	13 401	5631
parameters	295	749	325
R_1 [$I > 2\sigma(I)$][a]	0.0496	0.0313	0.0253
wR_2 (all reflns)[b]	0.1242	0.0708	0.0732
GooF on F^2[c]	1.206	1.092	1.309
largest diff peak/hole (e·Å^{-3})	3.387/−1.872	1.873/−1.599	2.764/−1.427

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

removed under vacuum to afford a solid. The solid was dissolved in CH_2Cl_2 and filtered. The filtrate was layered with toluene to afford **8** as pale brown crystals in 92% (151 mg, 0.220 mmol) yield. Mp (DSC): 225.6 °C. FT-IR (KBr, cm^{-1}): ν(NH) 3436 (sh), 3392 (m); ν(C═N) 1618 (vs); ν(S═O) 1117 (m). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.35, 3.48 (each br, 2 × 3H, $(CH_3)_2S(O)$), 3.79, 3.85, 4.08 (each s, 3 × 3H, OCH_3), 6.67 (d, $J_{H,H}$ = 8.1 Hz, 1H, Ar*H*), 6.90−6.99 (m, 5H, Ar*H*), 7.11−7.23 (m, 4H, Ar*H*), 7.53 (d, $J_{H,H}$ = 8.1 Hz, 1H, Ar*H*), 7.87, 7.90 (each s, 2H, N*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 46.2, 46.8 ($(CH_3)_2S(O)$), 55.2, 55.8, 56.1 (OCH_3), 106.2, 111.0, 111.3, 119.4, 120.7, 121.2, 122.0, 123.4, 125.5, 126.6, 126.7, 127.5, 130.0, 131.0, 134.8, 146.6, 148.1, 150.8 (Ar*C* and Ar*C*H), 154.3 (*C*═N). ^{195}Pt{^{1}H} NMR (85.8 MHz, $CDCl_3$): δ −3737. MS (TOF-ES$^+$), m/z (intensity %), [ion]: 608 (53), $[M + H - S(O)Me_2]^+$; 572 (100), $[M - Cl - S(O)Me_2]^+$; 555 (72), $[M - S(O)Me_2 - HCl - Me]^+$; 493 (69), $[L^{2\text{-anisyl}} + Cs - Me]^+$; 477 (20), $[L^{2\text{-anisyl}} + Cs - OMe]^+$; 378 (33), $[LH_3^{2\text{-anisyl}}]^+$; 376 (28), $[LH^{2\text{-anisyl}}]^+$. Anal. Calcd for $C_{24}H_{28}N_3O_4SClPt$ (M_w 685.10): C, 42.08; H, 4.12; N, 6.13; S, 4.68. Found: C, 41.94; H, 4.17; N, 5.93; S, 4.60. Pale yellow crystals of **8** for X-ray diffraction were grown from methanol/CH_2Cl_2 mixture at ambient temperature over a period of several days.

Complex 9. *cis*-$[Cl_2Pt(S(O)Me_2)_2]$ (100 mg, 0.237 mmol), $LH_2^{2\text{-tolyl}}$ (82.0 mg, 0.249 mmol), and NaOAc (20.0 mg, 0.244 mmol) were charged into a 25 mL round-bottom flask in methanol (10 mL), and the flask was fitted to a water condenser capped with an anhydrous $CaCl_2$ guard tube. The reaction mixture in the flask was simultaneously stirred and refluxed for 12 h and subsequently cooled to ambient temperature. The volatiles from the reaction mixture were removed under vacuum to afford a solid. The solid was dissolved in CH_2Cl_2 and filtered, and the filtrate was layered with toluene to afford **9**·$S(O)Me_2$ as pale-brown crystalline material in 79% (134 mg, 0.187 mmol) yield. Mp: 181.0 °C (decomp). FT-IR (KBr, cm^{-1}): ν(NH) 3433 (br, s), 3378 (sh, s), 3294 (m); ν(C═N) 1620 (vs); ν(S═O) 1142 (m). FT-IR ($CHCl_3$, cm^{-1}): ν(NH) 3387 (br, m); ν(C═N) 1622 (vs); ν(S═O) 1129 (br, m). The ^{1}H NMR spectrum of **9** indicated the presence of four major isomers, one intermediate isomer, and two minor isomers in about 1:1:1:1:0.23:0.12:0.11 ratios as estimated from the integrals of CH_3 protons of the guanidine unit. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.64 (s, 3H, CH_3, major isomer), 1.89, 1.90 (each s, 2 × 3H, CH_3, minor isomer 2), 1.94, 1.96 (each s, 2 × 3H, CH_3, major isomer), 1.98 (s, 3H, CH_3, minor isomer 2), 2.04, 2.06 (each s, 2 × 3H, CH_3, major isomer), 2.10 (s, 3H, CH_3, intermediate isomer), 2.12 (s, 3H, CH_3, major isomer), 2.19 (s, 3H, CH_3, intermediate isomer), 2.24, 2.28, 2.33 (each s, 3 × 3H, CH_3, major isomer), 2.36 (s, 3H, CH_3, intermediate isomer), 2.43 (s, 3H, CH_3, minor isomer 1), 2.49 (s, 3H, CH_3, major isomer), 2.58 (s, 3H, CH_3, minor isomer 1), 2.59, 2.62 (each s, 2 × 3H, CH_3, major isomer), 2.70 (s, 3H, CH_3, minor isomer 1), 3.26, 3.27 (each s, 2 × 3H, $(CH_3)_2S(O)$, intermediate isomer), 3.29 (s, 3H, $(CH_3)_2S(O)$, minor isomer 2), 3.30 (s, 2 × 3H, $(CH_3)_2S(O)$, one major isomer and minor isomer 2), 3.32 (s, 3 × 3H, $(CH_3)_2S(O)$, three major isomers), 3.40 (s, 3H, $(CH_3)_2S(O)$, minor isomer 1), 3.42 (s, 3H, $(CH_3)_2S(O)$, major isomer), 3.44 (s, 3H, $(CH_3)_2S(O)$, minor isomer 1), 3.49 (s, 3H, $(CH_3)_2S(O)$, major isomer), 3.52 (s, 2 × 3H, $(CH_3)_2S(O)$, two major isomers), 5.56 (s, 1H, N*H*, minor isomer 2), 5.61 (s, 3 × 1H, N*H*, two major isomers and one intermediate isomer), 6.23 (s, 1H, N*H*, major isomer), 6.32 (s, 1H, N*H*, minor isomer 1), 6.41 (s, 1H, N*H*, major isomer), 6.72−6.81 (m, 13H, Ar*H*), 6.83−6.92 (m, 13H, Ar*H*), 6.94−7.09 (m, 16H, Ar*H*), 7.12−7.21 (m, 16H, Ar*H*), 7.26−7.32 (m, 11H, Ar*H*), 7.43 (d, $J_{H,H}$ = 8.1 Hz, 2H, Ar*H*), 7.61−7.69 (m, 6H, Ar*H* (5H) and N*H* (1H) for major isomer), 7.75 (d, $J_{H,H}$ = 7.4 Hz, 1H, Ar*H*), 7.79 (s, 1H, N*H*, major isomer), 8.03 (s, 1H, N*H*, minor isomer 2), 9.82 (s, 1H, N*H*, intermediate isomer), 10.15 (s, 1H, N*H*, minor isomer 1), 10.56 (s, 2H, N*H*, two major isomers). ^{195}Pt{^{1}H} NMR ($CDCl_3$, 85.8 MHz): δ −2645 (minor), −2710 (major), −2760 (minor), −2839 (minor), −2851 (minor), −2958 (major), and −2995 (minor). MS (TOF-ES$^+$), m/z (intensity %), [ion]: 641 (20), $[M + K - Cl]^+$; 638 (22), $[M + H]^+$; 621 (15), $[M - H, Me]^+$; 601 (100) $[M - Cl]^+$; 330 (15), $[LH_3^{2\text{-tolyl}}]^+$. Anal. Calcd for $C_{24}H_{28}N_3OSClPt\cdot(CH_3)_2S(O)$ (M_w 715.23): C, 43.66; H, 4.79; N, 5.88; S, 8.97. Found: C, 43.59; H, 4.83; N, 5.85; S, 8.92.

Complex **9** was crystallized from a $CHCl_3$/methanol mixture at ambient temperature over a period of 1 week to afford crystals of one of the major isomers. The ^{1}H NMR spectral data of this isomer is

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Table 2. Crystallographic Data for $5{\cdot}C_7H_8$, $6{\cdot}S(O)Me_2$, and 8

	$5{\cdot}C_7H_8$	$6{\cdot}S(O)Me_2$	8
formula	$C_{34}H_{43}Cl_2N_3OPtS$	$C_{28}H_{38}ClN_3O_4PtS_2$	$C_{24}H_{28}ClN_3O_4PtS$
fw	807.76	775.27	685.09
temp. (K)	100(2)	100(2)	100(2)
wavelength (λ)	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.968(5)	10.8407(8)	8.8240(8)
b (Å)	11.004 (5)	11.8760(9)	10.6295(10)
c (Å)	15.910(4)	12.3107(9)	13.7122(13)
α (deg)	88.421(5)	92.791(4)	75.839(4)
β (deg)	76.519(4)	106.147(5)	82.686(5)
γ (deg)	81.102(5)	93.814(4)	84.765(4)
vol. (Å^3)	1508.4(12)	1515.30(19)	1234.5(2)
Z	2	2	2
ρ_{calcd} (g cm^{-3})	1.779	1.699	1.843
$F(000)$	808	772	672
μ(Mo Kα) (mm^{-1})	4.932	4.894	5.912
θ range (deg)	1.32−26.37	1.72−26.37	1.98−26.37
no. of reflns collected	24 915	31 530	17 879
no. of reflns used	6146	6157	5017
parameters	337	343	321
R_1 [$I > 2\sigma(I)$][a]	0.0275	0.0348	0.0228
wR_2 (all reflns)[b]	0.0784	0.0955	0.0591
GooF on F^2[c]	1.271	1.231	1.401
largest diff peak/hole (e·Å^{-3})	2.429/−0.971	2.702/−1.421	2.056/−1.475

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

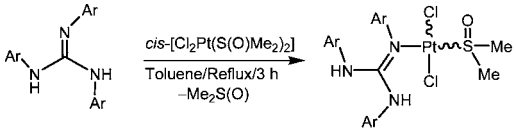
given below. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.96, 2.33, 2.60 (each s, 3 × 3H, CH_3), 3.30, 3.32 (each s, 2 × 3H, $(CH_3)_2S(O)$), 5.61 (s, 1H, NH), 6.83 (s, 1H, ArH), 6.84−6.87 (m, 1H, ArH), 6.89−6.93 (m, 1H, ArH), 6.93−6.96 (m, 1H, ArH), 6.98−7.02 (m, 2H, ArH), 7.06 (d, J_{HH} = 7.3 Hz, 1H, ArH), 7.10−7.14 (m, 1H, ArH), 7.17−7.21 (m, 2H, ArH), 7.75 (d, $J_{H,H}$ = 6.6 Hz, 1H, ArH), 7.79 (s, 1H, NH). Other data could not be obtained for this isomer due to paucity of the sample.

X-ray Crystallography. Details of data collections, structure solutions, and refinements are presented in Tables 1 and 2. Further details may be found in the Supporting Information.

RESULTS AND DISCUSSION

i. Platinum(II) Guanidine Complexes (1−5). *Synthesis.* Reaction of *cis*-$[Cl_2Pt(S(O)Me_2)_2]$ with 1 equiv of $LH_2^{2\text{-tolyl}}$, $LH_2^{2\text{-anisyl}}$, $LH_2^{4\text{-tolyl}}$, $LH_2^{2,5\text{-xylyl}}$, and $LH_2^{2,6\text{-xylyl}}$ carried out separately in toluene under reflux condition for 3 h afforded **1**, **2**, **3**, **4**, and **5**, respectively, in high yield as illustrated in Scheme 1. The products from the reaction mixture were isolated by evaporation of the mother liquor at ambient condition to afford a solid followed by crystallization of the solid from either $CHCl_3$/toluene mixture (**1**, **2**, **3**, **5**) or CH_2Cl_2/toluene mixture (**4**) at ambient condition. Complexes **1**−**5** are soluble in $CHCl_3$ and CH_2Cl_2 and sparingly soluble in acetone, methanol, and toluene.

Scheme 1. Syntheses of Complexes 1−5



LH_2^{Aryl}	Ar		Yield (%)
$LH_2^{2\text{-tolyl}}$	2-MeC_6H_4	**1**	96
$LH_2^{2\text{-anisyl}}$	2-$(MeO)C_6H_4$	**2**	83
$LH_2^{4\text{-tolyl}}$	4-MeC_6H_4	**3**	93
$LH_2^{2,5\text{-xylyl}}$	2,5-$Me_2C_6H_3$	**4**	94
$LH_2^{2,6\text{-xylyl}}$	2,6-$Me_2C_6H_3$	**5**	93

Single-Crystal X-ray Diffraction. Molecular structures of **1**, **2**, **4**, and **5** were determined by single-crystal X-ray diffraction and are depicted in Figure 1. Selected bond distances and bond angles are listed in Table 3. Two molecules are observed in an asymmetric unit of **2**, but the molecular structure and bond parameters are given only for molecule 1. The platinum atom is surrounded by two chlorides, the imine nitrogen of guanidine, and the sulfur atom of DMSO and displayed a slightly distorted square planar geometry. Two chlorides are located trans to each other around the platinum atom as are the sulfur atom of DMSO and the imine nitrogen of guanidine in **1**, **4**, and **5**. On the contrary, the aforementioned pairs of substituents are located cis to each other around the platinum atom in **2**. Complexes of the type $[Cl_2Pt(S(O)R_2)_2]$ have been shown to be stable in cis form due to the effective (d−d) π bonding, but the trans form becomes stable with sterically more demanding R substituent, such as isoamyl.[32] In the present study, the guanidine in **2** is sterically less hindered and perhaps more π accepting than the guanidine in **1**, **4**, and **5**. Thus, the configuration of the platinum atom in **1**, **4**, and **5** is predominantly influenced by steric factor, while the electronic factor dictates the configuration of the platinum atom in **2**. The guanidine units in complexes displayed anti−anti conformation ($\tau_{(CNC=N)}$ −146.7(8)°, −154.7(8)° (**1**); −147.4(4)°, −147.1(4)° (**2**); 150.0(4)°, 151.1(4)° (**4**), and −151.1(4)°, −150.2(4)° (**5**)) irrespective of their conformations in uncoordinated form ($LH_2^{2\text{-tolyl}}$ and $LH_2^{2,5\text{-xylyl}}$ anti−anti and $LH_2^{2\text{-anisyl}}$ and $LH_2^{2,6\text{-xylyl}}$ syn−anti).[33] The anti−anti conforma-

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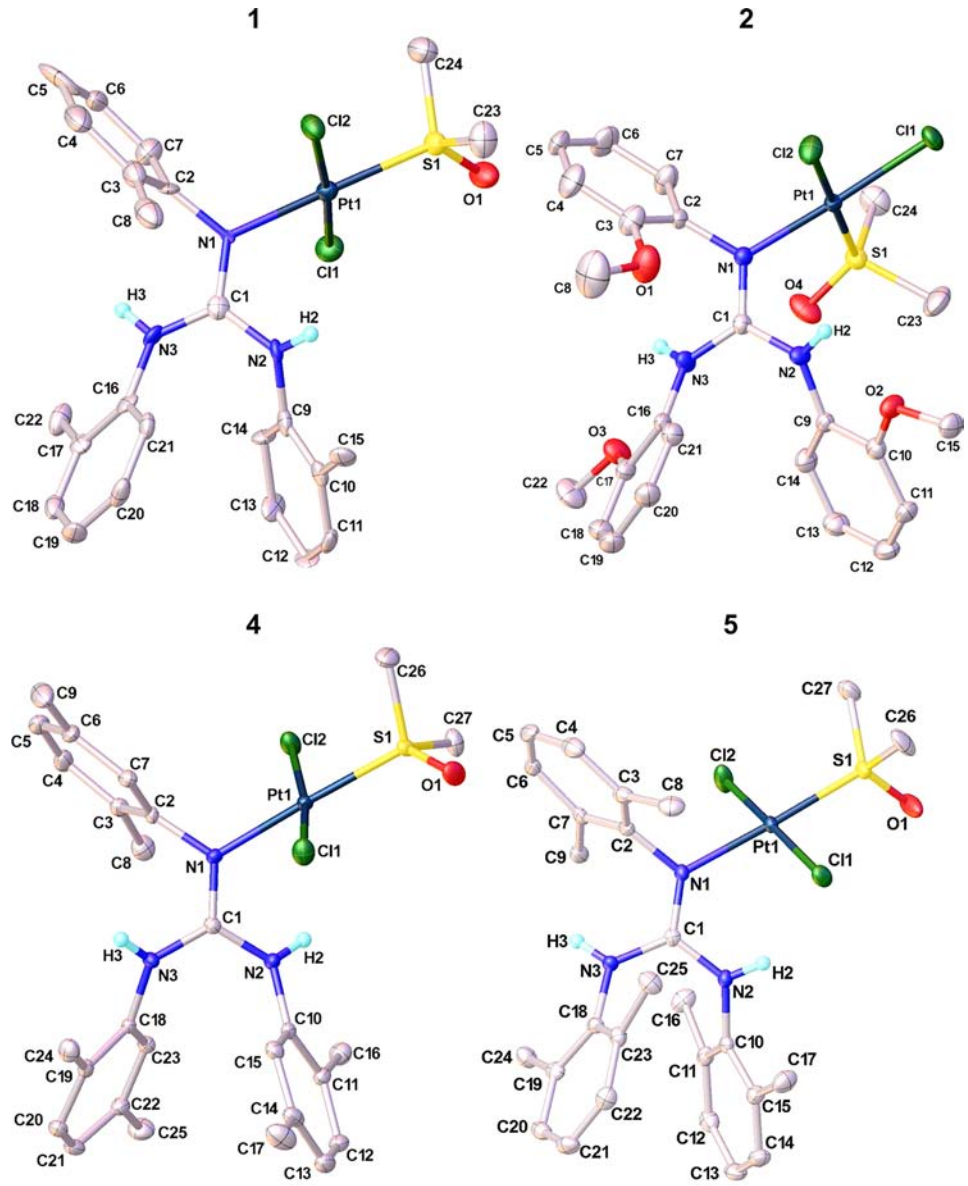

Figure 1. Molecular structures of **1**, **2**, **4**, and **5** at the 50% probability level. Only hydrogen atoms of the amino moieties are shown for clarity.

Table 3. Selected Bond Distances (Angstroms) and Bond Angles (degrees) for 1, 2, 4, and 5

	1	2	4	5
Pt1−Cl1	2.297(3)	2.306(1)	2.301(1)	2.326(1)
Pt1−Cl2	2.294(3)	2.318(1)	2.297(1)	2.300(1)
Pt1−S1	2.210(3)	2.206(1)	2.209(1)	2.224(1)
Pt1−N1	2.057(7)	2.033(3)	2.041(4)	2.086(4)
N1−C1	1.327(13)	1.318(5)	1.318(5)	1.318(6)
N2−C1	1.374(14)	1.362(5)	1.359(5)	1.361(5)
N3−C1	1.330(14)	1.350(5)	1.355(5)	1.366(5)
S1−O1/S1−O4	1.468(8)	1.468(3)	1.472(3)	1.462(4)
Cl1−Pt1−Cl2	173.5(1)	90.47(5)	170.57(4)	175.95(4)
S1−Pt1−Cl1	90.5(1)	90.13(5)	93.57(5)	90.21(5)
S1−Pt1−Cl2	92.8(1)	177.14(4)	90.52(5)	88.95(5)
N1−Pt1−Cl1	88.1(2)	177.7(1)	88.0(1)	90.8(1)
N1−Pt1−Cl2	88.7(2)	88.1(1)	88.3(1)	90.2(1)
N1−Pt1−S1	178.0(2)	91.4(1)	176.87(9)	178.0(1)

tion of the guanidine unit in complexes probably imparts minimum steric pressure on the platinum atom.

Δ_{CN}, Δ_{CN}', and ρ parameters[34,35] defined in Chart 2 can be used to understand the structure and bonding of the guanidine

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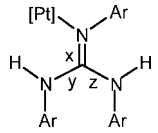
Chart 2. Definition of Δ_{CN}, Δ_{CN}', and ρ Parameters for 1, 2, 4, and 5[a]



[a] $\Delta_{CN} = y - x$; $\Delta_{CN}' = z - x$; $\rho = 2x/(y + z)$; [Pt] $Cl_2Pt(S(O)Me_2)$.

unit in **1**, **2**, **4**, and **5**. The Δ_{CN} and Δ_{CN}' value of 0.0 and the ρ value of 1.0 indicate a maximum $n-\pi$ conjugation involving the lone pair of the amino nitrogen atoms with the C=N π^* orbital, and any deviation from these values indicate a hampered $n-\pi$ conjugation. Δ_{CN} and Δ_{CN}' values in complexes (Δ_{CN}, Δ_{CN}' = 0.047(19), 0.003(19) Å (**1**); 0.044(5), 0.032(5) Å (**2**); 0.041(5), 0.037(5) Å (**4**); and 0.043(8), 0.048(6) Å (**5**)) are smaller than the corresponding values known for the respective uncoordinated guanidines (Δ_{CN}, Δ_{CN}' = 0.095(6), 0.098(6) Å ($LH_2^{2\text{-tolyl}}$); 0.100(6), 0.111(6) Å ($LH_2^{2\text{-anisyl}}$); 0.097(3), 0.098(3) Å ($LH_2^{2,5\text{-xylyl}}$); and 0.083(6), 0.090(6) Å ($LH_2^{2,6\text{-xylyl}}$))[33] (see also the Supporting Information). The ρ value in complexes (ρ = 0.98 (**1**) and 0.97 (**2**, **4**, and **5**)) is greater than that known for the respective uncoordinated guanidines (ρ = 0.93 ($LH_2^{2\text{-tolyl}}$, $LH_2^{2,5\text{-xylyl}}$, and $LH_2^{2,6\text{-xylyl}}$) and 0.92 ($LH_2^{2\text{-anisyl}}$)).[33] Moreover, the amino nitrogen atoms are planar in complexes.

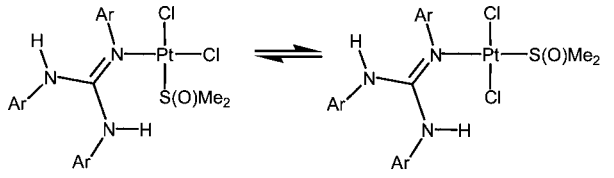
The aforementioned structural parameters indicate a greater $n-\pi$ conjugation in complexes as compared with the respective guanidines. However, $n-\pi$ conjugation in complexes is not at its maximum, and this feature is partly ascribed to the interaction of the lone pair of the amino nitrogen atoms with the π electrons of the aryl ring and partly ascribed to the steric clash between the central CN_3 unit and the NC_2H unit of the amino nitrogen atoms caused by the aryl substituent of the latter unit. The angle between two mean planes constituted by the CN_3 unit and the NC_2H unit are 33.7(6)°, 24.8(7)° (**1**), 32.5(2)°, 32.9(3)° (**2**), 29.8(2)°, 29.1(2)° (**4**), and 29.2(2)°, 29.5(2)° (**5**).

IR and NMR Spectroscopy. IR spectra of **1**–**5** revealed characteristic band(s) for the NH and C=N moieties of guanidines. Further, the DMSO molecule in **1**–**5** revealed one band in the 1116–1157 cm^{-1} interval assignable to the ν(S(O)) stretch, and these values are greater than that reported for free DMSO (ν(S(O)) 1055 cm^{-1} in the solid state and 1070 cm^{-1} in CCl_4[36]), indicating sulfur coordination of DMSO to the platinum atom in the complexes.

Platinum(II) imine complexes and imine-derived platinacycles are amenable to $^{195}Pt\{^1H\}$ NMR studies. The $\delta(^{195}Pt)$ values are sensitive to the coordination environment around the platinum atom and steric/electronic properties of the surrounding ligands.[37] The $\delta(^{195}Pt)$ values are useful to distinguish not only cis and trans configurations of the platinum but also *E* and *Z* configurations of the imine unit in $[Cl_2Pt(S(O)Me_2)(\text{ferrocenyl imine})]$.[5a,b,8a] The $^{195}Pt\{^1H\}$ NMR spectra of **1**, **4**, and **5** revealed one signal at $\delta(^{195}Pt)$ −2967, −2959, and −2893, respectively, and these $\delta(^{195}Pt)$ values agree with those reported for the ^{195}Pt nucleus surrounded by "N,Cl_2,S_{DMSO}" set of donor atoms.[5b,8a] The $^{195}Pt\{^1H\}$ NMR spectrum of **2** revealed a closely separated pair of resonances at $\delta(^{195}Pt)$ −2721 (major) and −2771 (minor), while that of **3** revealed a widely separated pair of resonances at $\delta(^{195}Pt)$ −2898 (minor) and −3009 (major). It has been shown that $\delta(^{195}Pt)$ values of *cis*-$[Cl_2Pt(S(O)R_2)L]$ (L = σ-donor/π-acceptor ligands) are downfield shifted with respect to their trans analogues, and this has been ascribed to a better (d–d)π bonding in the former isomer.[37] Hence, the major $\delta(^{195}Pt)$ signal of **2** and the minor $\delta(^{195}Pt)$ signal of **3** are assigned to the cis isomer, and the minor $\delta(^{195}Pt)$ signal of **2** and the major $\delta(^{195}Pt)$ signal of **3** are assigned to the trans isomer. The $\Delta\delta(\delta_{cis} - \delta_{trans})$ values for **2** and **3** are 50 and 111, respectively. Upon comparing the $\delta(^{195}Pt)$ value of the trans isomer of **2** with that of **1** it appears that the guanidine in the former complex is a better π acceptor than that present in the latter complex, although the steric factor can also influence $\delta(^{195}Pt)$ values to some extent.[38]

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** and **5** indicated the presence of a single isomer in solution. However, the ^1H NMR spectrum of **2** revealed the presence of two isomers in about a 1.0:2.1 ratio, as estimated from the integrals of OCH_3 and N*H* protons of the guanidine unit. The major set of signals is assigned to the cis isomer as observed in the solid state, and the minor set of signals is assigned to the trans isomer as also suggested by $^{195}Pt\{^1H\}$ NMR spectroscopy. The ^1H NMR spectrum of a freshly prepared solution of **3** revealed the presence of one isomer only, but upon storing the solution for 48 h, formation of two isomers in about a 1.0:0.2 ratio was noticed. From the ^1H and $^{195}Pt\{^1H\}$ NMR spectroscopic studies, the major set of signals is assigned to the trans isomer and the minor set of signals to the cis isomer. The cis–trans isomerization event and isomeric composition of **2** and **3** are summarized in Scheme 2.

Scheme 2. Cis–Trans Isomerization of 2 and 3



major	Ar = 2-(MeO)C_6H_4 (**2**)	minor
minor	Ar = 4-MeC_6H_4 (**3**)	major

cis-$[Cl_2Pt(S(O)R_2)(L)]$ (L = π-acceptor ligand such as sulfoxide[32] and pyrimidine;[38] R = alkyl and aryl) is more stable than its trans analogue due to enhanced (d–d)π bonding. However, with sterically more demanding sulfoxide such as diphenyl sulfoxide only *trans*-$[Cl_2Pt(S(O)Ph_2)(L)]$ (L = pyrimidine) has been isolated, but even this complex in CD_2Cl_2 has been shown to slowly isomerize to its cis analogue after a few weeks.[38] The solution behavior of **3** closely resembles the solution behavior of *trans*-$[Cl_2Pt(S(O)Ph_2)$-(pyrimidine)].

The ^1H NMR spectrum of **4** measured at 0.004, and 0.042 mM (400 MHz) revealed the presence of one major isomer and a very small quantity of minor isomer as identified from the signals of CH_3 protons of DMSO or from those of guanidine and DMSO. ^1H NMR patterns did not change even after 48 h. The ratio of the two isomers at 0.154 mM (400 MHz) as estimated from the integrals of the alkyl protons was 1.00:0.12. ^1H NMR spectral features of **4** could arise due to formation of (i) cis and trans isomers as discussed previously for **2** and **3**, (ii) trans-configurated **4** with anti–anti and syn–anti conformations of the guanidine unit, and (iii) three rotamers, namely, **A**, **B**, and **C**, that arise due to the restricted Pt–S bond rotation of

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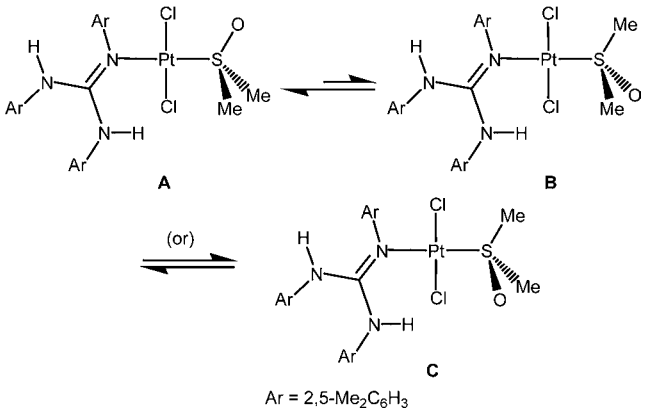
the trans configurated **4** as illustrated in Scheme 3. Formation of the cis isomer is ruled out due to the mutual repulsive

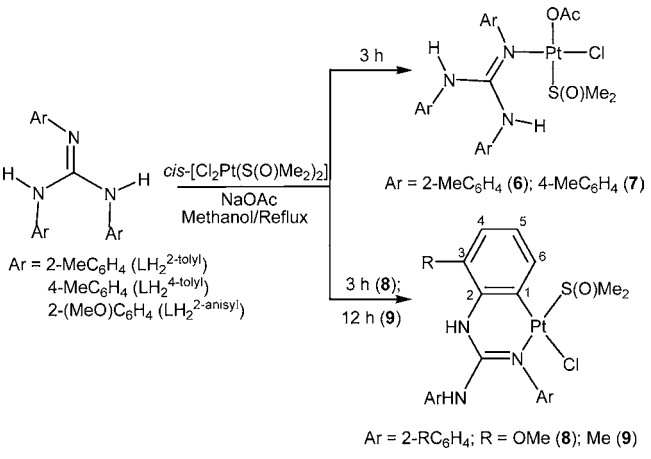
Scheme 3. Restricted Pt−S Bond Rotation That Leads to Formation of Three Rotamers of 4 in Solution



interaction between DMSO and the guanidine unit. Formation of the syn−anti conformer for the guanidine unit is also ruled out as it involves C−N(H) single-bond rotation, and we believe that this high-energy process is less likely. Thus, the ^{1}H NMR spectral behavior of **4** could be attributed to the presence of one major rotamer **A** as found in the solid state and the minor rotamer **B** or **C** at higher concentration. The presence of two rotamers in solution could arise due to the change in intermolecular hydrogen-bonding pattern associated with the oxygen atom of DMSO with concentration.

ii. Substitution versus Cycloplatination. *Synthesis.* Reaction of *cis*-$[Cl_2Pt(S(O)Me_2)_2]$ with 1 equiv of $LH_2^{2\text{-tolyl}}$ and $LH_2^{4\text{-tolyl}}$ in the presence of 1 equiv of NaOAc in methanol carried out separately under reflux condition for 3 h afforded acetate-substituted products **6** and **7** in 83% and 84% yields, respectively. Interestingly, the circuitous route involving reaction of **1** with 1 equiv of NaOAc in methanol under reflux condition for 3 h also afforded **6** in 85% yield. Reaction of *cis*-$[Cl_2Pt(S(O)Me_2)_2]$ with 1 equiv of $LH_2^{2\text{-anisyl}}$ in the presence of 1 equiv of NaOAc in methanol under reflux condition for 3 h afforded platinacycle **8** in 92% yield, and the analogous reaction carried out with bulkier $LH_2^{2\text{-tolyl}}$ for 12 h afforded **9** in 79% yield. Syntheses of **6**−**9** are illustrated in Scheme 4.

Scheme 4. Syntheses of Complexes 6−9



Single-Crystal X-ray Diffraction. The molecular structure and selected bond parameters of **6** are depicted in Figure 2.

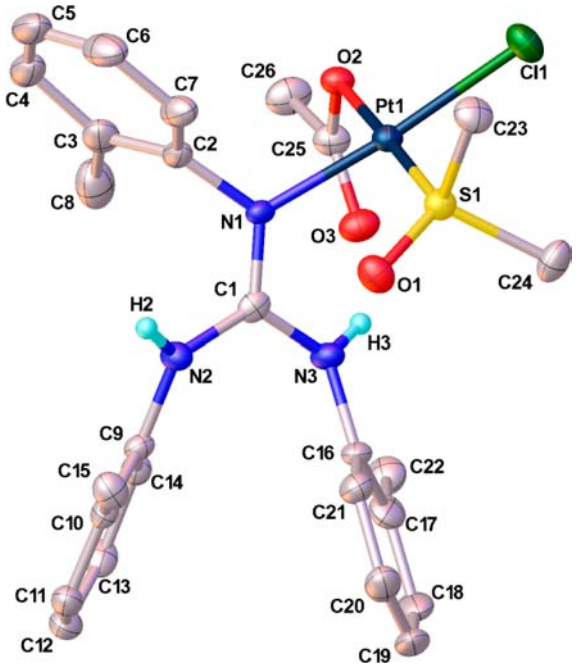


Figure 2. Molecular structure of **6** at the 50% probability level. Only hydrogen atoms of the amino moieties are shown for clarity. Selected bond distances (Angstroms) and bond angles (degrees): Pt1−Cl1 2.306(2), Pt1−O2 2.046(4), Pt1−S1 2.188(1), Pt1−N1 2.028(4), N1−C1 1.308(7), N2−C1 1.369(7), N3−C1 1.349(7), O2−C25 1.297(7), O3−C25 1.228(7); Cl1−Pt1−O2 89.1(1), S1−Pt1−Cl1 91.92(5), S1−Pt1−O2 178.3(1), N1−Pt1−Cl1 175.4(1), N1−Pt1−O2 87.7(2), N1−Pt1−S1 91.4(1).

The platinum atom is surrounded by the imine nitrogen of the guanidine, oxygen atom of the monodentate acetate, chloride, and the sulfur atom of DMSO. The bond parameters around the platinum atom indicate a slightly distorted square planar geometry. The oxygen atom of the acetate moiety and the sulfur atom of DMSO are placed trans to each other around the platinum atom as are the imine nitrogen of the guanidine and the chloride. Thus, the platinum atom in **6** revealed a cis configuration that contrasts with the trans configuration of the platinum atom observed in **1**.

The oxygen atom O3 of the acetato ligand in **6** acts as a trifurcated hydrogen-bond acceptor by forming one intramolecular N−H···O hydrogen bonding with the hydrogen atom H3 of the amino moiety and two intermolecular C−H···O hydrogen bondings, one with H13 of the tolyl unit of the adjacent molecule and the other with H24B of DMSO of another adjacent molecule, both the neighbors being related to the reference molecule by inversion symmetry (see the Supporting Information). The aforementioned noncovalent interactions are absent in **1** and believed to be at least partly responsible for the cis configuration of the platinum atom in **6**. The Δ_{CN}' (0.061(7) Å), Δ_{CN} (0.041(7) Å), and ρ (0.96) values in conjunction with the planarity of the amino nitrogen atoms in **6** suggest a partial $n-\pi$ conjugation between the lone pair of the amino nitrogen atoms with the C=N π^* orbital. To the best of our knowledge, the molecular structure of **6** represents the first crystallographically characterized acetate-substituted product formed prior to formation of [*C*,*N*] platinacycles from

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reactions of nitrogen donor ligands with Pt(II) precursor carried out in the presence of NaOAc[39] (see later).

The molecular structure and selected bond parameters of **8** are depicted in Figure 3. The platinum atom is surrounded by

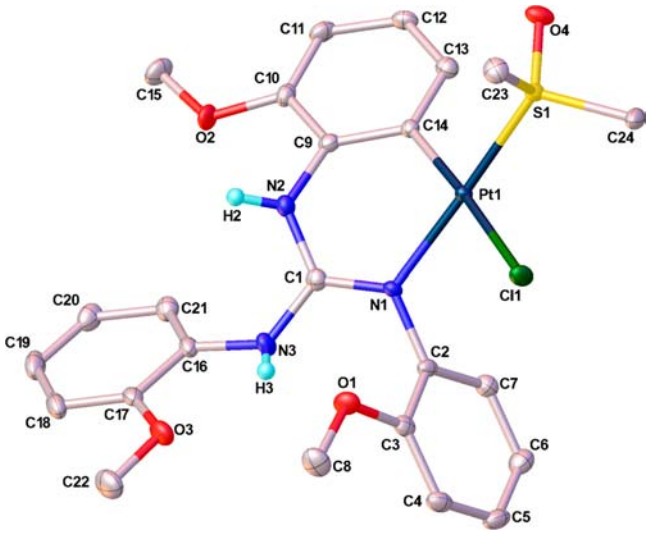

Figure 3. Molecular structure of **8** at the 50% probability level. Only hydrogen atoms of the amino moieties are shown for clarity. Selected bond distances (Angstrsoms) and bond angles (degrees): Pt1–Cl1 2.404(1), Pt1–N1 2.060(4), Pt1–S1 2.213(1), Pt1–C14 2.014(4), N1–C1 1.317(6), N2–C1 1.352(6), N3–C1 1.364(6), N2–C9 1.412(5), C9–C14 1.402(6); N1–Pt1–Cl1 89.6(1), N1–Pt1–S1 174.8(1), N1–Pt1–C14 87.9(2), S1–Pt1–C14 94.4(1), Cl1–Pt1–C14 176.9(1), S1–Pt1–Cl1 87.98(4).

the imine nitrogen, anisyl carbon, sulfur atom of DMSO, and chloride and thus revealed a slightly distorted square planar geometry. In **8**, DMSO is coordinated to the platinum atom in the cis relation with respect to the Pt–C bond, and this feature contrasts with that observed in the guanidine-derived six-membered palladacycles, [Pd{κ^2(*C*,*N*)-C_6H_3(OMe)-3(NHC(NHAr)(=NAr))-2}Br(L)] (Ar = 2-(MeO)C_6H_4; L = $NC_5H_3Me_2$-2,6 (**I**) and $NC_5H_3Me_2$-2,4 (**II**)) wherein lutidine is placed trans to the Pd–C bond.[31c] In a hypothetical trans isomer of **8**, there would be a repulsive interaction between DMSO and the anisyl moiety of the =NAr unit. Thus, the steric factor appears to predominantly dictate the cis configuration of the platinum atom in **8** (see above).

The six-membered "[*C*,*N*]Pt" ring in **8** revealed a pseudo-boat α conformation with N1, C1, C9, and C14 atoms defining the basal plane of the boat while Pt1 and N2 atoms defining the tips of the boat.[40] The Pt1–N1 distance, 2.060(4) Å, is comparable to the predicted value of 2.07 Å, but the Pt1–C14 distance, 2.014(4) Å, is slightly shorter than the predicted value of 2.09 Å (covalent radii *r*(Pt(II)) 1.36 Å, *r*(N) 0.71 Å, *r*(C(sp^2)) 0.73 Å), indicating some degree of Pt–C multiple-bond character. The Δ_{CN}' (0.047(6) Å) and Δ_{CN} (0.035(6) Å) values for the guanidine unit of **8** are smaller than those previously reported for **I** (Δ_{CN}' = 0.077(6) Å; Δ_{CN} = 0.067(6) Å), **II** (Δ_{CN}' = 0.065(4) Å; Δ_{CN} = 0.064(4) Å), and LH_2[2-anisyl] (see above).[31c,33] The endocyclic amino nitrogen atom is planar, while the exocyclic amino nitrogen atom deviates significantly from planarity ($\sum$N2 = 360°; $\sum$N3 = 343°).

IR and NMR Spectroscopy. IR spectra of **6**–**9** revealed characteristic band(s) for the NH and C=N moieties of guanidines. Complexes **6** and **7** also revealed a pair of bands at 1623 and 1384 cm^{-1} and 1626 and 1377 cm^{-1}, respectively, for the acetate moiety assignable to ν_a(OCO) and ν_s(OCO) stretches, respectively. The $\Delta\nu$ = 239 (**6**) and 249 cm^{-1} (**7**) values clearly indicated monodentate acetate coordination mode.[41] Complexes **6**–**9** revealed one band in the 1117–1142 cm^{-1} interval assignable to the ν(S(O)) stretch of the sulfur-coordinated DMSO.[36]

The $^{195}Pt\{^1H\}$ NMR spectrum of **6** revealed one resonance at $\delta(^{195}Pt)$ −2718, and this value is more deshielded than that observed for **1** ($\delta(^{195}Pt)$ −2967). The $^{195}Pt\{^1H\}$ NMR spectrum of **7** revealed one resonance at $\delta(^{195}Pt)$ −2891, and this value is comparable with that revealed by the cis isomer of **3** but more deshielded than that revealed by its trans analogue ($\delta(^{195}Pt)$ −2898 (cis) and −3009 (trans)). $^{195}Pt\{^1H\}$ NMR spectroscopy thus indicated the cis configuration for the platinum atom in **7**. The $\Delta\delta(\delta_{OAc} - \delta_{Cl})$ value of **7** for the **3**/**7** pair favorably matches with that known for the *cis*-[Cl_2Pt(*N*,*N*′)]/*cis*-[(AcO)ClPt(*N*,*N*′)] pair (*N*,*N*′ = (η^5-C_5H_5)Fe[(η^5-C_5H_4)CH=N$(CH_2)_3NMe_2$; $\Delta\delta$ 7) wherein OAc has been suggested to lie trans to the imine nitrogen.[5c] Thus, the $\Delta\delta(\delta_{OAc} - \delta_{Cl})$ value of 249 for the **1**/**6** pair appears to arise largely from the change in the configuration of the platinum atom in conjunction with the steric factor rather than from the substituent effect. ^1H NMR spectra of **6** and **7** indicated the presence of three sets of signals in the alkyl region in about 3:2:1 ratios assignable to CH_3 protons of the guanidine, DMSO, and acetate moiety, respectively. The diagnostic $^{13}C\{^1H\}$ NMR signals for CH_3 and OC(O) carbon nuclei of **6** and **7** further corroborated the structures determined by X-ray diffraction and $^{195}Pt\{^1H\}$ NMR studies.

The $^{195}Pt\{^1H\}$ NMR spectrum of **8** revealed one resonance at $\delta(^{195}Pt)$ −3737, and this value is upfield shifted relative to that observed for **2** (cis isomer; $\delta(^{195}Pt)$ −2721). This trend is in line with the literature trend reported for the [Cl_2PtL(S(O)Me_2)]/[ClPt(*C*,*N*)(S(O)Me_2)] pair (L = imine ligands, and *C*,*N* = imine-derived monoanionic κ^2*C*,*N* scaffolds).[4b,5a,8a] ^1H and $^{13}C\{^1H\}$ NMR spectra of **8** revealed the presence of one isomer in solution, and these spectral features contrast with those reported for **I** and **II** wherein two boat conformers interconvert through a planar intermediate via the six-membered "[*C*,*N*]Pd" ring inversion as revealed by a detailed ^1H NMR studies.[31c] The presence of a single isomer of **8** in solution could arise due to the bulky nature of DMSO or its more strongly π-accepting nature, but we believe that the former feature predominantly dictates the number of solution isomers.

The ^1H NMR spectrum of **9** indicated the presence of seven isomers in about 1:1:1:1:0.23:0.12:0.11 ratios as estimated from the integrals of CH_3 protons of the guanidine moiety. Further, the $^{195}Pt\{^1H\}$ NMR spectrum of **9** revealed seven resonances at $\delta(^{195}Pt)$ −2645, −2710, −2760, −2839, −2851, −2958, and −2995. Platinacycle **9** upon fractional crystallization in $CHCl_3$/methanol mixture once afforded one of the isomers as revealed by ^1H NMR spectroscopy (see Experimental Section). Intriguingly, the $\delta(^{195}Pt)$ values of **9** are more deshielded than that observed for **8**. IR and ^1H NMR spectroscopic data of metal sulfoxides were shown to be useful to assign the coordination modes of sulfoxides.[36,42] The IR spectrum of **9** was also measured in $CHCl_3$, which revealed one broad band at 1129 cm^{-1}, and this value is greater than that reported for free DMSO (see above). Also, the ^1H NMR chemical shifts of CH_3 protons of the coordinated DMSO in **9** lie in the interval δ

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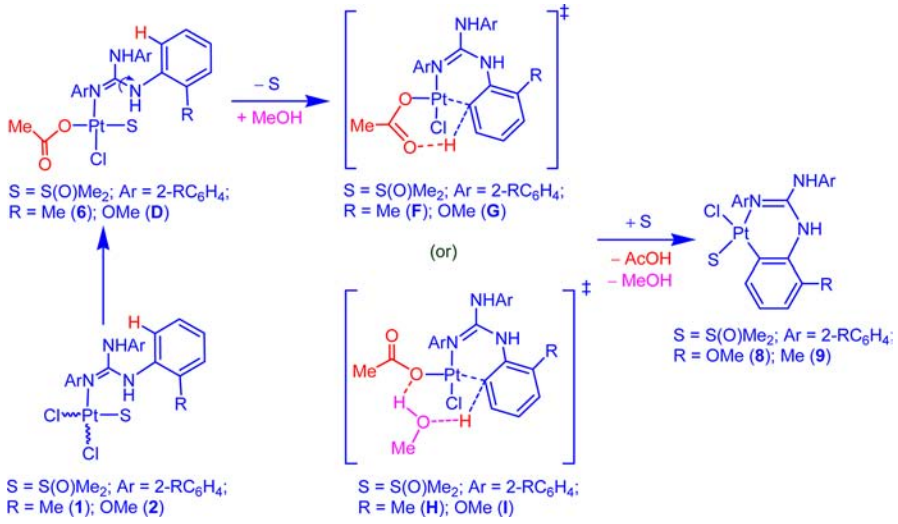
Scheme 5. Plausible Mechanism of Cycloplatination



3.26−3.52, and these values are more downfield shifted from the ^{1}H NMR chemical shift of free DMSO (δ 2.53), suggesting the presence of S-bonded DMSO in solution. For O-bonded DMSO, a smaller downfield shift (δ 2.59−3.03) has been suggested.[42]

In principle, the platinum atom in platinacycle such as **9** can have either the cis or the trans configuration, and hence two configurational isomers are possible. Each configurational isomer in turn can have six conformational isomers either due to three distinct orientations of DMSO with respect to the square plane of the platinum or due to two distinct orientations of *o*-Me substituent of the =NAr unit. The structures of 12 possible isomers of **9** are illustrated in Charts S1 and S2, Supporting Information. It is difficult to assign specific structures for seven isomers detected by NMR studies in the present investigation from those given in Charts S1 and S2, Supporting Information. ^{1}H NMR spectra of **8** and that of **9** that contained one major isomer along with a small proportion of other isomers did not change significantly with temperature (see the Supporting Information).

iii. Stereochemical Requirements and Mechanistic Aspects of Cycloplatination Reaction. The mechanism of cyclometalation in general[9a,b,43] and the role of metal-bound carboxylate in such reaction[44] in particular have been investigated in detail by both experimental and accurate computational methods. Palladium acetate is one of the useful precursors for the synthesis of a range of [*C*,*N*] palladacycles, but synthesis of the corresponding [*C*,*N*] platinacycles was hampered mainly due to commercial unavailability and difficulty associated with preparation of platinum(II) acetate.[45] In 1974, Shaw and co-workers for the first time used NaOAc as an external base in the cyclometalation reaction to accelerate the reaction rate.[46] Since then NaOAc has became one of the essential reagents in both stoichiometric[4a] and recently in catalytic C−H activation processes.[47] Only rarely was cycloplatination of imine ligands carried out in the absence of NaOAc.[48] One of the convenient routes for [*C*,*N*] platinacycles involves reaction of *cis*-[$Cl_2Pt(S(O)Me_2)_2$] with *N*-donor ligands in the presence of a stoichiometric amount of NaOAc in methanol under reflux condition. In this reaction, it has been proposed that NaOAc plays a dual role, as a nucleophile and as an internal base.[4a,d] Formation of an acetate-substituted product prior to formation of [*C*,*N*] platinacycle in a reaction of nitrogen-donor ligand with platinum(II) precursor in the presence of NaOAc was only detected by ^{1}H NMR spectroscopy,[3] and in one publication such products were isolated in unspecified low yields.[5c] In this context, the high-yield syntheses of **6** and **7** and the molecular structure of the former represent a significant advancement in the chemistry of [*C*,*N*] platinacycles. Thermolysis of **6** carried out in methanol for 9 h followed by solvent evaporation afforded a brown solid whose ^{1}H NMR spectrum revealed the formation of **9**. This experiment suggests that **9** is formed from the platinum precursor, the guanidine, and NaOAc possibly via **6**. Other crucial factors that are responsible for formation of five-membered [*C*,*N*] platinacycles include the cis configuration rather than the trans configuration for the platinum atom and the *E* configuration rather than the *Z* configuration for the imine unit in the precursor, [$Cl_2Pt(S(O)Me_2)$(arylimine)].[2d,5b] In case the arylimine in *cis*-[$Cl_2Pt(N,N')$] (N,N' = PhCH=$N(CH_2)_2NMe_2$ and ArCH=$N(CH_2)_2$N=CHAr; Ar = 9-$C_{14}H_9$) possesses the *Z* configuration then isomerization to *E* configuration precedes cycloplatination.[3,7]

Though $LH_2^{2\text{-anisyl}}$ and $LH_2^{2,6\text{-xylyl}}$ revealed the syn−anti conformation in the solid state, the former was successfully cycloplatinated while the latter was not. Probably, the acetate-substituted product [(AcO)ClPt(S(O)Me_2)(ArN=C-$(NHAr)_2$)] (Ar = 2-(MeO)C_6H_4; **D**) was formed transiently before forming platinacycle, **8**. The inability of $LH_2^{2,6\text{-xylyl}}$ to form acetate-substituted product [(AcO)ClPt(S(O)Me_2)-(ArN=C$(NHAr)_2$)] (Ar = 2,6-$Me_2C_6H_3$; **E**) is ascribed to greater steric encumbrance around the platinum atom in the supposedly formed intermediate **5**. Formation of primary amine-derived five-membered platinacycles is promoted by steric factor.[30a] However, sterically more hindered **9** is formed in 12 h, while sterically less hindered **8** is formed in 3 h, and this difference in time scale of cycloplatination could be ascribed to the difficulty with which the C−N(H) single bond rotates in the acetate-substituted product **6** before forming **9** as compared with hitherto unknown **D** in the formation of **8** as outlined below. Reaction of **1**/**2**, for example, with NaOAc in methanol could produce acetate-substituted products **6**/**D**, and these intermediates are presumed to undergo the C−N(H) single-bond rotation, solvent dissociation, followed by an

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intramolecular C−H activation process either through intermediates **F**/**G** via ambiphilic metal ligand activation (AMLA)[44b] or through intermediates **H**/**I** via a solvent-assisted concerted metalation deprotonation (CMD) pathway[49] to afford **8**/**9** as shown in Scheme 5.

Cyclopalladation of dimethylbenzylamine with $Pd(OAc)_2$ was suggested to involve a Wheland-type intermediate, but this experimental finding was later refined by accurate DFT calculations and subsequently shown to involve an agostic intermediate rather than a Wheland intermediate.[50,51] The cis configuration of the platinum atom in **6** to form **9** is probably ascribed to the flexible nature of two six-membered rings spanned by the platinum atom in intermediates **F**/**G** or **H**/**I**.

CONCLUSION

Judicious choice of aryl substituents of *sym*-*N*,*N*′,*N*″-triarylguanidines allowed us to isolate three classes of platinum(II) guanidine complexes, namely, $[Cl_2Pt(S(O)Me_2)L]$ (**1**−**5**), $[(AcO)ClPt(S(O)Me_2)L]$ (**6** and **7**), and $[ClPt(S(O)Me_2)(C,N)]$ (**8** and **9**), in high yield, and these complexes were characterized by analytical and spectroscopic techniques. The molecular structures of $LH_2^{2,5\text{-xylyl}}$, **1**, **2**, **4**, **5**, and **8** including one novel acetate-substituted product **6** were determined by single-crystal X-ray diffraction. The cis configuration of the platinum atom, sterically less hindered ortho substituent on the aryl rings of the guanidine, and π-accepting nature of the guanidine in precursor such as **2** appear to be suitable features for the facile cycloplatination reaction. The molecular structures of the new compounds allowed us to draw a plausible mechanism of the cycloplatination reaction. Further, the dual role of OAc^- as a nucleophile and as an internal base in the cycloplatination reaction was indicated. The subtle difference in the substitution pattern on the aryl rings of guanidines was shown to influence not only the configuration of the platinum atom but also the number and nature of solution species of the resulting complexes. The outcome of the present investigation is believed to be useful to further understand the intricacies of the mechanistic aspects of both stoichiometric and catalytic C−H activation processes.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format, packing diagram of **6**, general considerations, materials, experimental details pertinent to X-ray diffraction, synthesis, analytical, spectroscopic data of *sym*-*N*,*N*′-bis(2,5-xylyl)thiourea and $LH_2^{2,5\text{-xylyl}}$, figure showing the molecular structure, table of crystallographic parameters, and selected bond parameters of $LH_2^{2,5\text{-xylyl}}$, charts illustrating 12 probable solution isomers of **9**, $^{195}Pt\{^1H\}$ NMR spectra of **1**−**9**, ^1H, $^{13}C\{^1H\}$, $^1H-^{13}C$ HETCOR, DEPT 90 NMR spectra of **4**, ^1H NMR spectrum of one of the seven isomers of **9** crystallized from $CHCl_3$/methanol mixture, and variable-temperature ^1H NMR spectra of **8** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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