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Synthesis and Structural Characterization of New Chiral (Biscarbene)platinum(II) Complexes

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New chiral bis(triazolium) salts have been prepared in good yields. The corresponding mononuclear platinum(II) complexes [Pt{bis(NHC)}X_2] (X = Br, I) have been synthesized and spectroscopically characterized. One of the synthesized biscarbene complexes has also been characterised by X-ray crystallography. These complexes are efficient catalyst precursors for the hydrosilylation of 1-octene.

Introduction

An important aspect of organometallic chemistry is complex stability, particularly if such compounds may find synthetic or catalytic applications. As observed for phosphanes, the introduction of chelating ability to carbenes confers additional stabilizing character to the ligand.[1–3] Over the past two decades, N-heterocyclic carbenes (NHCs) have emerged as a new class of ancillary ligands for a broad range of transition-metal-mediated catalytic reactions.[4–8] NHCs are excellent σ-donors and form strong M–C bonds, often giving rise to complexes with a higher stability compared to complexes containing phosphanes. Thus, as a logical extension of this work, the development of chiral versions of NHC, e.g. as ligands for stereoselective catalysis, is of interest. The quest for chiral NHC ligands began in 1996 with the pioneering efforts of Herrmann et al.[9] and Enders et al.[10] Since then, the impact of these ligands in enantioselective catalysis has been significant. A wide range of stereoselective catalytic transformations catalyzed by chiral di-NHC complexes has been reported, e.g., hydrosilylation,[11–14] hydrogenation,[15] enantioselective 1,4-conjugate addition[16–17] and transfer hydrogenation.[18] As chirality transfer is a topic of continuously increasing interest, a number of review articles have been published in this field within the past few years, focussing on both successful chirality transfer, and on the limits of strategies designed to extend this very valuable research field into industry.[3,19–23]

Previously, we have focussed on the synthesis of novel chelating bidentate bis(NHC) ligands based on 1,2,4-triazoles and have reported some of their rhodium(I) complexes.[24]

On the basis of our experience in the coordination of chelating bis(triazol-2-ylidenes), we have extended this work to platinum. Herein, we describe the synthesis of the first chiral platinum(II) complexes with chelating bis(NHC) ligands and discuss their application in hydrosilylation reactions. The crystal structure of one of the complexes is also described.

Results and Discussion

Synthesis of Chiral (Biscarbene)platinum(II) Complexes

The chiral bis(triazolium) salts **2** and **4** were prepared from (–)-(*R*,*R*)-1,2-diaminocyclohexane and (+)-(*R*,*R*)-1,2-diphenylethane-1,2-diamine (see Scheme 1).

The neutral bis(triazoles) **1** and **3** are readily formed by treating triethyl orthoformate and formylhydrazine with commercially available amines in methanol at 90 °C. The bis(triazolium) salts **2** and **4** are generated by alkylation with the corresponding alkyl halide in acetonitrile at 100 °C.

^{1}H and ^{13}C{^{1}H} NMR spectra of compounds **2** and **4** reflect the C_2 symmetry of the complexes. The ^{1}H NMR spectra display two signals between δ = 9.18 (NNC*H*N) and 10.57 (NC*H*N) ppm, which are characteristic of triazolium cations.

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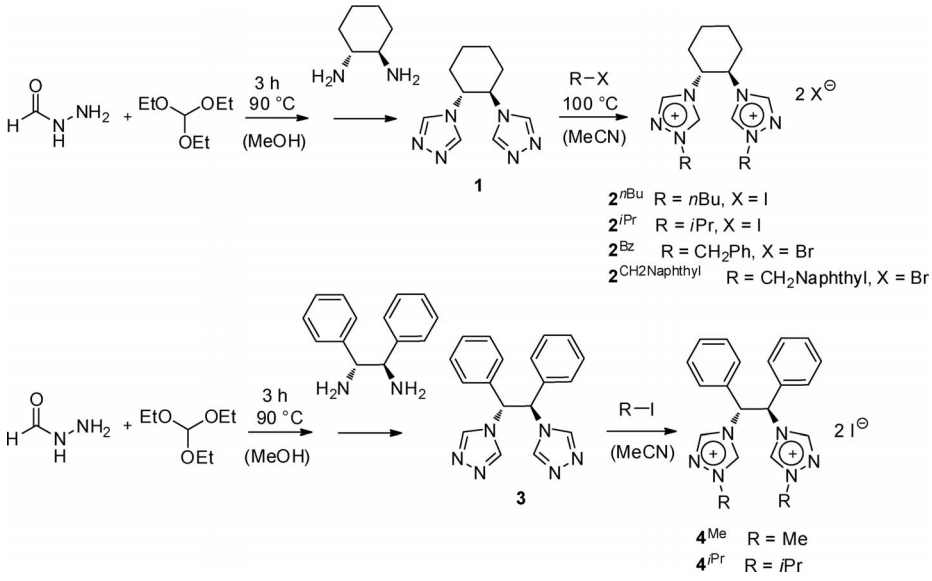
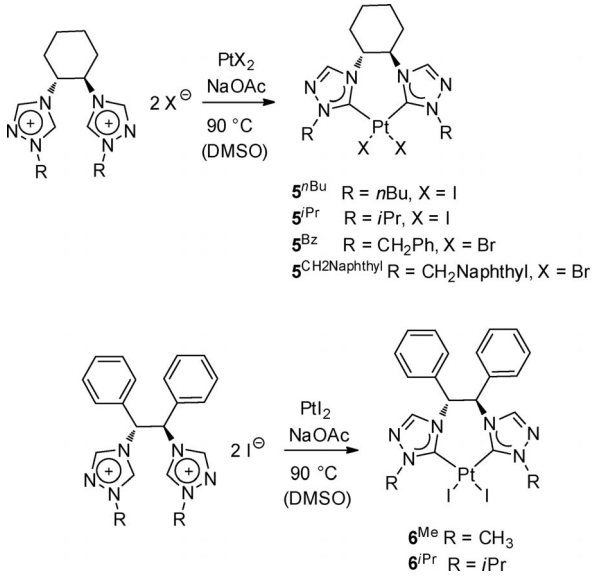


Scheme 1. Preparation of the chiral bis(triazolium) salts.[24]

The chiral complexes **5** and **6** (Scheme 2) have been synthesized according to a slightly modified literature procedure, by treating the platinum precursor with the triazolium salt in the presence of NaOAc as external base in dimethyl sulfoxide at 90 °C. [25] In order to avoid halogen scrambling during the reaction, the platinum(II) halides were treated with triazolium salts bearing the same halide counter anions. In contrast to other reports in the literature,[26] all complexes show optical activity in dimethyl sulfoxide, indicating that no racemisation took place. The complexes are air- and moisture-stable and can be stored for a prolonged period of time without apparent decomposition, as confirmed by NMR spectroscopy.



Scheme 2. Preparation of the chiral (biscarbene)Pt^{II} complexes.

^1H and $^{13}C\{^1H\}$ NMR patterns of all complexes are diagnostic of the C_1 symmetry of the structures. The assignment of the proton and carbon atoms is also confirmed by COSY and heteronuclear multiple quantum coherence (HMQC) spectroscopy. As a representative example of the Pt^{II} complexes, the spectra of complex $\mathbf{5}^{CH2Naphthyl}$ are discussed herein. The $^{13}C\{^1H\}$ NMR spectrum of this complex shows carbene carbon atom signals at δ = 152.1 and 145.7 ppm, indicating bidentate coordination of the ligand. A distinct multiplet in the ^1H NMR spectrum, attributed to one of the $^{c\text{-}hex}CH$ protons of the cyclohexylene bridge, is observed downfield at δ = 6.21 ppm and the other $^{c\text{-}hex}CH$ proton gives rise to a multiplet at δ = 4.60 ppm (see Figure 1). The close proximity of the platinum metal centre to one of the protons is most likely the reason for the downfield shift observed for one of the signals.

Structure Determination of $\mathbf{5}^{i\mathrm{Pr}}$

Single crystals of $\mathbf{5}^{i\mathrm{Pr}}$ suitable for X-ray diffraction were grown by diffusion of diethyl ether into a solution of $\mathbf{5}^{i\mathrm{Pr}}$ in acetonitrile. The molecular structure of the complex is depicted in Figure 2.

The platinum(II) centre is coordinated to the two carbene moieties of the chiral bidentate bis(NHC) ligand. The complex adopts a distorted square-planar geometry, with C–Pt–C angles slightly deviating from 90°, in particular the C1–Pt1–C3 angle is 85.3(2)°. The Pt–$C_{carbene}$ bond lengths are 1.963(5) and 1.974(6) Å, which fall within the range of bond lengths reported for other Pt^{II}\{bis(NHC)\} complexes. [28] The Flack parameter was used to determine the absolute configuration of the complex, which was found to contain two chiral centres, C5 and C6 with (*R*) configuration. To ensure that the same configuration is valid for all molecules in the sample, the angle of rotation was determined for the whole sample by polarimetry.

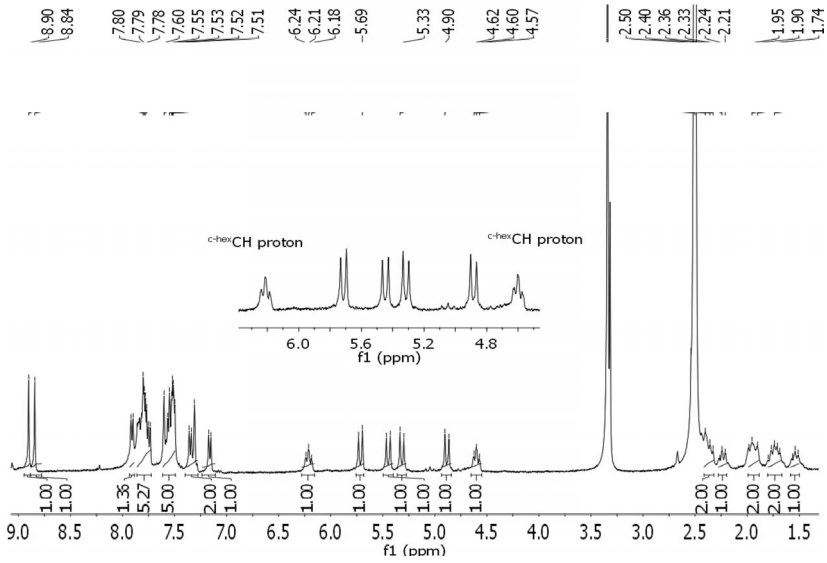


Figure 1. ^{1}H NMR spectrum of $\mathbf{5}^{CH2Naphthyl}$ in [D$_6$]dmso.

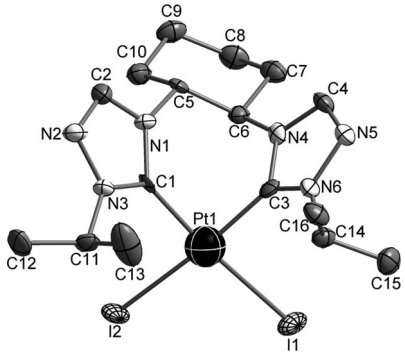
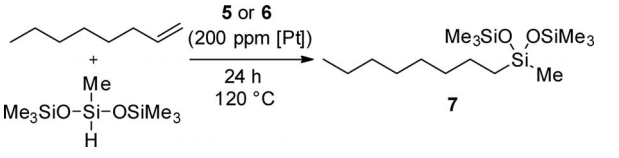


Figure 2. The structure of $\mathbf{5}^{iPr}$ as determined from XRD. The thermal ellipsoids are drawn at the 50% probability level. [27] Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1–C1 1.963(5), Pt1–C3 1.974(6), Pt1–I1 2.6588(5), Pt1–I2 2.6503(4), C1–Pt1–C3 85.3(2), I1–Pt1–I2 93.44(2), C1–Pt1–I2 91.8(2), C3–Pt1–I1 89.3(2), C1–Pt1–I1 174.6(2), C3–Pt1–I2 172.8(2).

Table 1. Hydrosilylation of 1-octene with bis(trimethylsiloxy)methylsilane catalyzed by **5** and **6**.



Entry	Complex	Yield of **7** [%][a]
1	$\mathbf{5}^{n\mathrm{Bu}}$	75
2	$\mathbf{5}^{i\mathrm{Pr}}$	81
3	$\mathbf{5}^{\mathrm{Bz}}$	71
4	$\mathbf{5}^{\mathrm{CH2Naphthyl}}$	77
5	$\mathbf{6}^{\mathrm{Me}}$	71
6	$\mathbf{6}^{i\mathrm{Pr}}$	72

[a] Yield determined with ^{1}H NMR spectroscopy; averaged over 3 runs.

Catalytic Application in the Hydrosilylation Reaction

The hydrosilylation of alkynes with platinum compounds as catalysts is a versatile reaction in organosilicon chemistry. The classical systems such as the Karstedt[29] and Speier[30] catalysts are well established as they display high activity even at very low catalyst loadings. However, some drawbacks to these catalysts, such as the precipitation of black inactive colloidal platinum, have led to the search for new catalysts. Thus, the catalytic activities of the new complexes **5** and **6** were tested in a model reaction, namely the hydrosilylation reaction of 1-octene with bis(trimethylsiloxy)methylsilane, with a catalyst loading of 200 ppm at 120 °C. This silane was chosen as it mimics a polysiloxane backbone (Table 1).

All complexes show good activity in the hydrosilylation reaction, even at a catalyst loading of only 200 ppm (0.034 mol-%). The best results are obtained with the complex bearing an isopropyl moiety as the *N*-substituent and a cyclohexylene bridge (Table 1, Entry 2); the complex with the same substituent but a different bridge type shows a lower activity (Table 1, Entry 6). Similar to other platinum complexes, complete regiocontrol is observed, and only the anti-Markovnikov adduct is obtained.[31–32] No formation of platinum black was observed at any time. The catalysts were isolated after a catalytic run, and shown to still be intact. All attempts to use prochiral alkenes such as α-methylstyrene or 2-methyl-1-pentene did not lead to the formation of the corresponding hydrosilylated product, even when the siloxane was changed to Et_3SiH; steric reasons are most likely to be responsible for this behaviour.

Conclusions

New chiral platinum(II) complexes have been synthesized in good yields by a simple synthetic route. One of the square-planar complexes has also been crystallographically characterized. These moisture- and air-stable compounds are efficient catalysts for the hydrosilylation of 1-octene at very low catalyst loadings. However, the use of prochiral alkenes in the reaction did not lead to the formation of the desired products. Further work is currently underway in our laboratories to elucidate the reaction mechanism and to determine the ligand or complex modifications necessary to allow for chirality transfer.

Experimental Section

General: The syntheses of the metal complexes were carried out with standard Schlenk techniques under argon. All reagents were purchased from commercial sources and used without further purification. All solvents were dried and degassed by standard methods prior to use.[33] The term filtration refers to filtration by cannula and a Whatman GF/B filter. Elemental analyses were carried out by the Microanalytical Laboratory of the Technische Universität München. FAB mass spectra were acquired by the Technische Universität München Mass Spectrometry Laboratory with a Finnigan MAT 90 spectrometer equipped with an FAB ionization chamber. ESI mass spectra were measured with an LCQ Finnigan instrument. NMR spectra were recorded with a JEOL-JMX-GX 400 MHz or a Bruker Avance DPX 400 spectrometer. NMR multiplicities are abbreviated as follows: s, singlet; d, doublet; t, triplet; sept, septet; m, multiplet. Coupling constants J are given in Hz. The spectra were referenced to the residual ^{1}H and ^{13}C{^{1}H} signals of the solvents.

Single-Crystal X-ray Structure Determination of Compound $5^{i\mathrm{Pr}}$:[34] Crystal data and details of the structure determination are as follows: $C_{16}H_{26}I_2N_6Pt$; Mr = 1502.6; crystal colour and shape: colourless fragment; crystal dimensions = 0.32 × 0.15 × 0.05 mm; crystal system: monoclinic; space group: $P2_1$ (no. 14); a = 9.8275(5), b = 8.7788(6), c = 13.0436(8) Å; β = 100.325(2)°, V = 1107.10(12) Å^3; Z = 2; μ(Mo-K_α) = 9.137 mm^{-1}; $\rho_{calcd.}$ = 2.254 g cm^{-3}; θ range = 2.81–25.24°; data collected: 14673; independent data [$I_o < 2\sigma(I_o)$/all data/R_{int}]: 3678/3812/0.0386; data/restraints/parameters: 3679/1/230; $R1$ [$I_o < 2\sigma(I_o)$/all data]: 0.0193/0.0205; $wR2$ [$I_o < 2\sigma(I_o)$/all data]: 0.0453/0.0458; GOF = 0.909; $\Delta\rho_{max/min}$: 0.81/–0.98 e Å^{-3}. Suitable single crystals for the X-ray diffraction study were grown from a mixture of diethyl ether and acetonitrile. Preliminary examination and data collection were carried out with an area detecting system (APEX II, κ-CCD) at the window of a rotating anode (Bruker AXS, FR591) and with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection was performed at 173 K (Oxford Cryosystems). Raw data were corrected for Lorentz polarization and, arising from the scaling procedure, for latent decay and absorption effects. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were assigned to ideal positions and refined by using the riding model. Matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the *International Tables for Crystallography*. CCDC-785511 ($\mathbf{5}^{i\mathrm{Pr}}$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the Synthesis of 3: Formylhydrazine (1.13 g, 18.8 mmol) and triethyl orthoformate (6.28 mL, 37.7 mmol) were dissolved in methanol (20 mL) and heated at 90 °C in an ACE pressure tube® (V = 35 mL) for 3 h. Then (+)-(*R*,*R*)-1,2-diphenylethane-1,2-diamine (1.00 g, 4.71 mmol) was added. The reaction mixture was kept at 110 °C for 72 h, before the resulting white solid was filtered off, washed with thf and pentane and dried in vacuo. Yield: 0.89 g (60%). $[\alpha]_D^{20}$ = –8.9 (c = 0.0071, dmso). ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 6.91 (s, 2 H, C*H*Ph), 7.23 (t, 2 H, CH_{para}), 7.31 (t, 4 H, CH_{meta}), 7.54 (d, 4 H, CH_{ortho}), 8.74 (s, 4 H, NC*H*N) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, [D$_6$]dmso): δ = 60.6 (C*H*Ph), 127.7 (CH_{meta}), 128.8 (CH_{para}), 129.0 (CH_{ortho}), 136.1 (C_{quat}), 141.6 (N*C*HN) ppm. $C_{18}H_{16}N_6$ (316.36): calcd. C 68.34, H 5.10, N 26.56; found C 68.35, H 5.09, N 26.35. MS-ESI: m/z = 971.1 [3 M + Na]$^+$, 655.1 [2 M + Na]$^+$, 317.0 [M + H]$^+$.

General Procedure for the Synthesis of 2: Compound **1** (400 mg, 1.83 mmol), alkyl halide (4.58 mmol) and MeCN (1.0 mL) were heated in an ACE pressure tube® (V = 35 mL) at 100 °C for 48 h. The precipitate was isolated by filtration, washed three times with thf (5 mL) and pentane and dried under reduced pressure to obtain the solid.

$2^{n\mathrm{Bu}}$: Yield: 903 mg (84%). $[\alpha]_D^{20}$ = –12.7 (c = 0.011, CH_2Cl_2). ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 0.89 (t, ^3J = 7.4 Hz, 6 H, CH_3), 1.26 (sext, ^3J = 7.4 Hz, 4 H, CH$_3$CH_2), 1.50 (m, 2 H, $^{c\text{-hex}}$CH_2), 1.82 (quint, ^3J = 7.4 Hz, 4 H, CH$_3$CH$_2$CH_2), 1.93 (m, 2 H, $^{c\text{-hex}}$CH_2), 2.16 (m, 2 H, $^{c\text{-hex}}$CH_2), 2.41 (m, 2 H, $^{c\text{-hex}}$CH_2), 4.33 (t, ^3J = 7.4 Hz, 4 H, NCH_2), 5.02 (m, 2 H, $^{c\text{-hex}}$C*H*), 9.27 (s, 2 H, NC*H*N), 10.34 (s, 2 H, NC*H*N) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, [D$_6$]dmso): δ = 13.1 (CH_3), 18.6 (CH$_3$CH_2), 23.3 ($^{c\text{-hex}}$CH_2), 29.5 ($^{c\text{-hex}}$CH_2), 30.9 (CH$_3$CH$_2$CH_2), 51.7 (NCH_2), 60.4 ($^{c\text{-hex}}$C*H*), 141.8 (N*C*HN), 143.3 (N*C*HN) ppm. $C_{18}H_{32}I_2N_6$ (586.08): calcd. C 36.87, H 5.50, N 14.33; found C 36.69, H 5.54, N 14.18. MS-FAB: m/z (%) = 458.8 (12.96) [M + I]$^+$, 330.9 (100) [M]$^{2+}$.

$2^{i\mathrm{Pr}}$: Yield: 963 mg (94%). $[\alpha]_D^{20}$ = –17.0 (c = 0.0034, dmso). ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 1.49 (d, ^3J = 6.6 Hz, 14 H, 12 H, CH_3, 2 H, $^{c\text{-hex}}$CH_2), 1.96 (m, 2 H, $^{c\text{-hex}}$CH_2), 2.19 (m, 2 H, $^{c\text{-hex}}$CH_2), 2.39 (m, 2 H, $^{c\text{-hex}}$CH_2), 4.76 (sept, ^3J = 6.6 Hz, 2 H, C*H*CH$_3$), 4.89 (m, 2 H, $^{c\text{-hex}}$C*H*), 9.18 (s, 2 H, NC*H*N), 10.28 (s, 2 H, NC*H*N) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, [D$_6$]dmso): δ = 20.9 (CH_3), 21.0 (CH_3), 23.4 ($^{c\text{-hex}}$CH_2), 30.6 ($^{c\text{-hex}}$CH_2), 55.7 (C*H*CH$_3$), 60.8 ($^{c\text{-hex}}$C*H*), 140.7 (N*C*HN), 143.4 (N*C*HN) ppm. $C_{16}H_{28}I_2N_6$ (558.05): calcd. C 34.42, H 5.06, N 15.05; found C 32.98, H 5.04, N 14.44. MS-FAB: m/z (%) = 430.0 (25) [M + I]$^+$, 302.6 (100) [M]$^{2+}$.

2^{Bz}: Yield: 791 mg (78%). $[\alpha]_D^{20}$ = –39.2 (c = 0.0036, CH_2Cl_2). ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 1.49 (m, 2 H, $^{c\text{-hex}}$CH_2), 1.93 (m, 2 H, $^{c\text{-hex}}$CH_2), 2.15 (m, 2 H, $^{c\text{-hex}}$CH_2), 2.40 (m, 2 H, $^{c\text{-hex}}$CH_2), 5.12 (m, 2 H, $^{c\text{-hex}}$C*H*), 5.60 (m, 4 H, NCH_2), 7.42 (s, 10 H, aryl), 9.32 (s, 2 H, NC*H*N), 10.57 (s, 2 H, NC*H*N) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, [D$_6$]dmso): δ = 23.5 ($^{c\text{-hex}}$CH_2), 31.1 ($^{c\text{-hex}}$CH_2), 55.1 (NCH_2), 60.6 ($^{c\text{-hex}}$C*H*), 128.8 (aryl), 129.0 (aryl), 132.7 ($C_{quat.}$), 142.4 (N*C*HN), 143.9 (N*C*HN) ppm. $C_{24}H_{28}Br_2N_6$ (560.33): calcd. C 51.44, H 5.04, N 15.00; found C 51.11, H 5.04, N 14.80. MS-FAB: m/z (%) = 479.1 (9) [M + Br]$^+$, 399.2 (100) [M]$^{2+}$.

General Procedure for the Synthesis of 4: Compound **3** (0.47 mmol), alkyl halide (1.2 mmol) and MeCN (1.0 mL) were heated in an ACE pressure tube® (V = 35 mL) for the times reported below. The solvent was removed under vacuum, and the precipitate washed

three times with diethyl ether (2 mL) and pentane and dried under reduced pressure to obtain the solid.

4^{Me}: Required reaction time: 24 h. Yield: 228 mg (80%). $[\alpha]_D^{20}$ = –25.8 (c = 0.0042, dmso). ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 4.06 (s, 6 H, CH_3), 7.32 (t, 2 H, CH_{para}), 7.37 (t, 4 H, CH_{meta}), 7.43 (s, 2 H, CHPh), 7.60 (d, 4 H, CH_{ortho}), 9.50 (s, 2 H, NCHN), 10.30 (s, 2 H, NCHN) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, [D$_6$]dmso): δ = 30.7 (CH_3), 62.7 (CHPh), 128.4 (CH_{meta}), 129.4 (CH_{ortho}), 130.0 (CH_{para}), 132.8 (C_{quat}), 142.4 (NCHN), 142.9 (NCHN) ppm. $C_{20}H_{22}I_2N_6$ (600.24): calcd. C 40.02, H 3.69, N 14.00; found C 39.83, H 3.76, N 13.89. MS-FAB: m/z (%) = 473.1 (41) [M + I]$^+$, 345.3 (100) [M]$^{2+}$.

4^{iPr}: Required reaction time: 4 d. Yield: 266 mg (86%). $[\alpha]_D^{20}$ = –41.0 (c = 0.0051, CH_2Cl_2). ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 1.48 (pseudo-t, ^3J = 6.4 Hz, 12 H, CH_3), 4.87 (sept, ^3J = 6.4 Hz, 2 H, CHCH$_3$), 7.30 (s, 2 H, CHPh), 7.38 (m, 6 H, CH_{para}, CH_{meta}), 7.62 (d, 4 H, CH_{ortho}), 9.48 (s, 2 H, NCHN), 10.40 (s, 2 H, NCHN) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, [D$_6$]dmso): δ = 21.0 (CH_3), 55.9 (CHCH$_3$), 63.2 (CHPh), 128.6 (CH_{meta}), 129.4 (CH_{ortho}), 130.1 (CH_{para}), 132.1 (C_{quat}), 140.8 (NCHN), 143.3 (NCHN) ppm. $C_{24}H_{30}I_2N_6$ (656.34): calcd. C 43.92, H 4.61, N 12.80; found C 44.16, H 4.92, N 12.51. MS-FAB: m/z (%) = 529.2 (86) [M + I]$^+$, 401.3 (100) [M]$^{2+}$.

Synthesis of 5 and 6: PtI_2 (60 mg, 0.13 mmol) or $PtBr_2$ (47.4 mg, 0.13 mmol), the corresponding ligand salt (0.13 mmol), and sodium acetate (21.9 mg, 0.27 mmol) were suspended in dimethyl sulfoxide (5 mL). The reaction mixture was heated at 90 °C for 12 h. The resulting solution was filtered before the solvent was removed at reduced pressure. The crude product was washed three times with water and pentane and then dried under reduced pressure.

5^{iPr}: Yield: 85.4 mg (85%). $[\alpha]_D^{20}$ = +13.0 (c = 1.9 × 10^{-3}, dmso). ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 1.27 (m, 6 H, CH_3), 1.45 (d, ^3J = 6.7 Hz, 6 H, CH_3), 1.60 (m, 3 H, $^{c\text{-hex}}$CH_2), 1.93 (m, 2 H, $^{c\text{-hex}}$CH_2), 2.19 (m, 1 H, $^{c\text{-hex}}$CH_2), 2.33 (m, 2 H, $^{c\text{-hex}}$CH_2), 4.48 (m, 1 H, $^{c\text{-hex}}$CH), 5.19 [sept, ^3J = 6.7 Hz, 1 H, CH(CH$_3$)$_2$], 5.61 [sept, ^3J = 6.7 Hz, 1 H, CH(CH$_3$)$_2$], 6.16 (m, 1 H, $^{c\text{-hex}}$CH), 8.80 (s, 1 H, NCHN), 8.88 (s, 1 H, NCHN) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, [D$_6$]dmso): δ = 20.7 (CH_3), 21.2 (CH_3), 21.9 (CH_3), 22.1 (CH_3), 24.0 ($^{c\text{-hex}}$CH_2), 24.2 ($^{c\text{-hex}}$CH_2), 28.9 ($^{c\text{-hex}}$CH_2), 34.9 ($^{c\text{-hex}}$CH_2), 53.3 [CH(CH$_3$)$_2$], 55.0 [CH(CH$_3$)$_2$], 57.6 ($^{c\text{-hex}}$CH), 62.0 ($^{c\text{-hex}}$CH), 141.5 (NCHN), 145.6 (NCHN), 147.9 (carbene), 152.7 (carbene) ppm. MS-FAB: m/z (%) = 624.0 (100) [M – I]$^+$. $C_{16}H_{26}I_2N_6Pt$ (753.32): calcd. C 25.58, H 3.49, N 11.19; found C 25.52, H 3.69, N 11.05.

5^{nBu}: Yield: 64.6 mg (62%). $[\alpha]_D^{20}$ = +11.2 (c = 2.2 × 10^{-3}, dmso). ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 0.88 (t, ^3J = 7.4 Hz, 3 H, CH_3), 0.91 (t, J = 7.4 Hz, 3 H, CH_3), 1.23–1.43 (m, 4 H, CH$_3$CH_2), 1.58 (m, 1 H, $^{c\text{-hex}}$CH_2), 1.68–2.05 (m, 9 H, CH$_3$CH_2CH_2, $^{c\text{-hex}}$CH_2), 2.21 (m, 1 H, $^{c\text{-hex}}$CH_2), 2.44 (m, 1 H, $^{c\text{-hex}}$CH_2), 4.05 (m, 1 H, $^{c\text{-hex}}$CH), 4.24–4.42 (m, 3 H, NCH_2), 4.64 (m, 1 H, 1 H, NCH_2), 6.49 (m, 1 H, $^{c\text{-hex}}$CH), 7.86 (s, 1 H, NCHN), 7.98 (s, 1 H, NCHN) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, [D$_6$]dmso): δ = 13.4 (CH_3), 13.5 (CH_3), 19.07 (CH$_3$CH_2), 19.13 (CH$_3$CH_2), 24.0 ($^{c\text{-hex}}$CH_2), 24.2 ($^{c\text{-hex}}$CH_2), 28.8 ($^{c\text{-hex}}$CH_2), 30.4 (CH$_3$CH$_2$CH_2), 30.5 (CH$_3$CH$_2$CH_2), 34.9 ($^{c\text{-hex}}$CH_2), 51.2 (NCH_2), 53.3 (NCH_2), 57.6 ($^{c\text{-hex}}$CH), 61.9 ($^{c\text{-hex}}$CH), 141.2 (NCHN), 145.2 (NCHN), 148.5 (carbene), 153.6 (carbene) ppm. $C_{18}H_{30}I_2N_6Pt$ (779.36): calcd. C 27.74, H 3.88, N 10.78; found C 28.13, H 3.73, N 10.32. MS-FAB: m/z (%) = 652.0 (100) [M + I]$^+$, 521.1 (64) [M]$^{2+}$.

5^{Bz}: Yield: 92.9 mg (73%). $[\alpha]_D^{20}$ = 24.5 (c = 2.9 × 10^{-3}, dmso). ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 1.52 (m, 1 H, $^{c\text{-hex}}$CH_2), 1.70 (m, 2 H, $^{c\text{-hex}}$CH_2), 1.94 (m, 2 H, $^{c\text{-hex}}$CH_2), 2.21 (m, 1 H, $^{c\text{-hex}}$CH_2), 2.37 (m, 2 H, $^{c\text{-hex}}$CH_2), 4.56 (m, 1 H, $^{c\text{-hex}}$CH), 5.01 (d, ^2J = 14.8 Hz, 1 H, NCH_2), 5.45 (d, ^2J = 14.8 Hz, 1 H, NCH_2), 5.56 (d, ^2J = 14.8 Hz, 1 H, NCH_2), 5.62 (d, ^2J = 14.8 Hz, 1 H, NCH_2), 6.19 (m, 1 H, $^{c\text{-hex}}$CH), 7.24 (m, 2 H, H_{aryl}), 7.33 (m, 8 H, H_{aryl}), 8.81 (s, 1 H, NCHN), 8.87 (s, 1 H, NCHN) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, [D$_6$]dmso): δ = 23.96 ($^{c\text{-hex}}$CH_2), 24.04 ($^{c\text{-hex}}$CH_2), 28.9 ($^{c\text{-hex}}$CH_2), 35.1 ($^{c\text{-hex}}$CH_2), 53.8 (NCH_2), 55.6 (NCH_2), 58.0 ($^{c\text{-hex}}$CH), 62.3 ($^{c\text{-hex}}$CH), 127.9 (C_{aryl}), 128.32 (C_{aryl}), 128.38 (C_{aryl}), 128.42 (C_{aryl}), 128.44 (C_{aryl}), 134.8 (C_{quat}), 135.4 (C_{quat}), 141.6 (NCHN), 145.5 (carbene), 145.6 (NCHN), 151.9 (carbene) ppm. MS-FAB: m/z (%) = 672.9 (100) [M + Br]$^+$, 592.0 (37) [M]$^{2+}$. $C_{24}H_{26}Br_2N_6Pt$ (753.39): calcd. C 38.26, H 3.48, N 11.15; found C 37.82, H 3.39, N 10.80.

$5^{CH2\text{-}Naphthyl}$: Yield: 116.9 mg (81%). $[\alpha]_D^{20}$ = +9.6 (c = 1.9 × 10^{-3}, dmso). ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 1.54 (m, 1 H, $^{c\text{-hex}}$CH_2), 1.74 (m, 2 H, $^{c\text{-hex}}$CH_2), 1.95 (m, 2 H, $^{c\text{-hex}}$CH_2), 2.25 (m, 1 H, $^{c\text{-hex}}$CH_2), 2.40 (m, 2 H, $^{c\text{-hex}}$CH_2), 4.60 (m, 1 H, $^{c\text{-hex}}$CH), 4.88 (d, ^2J = 15.2 Hz, 1 H, NCH_2), 5.32 (d, ^2J = 14.8 Hz, 1 H, NCH_2), 5.45 (d, ^2J = 15.2 Hz, 1 H, NCH_2), 5.71 (d, ^2J = 14.8 Hz, 1 H, NCH_2), 6.21 (m, 1 H, $^{c\text{-hex}}$CH), 7.16 (m, 1 H, H_{aryl}), 7.33 (m, 2 H, H_{aryl}), 7.50–7.60 (m, 5 H, H_{aryl}), 7.73–7.83 (m, 5 H, H_{aryl}), 7.91 (m, 1 H, H_{aryl}), 8.84 (s, 1 H, NCHN), 8.90 (s, 1 H, NCHN) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, [D$_6$]dmso): δ = 23.95, 24.04 ($^{c\text{-hex}}$CH_2), 28.9 ($^{c\text{-hex}}$CH_2), 35.1 ($^{c\text{-hex}}$CH_2), 53.8 (NCH_2), 55.6 (NCH_2), 58.0 ($^{c\text{-hex}}$CH), 62.3 ($^{c\text{-hex}}$CH), 125.5 (C_{aryl}), 126.1 (C_{aryl}), 126.3 (C_{aryl}), 126.41 (C_{aryl}), 126.43, (C_{aryl}), 126.6 (C_{aryl}), 127.5 (C_{aryl}), 127.55 (2 × C_{aryl}), 127.57 (2 × C_{aryl}), 127.6 (C_{aryl}), 127.8 (C_{aryl}), 128.0 (C_{aryl}), 132.3 (C_{quat}), 132.38 (C_{quat}), 132.40 (C_{quat}), 132.48 (C_{quat}), 132.53 (C_{quat}), 132.8 (C_{quat}), 141.6 (NCHN), 145.5 (NCHN), 145.7 (carbene), 152.1 (carbene) ppm. MS-FAB: m/z (%) = 773.0 (100) [M – Br]$^+$. $C_{32}H_{30}Br_2N_6Pt$·dmso (853.51 + 78.13): calcd. C 43.83, H 3.89, N 9.02; found C 43.96, H 3.60, N 9.24.

6^{Me}: Yield: 76.4 mg (72%). $[\alpha]_D^{20}$ = +39.3 (c = 2.1 × 10^{-3}, dmso). ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 3.90 (s, 3 H, CH_3), 4.04 (s, 3 H, CH_3), 6.75 (d, ^2J = 11.6 Hz, 1 H, CHPh), 7.25 (m, 3 H, CH_{aryl}), 7.48 (m, 3 H, CH_{aryl}), 7.64–7.76 (m, 5 H, CHPh, CH_{aryl}), 8.39 (s, 1 H, NCHN), 8.71 (s, 1 H, NCHN) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, [D$_6$]dmso): δ = 41.6 (CH_3), 63.3 (CHPh), 63.7 (CHPh), 128.0 (2 × C_{aryl}), 128.9 (2 × C_{aryl}), 129.1 (C_{aryl}), 129.7 (2 × C_{aryl}), 129.8 (2 × C_{aryl}), 130.3 (C_{aryl}), 130.9 (C_{quat}), 136.8 (C_{quat}), 141.8 (NCHN), 145.4 (NCHN), 150.1 (carbene), 155.2 (carbene) ppm. $C_{20}H_{20}I_2N_6Pt$ (793.30): calcd. C 30.28, H 2.54, N 10.59; found C 29.98, H 2.69, N 10.06. MS-ESI: m/z = 1459.0 (2 M – I)$^+$, 706.9 [M – I + CH$_3$CN]$^+$.

6^{iPr}: Yield: 73.9 mg (65%). $[\alpha]_D^{20}$ = +25.3 (c = 2.1 × 10^{-3}, dmso). ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 1.33 (d, ^3J = 6.6 Hz, 3 H, CHCH_3), 1.36 (d, ^3J = 6.6 Hz, 3 H, CHCH_3), 5.28 (sept, ^3J = 6.4 Hz, 1 H, CHCH$_3$), 5.69 (sept, ^3J = 6.6 Hz, 1 H, CHCH$_3$), 6.67 (d, ^3J = 11.6 Hz, 1 H, CHPh), 7.23 (t, ^3J = 7.4 Hz, 1 H, CH_{aryl}), 7.27 (t, ^3J = 7.4 Hz, 2 H, CH_{aryl}), 7.34 (t, ^3J = 7.4 Hz, 1 H, CH_{aryl}), 7.43 (t, ^3J = 7.4 Hz, 2 H, CH_{aryl}), 7.61 (d, ^3J = 7.4 Hz, 2 H, CH_{aryl}), 7.69 (d, ^3J = 7.4 Hz, 2 H, CH_{aryl}), 7.69 (d, ^3J = 11.6 Hz, 1 H, CHPh), 7.75 (m, 2 H, CH_{aryl}), 8.39 (s, 1 H, NCHN), 8.77 (s, 1 H, NCHN) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, [D$_6$]dmso): δ = 20.8 (CH_3), 21.2 (CH_3), 21.9 (CH_3), 22.0 (CH_3), 53.5 [CH(CH$_3$)$_2$], 55.1 [CH(CH$_3$)$_2$], 63.6 (CHPh), 63.8 (CHPh), 128.0 (2 × C_{aryl}), 128.9 (2 × C_{aryl}), 129.1 (C_{aryl}), 129.8 (4 × C_{aryl}), 130.3 (C_{aryl}), 131.0 (C_{quat}), 136.8 (C_{quat}), 142.5 (NCHN), 146.2 (NCHN), 149.3 (carbene), 154.1 (carbene) ppm. $C_{24}H_{28}I_2N_6Pt$ (849.41): calcd. C 33.94, H 3.32, N 9.89; found C 33.54, H 2.94, N 9.88. MS-ESI: m/z = 762.9 [M – I + CH$_3$CN]$^+$, 635.0 [M – 2 I – CH$_3$CN]$^+$, 594.3 [M – 2 I]$^+$.

General Procedure for Hydrosilylation Catalysis Reactions: An ACE pressure tube® was charged with methylbis(trimethylsilyloxy)silane (4.00 g, 0.018 mol) and *n*-octene (2.02 g, 0.018 mol). Then the catalyst (200 ppm Pt in relation to the total weight, 0.0062 mmol) was added, and the reaction mixture was heated at 120 °C. After 24 h, the reaction mixture was cooled, and the product yield was determined by ^{1}H NMR spectroscopy.

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