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Synthesis and Reactivity of Platinum(II) *cis*-Dialkyl, *cis*-Alkyl Chloro, and *cis*-Alkyl Hydrido Bis-*N*-heterocyclic Carbene Chelate Complexes

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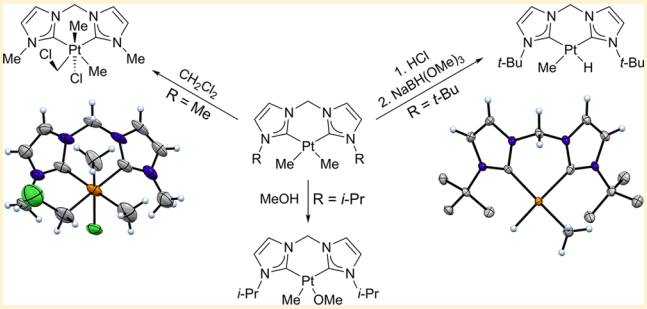
Supporting Information

ABSTRACT: Platinum(II) *cis*-dimethyl and *cis*-dineopentyl complexes bearing the alkyl-substituted bis-NHC ligands $L^{t\text{-}Bu}$, L^{Me}, and $L^{i\text{-}Pr}$ ($L^{t\text{-}Bu}$ = 1,1′-di-*tert*-butyl-3,3′-methylenediimidazolin-2,2′-diylidene, L^{Me} = 1,1′-dimethyl-3,3′-methylenediimidazolin-2,2′-diylidene, $L^{i\text{-}Pr}$ = 1,1′-diisopropyl-3,3′-methylenediimidazolin-2,2′-diylidene) as well as novel *cis*-alkyl chloro and *cis*-alkyl hydrido compounds were synthesized. The reactivity of the dimethyl complexes toward dichloromethane and methanol was investigated. Reductive elimination of alkanes from *cis*-alkyl hydrido complexes requires much higher temperatures than in related bisphosphine systems, which limits their applicability for the generation of reactive, bent platinum(0) d^{10}-ML_2 fragments for bond-activation chemistry. The platinum(II) complexes were characterized by NMR and IR spectroscopy, mass spectrometry, elemental analysis, and X-ray diffraction in most cases.



INTRODUCTION

Hydrocarbons are major constituents of natural gas and petroleum. Thus, the selective transformation of C−H bonds to other functional groups is a field of great interest not only in academic but in industrial research as well. One option to activate C−H or other relative inert bonds is the oxidative addition to electron-rich, low-valent complexes of late transition metals like d^{10}-ML_2 fragments (isolobal to $^1CH_2$).[1] Whitesides et al.[2] and our group[3] were able to confirm this by experiments with platinum complexes of chelating bisphosphines. The reactivity of these fragments depends on the electron density at the metal center and the bite angle of the ligand. MO model calculations suggest a higher reactivity for smaller bite angles in bond-activation reactions due to an increase of the total energy and an electronic structure change of the frontier orbitals.[4] It is well recognized that the replacement of phosphine ligands by *N*-heterocyclic carbenes (NHCs) can provide complexes with enhanced catalytic performance and higher ligand-to-metal bond stability.[5] The first chelating bis(carbene) complex used in catalysis was described by Herrmann et al. in 1995, who tested $L^{Me}PdI_2$ successfully as a catalyst in the Heck reaction.[6]

There are two possible routes to access the desired platinum(0) fragments bearing bis-NHC units as spectator ligands: Either the direct conversion of a platinum(0) precursor with a preformed bis(carbene), or reductive elimination from a bis-NHC platinum(II) compound. We successfully applied the first strategy to synthesize [$L^{t\text{-}Bu}$Pt(η^2-cod)] (cod = 1,5-cyclooctadiene) as the first example of a bis-NHC platinum(0) complex.[7] This one-step approach provides a fast access to complexes bearing differently substituted bis-NHCs. However, the olefin ligand, which has to dissociate prior to or in course of the reaction, could hamper reactions of the 14 VE fragment or interfere with product formation. This problem can be avoided with the second route based upon irreversible reductive elimination of e.g. a gaseous alkane from an appropriate *cis*-dialkyl or a *cis*-alkyl hydrido Pt(II) precursor. In case of established bisphosphine systems, *cis*-neopentyl hydrido platinum(II) complexes were successfully used. The reductive elimination takes place at room temperature for [(dtbpm)PtNpH][3a] (dtbpm = bis(di-*tert*-butylphosphino)ethane; Np = neopentyl) and above 45 °C in case of [(dcpe)PtNpH] (dcpe = bis(dicyclohexylphosphino)ethane).[2a] However, bis-NHC chelate complexes of platinum bearing two *cis*-alkyl ligands are scarce. Jamali et al. synthesized the dialkyl complex [$L^{t\text{-}Bu}PtMe_2$] by reaction of an in situ generated silver cluster with [$PtMe_2(\mu\text{-}SMe_2)]_2$. Following this procedure with the isopropyl-substituted ligand $L^{i\text{-}Pr}$, a cluster containing two silver and four platinum centers was formed.[8] A dimethyl platinum(II) complex bearing an aryl-substituted bis-NHC ligand was synthesized by the reaction of the same platinum precursor with the isolated bis(carbene).[9]

The goal of this study was the development of a flexible protocol for the synthesis of *cis*-dialkyl platinum(II) complexes bearing methyl and neopentyl groups, which do not allow β-H elimination. These compounds incorporating the bis-NHC chelate ligands $L^{t\text{-}Bu}$, L^{Me}, and $L^{i\text{-}Pr}$ (Figure 1) should then be further functionalized via *cis*-alkyl chloro to *cis*-alkyl hydrido complexes in order to investigate the reductive elimination of alkanes from the latter.

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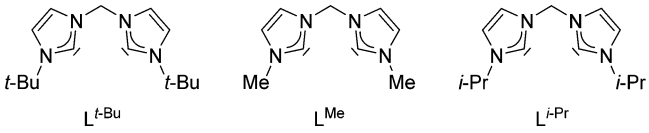


$L^{t\text{-Bu}}$ L^{Me} $L^{i\text{-Pr}}$

Figure 1. Bis-NHC ligands used in this study.

RESULTS AND DISCUSSION

Our first strategy for the preparation of platinum(II) dialkyl complexes with chelating bis-NHC ligands started with the synthesis of the corresponding dichloro complexes. Analogously to our work on bisphosphine platinum(II) complexes,[3a] these compounds should then in a second step be transformable with alkyl lithium reagents into the corresponding *cis*-dialkyl analogs.

The reaction of $[(cod)PtCl_2]$ with the isolated bis(carbene) $L^{t\text{-Bu}}$ in dichloromethane afforded the *cis*-dichloro complex $[L^{t\text{-Bu}}PtCl_2]$ (**1**) in 52% yield. Single crystals suitable for X-ray analysis precipitated from the reaction mixture at room temperature (Figure 2). The six-membered platinacycle exhibits

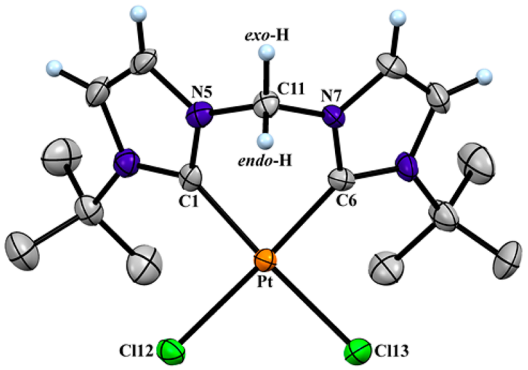


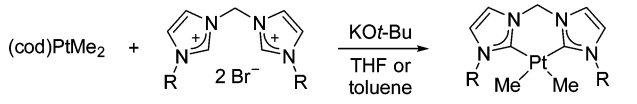
Figure 2. Solid-state molecular structure of **1** with ellipsoids drawn at the 50% probability level. Hydrogen atoms of *tert*-butyl groups and a non-coordinated dichloromethane molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt–C1 1.982(5), Pt–C6 1.974(5), Pt–Cl12 2.3731(13), Pt–Cl13 2.3764(14), C1–Pt–C6 84.6(2), Cl12–Pt–Cl13 88.02(5), N5–C11–N7 107.8(4).

the typical boat conformation found in methylene-bridged bis-NHC complexes, resulting in two diastereotopic methylene protons denominated *exo*- and *endo*-H. Due to the weaker *trans* influence of the chloro ligands, the platinum–carbene bond lengths in **1** are shorter than those in $[L^{t\text{-Bu}}PtMe_2]$.[8] In comparison to the dimethyl complex, the bite angle in the dichloro complex of 84.6(2)° is 1.6(2)° larger.

This air-stable compound has a very low solubility in most common organic solvents. In DMSO-d_6 the solubility was sufficient for the recording of a ^{1}H NMR spectrum, which shows two doublets at 5.97 and 6.18 ppm for the bis-NHC ligand's methylene bridge. Hence, the inversion of the platinacycle's boat conformers does not take place at room temperature in solution.

Presumably due to the low solubility of **1**, reactions with alkyl lithium compounds were not successful, and another route had to be developed for the synthesis of *cis*-platinum(II) dialkyl complexes. Starting from $[(cod)PtCl_2]$, the alkyl groups were introduced prior to the bis-NHC ligand. In contrast to the preparation of **1**, the bis(carbenes) were generated in situ as they turned out to be very temperature-sensitive. The dimethyl complexes $[L^{t\text{-Bu}}PtMe_2]$ (**2a**), $[L^{Me}PtMe_2]$ (**2b**), and $[L^{i\text{-Pr}}PtMe_2]$ (**2c**) were synthesized by the reaction of the corresponding bis(imidazolium) salts, potassium *tert*-butoxide, and $[(cod)PtMe_2]$ in THF or toluene at room temperature in yields between 61% and 87% (Scheme 1). As the products are unreactive toward water, it was possible to quench the reaction mixtures, and the complexes were extracted with dichloromethane.

Scheme 1. Synthesis of the Dimethyl Complexes 2a–c



$L^RH_2Br_2$ R = *t*-Bu (**2a**), Me (**2b**), *i*-Pr (**2c**)

Suitable single crystals for X-ray crystallography were obtained by slow evaporation of THF solutions of the complexes. The structures of the two new compounds **2b** (C_1-symmetry) and **2c** (C_s-symmetry) are depicted in Figure 3.

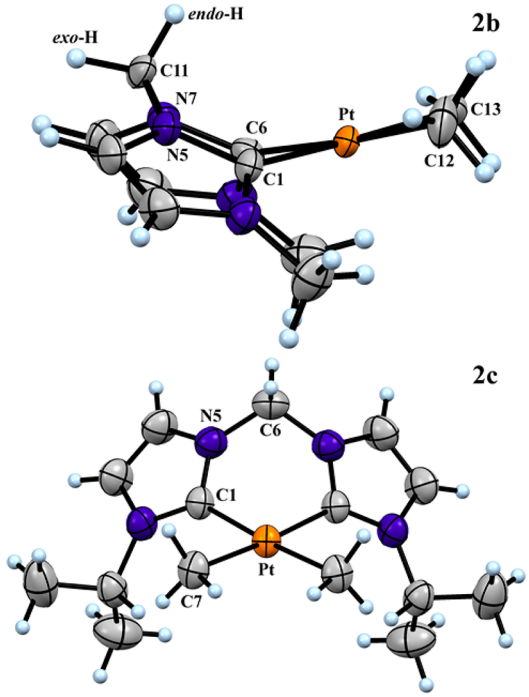


Figure 3. Solid-state molecular structures of **2b** and **2c** with ellipsoids drawn at the 50% probability level. A non-coordinated THF molecule in case of **2c** is omitted for clarity. Selected bond lengths (Å) and angles (deg): $[L^{Me}PtMe_2]$ (**2b**), Pt–C1 2.011(4), Pt–C6 2.024(4), Pt–C12 2.090(5), Pt–C13 2.127(4), C1–Pt–C6 84.56(17), C12–Pt–C13 85.9(2), N5–C11–N7 108.9(3); $[L^{i\text{-Pr}}PtMe_2]$ (**2c**), Pt–C1 2.013(5), Pt–C7 2.104(5), C1–Pt–C1′ 85.5(3), C7–Pt–C7′ 86.6(3), N5–C6–N5′ 109.0(6).

The bite angles of the bis-NHC ligands in the two structurally characterized dimethyl complexes are similar and lie between 85.5(3)° in **2c** and 83.0(1)° in **2a**.[8] In comparison to the latter, the platinum–carbene bond lengths in **2b** and **2c** are about 0.03 Å shorter.

In the ^{1}H NMR spectra, the methyl ligands appear as singlets between 0.2 and 0.3 ppm complemented by platinum satellites with ^2J coupling constants of 66–68 Hz. The protons of the bis-NHC ligands' methylene bridges give rise to two doublets

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with ^2J coupling constants between 12 and 13 Hz. As in complex **1**, this shows the rigidity of the six-membered platinacycles' boat conformations at room temperature. In each compound, one of the methylene protons, which was identified by ROESY as the one directing toward the metal center (*endo*-H), additionally couples with the platinum atom (^4J = 11−19 Hz). Remarkably, in complex **2b** all protons couple with the metal center except for the *exo*-H of the methylene bridge. The ^{13}C NMR signals of the carbene carbon atoms between 180.52 and 186.89 ppm are shifted to higher field in comparison to the platinum(0) complex [L$^{t\text{-Bu}}$Pt(η^2-cod)] (193.49 ppm).[7]

High-temperature NMR measurements in DMSO-d_6 for **2b** bearing the *N*-methyl-substituted bis(carbene) showed coalescence of the methylene protons at 57 °C. As expected, the inversion takes place at higher temperatures with increasing steric bulk of the ligand's substituents. Figure 4 shows the ^{1}H

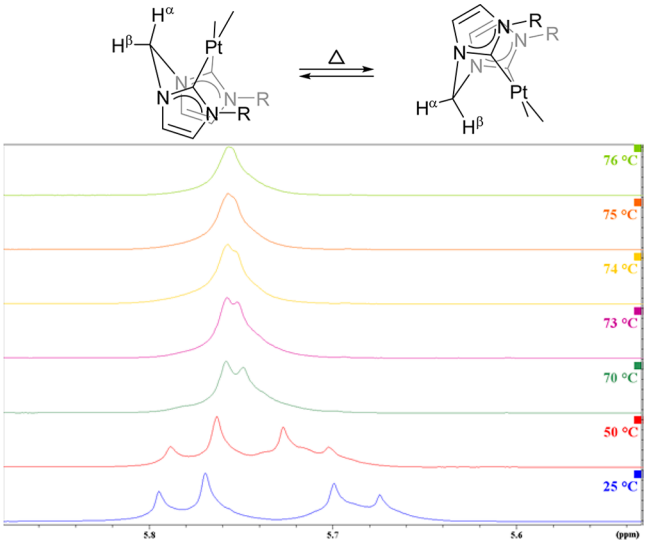

Figure 4. Determination of the methylene protons coalescence point using VT ^{1}H NMR spectroscopy of **2c**.

NMR spectra for **2c** with a coalescence temperature of 76 °C. In the *tert*-butyl system **2a**, no inversion was observed until 150 °C. In spite of this high temperature, no decomposition of the complex was visible in its NMR spectra.

While the sterically most crowded dimethyl complex **2a** based on ligand L$^{t\text{-Bu}}$ is stable in dichloromethane at room temperature, **2b** and **2c** slowly reacted with this solvent within about 5 days. X-ray structure analysis of single crystals formed by slow evaporation of a dichloromethane solution of [L^{Me}PtMe$_2$] showed that oxidative addition to the complex takes place (Figure 5). The octahedral, 5-fold *C*-ligated platinum(IV) complex [L^{Me}PtMe$_2$(CH$_2$Cl)Cl] (**3**) is the product of a formal *cis*-addition of a C−Cl bond to Pt(II) and—with about 50%—is the main component of the crystals. It is superimposed by several other stereoisomers holding the chloromethylene moiety in a *cis*- or *trans*-arrangement to the chloro ligand. The only group not involved in this multiple disorder pattern is the chloro ligand. Due to this disorder, we refrain from a geometrical discussion. Known structurally characterized compounds resulting from the oxidative addition of dichloromethane to platinum(II) dimethyl complexes exhibit *trans* arrangements of the methyl ligands due to a fast isomerization of the initially formed *cis* product.[10] This

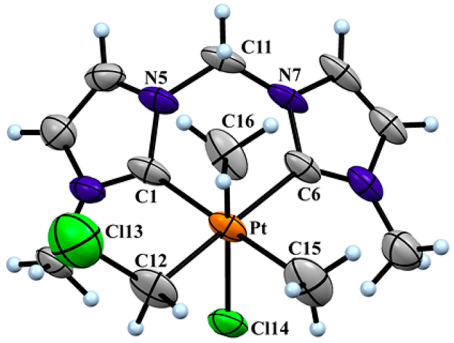

Figure 5. Main component of the solid-state structural isomers of **3** with ellipsoids drawn at the 50% probability level.

isomerization might in case of the bis-NHC system be slower because of the strong platinum−carbene bonds hampering an opening of the chelate ring.

Due to the nonplanar chelate ring, seven diastereotopic products for the oxidative addition are in principle possible. The ^{1}H NMR spectrum in Figure 6 was recorded 8 days after

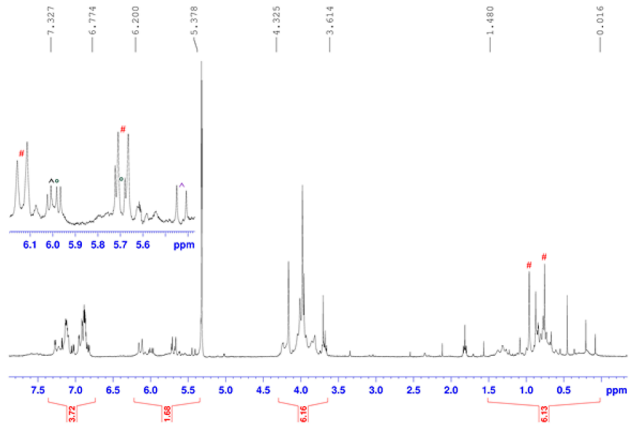

Figure 6. ^{1}H NMR spectrum of **2b** after 8 days in CD_2Cl_2.

[L^{Me}PtMe$_2$] was dissolved in CD_2Cl_2. It shows no remaining starting material, but a complicated product mixture. The integrals over the selected regions are in accordance with the formation of oxidative addition products: six protons for the methyl ligands at high field, six protons for the methyl substituents of the bis-NHC in the area around 4 ppm as well as two and four protons at lower field representing the methylene bridge and the imidazole protons, respectively. The deuterated chloromethylene ligand is not visible. In a COSY experiment, the diastereotopic sets of the methylene bridges of three main products (marked #, ○, and ^ in Figure 6) could be identified. These compounds were observed in a ratio of about 10:3:2.

Also in case of [L$^{i\text{-Pr}}$PtMe$_2$] single crystals were harvested from a dichloromethane solution. However, their X-ray analysis revealed them as the known complex [L$^{i\text{-Pr}}$PtCl$_2$].[11] Due to the isopropyl groups, superimpositions of the signals did not allow an interpretation of the NMR data of the product mixture in this case.

When dissolved in methanol-d_4, each of the three dimethyl complexes reacted to a new species within about 1 day at room temperature. These transformations were accompanied by the appearance of a singlet at 0.20 ppm and a triplet at 0.18 ppm in the ^{1}H NMR spectra, indicating the formation of methane and

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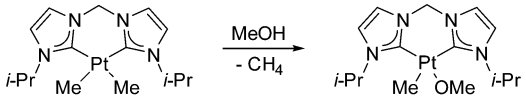
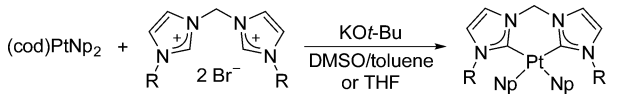
monodeuterated methane, respectively. Subsequently, the new compounds further reacted to a complicated product mixture of several secondary products. This reactivity was investigated in detail for **2c**. A quantitative transformation to the first product (**4**) without the observation of byproducts is observed after 2 days at 5 °C in methanol. In comparison to the dimethyl complex, C_s-symmetry is broken: the isopropyl methine hydrogens give rise to two septets in the ^{1}H NMR spectrum. A signal at 0.45 ppm representing a platinum bound methyl group has an integral of three protons and, in contrast to the product from the reaction with deuterated methanol, a new singlet with the same integral at 3.77 ppm is observed. This group obviously originates from the solvent and—in accordance with the formation of methane—suggests that the product is a platinum(II) methoxy methyl complex (Scheme 2). Although various attempts to obtain single crystals for X-ray analysis were not successful, the LIFDI mass spectrum and a correct elemental analysis confirm the identity of **4**.

Scheme 2. [L$^{i\text{-Pr}}$PtMe$_2$] Reacts with Methanol under Liberation of Methane To Give the Methoxy Methyl Complex 4



The syntheses of [L$^{t\text{-Bu}}$PtNp$_2$] (**5a**) and [L^{Me}PtNp$_2$] (**5b**) were performed in a similar procedure to that of the dimethyl complexes using [(cod)PtNp$_2$] as precursor (Scheme 3). In

Scheme 3. Preparation of the Dineopentyl Complexes 5a and 5b



contrast to known procedures using a Grignard reagent to prepare this platinum(II) complex,[12] we developed a synthesis employing neopentyl lithium to give [(cod)PtNp$_2$] in high yield and purity.

The dineopentyl complexes were isolated as colorless solids in 76% (**5a**) and 67% (**5b**) yield, respectively. As the rotation of the neopentyl groups is sterically hindered in both complexes, the hydrogen atoms of the platinum-bound methylene groups are diastereotopic and give rise to two doublets in the ^{1}H NMR spectra. Single crystals were obtained from a saturated dichloromethane solution (**5a**) and by layering a THF solution of **5b** with *n*-hexane. The solid-state structures show a slight decrease of the bite angles in comparison to the corresponding dimethyl complexes (Figure 7). In the dimethyl as well as in the dineopentyl complexes, the platinum−carbene bonds in compounds bearing L^{Me} and L$^{i\text{-Pr}}$ are shorter than those in complexes of the bulky L$^{t\text{-Bu}}$.

The methyl chloro bis-NHC platinum(II) complexes **6a** and **6b** were synthesized from the corresponding dimethyl complexes by reaction with 1 equiv of hydrochloric acid (Scheme 4). The acid was generated in situ by the reaction of

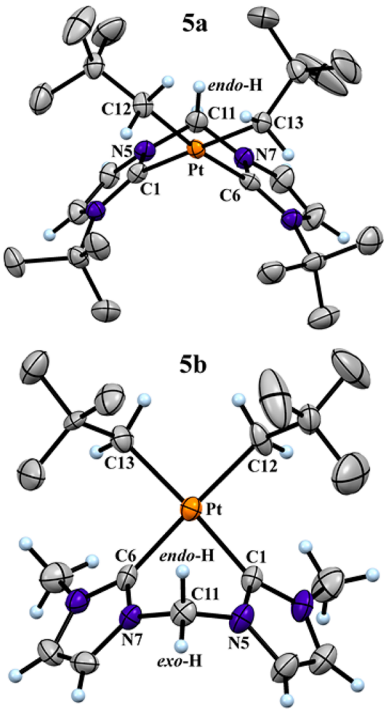
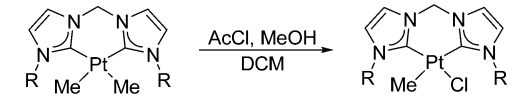


Figure 7. Solid-state molecular structures of **5a** and **5b** with ellipsoids drawn at the 50% probability level. Hydrogen atoms of *tert*-butyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): [L$^{t\text{-Bu}}$PtNp$_2$] (**5a**), Pt−C1 2.050(3), Pt−C6 2.059(3), Pt−C12 2.101(3), Pt−C13 2.098(3), C1−Pt−C6 81.77(11), C12−Pt−C13 86.25(11), N5−C11−N7 109.2(2); [L^{Me}PtNp$_2$] (**5b**) (two independent molecules were found in the unit cell; the values given are averaged), Pt−C1 2.021, Pt−C6 2.018, Pt−C12 2.108, Pt−C13 2.116, C1−Pt−C6 82.3, C12−Pt−C13 89.3, N5−C11−N7 108.7.

acetyl chloride with methanol. The products were obtained as colorless solids in 94% (**6a**) and 79% (**6b**) yield.

Scheme 4. Synthesis of Bis-NHC *cis*-Methyl Chloro Complexes



In contrast to the dimethyl complexes, the solubility in THF and toluene is low, and NMR data were obtained from CD_2Cl_2 solutions. Due to the asymmetric substitution, the signal sets for the imidazole rings and ligand substituents are doubled in comparison to the starting materials. Single crystals were obtained from a dichloromethane solution in case of **6a**. The solid-state structure shows that the shorter platinum−carbene bond distance is *trans* to the chloro ligand (Figure 8).

For the synthesis of the neopentyl chloro complex **7** the employment of AcCl/MeOH led to the formation of side products. Better results were obtained by slow addition of a hydrogen chloride stock solution in diethyl ether to a saturated THF solution of the dineopentyl complex (Scheme 5). The product precipitated and was obtained in 91% yield.

The solid-state structure shows that the bite-angle of 84.38(9)° in **7** is larger than in the dineopentyl complex (Figure 9). As in the other alkyl chloro complexes, the

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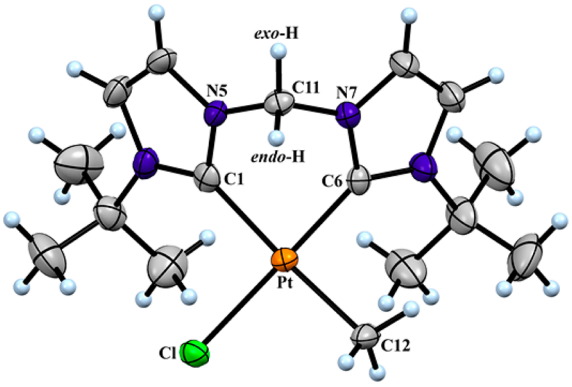
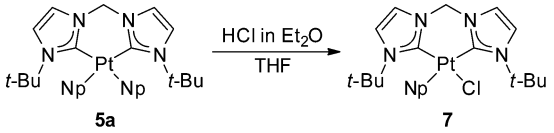


Figure 8. Solid-state molecular structure of **6a** with ellipsoids drawn at the 50% probability level. A non-coordinated dichloromethane molecule is omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt−C1 2.060(4), Pt−C6 1.961(4), Pt−Cl 2.3724(13), Pt−C12 2.121(8), C1−Pt−C6 85.21(17), Cl−Pt−C12 86.6(3), N5−C11−N7 108.9(3).

Scheme 5. Preparation of the *cis*-Neopentyl Chloro Complex 7



platinum−carbene bond *trans* to the chloro ligand is the shorter one.

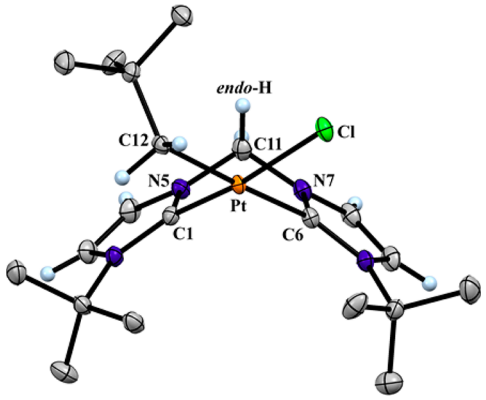
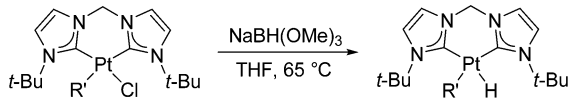


Figure 9. Solid-state molecular structure of **7** with ellipsoids drawn at the 50% probability level. Hydrogen atoms of *tert*-butyl groups and a non-coordinated dichloromethane molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt−C1 1.970(2), Pt−C6 2.061(2), Pt−Cl 2.3894(5), Pt−C12 2.097(2), C1−Pt−C6 84.38(9), Cl−Pt−C12 90.07(6), N5−C11−N7 108.54(19).

Alkyl hydrido complexes were synthesized for the L$^{t\text{-Bu}}$ systems, as the steric bulk of the *tert*-butyl groups is expected to facilitate the reductive elimination and makes the complexes less prone to side reactions resulting from oxidative additions. L$^{t\text{-Bu}}$PtMeH (**8**) and L$^{t\text{-Bu}}$PtNpH (**9**) are accessible from the reaction of the appropriate alkyl chloro complexes with 5−10 equiv of sodium trimethoxyborohydride at 65 °C (Scheme 6). The products were obtained by extraction with toluene in yields of 78% (**8**) and 87% (**9**).

In the ^{1}H NMR spectra, the hydrido ligands give rise to singlets at −7.58 (**8**) and −7.12 ppm (**9**) with ^1J(Pt,H)

Scheme 6. Preparation of the Alkyl Hydrido Complexes 8 and 9



coupling constants of 1047 and 1083 Hz, respectively. The rotation of the sterically demanding neopentyl ligand in **9** is hindered at room temperature resulting in two doublets for its methylene groups with ^2J couplings of 12 Hz between the hydrogen atoms and 78−84 Hz to the metal center. Whereas the ^{13}C resonance of the neopentyl methylene group in **9** is only slightly shifted to higher field compared to that of the dineopentyl complex **5a**, the ^{13}C signal of the methyl ligand in **8** is shifted 15.7 ppm upfield in comparison to the methyl ligands of **2a** and is observed at −23.91 ppm.

Crystallization from a saturated THF solution yielded single crystals of **8**. Due to the strong *trans* influence of the hydrido ligand, the platinum−carbene bond opposite to it is weakened and exhibits the longest NHC carbon-to-metal distance of the platinum(II) complexes discussed in this study with 2.072(4) Å (Figure 10). The platinum−hydride bond length measures

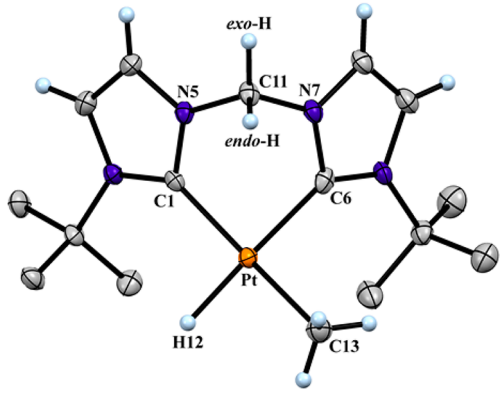


Figure 10. Solid-state molecular structure of **8** with ellipsoids drawn at the 50% probability level. Hydrogen atoms of *tert*-butyl groups and a non-coordinated THF molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt−C1 2.036(4), Pt−C6 2.072(4), Pt−H12 1.72(4), Pt−C13 2.114(4), C1−Pt−C6 84.14(15), H−Pt−C13 79.0(14), N5−C11−N7 108.5(3).

1.72(4) Å and is longer than that in the neopentyl hydrido bisphosphine systems (dcpe: 1.56(5) Å;[2a] dtbpm: 1.58(5) Å[3a]). This is in line with the IR stretching frequency of 2002 cm^{-1} in **8**, which is lower than 2010 cm^{-1} in [(dcpe)PtNpH].[2a] In the bis-NHC neopentyl hydrido complex **9**, an even lower frequency of 1986 cm^{-1} is observed.

As stated in the introduction, reductive elimination of neopentane from bisphosphine platinum(II) neopentyl hydrido complexes takes place at rather mild temperatures. In case of the bis-NHC complexes **8** and **9**, no reaction was observed within 2 days in THF-d_8 at 65 °C. After 1 day at 100 °C in toluene-d_8, about 20% of **9** had reductively eliminated neopentane, giving rise to a singlet in the ^{1}H NMR spectrum at 0.90 ppm. The conversion of **8** is about 5 times slower, which is attributed to less steric bulk of the methyl ligand. In both reactions, a yellow suspension is formed. The solid is hardly soluble in any common organic solvent, and the reaction

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product(s) could not be identified to date. First experiments show that the addition of electron-deficient olefins lowers the required temperatures to a certain extent. This is attributed to the associative formation of platinum(0) olefin complexes. Nevertheless, the high temperatures needed limit the scope of the neopentyl hydrido complexes as precursors for reactive d^{10}-ML_2 fragments in bond-activation reactions, as potential activation products might not be stable under these conditions. The chemistry of the *cis*-alkyl hydrido complexes **8** and **9** will be reported in due course.

CONCLUSION

In summary, we have presented the syntheses of *cis*-dimethyl and *cis*-dineopentyl platinum(II) complexes bearing alkyl-substituted bis-NHC chelate ligands. The reactivity of the *cis*-dimethyl complexes toward methanol and dichloromethane was investigated. In the first case, *cis*-methoxy methyl complexes are formed. Oxidative addition of dichloromethane does not take place with the bulky *tert*-butyl-substituted complex. In case of methyl substitution, a 5-fold *C*-ligated platinum(IV) product was structurally characterized. By the reaction of the *cis*-dialkyl complexes with hydrogen chloride, the corresponding *cis*-alkyl chloro complexes were prepared, which were further functionalized to *cis*-alkyl hydrido compounds. Reductive elimination of alkanes from these complexes requires high temperatures of about 100 °C, which limits their usefulness as convenient precursors for 14 VE fragments of the d^{10}-ML_2 type in bond-activation reactions. Therefore, future studies in this field should better focus on employment of the conveniently accessible platinum(0) complex $L^{t\text{-}Bu}Pt(\eta^2\text{-cod})$ as the source for the desired reactive intermediates.

EXPERIMENTAL SECTION

General Methods. All manipulations were performed under an inert atmosphere of argon using standard Schlenk and glovebox techniques. Dichloromethane, diethyl ether, *n*-hexane, THF, and toluene were taken from an MBraun SPS-800 solvent purification system. Pentane was distilled from sodium, methanol from magnesium, and DMSO from calcium hydride. All solvents were degassed by freeze−pump−thaw cycles, saturated with argon, and stored over molecular sieves (3 Å). Chemicals were prepared according to published procedures: $L^{t\text{-}Bu}$,[13] 1,1′-di-*tert*-butyl-3,3′-methylenediimidazolium dibromide ($L^{t\text{-}Bu}H_2Br_2$),[7] 1,1′-dimethyl-3,3′-methylenediimidazolium dibromide ($L^{Me}H_2Br_2$),[14] 1,1′-diisopropyl-3,3′-methylenediimidazolium dibromide ($L^{i\text{-}Pr}H_2Br_2$),[14] [(cod)-$PtCl_2$],[15] and [(cod)$PtMe_2$].[16] Neopentyl lithium was synthesized according to a procedure by Schrock et al.[17a] using ultrasonic irradiation as described by Matsumoto et al.[17b] NMR data are reported in units of δ relative to tetramethylsilane referenced to the residual solvent resonance as internal standard.

[(cod)$PtNp_2$]. At −30 °C a colorless solution of neopentyllithium (673 mg, 8.62 mmol) in diethyl ether (30 mL) was added dropwise over a period of 20 min to a colorless suspension of [(cod)$PtCl_2$] (1.075 g, 2.87 mmol) in diethyl ether (30 mL). The yellowish reaction mixture was stirred for 2 h and allowed to warm to 5 °C during that time. The resulting yellow suspension was hydrolyzed with 30 mL of a saturated ammonium chloride solution. After the organic phase was separated and the aqueous phase extracted four times with 8 mL of diethyl ether, the combined organic phases were dried over magnesium sulfate. All volatile compounds were removed in vacuo. The remaining brown crude product was purified by column chromatography with petroleum ether, dissolved in pentane, and crystallized at −15 °C. Pale yellow crystals were obtained as product. Yield: 1.024 g (80%). Mp: 111−112 °C. Anal. Calcd for $C_{18}H_{34}Pt$ (445.54): C, 48.52; H, 7.69. Found: C, 48.60; H, 7.69. ^{1}H NMR (300.53 MHz, $CDCl_3$): δ 1.05 (s, 18H, CH_3), 1.88 (s+sat, ^2J(Pt,H) = 92.4 Hz, 4H, Pt-CH_2), 2.12−2.34 (m, 8H, C═CH−CH_2), 4.88 (s, ^2J(Pt,H) = 37.5 Hz, 4H, C═CH-CH_2). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 29.80 (C═CH-CH_2), 35.56 (^3J(Pt,C) = 50.0 Hz, CH_3), 36.08 (^1J(Pt,C) = 884.1 Hz, Pt-CH_2), 36.69 ($C(CH_3)_3$), 100.50 (s+sat, ^1J(Pt,C) = 44.6 Hz, C═C).

[$L^{t\text{-}Bu}PtCl_2$] (1). $L^{t\text{-}Bu}$ (50 mg, 0.19 mmol) and [(cod)$PtCl_2$] (72 mg, 0.19 mmol) were dissolved in dichloromethane (5 mL) and stirred for 2 h at room temperature. The colorless, crystalline product was isolated by filtration, washed two times with 0.5 mL of dichloromethane, and dried in vacuo. Yield: 53 mg (52%). Anal. Calcd for $C_{16}H_{26}Cl_4N_4Pt$ (526.37): C, 31.44; H, 4.29; N, 9.17. Found: C, 32.17; H, 4.44; N, 8.75 (the one non-coordinated dichloromethane molecule visible in the crystal structure is included). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 1.85 (s, 18H, CH_3), 5.97 (d, ^2J(H,H) = 13 Hz, 1H, CH_2), 6.18 (d, ^2J(H,H) = 13 Hz, 1H, CH_2), 7.55 (d, ^3J(H,H) = 2 Hz, 2H, CH-Im), 7.60 (d, ^3J(H,H) = 2 Hz, 2H, CH-Im). Due to the low solubility of **1a**, a ^{13}C NMR spectrum could not be measured. MS (FAB): m/z (%) 526.1 (4) $[M + H]^+$, 491.1 (29) $[M - Cl]^+$, 454.2 (100) $[M - 2Cl - H]^+$, 398.1 (75) $[M - 2Cl - t\text{-}Bu]^+$.

[$L^{t\text{-}Bu}PtMe_2$] (2a). A colorless suspension of [(cod)$PtMe_2$] (300 mg, 0.90 mmol), $L^{t\text{-}Bu}H_2Br_2$ (380 mg, 0.90 mmol), and potassium *tert*-butoxide (303 mg, 2.70 mmol) in toluene (40 mL) was stirred for 12 h at room temperature. Dichloromethane (20 mL) and water (40 mL) were added, and the organic phase was separated. The aqueous phase was extracted three times with 15 mL of dichloromethane. The combined organic phases were dried over magnesium sulfate. All volatile compounds were removed in vacuo. The remaining solid was washed with diethyl ether and dried in vacuo to give a colorless powder. Yield: 265 mg (61%). Mp: 157 °C dec. Anal. Calcd for $C_{17}H_{30}N_4Pt$ (485.52): C, 42.05; H, 6.23; N, 11.54. Found: C, 41.78; H, 6.14; N, 11.35. ^{1}H NMR (300.51 MHz, THF-d_8): δ 0.20 (s+sat, ^2J(Pt,H) = 68 Hz, 6H, Pt-CH_3), 1.72 (s, 18H, N-C(CH_3)$_3$), 5.39 (d, ^2J(H,H) = 12 Hz, 1H, *exo*-CH_2), 6.39 (d+sat, ^2J(H,H) = 12 Hz, ^4J(Pt,H) = 19 Hz, 1H, *endo*-CH_2), 7.04 (d, ^3J(H,H) = 2 Hz, 2H, CH-Im), 7.11 (d, ^3J(H,H) = 2 Hz, 2H, CH-Im). ^{13}C{^{1}H} NMR (125.47 MHz, THF-d_8): δ −8.25 (s+sat, ^1J(Pt,C) = 609 Hz, Pt-CH_3), 31.54 (s +sat, ^4J(Pt,C) = 8 Hz, N-C(CH_3)$_3$), 58.50 (N-C(CH_3)$_3$), 63.90 (CH_2), 117.47 (s+sat, ^3J(Pt,C) = 24 Hz, CH-Im), 118.27 (s+sat, ^3J(Pt,C) = 19 Hz, CH-Im), 186.89 (N_2C-Im). IR (KBr, cm^{-1}): 3132(w); 3097(w); 2974(m); 2795(m); 2360(w); 2340(w); 1477(s); 1368(s); 1229(s); 825(m). MS (LIFDI, CH_2Cl_2): m/z (%) 485.2 (100) $[M]^{+\bullet}$.

[$L^{Me}PtMe_2$] (2b). A colorless THF suspension (20 mL) of [(cod)$PtMe_2$] (150 mg, 0.45 mmol), $L^{Me}H_2Br_2$ (152 mg, 0.45 mmol), and potassium *tert*-butoxide (106 mg, 0.95 mmol) was stirred for 24 h at room temperature. Water (40 mL) and dichloromethane (20 mL) were added to the light yellow suspension, and the organic phase was separated. The aqueous phase was extracted three times with 20 mL of dichloromethane. After back-extraction of the combined organic phases with water (20 mL), they were dried over magnesium sulfate. All volatile compounds were removed in vacuo. The remaining colorless solid was washed three times with 4 mL of diethyl ether. Yield: 158 mg (87%). Mp: 237 °C dec. Anal. Calcd for $C_{11}H_{18}N_4Pt$ (401.38): C, 32.92; H, 4.52; N, 13.96. Found: C, 32.79; H, 4.48; N, 13.67. ^{1}H NMR (300.13 MHz, THF-d_8): δ 0.30 (s+sat, ^2J(Pt,H) = 66 Hz, 6H, Pt-CH_3), 3.66 (s+sat, ^4J(Pt,H) = 3,6 Hz, 6H, N-CH_3), 5.53 (d, ^2J(H,H) = 12 Hz, 1H, *exo*-CH_2), 5.84 (d+sat, ^2J(H,H) = 12 Hz, ^4J(Pt,H) = 11 Hz, 1H, *endo*-CH_2), 6.87 (d+sat, ^3J(H,H) = 2 Hz, ^4J(Pt,H) = 7 Hz, 2H, CH-Im), 7.08 (d+sat, ^3J(H,H) = 2 Hz, ^4J(Pt,H) = 4 Hz, 2H, CH-Im). ^{13}C{1H} NMR (75.47 MHz, THF-d_8): δ −8.34 (s+sat, ^1J(Pt,C) = 584 Hz, Pt-CH_3), 36.52 (s+sat, ^3J(Pt,C) = 23 Hz, N-CH_3), 63.21 (s+sat, ^3J(Pt,C) = 43 Hz, CH_2), 118.77 (s+sat, ^3J(Pt,C) = 19 Hz, CH-Im), 120.62 (s+sat, ^3J(Pt,C) = 23 Hz, CH-Im), 185.08 (s+sat, ^1J(Pt,C) = 788 Hz, N_2C-Im). IR (KBr, cm^{-1}): 3145(w); 3106(w); 2946(m); 2900(m); 2788(s); 1563(w); 1457(s); 1368(s). MS (LIFDI, toluene): m/z (%) 401.1 (100) $[M]^{+\bullet}$.

[$L^{i\text{-}Pr}PtMe_2$] (2c). $L^{i\text{-}Pr}H_2Br_2$ (355 mg, 0.90 mmol), potassium *tert*-butoxide (212 mg, 1.89 mmol), and [(cod)$PtMe_2$] (300 mg, 0.90 mmol) were suspended in THF (40 mL) and stirred at room

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temperature for 24 h. The light pink suspension was concentrated to half of its volume in vacuo, and dichloromethane (40 mL) and water (20 mL) were added. The phases were separated, and the aqueous phase was extracted three times with dichloromethane (5 mL). The combined organic phases were dried over magnesium sulfate, and two-thirds of the solvent was removed in vacuo. The brownish solution was layered with diethyl ether (10 mL) and stored overnight at −60 °C. The colorless solid was washed with cold diethyl ether and dried in vacuo. Yield: 230 mg (78%). Mp: 260 °C dec. Anal. Calcd for $C_{15}H_{26}N_4Pt$ (457.18): C, 39.38; H, 5.73; N, 12.25. Found: C, 39.33; H, 5.66; N, 11.90. ^{1}H NMR (300.51 MHz, DMSO-d_6): δ 0.17 (s+sat, ^2J(Pt,H) = 66 Hz, 6H, Pt-CH_3), 1.14 (d, ^3J(H,H) = 7 Hz, 6H, N-CH(CH_3)$_2$), 1.41 (d, ^3J(H,H) = 7 Hz, 6H, N-CH(CH_3)$_2$), 5.03 (sept, ^3J(H,H) = 7 Hz, 2H, N-CH(CH_3)$_2$), 5.67 (d+sat, ^2J(H,H) = 13 Hz, ^4J(Pt,H) = 12 Hz, 1H, *endo*-CH_2), 5.79 (d, ^2J(H,H) = 13 Hz, 1H, *exo*-CH_2), 7.27 (d, ^3J(H,H) = 2 Hz, 2H, CH-Im), 7.32 (d, ^3J(H,H) = 2 Hz, 2H, CH-Im). ^{13}C{^{1}H} NMR (75.56 MHz, DMSO-d_6): δ −7.51 (s+sat, ^1J(C,Pt) = 581 Hz, Pt-CH_3), 22.62 (N-CH(CH_3)$_2$), 23.41 (N-CH(CH_3)$_2$), 49.44 (N-C(CH_3)$_2$), 61.89 (CH_2), 115.63 (CH-Im), 119.73 (CH-Im), 180.52 (N_2C-Im). IR (ATR, cm^{-1}) = 3132(m); 2961(m); 2870(m); 2791(m); 1520(w); 1449(m); 1410(s); 1366(m); 1351(m); 1281(m); 1237(m); 1215(s); 1194(m); 1179(s); 1004(m); 797(m); 707(s); 669(s); 529(m); 534(m). MS (LIFDI, THF): *m*/*z* (%) 456.9 (100) [M]$^{+\bullet}$.

[L$^{i\text{-Pr}}$Pt(OMe)Me] (4). **2a** (211 mg, 0.46 mmol) was dissolved at 5 °C in methanol (15 mL) and stirred at this temperature for 2 days. All volatiles of the slightly turbid reaction mixture were removed in vacuo. The colorless product was dried in vacuo. Yield: 218 mg (100%). Mp: 107 °C dec. Anal. Calcd for $C_{15}H_{26}N_4OPt$ (473.48): C, 38.05; H, 5.53; N, 11.83. Found: C, 37.81; H, 5.43; N, 11.95. ^{1}H NMR (500.13 MHz, THF-d_8): δ 0.45 (s, 3H, Pt-CH_3), 1.21 (d, ^3J(H,H) = 7 Hz, 3H, N-CH(CH_3)$_2$), 1.27 (d, ^3J(H,H) = 7 Hz, 3H, N-CH(CH_3)$_2$), 1.44 (pseudo-t, 6H, N-CH(CH_3)$_2$), 3.77 (s, 3H, OCH_3), 4.90 (d, ^2J(H,H) = 12 Hz, 1H, *exo*-CH_2), 5.19 (sept, ^3J(H,H) = 9 Hz, 1H, N-CH(CH_3)$_2$), 6.13 (sept, ^3J(H,H) = 7 Hz, 1H, N-CH(CH_3)$_2$), 6.95 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im), 7.00 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im), 7.33−7.42 (m, 2H, *endo*-CH_2 and CH-Im), 8.16 (s, 1H, CH-Im). ^{13}C{^{1}H} NMR (125.76 MHz, THF-d_8): δ −5.27 (Pt-CH_3), 22.30 (N-CH(CH_3)$_2$), 22.73 (N-CH(CH_3)$_2$), 23.68 (N-CH(CH_3)$_2$), 24.42 (N-CH(CH_3)$_2$), 49.68 (N-C(CH_3)$_2$), 50.66 (N-C(CH_3)$_2$), 55.50 (OCH_3), 61.09 (CH_2), 115.36 (CH-Im), 115.43 (CH-Im), 120.11 (CH-Im), 120.92 (CH-Im), 156.28 (N_2C-Im), 181.86 (N_2C-Im). IR (ATR, cm^{-1}) = 2963(w); 2872(w); 2792(w); 2742(w); 1455(w); 1416(s); 1356(m); 1285(w); 1211(s); 1177(m); 1131(w); 1062(s); 1006(w); 880(w); 801(w); 717(m); 693(m); 674(m). MS (LIFDI, THF): *m*/*z* (%) 472.9 (100) [M]$^{+\bullet}$.

[L$^{t\text{-Bu}}$PtNp$_2$] (5a). [(cod)PtNp$_2$] (1.737 g, 3.90 mmol) and L$^{t\text{-Bu}}$H$_2$Br$_2$ (1.881 g, 4.29 mmol) were suspended in dimethyl sulfoxide (50 mL) and toluene (50 mL). Over a period of 1.5 h, a solution of potassium *tert*-butoxide (1.531 g, 13.65 mmol) in dimethyl sulfoxide (5 mL) and toluene (20 mL) was added, and the deep red solution was stirred for 12 h at room temperature. All volatile compounds apart from dimethyl sulfoxide were removed in vacuo. Dichloromethane (200 mL) and water (200 mL) were added to the remaining brown suspension. The organic phase was separated, and the aqueous phase was extracted four times with dichloromethane (50 mL). After the organic phase had been back-extracted three times with water (40 mL), the combined aqueous phases were extracted a last time with dichloromethane (35 mL). The combined organic phases were dried over magnesium sulfate and concentrated to 20 mL in vacuo. The colorless product crystallized at 8 °C and was washed with diethyl ether. Yield: 1.767 g (76%). Mp: 256 °C dec. Anal. Calcd for $C_{25}H_{46}N_4Pt$ (597.74): C, 50.23; H, 7.76; N, 9.37. Found: C, 49.97; H, 7.72; N, 9.26. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 0.79 (s, 18H, Pt-CH_2-C(CH_3)$_3$), 1.09 (d+sat, ^2J(H,H) = 12 Hz, ^2J(Pt,H) = 76 Hz, 2H, Pt-CH_2), 1.70 (s, 18H, N-C(CH_3)$_3$), 1.74 (d+sat, ^2J(H,H) = 12 Hz, ^2J(Pt,H) = 79 Hz, 2H, Pt-CH_2), 5.13 (d, ^2J(H,H) = 12 Hz, 1H, *exo*-CH_2), 6.87 (d, ^3J(H,H) = 2 Hz, 2H, CH-Im), 6.87 (d+sat, ^2J(H,H) = 12 Hz, ^4J(Pt,H) = 20 Hz, 1H, *endo*-CH_2), 7.02 (d, ^3J(H,H) = 2 Hz, 2H, CH-Im). ^{13}C{^{1}H} NMR (125.76 MHz, CD_2Cl_2): δ 31.56 (N-C(CH_3)$_3$), 34.18 (s+sat, ^1J(Pt,C) = 706 Hz, Pt-CH_2), 35.36 (s+sat, ^3J(Pt,C) = 45 Hz, Pt-CH_2-C(CH_3)$_3$), 36.10 (Pt-CH_2-C(CH_3)$_3$), 58.69 (N-C(CH_3)$_3$), 64.28 (s+sat, ^3J(Pt,C) = 64 Hz, CH_2), 117.81 (s+sat, ^3J(Pt,C) = 23 Hz, CH-Im), 118.86 (s+sat, ^3J(Pt,C) = 18 Hz, CH-Im), 188.44 (N_2C-Im). IR (KBr, cm^{-1}) = 3138(w); 3109(w); 2974(s); 2943(s); 2927(s); 2888(s); 2777(s); 1471(m); 1435(s); 1404(s); 1360(s); 1229(s); 821(m). MS (LIFDI, toluene) *m*/*z* (%) 526.3 (100) [M − Np]$^+$.

[L^{Me}PtNp$_2$] (5b). A colorless THF suspension (80 mL) of [(cod)PtNp$_2$] (500 mg, 1.12 mmol), L^{Me}H$_2$Br$_2$ (372 mg, 1.10 mmol), and potassium *tert*-butoxide (303 mg, 2.70 mmol) was stirred for 12 h at room temperature. Water and dichloromethane were added. The organic phase was separated, and the aqueous phase was extracted three times with 15 mL of dichloromethane. The organic phase was dried over magnesium sulfate. All volatile compounds were removed in vacuo. The remaining solid was washed with diethyl ether. Yield: 380 mg (67%). Mp: 242 °C dec. Anal. Calcd for $C_{19}H_{34}N_4Pt$ (513.58): C, 44.43; H, 6.67; N, 10.91. Found: C, 44.63; H, 6.51; N, 10.59. ^{1}H NMR (500.13 MHz, THF-d_8): δ 0.84 (s, 18H, Pt-CH_2-C(CH_3)$_3$), 1.22 (d+sat, ^2J(H,H) = 12 Hz, ^2J(Pt,H) = 80 Hz, 2H, Pt-CH_2), 2.06 (d+sat, ^2J(H,H) = 12 Hz, ^2J(Pt,H) = 72 Hz, 2H, Pt-CH_2), 3.66 (s, 6H, N-CH_3), 5.55 (d, ^2J(H,H) = 12 Hz, 1H, *exo*-CH_2), 6.15 (d +sat, ^2J(H,H) = 12 Hz,, ^4J(Pt,H) = 14 Hz, 1H, *endo*-CH_2), 6.78 (d, ^3J(H,H) = 2 Hz, 2H, CH-Im), 7.11 (d, ^3J(H,H) = 2 Hz, 2H, CH-Im). ^{13}C{^{1}H} NMR (125.76 MHz, THF-d_8): δ 34.82 (s+sat,^1J(Pt,C) = 673 Hz, Pt-CH_2), 36.42 (s+sat, ^3J(Pt,C) = 44 Hz, Pt-CH_2-C(CH_3)$_3$), 37.07 (s+sat, ^3J(Pt,C) = 23 Hz, N-CH_3), 36.59 (s, Pt-CH_2-C(CH_3)$_3$), 63.10 (s+sat, ^3J(Pt,C) = 48 Hz, CH_2), 119.02 (s+sat, ^3J(Pt,C) = 19 Hz, CH-Im), 120.73 (s+sat, ^3J(Pt,C) = 21 Hz, CH-Im), 187.88 (s+sat, ^1J(Pt,C) = 753 Hz, N_2C-Im). IR (KBr, cm^{-1}) = 3130(w); 2948(s); 2935(s); 2889(s); 2768(s); 1658(w); 1470(s); 1421(s). MS (LIFDI, toluene): *m*/*z* (%) 512.9 (100) [M]$^{+\bullet}$.

[L$^{t\text{-Bu}}$PtMeCl] (6a). Acetyl chloride (14.5 μL, 0.20 mmol) was added to a solution of **2a** (99 mg, 0.20 mmol) in dichloromethane (20 mL) and methanol (0.3 mL). The reaction mixture was stirred for 2 h at room temperature. All volatile compounds were removed in vacuo. The remaining solid was washed with THF. Yield: 97 mg (94%). Mp: 266 °C dec. Anal. Calcd for $C_{16}H_{27}ClN_4Pt$ (505.95): C, 37.98; H, 5.38; N, 11.07. Found: C, 37.76; H, 5.34; N, 10.78. ^{1}H NMR (300.51 MHz, CD_2Cl_2): δ 0.38 (s+sat, ^2J(Pt,H) = 59 Hz, 3H, Pt-CH_3), 1.78 (s, 9H, N-C(CH_3)$_3$), 1.83 (s, 9H, N-C(CH_3)$_3$), 5.30 (d, ^2J(H,H) = 12 Hz, 1H, *exo*-CH_2), 6.48 (d+sat, ^2J(H,H) = 12 Hz, ^4J(Pt,H) = 18 Hz, 1H, *endo*-CH_2), 7.00 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im), 7.02 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im), 7.09 (m, 2H, CH-Im). ^{13}C{^{1}H} NMR (125.76 MHz, CD_2Cl_2): δ −6.74 (s+sat, ^1J(Pt,C) = 553 Hz, Pt-CH_3), 31.52 (N-C(CH_3)$_3$), 31.82 (N-C(CH_3)$_3$), 59.53 (N-C(CH_3)$_3$), 64.44 (s+sat, ^3J(Pt,C) = 71 Hz, CH_2), 118.37 (s+sat, ^3J(Pt,C) = 22 Hz, CH-Im), 118.71 (CH-Im), 118.87 (CH-Im), 155.79 (N_2C-Im), 182.61 (N_2C-Im). IR (KBr, cm^{-1}): 3130(m); 2976(m); 2926(m); 2360(w); 2340(w); 1416(s); 1380(s); 1236(s). MS (LIFDI, CH_2Cl_2): *m*/*z* (%) 505.3 (100) [M]$^{+\bullet}$.

[L^{Me}PtMeCl] (6b). Acetyl chloride (14.5 μL, 0.20 mmol) was added to a solution of **2b** (75 mg, 0.19 mmol) in dichloromethane (30 mL) and methanol (1 mL). The reaction mixture was stirred for 1 h at room temperature. All volatile compounds were removed in vacuo. The remaining solid was washed with toluene. Yield: 62 mg (79%). Mp: 270 °C dec. Anal. Calcd for $C_{10}H_{15}ClN_4Pt$ (421.79): C, 28.48; H, 3.58; N, 13.28. Found: C, 28.40; H, 3.62; N,13.01. ^{1}H NMR (600.13 MHz, CD_2Cl_2): δ 0.44 (s+sat, ^2J(Pt,H) = 56 Hz, 3H, Pt-CH_3), 3.71 (s, 3H, N-CH_3), 3.96 (s, 3H, N-CH_3), 5.41 (d, ^2J(H,H) = 13 Hz, 1H, *exo*-CH_2), 6.07 (d+sat, ^2J(H,H) = 13 Hz, 1H, *endo*-CH_2), 6.82 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im), 6.85 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im), 7.03 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im), 7.05 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im). ^{13}C{^{1}H} NMR (150.90 MHz, CD_2Cl_2): δ −6.07 (s, Pt-CH_3), 37.47 (N-CH_3), 37.65 (N-CH_3), 63.27 (CH_2), 118.81 (CH-Im), 119.47 (CH-Im), 121.55 (CH-Im), 122.05 (CH-Im), 155.21 (N_2C-Im), 181.77 (N_2C-Im). IR (KBr, cm^{-1}): 3153(w); 3084(w); 2948(m);

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2918(m); 2797(s); 1668(w); 1564(m); 1464(s); 1434(s); 1401(s); 1248(s). MS (LIFDI, CH_2Cl_2): *m/z* (%) 422.0 (100) $[M + H]^+$.

[L$^{t\text{-Bu}}$PtNpCl] (7). To a solution of **5a** (195 mg, 0.33 mmol) in THF (15 mL) a solution of hydrogen chloride in diethyl ether (0.36 mL, 1.0 M) was added with a syringe pump over a period of 2 h at room temperature. The colorless suspension was stirred for 30 min, and all volatile compounds were removed in vacuo. The colorless solid was washed three times with 6 mL of toluene and dried in vacuo. Yield: 166 mg (91%). Mp: 227 °C dec. Anal. Calcd for $C_{20}H_{35}ClN_4Pt$ (562.06): C, 42.74; H, 6.28; N, 9.97. Found: C, 42.12; H, 6.02; N, 9.76. ^{1}H NMR (300.51 MHz, CD_2Cl_2): δ 0.79 (s, 9H, Pt-CH_2-C(CH_3)$_3$), 1.64 (s, 2H, Pt-CH_2), 1.81 (s, 9H, N-C(CH_3)$_3$), 1.82 (s, 9H, N-C(CH_3)$_3$), 5.27 (d, ^2J(H,H) = 12 Hz, 1H, *exo*-CH_2), 6.52 (d +sat, ^2J(H,H) = 12 Hz, ^4J(Pt,H) = 18 Hz, 1H, *endo*-CH_2), 6.98 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im), 7.02 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im), 7.07 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im), 7.09 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im). ^{13}C{^{1}H} NMR (125.76 MHz, CD_2Cl_2): δ 31.50 (N-C(CH_3)$_3$), 32.01 (N-C(CH_3)$_3$), 32.54 (Pt-CH_2), 34.57 (s+sat, ^3J(Pt,C) = 36 Hz, Pt-CH_2-C(CH_3)$_3$), 35.62 (Pt-CH_2-C(CH_3)$_3$), 59.43 (N-C(CH_3)$_3$), 59.52 (N-C(CH_3)$_3$), 64.56 (CH_2), 118.37 (CH-Im), 118.72 (CH-Im), 118.77 (CH-Im), 118.79 (CH-Im), 157.48 (N_2C-Im), 183.73 (N_2C-Im). IR (KBr, cm^{-1}) = 3130(m); 2975(s); 2943(s); 2889(m); 2847(m); 1418(s); 1376(s); 1322(m); 1235(s); 1211(s); 718(m). MS (LIFDI, CH_2Cl_2): *m/z* (%) 562.3 (100) $[M + H]^+$.

[L$^{t\text{-Bu}}$PtMeH] (8). A colorless THF suspension (40 mL) of **6** (50 mg, 0.10 mmol) and sodium trimethoxyborohydride (64 mg, 0.50 mmol) was stirred at 65 °C for 1 h. All volatile compounds were removed in vacuo. Toluene (40 mL) was added, and the solution was stirred for 15 min, filtered, and evaporated to dryness. The remaining solid was washed with *n*-hexane. Yield: 37 mg (78%). Mp: 162 °C dec. Anal. Calcd for $C_{16}H_{28}N_4Pt$ (471.50): C, 40.76; H, 5.98; N, 11.88. Found: C, 41.06; H, 6.00; N, 11.71. ^{1}H NMR (300.13 MHz, THF-d_8): δ −7.58 (s+sat, ^1J(Pt,H) = 1047 Hz, 1H, Pt-H), 0.48 (s+sat, ^2J(Pt,H) = 68 Hz, 3H, Pt-CH_3), 1.74 (s, 9H, N-C(CH_3)$_3$), 1.78 (s, 9H, N-C(CH_3)$_3$), 5.58 (d, ^2J(H,H) = 12 Hz, 1H, *exo*-CH_2), 6.16 (d+sat, ^2J(H,H) = 12 Hz, ^4J(Pt,H) = 17 Hz, 1H, *endo*-CH_2), 7.00 (d+sat, ^3J(H,H) = 2 Hz, ^4J(Pt,H) = 8 Hz, 1H, CH-Im), 7.10 (d, ^3J(H,H) = 2 Hz, 2H, CH-Im), 7.18 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im). ^{13}C{^{1}H} NMR (75.47 MHz, THF-d_8): δ −23.91 (Pt-CH_3), 30.23 (s+sat, ^4J(Pt,C) = 21 Hz, N-C(CH_3)$_3$), 31.78 (s+sat, ^4J(Pt,C) = 7 Hz, N-C(CH_3)$_3$), 58.47 (N-C(CH_3)$_3$), 58.65 (N-C(CH_3)$_3$), 63.91 (CH_2), 116.46 (CH-Im), 117.46 (CH-Im), 117.71 (CH-Im), 118.52 (CH-Im), 183.18 (N_2C-Im), 189.66 (N_2C-Im). IR (THF, cm^{-1}) = 3129(m); 2975(s); 2904(s); 2795(m); 2002(s, Pt-H); 1446(s); 1372(s); 1261(s); 705(m). MS (LIFDI, toluene): *m/z* (%) 455.2 (100) $[M - CH_4]^{+\bullet}$.

[L$^{t\text{-Bu}}$PtNpH] (9). A colorless THF suspension (50 mL) of **7** (208 mg, 0.37 mmol) and sodium trimethoxyborohydride (470 mg, 3.70 mmol) was stirred at 65 °C for 5 h. All volatile compounds were removed in vacuo. Toluene (50 mL) was added, and the solution was stirred for 15 min, filtered, and evaporated to dryness. The remaining colorless solid was washed with *n*-hexane. Yield: 170 mg (87%). Mp: 206 °C dec. Anal. Calcd for $C_{20}H_{36}N_4Pt$ (527.61): C, 45.53; H, 6.88; N, 10.62. Found: C, 45.51; H, 6.79; N, 10.73. ^{1}H NMR (500.13 MHz, toluene-d_8): δ −7.12 (s+sat, ^1J(Pt,H) = 1083 Hz, 1H, Pt-H), 1.61 (s, 9H, Pt-CH_2-C(CH_3)$_3$), 1.62 (s, 9H, N-C(CH_3)$_3$), 1.68 (s, 9H, N-C(CH_3)$_3$), 2.28 (d+sat, ^2J(H,H) = 12 Hz, ^2J(Pt,H) = 84 Hz, 1H, Pt-CH_2), 2.53 (d+sat, ^2J(H,H) = 12 Hz, ^2J(Pt,H) = 78 Hz, 1H, Pt-CH_2), 4.04 (d, ^2J(H,H) = 12 Hz, 1H, *exo*-CH_2), 5.98 (d+sat, ^2J(H,H) = 12 Hz, ^4J(Pt,H) = 17 Hz, 1H, *endo*-CH_2), 6.09 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im), 6.16 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im), 6.32 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im), 6.33 (d, ^3J(H,H) = 2 Hz, 1H, CH-Im). ^{13}C{^{1}H} NMR (125.76 MHz, THF-d_8): δ 30.17 (s+sat, ^4J(Pt,C) = 22 Hz, N-C(CH_3)$_3$), 30.45 (Pt-CH_2), 31.84 (N-C(CH_3)$_3$), 35.36 (s+sat, ^3J(Pt,C) = 60 Hz, Pt-CH_2-C(CH_3)$_3$), 35.49 (Pt-CH_2-C(CH_3)$_3$), 58.45 (N-C(CH_3)$_3$), 58.60 (N-C(CH_3)$_3$), 63.94 (s+sat, ^3J(Pt,C) = 63 Hz, CH_2), 116.37 (s+sat, ^3J(Pt,C) = 23 Hz, CH-Im), 117.30 (s+sat, ^3J(Pt,C) = 20 Hz, CH-Im), 117.89 (s+sat, ^3J(Pt,C) = 22 Hz, CH-Im), 118.57 (s+sat, ^3J(Pt,C) = 17 Hz, CH-Im), 184.18 (N_2C-Im), 191.14 (N_2C-Im). IR (THF, cm^{-1}) = 3141(w); 2979(s); 2926(s); 2846(m); 1986(s, Pt-H); 1413(s); 1372(s); 1292(s); 699(m). MS (LIFDI, toluene): *m/z* (%) 455.2 (100) $[M - NpH]^{+\bullet}$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, and CIF files, giving NMR spectra and crystallographic data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00204.

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Notes

The authors declare no competing financial interest.

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