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From NHC to Imidazolyl Ligand: Synthesis of Platinum and Palladium Complexes d^{10}-[$M(NHC)_2$] (M = Pd, Pt) of the NHC 1,3-Diisopropylimidazolin-2-ylidene

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Supporting Information

ABSTRACT: The widely held belief that N-heterocyclic carbenes (NHCs) act only as innocent spectator ligands is not always accurate, even in the context of well-explored reactions. Ligand exchange in the conversion of [Pt(PPh_3)$_2$(η^2-C_2H_4)] (**3**) to [Pt(iPr$_2$Im)$_2$] (**2**) depends critically on the particular reaction conditions employed, with slight changes leading to vastly different outcomes. In addition to [Pt(iPr$_2$Im)$_2$] (**2**), complexes [Pt(iPr$_2$Im)(PPh_3)(η^2-C_2H_4)] (**5**) and *trans*-[Pt(iPr$_2$Im)$_2$(iPr-Im*)(H)] (**6**) were isolated and in the case of **6** fully characterized. Complex **5** represents the first mixed-olefin complex in transition metal chemistry containing both an NHC and a phosphine ligand. Chemical degradation of the NHC was shown to yield the new imidazole-2-yl iPr-Im* in **6**. Therefore, the synthesis of [Pt(iPr$_2$Im)$_2$] (**2**) via metallic reduction of the ionic precursor [Pt(iPr$_2$Im)$_3$(Cl)]$^+$Cl$^-$ (**9**) is favorable, a procedure adaptable to analogous palladium compounds. While [Pd(iPr$_2$Im)$_3$(Cl)]$^+$Cl$^-$ (**8**) is the only product obtained from the reaction of iPr$_2$Im and $PdCl_2$, neutral [Pt(iPr$_2$Im)$_2$(Cl)$_2$] (**10**), formed as a mixture of its two stereoisomers ***cis*-10** and ***trans*-10**, is available through precise control of the stoichiometry in the reaction of $PtCl_2$ and exactly 2 equiv of iPr$_2$Im.

INTRODUCTION

The activation and functionalization of element−element bonds using transition metal complexes play a pivotal role in homogeneous catalysis. Bond activation is most often achieved by σ-bond metathesis or oxidative addition to low-valent, electron-rich transition metal complexes. In this respect, complexes of d^8-transition metals play a particularly important role.[1] Catalytic cycles proposed for group 10 transition metal catalysts typically involve d^{10}-[ML_2] complexes (L = neutral two-electron-donor ligand, e.g., a phosphine), with d^8-[ML_2(A)(B)] complexes (A, B = anionic two-electron-donor ligand, e.g., a halide), products of the oxidative addition of A−B to d^{10}-[ML_2], as key intermediates. Thus, in investigations concerning the isolation and reactivity of unsaturated, zerovalent transition metal complexes, palladium and platinum have been the focus of research for more than 50 years.[2] Complexes with electronically and coordinatively unsaturated d^{10}-metal centers serve either as starting materials for entrance into catalytic cycles or as precursors for model reactions. In addition, complexes that easily transfer unsaturated complex fragments, such as olefin complexes [$M^0(PR_3)_2(\eta^2$-$C_2H_4)$], [$M^0(PR_3)_n$] (n = 3, 4), and *in situ*-generated or isolated complexes [$M^0(PR'_3)_2$] (R′ = very bulky substituent) have also demonstrated a rich chemistry in terms of element−element bond activation reactions.[3] The first zerovalent complexes of the type [$M^0(PPh_3)_n$] (M = Ni, Pd) were reported by Malatesta and co-workers,[4] synthesized through the reduction of [$M(PPh_3)_2(Cl)_2$] using KOH in ethanol in the presence of excess PPh_3. Since these early investigations on ($M^0(PPh_3)_n$ (n = 2, 3, 4) complexes, bulky phosphine ligands have proven to be especially appropriate for the stabilization of two-coordinate 14-electron complexes.[5] Beyond catalysis, complexes of the type [$M^0(PR_3)_2$] (e.g., [Pt(PCy_3)$_2$]) have lately been used as metal bases for the stabilization of novel metal-only Lewis pairs with transition metal Lewis bases, as well as transition metal borylene, oxoboryl, iminoboryl, and diborene complexes.[6]

In the last two decades, N-heterocyclic carbenes (NHCs) have emerged as one of the most important classes of spectator ligands in organometallic chemistry.[7] Due to their superior σ-donor capabilities as compared to phosphines, these ligands are widely used in transition metal chemistry and catalysis. We recently communicated the syntheses of [Pd(iPr$_2$Im)$_2$] (**1**) (iPr$_2$Im = 1,3-diisopropylimidazolin-2-ylidene) and [Pt(iPr$_2$Im)$_2$] (**2**) via the reduction of [M(iPr$_2$Im)$_3$(Cl)]$^+$Cl$^-$ (M = Pd, **8**; Pt, **9**).[8] Herein we provide a more detailed account on synthetic pathways used to construct these basic-metal 14 valence electron (VE) complexes.

RESULTS AND DISCUSSION

Two major pathways may be envisioned for the synthesis of 14-VE metal(0) complexes starting from suitable metal(II) halides: One is implemented by a ligand exchange from suitable metal(0) precursors; the other involves the reduction of complexes in an oxidation state higher than 0. Metal(0)

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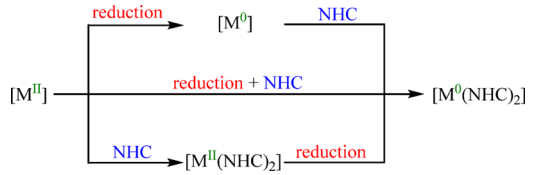
complexes suitable for ligand exchange reactions with NHC usually contain other 2-VE donor ligands, such as olefins or phosphines (Scheme 1, top). The metal(0) precursor used is usually also prepared via reduction of a metal halide derivative in the presence of these neutral donor ligands.[9] The other approach utilizes the introduction of the NHC ligand in a metal(II) halide (or in a higher formal oxidation state) with formation of NHC complexes in an oxidation state higher than 0 (e.g., +II, Scheme 1, bottom) followed by a reductive step to give the 14-VE $[M(NHC)_2]$. Both steps might be successfully combined in a one-pot approach starting directly from a metal(II) halide (Scheme 1, center).

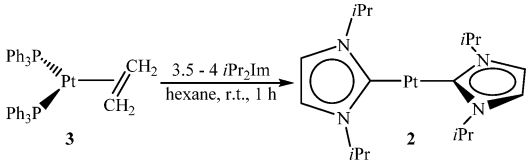
Scheme 1. Synthetic Strategies for $[M(NHC)_2]$ Synthesis, Starting from Metal(II) Precursor: (i) Reduction to a Metal(0) Complex Followed by a Ligand Exchange (Top); (ii) Reduction of a NHC-Stabilized Metal(II) Halide Complex and Subsequent Reduction of the NHC Metal(II) Complex (Bottom); (iii) Combination of Both Steps (i and ii) in a One-Pot Procedure (Center)



These pathways have been applied already for the synthesis of NHC complexes of the metals palladium and platinum.[10] For palladium, two major pathways for the synthesis of complexes $[M(NHC)_2]$ have been established: (i) ligand substitution at bis(tri-*ortho*-tolylphosphine)palladium(0), $[Pd(P\{oTol\}_3)_2]$ ($oTol$ = 2-CH_3-C_6H_4),[10a] and (ii) ligand substitution at dimeric methallyl(chlorido)palladium(II), $[(Pd(\eta^3\text{-}C_4H_7)(Cl)_2]$, in the presence of sodium dimethylmalonate.[10b] The latter procedure does not require the unappealing synthesis of the $[Pd(P\{oTol\}_3)_2]$ precursor,[11] but the stoichiometry has to be controlled carefully due to equilibration reactions.[10c] For platinum, complexes $[Pt(NHC)_2]$ have been isolated with the bulky NHCs Mes_2Im and $Dipp_2Im$ (Mes = 1,3,5-trimethylphenyl, Dipp = 2,6-diisopropylphenyl), starting from the NHC and $[Pt(COD)_2]$ or $[Pt(COD)(Me)_2]$, respectively.[12a,c] Intramolecular C−H bond activation of the ligand occurred for $[Pt(Mes_2Im)_2]$ in the latter case,[12c] and this approach also seems to be limited, since the use of tBu_2Im leads to formation of *cis*-$[Pt(tBu_2Im)(^atBu_2Im')(H)(Me)_2]$ (^{a} denotes coordination at the backbone as an "abnormal" NHC). Furthermore, the synthesis of $[Pt(Mes_2ImH_2)_2]$ (Mes_2ImH_2 = 1,3-di(mesityl)-imidazolidin-2-ylidene) via ligand exchange at $[Pt(PCy_3)_2]$ has been reported by Braunschweig et al., but the use of tBu_2Im as the carbene afforded mixed substituted $[Pt(tBu_2Im)(PCy_3)]$.[12d]

All attempts to synthesize $[Pd(iPr_2Im)_2]$ (**1**) in significant amounts using ligand exchange with a suitable palladium(0) precursor failed in our hands. Selective exchange of phosphine ligands did not occur, whereas reactions of $[Pd_2(dba)_3]$ with iPr_2Im led to cyclopropanation of the dibenzylideneacetone ligand by iPr_2Im.[13,14] In contrast, $[Pt(iPr_2Im)_2]$ (**2**) is accessible by ligand exchange reactions starting from the platinum complex $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ (**3**) and an excess (3.5−4 equiv) of iPr_2Im in 73% yield (see Scheme 2). Compound **3** emerged as the most suitable starting material, whereas homoleptic phosphine complexes such as $[Pt(PPh_3)_4]$, $[Pt(PPh_3)_3]$, and $[Pt(PCy_3)_2]$ did not afford $[Pt(iPr_2Im)_2]$ upon reaction with iPr_2Im. The use of $[Pt(COD)_2]$ led to complex **2** in small quantities, but this reaction seems to be in general more sensitive toward the degradation of the metal precursor into elemental platinum compared to the reaction of $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ (**3**).

Scheme 2. Synthesis of $[Pt(iPr_2Im)_2]$ (2) from $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ (3)



In the past decades various synthetic pathways for $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ (**3**) have been published,[15] whereof a procedure by Nagel et al.[15f] features the best results to our experience. This route involves the reduction of the Pt(II) precursor *cis*-$[Pt(PPh_3)_2(Cl)_2]$ (**4**) with $NaBH_4$ in ethanol in the presence of ethylene. *cis*-$[Pt(PPh_3)_2(Cl)_2]$ is readily prepared from $K_2[PtCl_4]$ and triphenylphosphine. Alternatively, *cis*-$[Pt(PPh_3)_2(Cl)_2]$ can be synthesized within 2 h from the reaction of hexachloroplatinic acid $H_2[PtCl_6]$ with an excess of PPh_3 in xylene at 140 °C in excellent yields (see Experimental Section). No *trans*-isomer has been detected from this reaction. Drew et al. applied a similar strategy for the synthesis of $[Pt(COD)(Cl)_2]$ from $H_2[PtCl_6]$ and 1,5-cyclooctadiene.[16]

Although $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ (**3**) can be converted to $[Pt(iPr_2Im)_2]$ (**2**) by reacting it with 3.5 equiv of iPr_2Im for 1 h at room temperature in *n*-hexane, this reaction is rather sluggish and reveals some peculiarities; that is, the outcome of this reaction is completely different if one of these parameters is modified. First of all, if a "stoichiometric" amount (2 equiv) of iPr_2Im was used for the reaction with $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$, a complex mixture of several compounds can be detected, which contains only minor amounts of $[Pt(iPr_2Im)_2]$ (**2**). Although we have not clarified the identity of each product in this mixture, we have obtained small amounts of single crystals of the complex $[Pt(iPr_2Im)(PPh_3)(\eta^2\text{-}C_2H_4)]$ (**5**) suitable for X-ray analysis in one case (see Figure 1). The four atoms (P, C1, C2, C3) attached to the platinum atom of this compound reveal an almost ideal coplanar alignment, resulting in a pseudo trigonal-planar coordination sphere at platinum (coordinated with the phosphine, the NHC, and the olefin). The C−C bond length of the ethylene ligand (C2−C3 1.458(9) Å) is in the range of a carbon−carbon single bond, as typically observed for olefins coordinated to electron-rich transition metals.

We recently reported the bis-NHC ethylene platinum complex $[Pt(iPr_2Im)_2(\eta^2\text{-}C_2H_4)]$, which is stable only in an ethylene atmosphere and decomposes to $[Pt(iPr_2Im)_2]$ (**2**) if the atmosphere is changed to argon or the system is evacuated.[8] Assuming that the bisphosphine complex $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ (**3**) as well as the mixed substituted complex $[Pt(iPr_2Im)(PPh_3)(\eta^2\text{-}C_2H_4)]$ (**5**) are stable compounds, we propose that the phosphine ligands of $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ are consecutively replaced by iPr_2Im in an equilibrium that ultimately leads to $[Pt(iPr_2Im)_2(\eta^2\text{-}C_2H_4)]$, which decomposes upon isolation/evacuation to $[Pt(iPr_2Im)_2]$ (**2**) (see Scheme 3). As a consequence of this equilibrium, an excess of iPr_2Im has to be used to obtain $[Pt(iPr_2Im)_2]$ (**2**) from the reaction of $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ (**3**) and iPr_2Im in a significant amount (*vide supra*). If the reaction of $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ with 2

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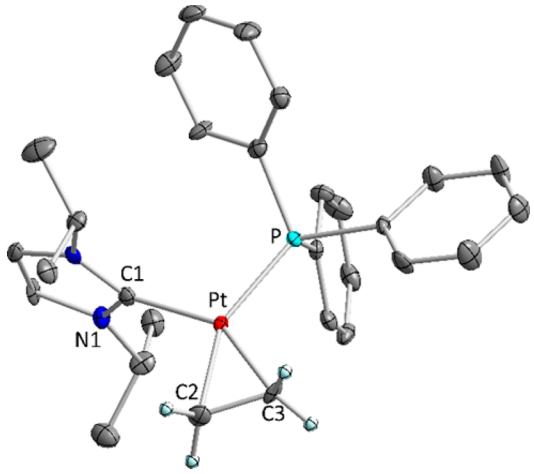
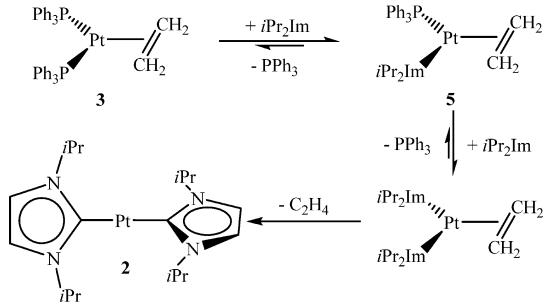


Figure 1. Molecular structure of $[Pt(iPr_2Im)(PPh_3)(\eta^2\text{-}C_2H_4)]$ (**5**) in the solid state (ellipsoids set at the 50% probability level). Hydrogen atoms have been omitted for clarity with the exception of the ethylene ligand. Selected bond lengths (Å) and angles (deg): Pt−P 2.2547(17), Pt−C1 2.059(7), Pt−(center C2−C3) 1.9720(4), C2−C3 1.458(9); P−Pt−C1 99.94(16), P−Pt−(center C2−C3) 132.60(4), C1−Pt−(center C2−C3) 127.46(18), (plane Pt−P−C1)−(plane Pt−C2−C3) 3.4(3).

Scheme 3. Stepwise Substitution of Phosphine Ligands with NHC in $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$-Type Complexes: $[Pt(iPr_2Im)_2(\eta^2\text{-}C_2H_4)]$ Transforms to $[Pt(iPr_2Im)_2]$ (2) upon Isolation

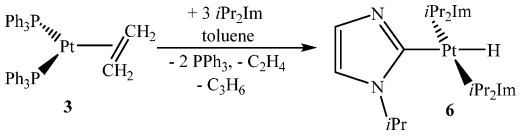


equiv of iPr_2Im is performed in an NMR tube, we indeed observe small amounts of $[Pt(iPr_2Im)_2(\eta^2\text{-}C_2H_4)]$ (**5**). A similar stepwise exchange of phosphine ligands with NHCs has been reported by Braunschweig et al. at $[PtL_2]$ complexes bearing bulky phosphines (L = PCy_3) and using the sterically demanding NHC Mes_2ImH_2.[12d]

As another consequence of this equilibrium, nonpolar solvents such as *n*-hexane are the solvent of choice. The complex $[Pt(iPr_2Im)_2]$, once formed, precipitates from *n*-hexane solutions and shifts the equilibrium to the side of the product. As another advantage, once precipitated, $[Pt(iPr_2Im)_2]$ is not available for further transformations. If this reaction is carried out in solvents such as benzene, toluene, or thf, in which complex **2** is soluble and remains dissolved, it readily reacts with additional NHC to give the complex *trans*-$[Pt(iPr_2Im)_2(iPr\text{-}Im^*)(H)]$ (**6**) (*i*Pr-Im* = 1-isopropylimidazole-2-yl) (see Scheme 4). Complex **6** was isolated from the reaction of $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ and iPr_2Im in 18% yield and characterized using IR, ^1H, $^{13}C\{^1H\}$, and ^{195}Pt NMR spectroscopy, and elemental and X-ray analysis.

Although isolated yields of **6** are considerably low, *trans*-$[Pt(iPr_2Im)_2(iPr\text{-}Im^*)(H)]$ is the major product if the reaction

Scheme 4. Synthesis of *trans*-$[Pt(iPr_2Im)_2(iPr\text{-}Im^*)(H)]$ (6) from $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ (3)



is performed on an NMR scale. Propylene can be detected in the reaction mixture, and, most significantly, a hydride resonance at −6.11 ppm evolves with platinum satellites ($^1J_{PtH}$ = 802.7 Hz). In the ^{195}Pt NMR spectrum, a broad resonance at −4465 ppm emerges, which is significantly shifted from the ^{195}Pt NMR resonance of **2** at δ = −5942 ppm. The carbene carbon atoms are detected at 175.8 ppm in the $^{13}C\{^1H\}$ NMR spectrum, whereas the deprotonated imidazolyl carbon atom gives rise to a resonance at 172.5 ppm. The allocation of both signals was validated in an $^1H-^{13}C$ HMBC analysis by the cross-peaks to the corresponding backbone protons (see Supporting Information). We propose that complex $[Pt(iPr_2Im)_2]$ (**2**) is formed during this reaction and subsequently reacts with another equivalent of iPr_2Im to give complex **6**, since the reaction of isolated **2** with 1 equiv of the NHC in C_6D_6 at 80 °C also leads to *trans*-$[Pt(iPr_2Im)_2(iPr\text{-}Im^*)(H)]$ (**6**) as the major product.

Colorless single crystals of **6** suitable for X-ray diffraction were grown by slow diffusion of *n*-hexane into a saturated solution of the compound in toluene (see Figure 2).

Complex **6** adopts a square-planar coordination spanned by two NHC ligands, one hydride ligand and the imidazolyl ligand. Although the imidazolyl ligand may look at first glance like an NHC, it has an entirely different electronic structure (see Figure 3). Consequently, the endocyclic bond distances within

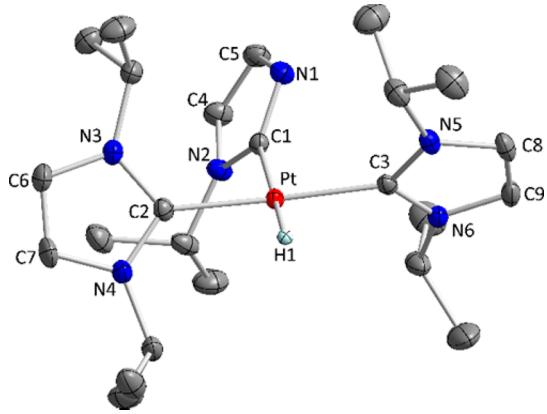


Figure 2. Molecular structure of *trans*-$[Pt(iPr_2Im)_2(iPr\text{-}Im^*)(H)]$ (**6**) in the solid state (ellipsoids set at the 50% probability level). All hydrogen atoms with exception of the isotropically refined H1 have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt−H1 1.64(3), Pt−C1 2.083(3), Pt−C2 2.018(3), Pt−C3 2.012(2), C1−N1 1.348(4), C1−N2 1.380(4), N1−C5 1.372(3), N2−C4 1.383(4), C4−C5 1.348(5), C2−N3 1.361(3), C2−N4 1.361(4), N3−C6 1.374(4), N4−C7 1.381(4), C6−C7 1.340(5), C3−N5 1.357(4), C3−N6 1.356(3), N5−C8 1.385(4), N6−C9 1.391(4), C8−C9 1.326(4), (plane C1−C2−C3−H1)−Pt 0.0811(2); C1−Pt−H1 175.98(9), C2−Pt−C3 173.21 (10), (plane Pt−C1−C2−C3−H1)−(plane N1−C1−N2) 57.51(14), (plane Pt−C1−C2−C3−H1)−(plane N−C2−N) 56.78(14), (plane Pt−C1−C2−C3−H1)−(plane N−C3−N) 67.31(11).

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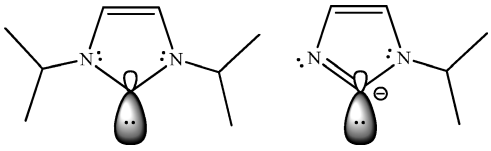


Figure 3. Electronic structure of the NHC ligand *i*Pr$_2$Im (left) and the imidazolyl ligand (right) in *trans*-[Pt(*i*Pr$_2$Im)$_2$(*i*Pr-Im*)(H)] (**6**).

the ring are significantly affected. The carbene carbon atom of *i*Pr$_2$Im features an electron sextet stabilized with a π system formed by the two endocyclic lone pairs of the nitrogen atoms and the C−C double bond of the backbone. For the imidazolyl ligand one of the lone pairs is located in an exocyclic nitrogen sp^2 orbital and the six electron π system contains two double bonds and the lone pair of the *i*Pr-substituted nitrogen atom (see Figure 3). This fact is nicely reflected in the X-ray crystal structure of complex **6**; that is, the distance N1−C1 (1.348(4) Å) is shorter than N2−C1 (1.380(4) Å), and the Pt−C1 bond (2.083(3) Å) is significantly enlarged compared to the Pt−C bonds to the NHC carbene carbon atoms (Pt−C2 2.018(3), Pt−C3 2.012(2) Å). These alternating bond lengths match with the Lewis structure given in Figure 3 and differ from the situation in the unimpaired *i*Pr$_2$Im ligands. Consequently, *i*Pr-Im* may be best described as an anionic vinyl/aryl substituent. Nolan and co-workers described the complex *cis*-[Pt(*t*Bu$_2$Im)-(^{a}*t*Bu$_2$Im)(Me)$_2$] containing a normal- and an abnormal (vinylic)-coordinated NHC ligand.[12c] Therein the Pt−^{a}C bond is slightly elongated (2.074(4) Å) compared to the Pt−C_{NHC} bond to the classical *t*Bu$_2$Im ligand (Pt−C 2.058(4) Å), and the Pt−^{a}C observed there is very close to the Pt−C1 length in **6**. However, the elongation of the imidazolyl Pt−C bond may also be caused by the structural *trans* effect of the hydride ligand, leading to an increase of up to 0.08 Å in square-planar [M(NHC)$_3$(H)] (M = Ni, Pd) complexes.[17]

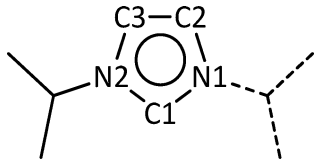
To our knowledge there is currently no example of (*i*Pr-Im*) as a ligand in organometallic chemistry, but a similar system was postulated in ruthenium chemistry by Whittlesey et al. as an intermediate in the degradation of NHC ligands.[18] Generally, imidazolyl (or imidazolinyl[19]) complexes are very reactive and rarely have been isolated.[20] Furthermore, there are some examples characterized in solution.[21] However, none of these emerged from the degradation of an NHC.

All structurally characterized imidazolyl complexes feature a slightly shorter bond of the coordinated carbon atom to the "naked" nitrogen atom, as observed in compound **6**.[20b,e,20h] Although the differences are borderline significant, we consider the structure given in Figure 3, as a dominant resonance form.

DFT calculations (TURBOMOLE, RIDFT, BP86/def2-TZVPP; see Supporting Information) reveal that the reaction of [Pt(*i*Pr$_2$Im)$_2$] with *i*Pr$_2$Im to give *trans*-[Pt(*i*Pr$_2$Im)$_2$(*i*Pr-Im*)(H)] (**6**) and propylene is favorable by −48.3 kJ/mol.

Since X-ray diffraction is generally not a very reliable method to distinguish between hydrogen atoms and lone pairs, the N2 atom might also be protonated to give an *i*PrHIm-type NHC ligand. However, *i*PrHIm would be a neutral ligand and *trans*-[Pt(*i*Pr$_2$Im)$_2$(*i*Pr-Im*)(H)] (**6**) thus a paramagnetic Pt(I) complex. Furthermore, we do not have any NMR spectroscopic indications for a N−H function in the molecule. Although we tried to minimize line broadening by using a nonpolar solvent (C_6D_6), we never observed a N−H signal or coupling to the backbone protons in the ^{1}H NMR spectrum nor cross-peaks in 2D NMR experiments (^{1}H−^{1}H COSY, ^{1}H−^{13}C HMBC). Furthermore, since *i*Pr-Im* is a novel ligand in transition metal chemistry, we performed DFT calculations (TURBOMOLE, RIDFT, BP86/def2-TZVPP; see Supporting Information) on *i*Pr$_2$Im and (*i*Pr-Im*)$^-$. A comparison of the experimentally observed bond lengths within the imidazole ring of *i*Pr$_2$Im and (*i*Pr-Im*)$^-$ of complex **6** and the calculated metric parameters of *i*Pr$_2$Im and (*i*Pr-Im*)$^-$ are given in Table 1. The elongation

Table 1. Experimentally Observed Bond Lengths of *i*Pr$_2$Im and the Imidazolyl Ligand *i*Pr-Im* in *trans*-[Pt(*i*Pr$_2$Im)$_2$(*i*Pr-Im*)(H)] (6) (X-ray) and a comparison to Calculated (DFT, BP86/TZVPP) Bond Lengths



	X-ray data of **6**		calculated free ligands	
	*i*Pr$_2$Im	(*i*Pr-Im*)$^-$	*i*Pr$_2$Im	(*i*Pr-Im*)$^-$
Pt−C	2.011	2.083		
C1−N1	1.359	1.348	1.372	1.365
C1−N2	1.359	1.380	1.372	1.414
N1−C2	1.380	1.372	1.391	1.382
N2−C3	1.386	1.382	1.391	1.392
C2−C3	1.333	1.348	1.363	1.379

of the C1−N2 distance calculated for (*i*Pr-Im*)$^-$ (1.414 Å) compared to *i*Pr$_2$Im (1.372 Å) is nicely reflected in the X-ray crystal structure of **6** (*i*Pr-Im*, 1.380 Å; *i*Pr$_2$Im, 1.359 Å).

Up to now we have demonstrated that the reaction of [Pt(PPh$_3$)$_2$(η^2-C$_2$H$_4$)] (**3**) with *i*Pr$_2$Im to give [Pt(*i*Pr$_2$Im)$_2$] (**2**) critically depends on the solvent and the stoichiometry employed, and the use of an excess of the NHC in *n*-hexane at room temperature has proven to be most advantageous for this transformation. However, even if these conditions are met, prolonged reactions times also lead to the almost quantitative formation of an unwanted reaction product. Under these conditions an ionic compound was isolated, which contains a square planar hydrido platinum(II) complex cation [Pt-(*i*Pr$_2$Im)$_3$(H)]$^+$ (**7**). The cation was identified using ^{1}H NMR spectroscopy, which reveals the typical spectroscopic signature of a T-shaped alignment of three *i*Pr$_2$Im ligands (as has been observed in [M(*i*Pr$_2$Im)$_3$(Cl)]$^+$Cl$^-$; M = Pd, **8**; Pt, **9**; see below). The resonances of the hydride ligand at −7.48 ppm ($^1J_{PtH}$ = 918.1 Hz) and the NHC backbone protons at 6.84 ppm ($^4J_{PtH}$ = 10.0 Hz) and 8.24 ppm ($^4J_{PtH}$ = 7.1 Hz) reveal ^{195}Pt satellites. Due to its low solubility, we could not characterize the anionic part of this compound properly. This complex is only poorly soluble in hydrocarbons or ethers and decomposes in other solvents. However, we have obtained crystals suitable for X-ray diffraction from a solution in methylene chloride, in which the anion was completely displaced by chloride and the hydride ligand was partially displaced (6%) by a chloride ligand, yielding a crystal of the molecular formula [M(*i*Pr$_2$Im)$_3$(Cl)$_{0.06}$H$_{0.94}$]$^+$Cl$^-$ (see Supporting Information).

All these drawbacks observed for the reaction of [Pt-(PPh$_3$)$_2$(η^2-C$_2$H$_4$)] (**3**) with *i*Pr$_2$Im led us to more closely investigate the reactivity of palladium(II) and platinum(II) chlorides with *i*Pr$_2$Im and the subsequent reduction of the NHC-stabilized halides. The reaction of PtCl$_2$ with 2 equiv of

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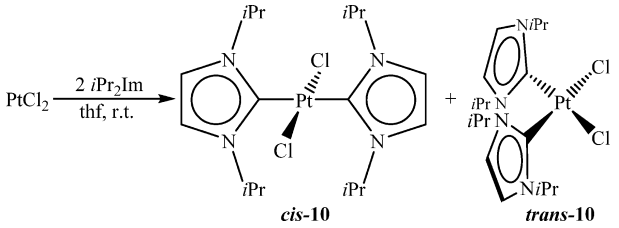
*i*Pr$_2$Im leads to a mixture of the two isomers *cis*-[Pt(*i*Pr$_2$Im)$_2$(Cl)$_2$] (***cis*-10**) and *trans*-[Pt(*i*Pr$_2$Im)$_2$(Cl)$_2$] (***trans*-10**) in a ratio of 1:3 in good yield (see Scheme 5). According to

Scheme 5. Reaction of PtCl$_2$ with Two Equivalents of *i*Pr$_2$Im: Synthesis of *cis*-[Pt(*i*Pr$_2$Im)$_2$(Cl)$_2$] (*cis*-10) and *trans*-[Pt(*i*Pr$_2$Im)$_2$(Cl)$_2$] (*trans*-10)



DFT calculations (TURBOMOLE, RIDFT, BP86/def2-TZVPP; see Supporting Information), the *trans* isomer is energetically favored by 17.8 kJ/mol. A synthetic procedure for ***trans*-10** starting from the organonitrile adducts of PtCl$_2$, [Pt(NCR)$_2$(Cl)$_2$] (R = Me, Ph), was already reported by Herrmann and co-workers in the patent literature.[22] Although this route produced exclusively the *trans*-isomer, the procedure in general is lacking in our experience, as it gives low yields (<10%). Similarly, the reaction of [Pt(COD)(Cl)$_2$] with *i*Pr$_2$Im selectively leads to ***cis*-8**, although the yields were very low for this reaction likewise.

Both isomers of **10** can be easily distinguished in the ^{1}H and ^{13}C{^{1}H} NMR spectrum. The D_{2h}-symmetric ***trans*-10** gives rise to only one set of signals for the NHC ligands, whereas for the C_{2v}-symmetric *cis*-isomer the methyl groups are split into two sets of resonances. The signals for the NHC carbene carbon atoms were detected at 144.9 (***cis*-10**) and 167.3 ppm (***trans*-10**), respectively. The highfield-shifted NHC carbene carbon atom resonance of ***cis*-10** is in accordance with observations made before for the analogous complex *cis*-[Pt(Cy$_2$Im)$_2$(Cl)$_2$] reported by Nolan et al.[23] Crystals of ***cis*-10** have been obtained from recrystallization of the mixture in methylene chloride, and the X-ray analysis (see Figure 4) confirmed the identity of this square planar complex.

Using PdCl$_2$ as a metal precursor, the reaction with 2 equiv of *i*Pr$_2$Im (or even less) at room temperature afforded only the ionic compound [Pd(*i*Pr$_2$Im)$_3$(Cl)]$^+$Cl$^-$ (**8**) and unreacted

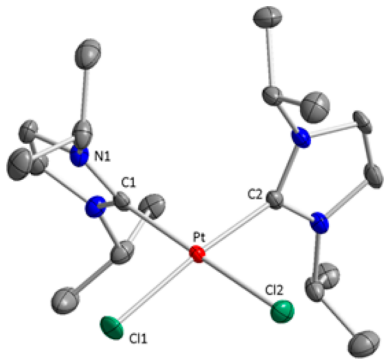
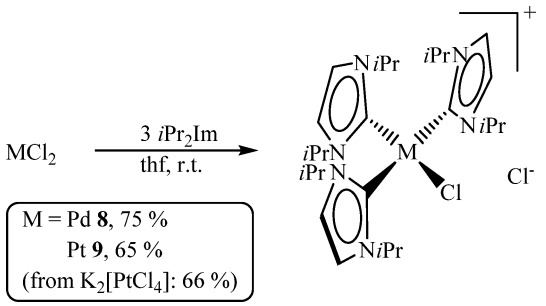


Figure 4. Molecular structure of *cis*-[Pt(*i*Pr$_2$Im)$_2$(Cl)$_2$] (***cis*-10**) in the solid state (ellipsoids set at the 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt−Cl1 2.359(11), Pt−Cl2 2.365(11), Pt−C1 1.985(4), Pt−C2 1.981(4), Cl1−Pt−Cl2 85.53(12), C1−Pt−C2 97.32(16).

PdCl$_2$. This complex **8** as well as the platinum analogue [Pt(*i*Pr$_2$Im)$_3$(Cl)]$^+$Cl$^-$ (**9**) can be conveniently synthesized in good to fair yields using 3 equiv or an excess of the NHC. Since [Pt(*i*Pr$_2$Im)$_2$(Cl)$_2$] (**10**) readily reacts with any excess of the NHC used in the reaction and a separation of **9** and **10** involves significant loss in yield, it is convenient for the synthesis of [Pt(*i*Pr$_2$Im)$_2$] (**2**) also to use complex **9** as starting material. Thus, air-stable complexes of the type [M(*i*Pr$_2$Im)$_3$(Cl)]$^+$Cl$^-$ (M = Pd, **8**; Pt, **9**) can be synthesized easily from the reaction of PdCl$_2$ and PtCl$_2$, with a slight excess of the *i*Pr$_2$Im (see Scheme 6). Furthermore, the use of K$_2$[PtCl$_4$] instead of PtCl$_2$

Scheme 6. Synthesis of [M(*i*Pr$_2$Im)$_3$(Cl)]$^+$Cl$^-$ (M = Pd, 8; Pt, 9)



as a platinum source in the reaction with *i*Pr$_2$Im leads selectively to [Pt(*i*Pr$_2$Im)$_3$(Cl)]$^+$Cl$^-$ (**9**), and we did not isolate compound **10** from any of these reactions, even if a substoichiometric amount of NHC was used. In some instances, however, the formation of the imidazolium salt *i*Pr$_2$Im·HCl as a side product was observed. The imidazolium salt and the complex cannot be separated easily, since both compounds reveal similar solubility in common organic solvents (soluble in methylene chloride or dmso, insoluble in ethers and hydrocarbons).

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **8** and **9** are those typically observed for a T-shaped alignment of three *i*Pr$_2$Im ligands. For the two *cis* NHC ligands (with respect to the chloride ligand) the methyl groups split up into those pointing to the chloride and those pointing to the central *i*Pr$_2$Im, whereas the *trans* NHC ligand reveals one set of resonances. This leads to ^{1}H NMR spectra consisting of two singlets for the NHC backbones and two septets for the methine units in a 2:1 ratio each and three doublets in a 1:1:1 ratio for the methyl protons. Analogous Me$_2$Im-substituted complexes have been described by Crabtree and co-workers.[24] Single crystals of [Pt(*i*Pr$_2$Im)$_3$(Cl)]$^+$Cl$^-$ (**8**) suitable for X-ray diffraction were grown by slow evaporation of the solvent from a saturated solution in methylene chloride at room temperature (see Figure 5).

The cation of [Pt(*i*Pr$_2$Im)$_3$(Cl)]$^+$Cl$^-$ (**9**) adopts a square planar structure with a T-shaped, propeller-like alignment of the three NHC ligands and a chloride ligand, which completes the square. It is closely related to the structure of [Pd(*i*Pr$_2$Im)$_3$(Cl)]$^+$Cl$^-$ (**8**) published recently.[8] The imidazole rings are propeller-like twisted with torsion angles of approximately 60°. Due to the weak structural *trans* effect of the chloride ligand, the central *i*Pr$_2$Im ligand reveals a significantly shorter Pt−C bond distance (Pt−C1 1.989(7) Å) compared to the *i*Pr$_2$Im ligands in *cis* alignment (Pt−C2 2.064(7), Pt−C3 2.038(7) Å). These NHC ligands are slightly

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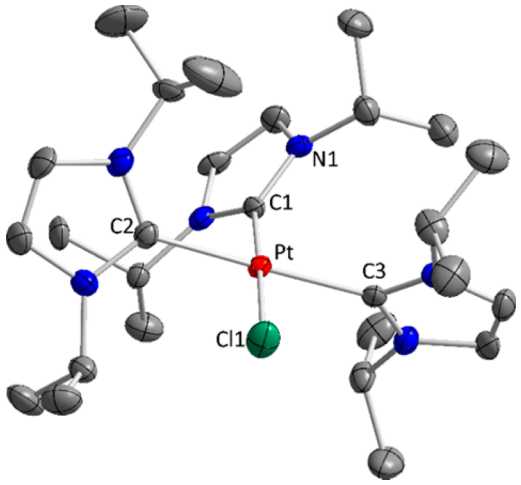
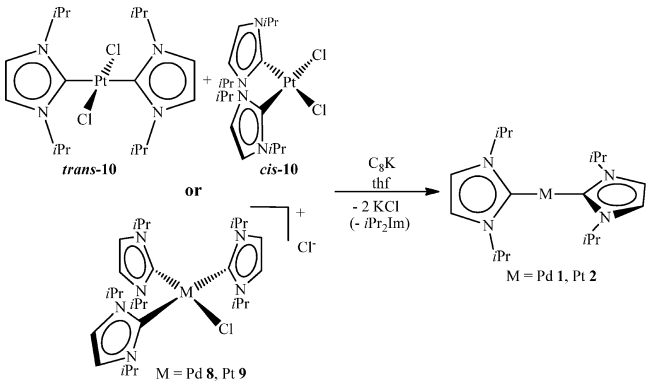


Figure 5. Molecular structure of the cation of $[Pt(iPr_2Im)_3(Cl)]^+Cl^-$ (**9**) in the solid state (ellipsoids set at the 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt−Cl1 2.363(2), Pt−C1 1.989(7), Pt−C2 2.064(7), Pt−C3 2.038(7); Cl1−Pt−C1 178.3(2), C2−Pt−C3 174.1(3), Cl1−Pt−C2 87.9(2), Cl1−Pt−C3 88.4(2), (plane Pt−Cl1−C1−C2−C3)−(plane N1−C1−N) 57.4(4), (plane Pt−Cl1−C1−C2−C3)−(plane N−C2−N) 58.7(5), (plane Pt−Cl1−C1−C2−C3)−(plane N−C3−N) 64.5(3).

bent toward the chloride ligand (Cl1−Pt−C2 87.9(2)°, Cl1−Pt−C3 88.4(2)°).

The complexes $[Pd(iPr_2Im)_3(Cl)]^+Cl^-$ (**8**) and $[Pt(iPr_2Im)_3(Cl)]^+Cl^-$ (**9**) as well as a mixture of the isomers of $[Pt(iPr_2Im)_2(Cl)_2]$ (**10**) are suitable precursors for the reductive synthesis of $[Pd(iPr_2Im)_2]$ (**1**) and $[Pt(iPr_2Im)_2]$ (**2**) using an excess of potassium graphite (see Scheme 7). As

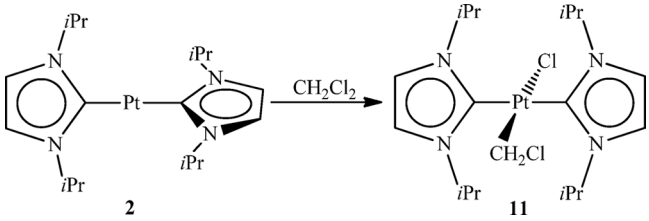
Scheme 7. Synthesis of $[M(iPr_2Im)_2]$ (M = Pd, 1; Pt, 2)



reported before for the reduction of $[Pd(iPr_2Im)_3(Cl)]^+Cl^-$ (**8**) and $[Pt(iPr_2Im)_3(Cl)]^+Cl^-$ (**9**), the reaction of $[Pt(iPr_2Im)_2(Cl)_2]$ (**10**) with potassium graphite has to be performed for several days at room temperature. In some cases colloidal metal is formed as a side product, which has to be separated by multiple filtrations through long columns of Celite. In contrast to the ligand exchange reactions using $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$, only traces of $[Pt(iPr_2Im)_3(H)]^+$ and *trans*-$[Pt(iPr_2Im)_2(iPr\text{-}Im^*)(H)]$ have been detected occasionally. The ^1H NMR chemical shifts of the resonances of both $[Pd(iPr_2Im)_2]$ (**1**) and $[Pt(iPr_2Im)_2]$ (**2**) are strongly dependent on the solvent used for dissolving the sample. The signals of $[Pd(iPr_2Im)_2]$ (**1**) are detected at 1.34 (methyl), 6.03 (methine), and 6.46 ppm (NHC backbone) in C_6D_6, whereas in thf-d_8 the methyl (1.42 ppm) and backbone resonances (6.83 ppm) are significantly shifted to lower fields. The methine resonances, in contrast, appear at higher fields (5.62 ppm). The same trends are observed for the analogous platinum complex $[Pt(iPr_2Im)_2]$ (**2**) (C_6D_6: 1.33, 6.26, 6.40 ppm; thf-d_8: 1.42, 5.83, 6.81 ppm).

$[Pt(iPr_2Im)_2]$ (**2**) is stable only in hydrocarbons and ethers as solvents. When dissolved in methylene chloride, oxidative addition of a C−Cl bond to the platinum center occurs within seconds to afford the neutral complex $[Pt(iPr_2Im)_2(CH_2Cl)(Cl)]$ (**11**) (see Scheme 8). The ^1H NMR spectrum consists of

Scheme 8. Reaction of $[Pt(iPr_2Im)_2]$ (2) with CH_2Cl_2 to Yield $[Pt(iPr_2Im)_2(CH_2Cl)(Cl)]$ (11)



one set of signals for the NHC ligands with two doublets for the chemically inequivalent methyl groups. Platinum satellites have been detected at the resonances of the backbone protons and the methylene protons (*CHCH*, $^4J_{PtH}$ = 9.0 Hz; *CH*$_2$, $^2J_{PtH}$ = 59.1 Hz). In the course of our investigation, it turned out that this reaction is extremely useful for the NMR spectroscopic determination of the purity of $[Pt(iPr_2Im)_2]$ (**2**) synthesized by various methods. Since most of the byproducts are poorly soluble in C_6D_6 (some of them in thf likewise), but readily soluble in methylene chloride, we have found it convenient to dissolve our reaction products in methylene chloride and to convert $[Pt(iPr_2Im)_2]$ quantitatively to complex $[Pt(iPr_2Im)_2(CD_2Cl)(Cl)]$ (***deutero*-11**) to quantify the ratio between $[Pt(iPr_2Im)_2]$ and byproduct.

CONCLUSION

Herein, we give a detailed account on the synthesis of the NHC-stabilized, two-coordinated palladium and platinum 14-VE complexes $[M(iPr_2Im)_2]$ (M = Pd, **1**; Pt, **2**). Although complex **2** can be synthesized by ligand exchange starting from $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ (**3**) in good yield, we have found it advantageous and convenient to use the metallic reduction of $[M(iPr_2Im)_3(Cl)]^+Cl^-$ (M = Pd, **8**; Pt, **9**), which can be conveniently synthesized from the reaction of MCl_2 or $K_2[Pt(Cl)_4]$. Ligand exchange of $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ (**3**) to give $[Pt(iPr_2Im)_2]$ (**2**) critically depends on the reaction conditions employed. Slight changes in these led to completely different outcomes of the reaction, and we have characterized the complexes $[Pt(iPr_2Im)(PPh_3)(\eta^2\text{-}C_2H_4)]$ (**5**) and *trans*-$[Pt(iPr_2Im)_2(iPr\text{-}Im^*)(H)]$ (**6**) as well as the cation $[M(iPr_2Im)_3(H)]^+$ (**7**) as other products of the reaction between **3** and iPr_2Im. Interestingly, performing the reaction of **3** with an excess of iPr_2Im in toluene or thf produced *trans*-$[Pt(iPr_2Im)_2(iPr\text{-}Im^*)(H)]$ (**6**), a complex substituted with the partially degraded NHC *i*Pr-Im*.

EXPERIMENTAL SECTION

General Considerations. All reactions and subsequent manipulations involving organometallic reagents were performed under a

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nitrogen or argon atmosphere using standard Schlenk techniques, as reported previously.[25] NMR spectra were recorded, if not noted otherwise, on Bruker DRX-300, Bruker Avance 200, Bruker Avance 400, or Bruker Avance 500 spectrometers at 298 K. ^{13}C NMR spectra were broad-band proton-decoupled ($^{13}C\{^1H\}$). NMR data are listed in parts per million (ppm) and are reported relative to tetramethylsilane. Coupling constants are quoted in hertz (Hz). Spectra are referenced internally to residual protio solvent resonances (^1H: C_6D_5H 7.15 ppm, $CDHCl_2$ 5.32 ppm, thf-d_7 3.58, 1.72 ppm, dmso-d_5 2.50 ppm) or natural-abundance carbon resonances (^{13}C: C_6D_6, 128.1 ppm, CD_2Cl_2 53.8 ppm, thf-d_8 67.2, 25.3 ppm, dmso-d_6 39.5 ppm) or external 85% H_3PO_4 in H_2O (^{31}P: 0 ppm) and external 1 M $Na_2[PtCl_6]$ in D_2O (^{195}Pt: 0 ppm), respectively. Elemental analyses were performed in the microanalytical laboratory of the University Würzburg with an Elementar Vario Micro cube. Infrared spectra were recorded on a Nicolet 380 FT-IR spectrometer as solids by using an ATR unit or in solution using a cell for measurement and are reported in cm^{-1}. The compounds *i*Pr_2Im,[26] $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$[15f] and $[Pt(i\text{Pr}_2\text{Im})_2]$[8] were prepared according to literature procedures.

All other reagents have been obtained from commercial sources and were used as received.

Synthesis of Complexes. *[Pt(iPr$_2$Im)$_2$] (**2**).* Via ligand exchange of $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$: 1.82 g (2.43 mmol) of $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ (**3**) was suspended in 20 mL of *n*-hexane, and 1.48 mL (1.48 g, 9.72 mmol) of *i*Pr_2Im was added. The solution turned red immediately. After stirring for 1 h at room temperature the precipitate was filtered off, washed twice with small (5 mL) portions of *n*-hexane, and dried *in vacuo*. Yield: 880 mg (1.76 mmol, 73%) of a yellow solid.

Via reduction of $[Pt(i\text{Pr}_2\text{Im})_2(Cl)_2]$ (**10**): A suspension of 350 mg (570 μmol) of $[Pt(i\text{Pr}_2\text{Im})_2(Cl)_2]$ (**10**) and 231 mg (1.71 mmol, 3.00 equiv) of potassium graphite in 40 mL of thf was stirred for 4 d at room temperature, resulting in a yellow solution and black graphite. All solid components were removed by filtration over a large pad of Celite and washed with 5 mL portions of thf until the eluent was colorless. After volatile components had been removed *in vacuo*, the crude product was suspended in small amounts of *n*-hexane (5 mL) and filtered off. The yellow solid obtained was washed twice with 5 mL of *n*-hexane and dried *in vacuo*. Yield: 232 mg (465 μmol, 88%) of a yellow solid. Anal. Calcd (found) for $C_{18}H_{32}N_4Pt$ [499.57 g·mol^{-1}]: C, 43.28 (43.68); H, 6.46 (6.39); N, 11.22 (11.05). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3162 (m, $\nu_{-C\text{-}H,str}$), 3113 (m, $\nu_{-C\text{-}H,str}$), 3056 (m, $\nu_{-C\text{-}H,str}$), 2973 (vs, $\nu_{-C\text{-}H,str}$), 2932 (s, $\nu_{-C\text{-}H,str}$), 2870 (s, $\nu_{-C\text{-}H,str}$), 2022 (w), 1658 (w), 1640 (w), 1630 (w), 1564 (w), 1465 (m), 1457 (s), 1425 (vs), 1410 (vs), 1393 (s), 1369 (s), 1339 (w), 1304 (s), 1271 (s), 1218 (vs, NHC-$\gamma_{=C-H,oop}$), 1169 (w), 1131 (m), 1109 (w), 1078 (w), 1064 (w), 1020 (s), 995 (w), 874 (w), 791 (m), 739 (w), 723 (m), 703 (s). ^1H NMR (500 MHz, C_6D_6): δ = 1.33 (d, 24 H, CH_3, $^3J_{HH}$ = 6.8 Hz), 6.26 (sept, 4 H, $CHMe_2$, $^3J_{HH}$ = 6.8 Hz), 6.40 (s_{sat}, 4 H, *CHCH*, $^4J_{PtH}$ = 19.0 Hz). ^1H NMR (200 MHz, thf-d_8): δ = 1.42 (d, 24 H, CH_3, $^3J_{HH}$ = 6.8 Hz), 5.83 (sept, 4 H, $CHMe_2$, $^3J_{HH}$ = 6.8 Hz), 6.81 (s_{sat}, 4 H, *CHCH*, $^4J_{PtH}$ = 19.3 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ = 23.1 (CH_3), 52.2 (sat, $CHMe_2$, $^3J_{PtC}$ = 108.5 Hz), 113.7 (sat, *CHCH*, $^3J_{PtC}$ = 45.1 Hz), 197.7 (*NCN*). ^{195}Pt NMR (107 MHz, 23.0 °C, C_6D_6): δ = −5942.

If the reaction mixture of $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ and *i*Pr_2Im was stirred for several days, cationic $[Pt(i\text{Pr}_2\text{Im})_3(H)]^+$ (**7**) occurred as the major product. The mixture was filtered off, and the brownish crude product was washed with 5 mL of *n*-hexane, 5 mL of toluene, and again 5 mL of *n*-hexane. After drying *in vacuo* $[Pt(i\text{Pr}_2\text{Im})_3(H)]^+$ (**7**) was obtained as a colorless solid. Single crystals of $[Pt(i\text{Pr}_2\text{Im})_3(H)]$-$((SiMe_2O)_3OH)^-$ suitable for X-ray diffraction were obtained from a saturated solution in thf at −30 °C (see Supporting Information). Anal. Calcd (found) for $C_{33}H_{68}N_6PtO_4Si_2$ [892.28 g·mol^{-1}]: C, 44.42 (45.12); H, 7.68 (7.54); N, 9.42 (10.11). ^1H NMR (500 MHz, C_6D_6): δ = −7.48 (s_{sat}, 1 H, *PtH*, $^1J_{PtH}$ = 918.1 Hz), 0.59 (s_{sat}, 6 H, $(Si(CH_3)_2O)_2(Si(CH_3)_2)$, $^2J_{SiH}$ = 7.3 Hz), 0.63 (s_{sat}, 12 H, $(Si(CH_3)_2O)_2(Si(CH_3)_2)$, $^2J_{SiH}$ = 7.0 Hz), 0.86 (d, 18 H, *cis*-CH_3, $^3J_{HH}$ = 6.8 Hz), 1.04 (d, 12 H, *trans*-CH_3, $^3J_{HH}$ = 6.8 Hz), 1.12 (d, 12 H, *cis*-CH_3, $^3J_{HH}$ = 6.8 Hz), 4.84 (sept, 2 H, *trans*-$CHMe_2$, $^3J_{HH}$ = 6.8 Hz), 5.01 (sept, 4 H, *cis*-$CHMe_2$, $^3J_{HH}$ = 6.8 Hz), 6.84 (s_{sat}, 4 H, *cis*-*CHCH*, $^4J_{PtH}$ = 10.0 Hz), 8.24 (s_{sat}, 2 H, *trans*-*CHCH*, $^4J_{PtH}$ = 7.1 Hz). ^1H NMR (500 MHz, CD_2Cl_2): δ = −7.96 (s_{sat}, 1 H, *PtH*, $^1J_{PtH}$ = 920.2 Hz), 1.04 (d, 12 H, CH_3, $^3J_{HH}$ = 6.8 Hz), 1.16 (d, 12 H, CH_3, $^3J_{HH}$ = 6.8 Hz), 1.39 (d, 12 H, CH_3, $^3J_{HH}$ = 6.8 Hz), 4.99 (m, 6 H, $CHMe_2$), 5.01 (sept, 4 H, *cis*-$CHMe_2$, $^3J_{HH}$ = 6.8 Hz), 7.06 (s_{sat}, 4 H, *cis*-*CHCH*, $^4J_{PtH}$ = 10.8 Hz), 7.11 (s_{sat}, 2 H, *trans*-*CHCH*, $^4J_{PtH}$ = 7.5 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ = 2.4 ($(Si(CH_3)_2O)_2(Si(CH_3)_2)$), 3.7 ($(Si(CH_3)_2O)_2(Si(CH_3)_2)$), 21.8 (*cis*-$CH_3$), 22.6 (*trans*-$CH_3$), 23.1 (*cis*-$CH_3$), 52.0 (*trans*-CHMe), 52.5 (*cis*-$CHMe_2$), 117.3 (*cis*-CHCH), 120.7 (*trans*-CHCH), 167.7 (*cis*-NCN), 172.5 (*trans*-NCN). ^{29}Si NMR (99.4 MHz, C_6D_6): δ = −23.2 ($(Si(CH_3)_2O)_2(Si(CH_3)_2)$), −22.9 ($(Si(CH_3)_2O)_2(Si(CH_3)_2)$).

The O−H proton was not detected. In CD_2Cl_2 solutions, the anion is rapidly exchanged by chloride.

*cis-[Pt(PPh$_3$)$_2$(Cl)$_2$] (**4**).* A 4.50 g (8.69 mmol) amount of $H_2[PtCl_6]\cdot H_2O$ (40% Pt) and 14.0 g (53.4 mmol) of PPh_3 were suspended in 60 mL of xylene. The reaction mixture was heated to 140 °C until no orange-colored $H_2[PtCl_6]$ was visible (approximately 2 h). After cooling to room temperature, the colorless precipitate formed was filtered off, washed subsequently with 30 mL portions of ethanol, water, and diethyl ether, and dried *in vacuo* to give *cis*-$[Pt(PPh_3)_2(Cl)_2]$. Yield: 6.75 g (8.54 mmol, 98%) of a colorless, air- and moisture-stable solid. ^1H NMR (200 MHz, CD_2Cl_2): δ = 7.21 (m, 12 H, *m*-*CH*), 7.49 (m, 18 H, *o*-*CH*, *p*-*CH*). ^{31}P NMR (80.9 MHz, CD_2Cl_2): δ = 13.9 (s_{sat}, $^1J_{PtP}$ = 3676.2 Hz).

trans-[Pt(iPr$_2$Im)$_2$(iPr-Im)(H)] (**6**).* A 250 mg (335 μmol) amount of $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ (**3**) was dissolved in 20 mL of toluene, and 203 mg (1.34 mmol, 203 μL, 4.00 equiv) of *i*Pr_2Im was added. The solution was heated to 90 °C for 4 d and filtered afterward over a pad of Celite. The solvent was removed *in vacuo*, and the residue was suspended in 20 mL of *n*-hexane. After filtration, the solid was washed twice with 5 mL portions of *n*-hexane, and the product was dried *in vacuo*. Yield: 37.5 mg (61.6 μmol, 18%) of an off-white solid. Anal. Calcd (found) for $C_{24}H_{42}N_6Pt$ [609.73 g·mol^{-1}]: C, 47.28 (47.50); H, 6.94 (6.94); N, 13.78 (13.28). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3168 (w, $\nu_{-C\text{-}H,str}$), 3124 (w, $\nu_{-C\text{-}H,str}$), 3090 (w, $\nu_{-C\text{-}H,str}$), 3058 (w, $\nu_{-C\text{-}H,str}$), 2968 (vs, $\nu_{-C\text{-}H,str}$), 2933 (m, $\nu_{-C\text{-}H,str}$), 2870 (m, $\nu_{-C\text{-}H,str}$), 1927 (s, $\nu_{Pt-H,str}$), 1611 (w), 1565 (w), 1472 (m), 1465 (m), 1458 (m), 1448 (w), 1426 (s), 1410 (s), 1394 (s), 1368 (s), 1339 (w), 1302 (s), 1262 (m), 1213 (vs, NHC-$\gamma_{=C-H,oop}$), 1175 (w), 1132 (s), 1086 (s), 1018 (s), 882 (w), 801 (m), 735 (w), 720 (w). ^1H NMR (500 MHz, C_6D_6): δ = −6.11 (s_{sat}, 1 H, *PtH*, $^1J_{PtH}$ = 802.7 Hz), 1.06 (d, 6 H, Im*-CH_3, $^3J_{HH}$ = 6.8 Hz), 1.20 (d, 24 H, CH_3, $^3J_{HH}$ = 6.8 Hz), 5.18 (sept, 1 H, Im*-$CHMe_2$, $^3J_{HH}$ = 6.8 Hz), 5.98 (sept, 4 H, $CHMe_2$, $^3J_{HH}$ = 6.8 Hz), 6.38 (s_{sat}, 4 H, *CHCH*, $^4J_{PtH}$ = 6.8 Hz), 7.00 (d, 1 H, Im*-*CHCH*, $^3J_{HH}$ = 1.2 Hz), 7.55 (d, 1 H, Im*-CHC*H*, $^3J_{HH}$ = 1.2 H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ = 22.8 (CH_3), 24.3 (Im*-CH_3), 48.2 (sat, Im*-$CHMe_2$, $^3J_{PtC}$ = 35.8 Hz), 52.0 (sat, $CHMe_2$, $^3J_{PtC}$ = 52.8 Hz), 111.3 (sat, Im*-CHCH, $^3J_{PtC}$ = 10.2 Hz), 115.0 (sat, *CHCH*, $^3J_{PtC}$ = 29.6 Hz), 131.4 (sat, Im*-CHCH, $^3J_{PtC}$ = 64.2 Hz), 172.5 (Im*-NCN), 175.8 (NCN). ^{195}Pt NMR (107 MHz, 23.0 °C, C_6D_6): δ = −4456 (m_{br}).

*[Pd(iPr$_2$Im)$_3$(Cl)]$^+$Cl$^-$ (**8**).* A 6.88 g (45.2 mmol, 4.00 equiv) amount of pure *i*Pr_2Im was added dropwise to a suspension of 2.00 g (11.3 mmol) of $PdCl_2$ in 40 mL of thf. The resulting mixture was stirred overnight at room temperature. During this time a grayish solid precipitated, which was filtered off, washed twice with 20 mL of diethyl ether, and dried *in vacuo*. To remove colloidal palladium, the crude product was dissolved in methylene chloride and filtered over a pad of Celite. After removal of the solvent $[Pd(i\text{Pr}_2\text{Im})_3(Cl)]^+Cl^-$ was obtained as a light grayish solid. Yield: 5.36 g (8.45 mmol, 75%). Crystals suitable for X-ray diffraction were grown at room temperature by slow evaporation of the solvent from a solution in methylene chloride. Anal. Calcd (found) for $C_{27}H_{48}Cl_2N_6Pd$ [634.04 g mol^{-1}]: C, 51.15 (51.27); H, 7.63 (7.64); N, 13.25 (12.94). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 704 (m), 740 (m), 779 (w), 817 (m), 1131 (m), 1180 (w), 1213 (vs), 1282 (w), 1300 (m), 1372 (s), 1398 (s), 1428 (), 1457 (m), 1635 (w), 1653 (w), 1684 (w), 1699 (w), 1717 (w), 1734 (w), 1792 (vw), 1844 (vw), 1928 (m), 2037 (m), 2877 (m), 2936 (m), 2976 (vs), 3054 (s), 3730 (w). ^1H NMR (500 MHz, CD_2Cl_2): δ = 1.04 (d,

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12 H, *trans*-CH_3, $^3J_{HH}$ = 6.7 Hz), 1.18 (d, 12 H, *cis*-CH_3, $^3J_{HH}$ = 6.7 Hz), 1.54 (d, 12 H, *cis*-CH_3, $^3J_{HH}$ = 6.7 Hz), 4.93 (sept, 2 H, *trans*-$CHMe_2$, $^3J_{HH}$ = 6.7 Hz), 5.17 (sept, 4 H, *cis*-$CHMe_2$, $^3J_{HH}$ = 6.7 Hz), 7.12 (s, 4 H, *cis*-CHCH), 7.42 (s, 2 H, *trans*-CHCH). ^{1}H NMR (500 MHz, dmso-d_6): δ = 0.97 (d, 12 H, *trans*-CH_3, $^3J_{HH}$ = 6.7 Hz), 1.13 (d, 12 H, *cis*-CH_3, $^3J_{HH}$ = 6.7 Hz), 1.48 (d, 12 H, *cis*-CH_3, $^3J_{HH}$ = 6.7 Hz), 4.69 (sept, 2 H, *trans*-$CHMe_2$, $^3J_{HH}$ = 6.7 Hz), 4.94 (sept, 4 H, *cis*-$CHMe_2$, $^3J_{HH}$ = 6.7 Hz), 7.65 (s, 4 H, *cis*-CHCH), 7.81 (s, 2 H, *trans*-CHCH). $^{13}C\{^1H\}$ NMR (126 MHz, dmso-d_6): δ = 21.5 (*cis*-CH_3), 21.9 (*trans*-CH_3), 24.2 (*cis*-CH_3), 52.5 (*cis*-$CHMe_2$), 52.9 (*trans*-$CHMe_2$), 119.1 (*cis*-CHCH), 120.2 (*trans*-CHCH), 155.4 (*trans*-NCN), 165.6 (*cis*-NCN).

[Pt(iPr$_2$Im)$_3$(Cl)]$^+$Cl$^-$ (**9**). A 1.14 g (7.48 mmol, 1.14 mL) amount of pure *i*Pr$_2$Im was added dropwise to a suspension of 500 mg (1.87 mmol) of $PtCl_2$ in 50 mL of thf, and the resulting mixture was stirred overnight at room temperature. During this time, a colorless solid precipitated, which was filtered off, washed twice with 20 mL of diethyl ether, and dried *in vacuo*. Yield: 876 mg (1.21 mmol, 65%) of a colorless solid. Anal. Calcd (found) for $C_{27}H_{48}Cl_2N_6Pt$ [722.71 g mol^{-1}]: C, 44.68 (44.18); H, 7.08 (7.53); N, 11.58 (11.23). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3164 (vw), 3127 (w), 3094 (w), 3054 (vw), 2975 (s), 2936 (w), 2875 (w), 2160 (w), 1658 (vw), 1565 (vw), 1473 (w), 1457 (w), 1434 (m), 1415 (m), 1395 (m), 1372 (m), 1305 (w), 1282 (w), 1215 (vs), 1179 (w), 1136 (w), 744 (w), 713 (m). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.04 (d, 12 H, *trans*-CH_3, $^3J_{HH}$ = 6.7 Hz), 1.17 (d, 12 H, *cis*-CH_3, $^3J_{HH}$ = 6.7 Hz), 1.54 (d, 12 H, *cis*-CH_3, $^3J_{HH}$ = 6.7 Hz), 4.93 (sept, 2 H, *trans*-$CHMe_2$, $^3J_{HH}$ = 6.7 Hz), 5.17 (sept, 4 H, *cis*-$CHMe_2$, $^3J_{HH}$ = 6.7 Hz), 7.12 (s, 4 H, *cis*-CHCH), 7.42 (s, 2 H, *trans*-CHCH). ^{1}H NMR (500 MHz, dmso-d_6): δ = 0.96 (d, 12 H, *trans*-CH_3, $^3J_{HH}$ = 6.5 Hz), 1.12 (d, 12 H, *cis*-CH_3, $^3J_{HH}$ = 6.7 Hz), 1.45 (d, 12 H, *cis*-CH_3, $^3J_{HH}$ = 6.7 Hz), 4.81 (sept, 2 H, *trans*-$CHMe_2$, $^3J_{HH}$ = 6.5 Hz), 5.04 (sept, 4 H, *cis*-$CHMe_2$, $^3J_{HH}$ = 6.7 Hz), 7.65 (s, 4 H, *cis*-CHCH), 7.74 (s, 2 H, *trans*-CHCH). $^{13}C\{^1H\}$ NMR (126 MHz, dmso-d_6): δ = 21.4 (*cis*-CH_3), 21.7 (*trans*-CH_3), 24.2 (*cis*-CH_3), 51.8 (*cis*-$CHMe_2$), 52.0 (*trans*-$CHMe_2$), 118.8 (*cis*-CHCH), 119.3 (*trans*-CHCH), 141.3 (*trans*-NCN), 161.6 (*cis*-NCN).

[Pt(iPr$_2$Im)$_2$(Cl)$_2$] (**10**). A solution of 1.15 g (7.52 mmol, 1.15 mL, 2.00 equiv) of *i*Pr$_2$Im was added dropwise to a suspension of 1.00 mg (3.76 mmol) of $PtCl_2$ in 40 mL of thf. The mixture was stirred overnight at room temperature. During this time, a colorless solid precipitated, which was filtered off, washed twice with 20 mL of diethyl ether, and dried *in vacuo*. The resulting product contained a mixture of the *cis*- and the *trans*-isomer of **10** with *trans*-[Pt(*i*Pr$_2$Im)$_2$(Cl)$_2$] as the main component. Yield: 1.48 g (2.59 mmol, 69%) of a colorless solid. Crystals of ***cis*-10** suitable for X-ray diffraction were grown at room temperature by slow diffusion of diethyl ether into a solution in methylene chloride. Anal. Calcd (found) for $C_{18}H_{32}Cl_2N_4Pt$ [570.47 g mol^{-1}]: C, 37.90 (37.42); H, 5.65 (6.01); N, 9.82 (9.80). *trans*-[Pt(*i*Pr$_2$Im)$_2$(Cl)$_2$]: IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3163 (vw), 3126 (w), 3095 (w), 2975 (m), 2936 (w), 2874 (vw), 2156 (vw), 1665 (vw), 1563 (vw), 1457 (w), 1434 (m), 1415 (m), 1395 (w), 1372 (m), 1306 (w), 1215 (vs), 1180 (w), 1136 (w), 882 (vw), 743 (w), 715 (m). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.55 (d, 24 H, CH_3, $^3J_{HH}$ = 6.9 Hz), 5.78 (sept, 4 H, $CHMe_2$, $^3J_{HH}$ = 6.9 Hz), 7.74 (s, 4 H, CHCH, $^4J_{PtH}$ = 5.4 Hz). ^{1}H NMR (200 MHz, dmso-d_6): δ = 1.47 (d, 24 H, CH_3, $^3J_{HH}$ = 6.8 Hz), 5.65 (sept, 4 H, $CHMe_2$, $^3J_{HH}$ = 6.8 Hz), 7.35 (s, 4 H, CHCH, $^4J_{PtH}$ = 5.4 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ = 23.3 (CH_3), 51.7 ($CHMe_2$), 116.3 (CHCH), 167.3 (NCN). *cis*-[Pt(*i*Pr$_2$Im)$_2$(Cl)$_2$]: IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3157 (w, $\nu_{-C\text{-}H,str}$), 3118 (m, $\nu_{-C\text{-}H,str}$), 3100 (m, $\nu_{-C\text{-}H,str}$), 2974 (vs, $\nu_{-C\text{-}H,str}$), 2936 (m, $\nu_{-C\text{-}H,str}$), 2876 (m, $\nu_{-C\text{-}H,str}$), 1572 (w), 1457 (s), 1430 (s), 1413 (s), 1376 (s), 1302 (m), 1216 (vs, NHC-$\gamma_{=C-H,oop}$), 1180 (m), 1134 (m), 1066 (w), 1034 (w), 747 (m), 734 (m), 711 (s). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.16 (d, 12 H, CH_3, $^3J_{HH}$ = 6.8 Hz), 1.51 (d, 12 H, CH_3, $^3J_{HH}$ = 6.8 Hz), 5.45 (sept, 4 H, $CHMe_2$, $^3J_{HH}$ = 6.8 Hz), 6.96 (s, 4 H, CHCH, $^4J_{PtH}$ = 12.7 Hz). ^{1}H NMR (200 MHz, dmso-d_6): δ = 1.09 (d, 12 H, CH_3, $^3J_{HH}$ = 6.8 Hz), 1.42 (d, 12 H, CH_3, $^3J_{HH}$ = 6.8 Hz), 5.22 (sept, 4 H, $CHMe_2$, $^3J_{HH}$ = 6.8 Hz), 7.51 (s, 4 H, CHCH). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ = 22.6 (CH_3), 24.5 (CH_3), 54.5 (sat, $CHMe_2$, $^3J_{PtC}$ = 38.2 Hz), 117.6 (sat, CHCH, $^3J_{PtC}$ = 38.8 Hz), 144.9 (sat, NCN, $^1J_{PtC}$ = 1479.6 Hz).

Trans-[Pt(iPr$_2$Im)$_2$(CH$_2$Cl)(Cl)] (**11**). A 30.0 mg (60.0 μmol) amount of [Pt(*i*Pr$_2$Im)$_2$] (**2**) was dissolved in 2 mL of methylene chloride to give a clear, colorless solution. All volatiles were removed *in vacuo* and the residue was suspended in 3 mL of *n*-Pentane. After decantation of the supernatant, the purification process was repeated. The resulting colorless solid was dried *in vacuo* to give 29.0 mg (49.6 μmol, 83%) of a colorless solid. Anal. Calcd (found) for $C_{19}H_{34}Cl_2N_4Pt$ [584.49 g·mol^{-1}]: C, 39.04 (39.62); H, 5.86 (5.95); N, 9.59 (9.26). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3054 (m, $\nu_{-C\text{-}H,str}$), 2973 (vs, $\nu_{-C\text{-}H,str}$), 2935 (m, $\nu_{-C\text{-}H,str}$), 2875 (w, $\nu_{-C\text{-}H,str}$), 1431 (s), 1411 (s), 1371 (s), 1302 (m), 1215 (vs, NHC-$\gamma_{=C-H,oop}$), 1134 (m), 1030 (w), 710 (w). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.26 (d, 12 H, CH_3, $^3J_{HH}$ = 6.8 Hz), 1.46 (d, 12 H, CH_3, $^3J_{HH}$ = 6.8 Hz), 4.27 (s_{sat}, 4 H, CH_2, $^2J_{PtH}$ = 59.1 Hz), 5.95 (sept, 4 H, $CHMe_2$, $^3J_{HH}$ = 6.8 Hz), 6.35 (s_{sat}, 4 H, CHCH, $^4J_{PtH}$ = 9.0 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ = 13.5 (CH_2), 22.8 (CH_3), 23.8 (CH_3), 51.8 (sat, $CHMe_2$, $^3J_{PtC}$ = 38.3 Hz), 115.6 (sat, CHCH, $^3J_{PtC}$ = 30.0 Hz), 176.8 (NCN). [Pt(*i*Pr$_2$Im)$_2$] (**2**) dissolved in CD_2Cl_2: [Pt(*i*Pr$_2$Im)$_2$(CD_2Cl)(Cl)] (**deutero-11**): ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.49 (d, 12 H, CH_3, $^3J_{HH}$ = 6.8 Hz), 1.52 (d, 12 H, CH_3, $^3J_{HH}$ = 6.8 Hz), 5.64 (sept, 4 H, $CHMe_2$, $^3J_{HH}$ = 6.8 Hz), 6.97 (s_{sat}, 4 H, CHCH, $^4J_{PtH}$ = 9.0 Hz).

Crystallographic Details. Crystal data collection and processing parameters are given in Table S1 (see Supporting Information). Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Bruker D8 Apex-1 diffractometer with a CCD area detector and graphite-monochromated Mo Kα radiation equipped with a noncommercial low-temperature device or a Bruker D8 Apex-2 diffractometer with CCD area detector and graphite-monochromated or helios multilayer-monochromated Mo Kα radiation equipped with an Oxford Cryosystems low-temperature device. Data were collected at 168 K (Apex-1) and 100 K (Apex-2), respectively. The images were processed with the Bruker software packages, and equivalent reflections were merged. Corrections for Lorentz−polarization effects and absorption were performed if necessary, and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. Extinction corrections were applied as required. Crystallographic calculations were performed using the SHELXTL software package.[27] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factor calculations.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1055814 (**5**), 1055815 (**6**), 1055816 (**9**), and 1055817 (***cis*-10**). Copies of the data can be obtained free of charge on application to the CCDC.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, spectra, and CIF and XYZ files giving experimental and computational details. Crystallographic data, DFT-optimized energies, and coordinates. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00277.

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Notes

The authors declare no competing financial interest.

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