## Unusual reactivities of *N*-heterocyclic carbenes upon coordination to the platinum(II)–dimethyl moiety<sup>†</sup>

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Unsaturated NHCs of varying steric bulk undergo a series of unusual oxidative addition and reductive elimination processes upon binding to the  $Pt(Me)_2$  fragment.

N-Heterocyclic carbenes are now well-established and versatile entities for late-transition metal compounds and have proven to be often superior ancillary ligands in homogeneous catalytic processes.<sup>1</sup> Among such catalytic transformations, alkane (and in particular methane) C-H bond activation and functionalization certainly remains one of the most challenging tasks.<sup>2</sup> While a variety of homogeneous metal compounds have shown potential for this kind of process, results with platinum complexes of the Shilov-type are particularly interesting for the functionalization of methane. Intense research has gone into trying to understand individual steps of the Shilov chemistry with Pt(II)-dimethyl or Pt(IV)-methyl model compounds surrounded with neutral or anionic nitrogen-based chelates and phosphine ligands.<sup>3</sup> These findings have subsequently been implemented in an improved catalytic process for the conversion of methane.<sup>4</sup> Despite the obvious similarity between NHCs and the ligands normally used in this type of chemistry and despite the fact that interesting palladium-catalyzed methane reactivity has been disclosed using a chelating N-heterocyclic carbene ligands,<sup>5</sup> efforts to develop Shilov-type chemistry with platinum-NHC compounds have been minimal. For instance, reports in the literature where NHC ligands are part of alkyl- or aryl-containing platinum species are exceedingly scarce,<sup>6</sup> and apparently simple model compounds such as (NHC)<sub>2</sub>Pt(Me)<sub>2</sub> or (NHC)<sub>2</sub>Pt(Me)Cl are unknown at present.

Herein, we report our results on the coordination behavior of monodentate, unsaturated NHCs of varying steric bulk (Scheme 1) with  $(COD)Pt(Me)_2$ ,<sup>7</sup> and show how the bulkier ligand members undergo a series of unusual oxidative addition



Scheme 1 Unsaturated *N*-heterocyclic carbones used with corresponding  $%V_{bur}$  steric parameter values.<sup>7</sup>

(C–H) and reductive elimination (C–H and C–C) processes upon binding to the platinum center.

We anticipated a rather straightforward reactivity between relatively small *N*-heterocyclic carbene ligands <sup>Me</sup>IMe (% $V_{bur} = 25.5$ ), ICy (% $V_{bur} = 26.1$ ), or <sup>Me</sup>I'Pr (% $V_{bur} =$ 27.9) and (COD)Pt(Me)<sub>2</sub>.<sup>8</sup> Indeed, mixing (COD)Pt(Me)<sub>2</sub> with 2 equivalents of the respective ligand in benzene at room temperature leads to fast substitution of the COD moiety and, after appropriate workup, to high yields of complexes cis-(<sup>Me</sup>IMe)<sub>2</sub>Pt(Me)<sub>2</sub> (1), cis-(ICy)<sub>2</sub>Pt(Me)<sub>2</sub> (2), and cis-(MeI<sup>i</sup>Pr)<sub>2</sub>Pt(Me)<sub>2</sub> (3). Since these compounds represented a new class of NHC-platinum complexes, complete characterization included X-ray diffraction studies. Ball-and-stick drawings of cis-1, cis-2 and cis-3 are incorporated in Scheme 2. Due to the steric crowding of the two cis-configured NHC ligands in these compounds, deviations from the expected square-planar geometry are already apparent in these complexes. The bond angles between the NHCs and the platinum center increase when going from cis-1 to cis-2 to cis-3, and lead to a contraction in the CH<sub>3</sub>-Pt-CH<sub>3</sub> angles (Table S1).<sup>†</sup>

The increasing distortions in complexes 1–3 already hinted to possible problems when accommodating sterically more



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<sup>&</sup>lt;sup>+</sup> Electronic supplementary information (ESI) available: Table SI with selected bond lengths and angles of complexes 1–7, experimental procedures. CCDC 741808–741813 (1–6) and 756172 (7). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b920482b

demanding NHC ligands. For the next bulkier ligand in our series, namely IMes ( $V_{bur} = 34.2$ ), reaction with (COD)Pt(Me)<sub>2</sub> in benzene and subsequent evaporation gave two compounds in variable ratio depending on the reaction time. In situ reactions in  $C_6D_6$  revealed relatively fast displacement of COD by the two IMes ligands. Based on these studies. preparative reactions were devised. Workup of the reaction after 10 minutes gave the first complex in pure form, while extended reaction times and slight heating led to exclusive generation of the second compound. This latter complex was fully characterized and turned out to be the unusual. cyclometallated derivative cis-(IMes)(IMes')Pt(Me) (5).† The X-ray structure of 5 (Scheme 3, below) shows that the two NHC ligands remain in a cis orientation with the cyclometallated side chain trans to the normal IMes ligand. In spite of its ready transformation into 5, <sup>1</sup>H and <sup>13</sup>C NMR characterization of the first compound, that we presumed to be cis-(IMes)<sub>2</sub>Pt(Me)<sub>2</sub> (4), was possible. In addition, when a benzene solution of 4 is layered with diethyl ether, X-ray quality crystals are swiftly formed and permit the unequivocal confirmation of its structure (Scheme 3, above).† The cis orientation of the ligands, together with the steric requirements of the mesityl wingtips of IMes, leads to a highly distorted structure in the solid state. In order to accommodate both IMes ligands, the imidazole rings cannot acquire the usual coordination mode and tilt away and towards the two Pt-methyl groups (dihedral angles between the plane of the imidazole ring and platinum in 4:  $159.2(1)^{\circ}$  and  $163.0(1)^{\circ}$ ). Furthermore, one of the o-methyl groups of IMes approaches the metal center (3.569(5) Å). The overall structure certainly helps explain the propensity of 4 to undergo subsequent intramolecular C-H activation of one of the benzylic positions of the ligand. A straightforward reaction pathway accounting

Scheme 3 Probable reaction pathway for the formation of 4 and 5 with ball-and-stick drawings of cis-(IMes)<sub>2</sub>Pt(Me)<sub>2</sub> (4), and of cyclometallated (IMes)(IMes')Pt(Me) (5).

Me-H

+ 2 IMes

- COD

(COD)Pt

C42 Pt

C22

C-H act

Mes

Pt1



Scheme 4 Proposed reaction pathway for the formation of 6 with ball-and-stick drawing of  $(IPr)_2Pt(6)$ .

for the formation of **5** is outlined in Scheme 3 and involves initial C–H activation of **4** to give a six-coordinate platinum(IV) complex which subsequently undergoes reductive elimination of a molecule of methane to give **5**. It should be noted that while intramolecular activation of the benzylic C–H bond of the aromatic side chain in IMes is known for both Ru and Rh,<sup>9</sup> the example here represents the first case of such reactivity with a group 10 metal.

Activation of the isopropyl groups of the aromatic side chains in IPr is more difficult than benzylic C-H activation in IMes.<sup>10</sup> We therefore turned our attention to the interaction of IPr (% $V_{\text{bur}} = 35.8$ ) with (COD)Pt(Me)<sub>2</sub>. Here, reaction of 2 equivalents of IPr with (COD)Pt(Me)<sub>2</sub> at room temperature was less straightforward and led to a mixture of complexes. Gratifyingly, slight heating of the benzene or toluene solution (50-80 °C) gave a yellow-orange fluorescent solution from which a single, bright vellow complex was isolated in high overall yield after workup. Complete characterization showed the compound to be the homoleptic 14-electron platinum(0) complex (IPr)<sub>2</sub>Pt (6).<sup>+</sup> The most likely reaction pathway leading to 6 is shown in Scheme 4 and involves initial coordination of two IPr ligands. The resulting cis-configured (IPr)<sub>2</sub>Pt(Me)<sub>2</sub> species would then undergo ready C-C reductive elimination of ethane because of the steric pressure exerted by the two IPr ligands on the methyl groups. Such reactivity is highly unusual and we are not aware of reports on C-C reductive elimination of simple methyl/alkyl groups from platinum(II) compounds.<sup>11</sup> In the solid state, complex **6** shows the expected linear two-coordinate arrangement with somewhat shorter NHC-Pt bond lengths than in the Pt(II) complexes (Table S1).<sup>†</sup>

The bulkiest NHC member in our series, namely I'Bu (% $V_{\rm bur} = 37.0$ ), chooses yet another reactivity pathway to alleviate the severe steric crowding which would arise from a compound of formula cis-(NHC)2Pt(Me)2. Reaction of 2 equivalents of I'Bu with  $(COD)Pt(Me)_2$  in diethyl ether leads to slow precipitation of a white powder that is isolated in good yield after workup. The <sup>1</sup>H NMR spectrum showed a 1 : 1 stoichiometry between the methyl and I<sup>t</sup>Bu ligands, but several resonances indicated that the complex formed was not cis- $(I^{t}Bu)_{2}Pt(Me)_{2}$ . To elucidate the structure of the compound, crystals were grown from slow diffusion of diethyl ether into a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution and were subjected to an X-ray diffraction study.<sup>†</sup> The crystal structure of  $cis(nI^{t}Bu)(aI^{t}Bu)Pt(Me)_{2}$  (7, Scheme 5) shows coordination of one of the two I'Bu moieties via the C4 position of the central imidazole ring. By repositioning one of the 'Bu side chains through abnormal binding of  $I^{t}Bu$ , the overall



Scheme 5 Possible reaction pathway leading to the formation of 7 with ball-and-stick drawing of  $cis-(nI'Bu)(aI'Bu)Pt(Me)_2$  (7). C(7)–Pt and C(11)–Pt distances: 3.278(8) and 3.193(8) Å.

crowding is considerably reduced and the X-ray structural data permit the quantification of the steric pressure around the Pt center. This can be gauged by measuring the  $\% V_{bur}$  values for both normal (37.0) and abnormal (29.4) I'Bu ligands present in 7. As the numbers clearly indicate, an abnormal binding mode significantly relieves the bulk around the Pt center, rendering the sterics of this coordination mode more similar to the overall  $\% V_{bur}$  values of less sterically demanding, normally bound complexes 1–3.

A closer inspection of the X-ray structure of 7 also indicates that the 'Bu groups of the normally bound I'Bu ligand approach the metal considerably and both C(7)-Pt and C(11)–Pt distances are within the range of weak agostic interactions (3.278(8) Å and 3.193(8) Å; closest H-Pt distances; 2.45(7) Å and 2.61(7) Å).<sup>12</sup> Both these X-ray data as well as the fact that I'Bu is sterically more demanding than IMes and IPr support the mechanistic proposal for its generation (Scheme 5). Accordingly, the pathway to 7 would proceed via intermolecular C-H activation of the alkenyl C-H bond of the imidazole fragment by a transient  $(I'Bu)Pt(Me)_2$ complex to give an unsaturated Pt(IV) species. Subsequent formal C-H reductive elimination via hydrogen migration from the platinum center to the C2 position of the imidazole moiety would generate the observed complex 7. Formation of monometallic complex 7 is very unusual because the abnormal NHC binding mode is directly generated from the free monodentate carbene ligand.<sup>13</sup>

In conclusion, the present results indicate that *N*-heterocyclic carbene ligands can be used to generate a remarkable range of high-yielding, unusual products when reacted with platinum–dimethyl precursors. All of the NHCs studied bind readily to  $(COD)Pt(Me)_2$ .<sup>14</sup> With the bulkier members of the NHCs tested, a series of unprecedented transformations have been uncovered. Studies aimed at exploiting the reactivities found here are ongoing in our laboratories.

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