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Unusually large ‘yaw’ angle upon coordination of a new bulky unsymmetrical 3-hydroxyadamantyl-functionalized N-heterocyclic carbene ligand to rhodium(I)

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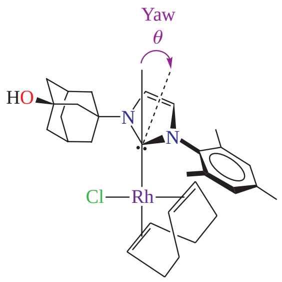
The facile synthesis of a new 3-hydroxyadamantyl-functionalized N-heterocyclic carbene (NHC) ligand and its corresponding rhodium complex [Rh(NHC)(COD)Cl] is described. This complex features an unusually large yaw distortion angle (θ = 6.8°) for a monodentate NHC species, which is attributed to its unsymmetrical nature and the steric imbalance between its two wingtips. The comprehensive analysis of the yaw distortion angles in 85 related Rh species featuring various N-substituents is reported to support this hypothesis.

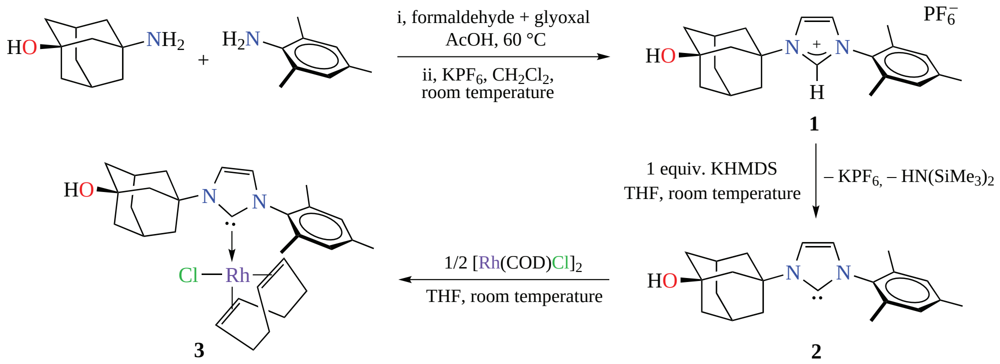


Keywords: rhodium, functional NHC ligand, organometallic complex, yaw distortion angle, carbene coordination, steric effects.

Stereoelectronic effects play an important role in metal–carbene bonding and thus in the reactivity of N-heterocyclic carbene (NHC) complexes.[1–8] Combining a bulky N-substituent with a N′ moiety of smaller steric profile in NHCs can drastically impact the metal access, and accordingly unsymmetrical NHCs[9–12] have demonstrated significant benefit over C_2-symmetrical NHCs for a number of challenging catalytic transformations.[13–17] In recent years there is also a growing interest in the design of unsymmetrical NHCs with additional functionalities for the introduction of hemilabile, chelating, or stimuli-responsive ligand properties.[18,19] Quite interestingly, in a recent contribution, Semwal *et al.* have shown that the hydride-transfer activity of iridium–NHC complexes is correlated with the geometric arrangement (yaw and bite angles) of the chelating NHC ligands.[20] In this context, our group developed an N-heterocyclic carbene (NHC) ligand functionalized with an alkoxy-containing pendant arm and demonstrated the interest of this platform to prepare a range of monometallic and heterobimetallic complexes.[21–23] Following a similar synthetic strategy, we chose to extend this chemistry to the more bulky hydroxyl-adamantyl wingtip to tune the steric profiles of these NHC complexes.

The unsymmetrical imidazolium hexafluorophosphate salt **1** (Scheme 1) is readily prepared using a simple multicomponent one-step synthetic procedure[10–12,22] from 3-amino-1-adamantanol and mesitylaniline. Compound **1** can be synthesized on a multi-gram scale with a yield of 69% after purification by silica-gel chromatography, which is required to separate **1** from the symmetrical imidazolium side-products. This salt was fully characterized, including a single-crystal X-ray diffraction analysis (see Online Supplementary Materials).

Deprotonation of **1** with one equivalent of potassium bis(trimethylsilyl)amide (KHMDS) quantitatively yields the free hydroxyl-carbene species, **2** (Scheme 1). The ^{1}H and ^{13}C NMR data for **2** closely match those described for the hydroxyalkyl-functionalized NHC compound 1-mesityl-3-(2-hydroxyisobutyl)imidazol-2-ylidene,[22] and fully support the proposed structure. As a result of ligand deprotonation, the characteristically downfield imidazolium ^{1}H NMR signal (δ 8.47 ppm in **1**) is not seen in **2**. The imidazolyl backbone protons are observed as



Scheme 1 Synthesis of the unsymmetrical NHC ligand **2** and its coordination to rhodium.

doublets ($^3J_{HH}$ = 1.7 Hz) at δ 7.24 and 6.82 ppm, respectively, as expected for an unsymmetrical carbene system. The hydroxyl proton of the pendent adamantyl group appears at *ca.* δ 5.03 ppm, and the ^{13}C NMR carbene resonance is observed at δ 211.86 ppm, which is in the range of values (210–220 ppm) reported in the literature for free imidazol-2-ylidenes.[24]

Rh–NHC complexes have found numerous applications in catalysis,[25,26] which motivated us to prepare novel Rh carbene species. Treatment of **2** with half equivalent of $[Rh(COD)Cl]_2$ in THF at room temperature affords the rhodium complex Rh(L)(COD)Cl, **3**, in good 70% isolated yield. Complex **3** is stable for months in the solid state and at least 1 week in THF solution at room temperature under inert atmosphere. The NHC binding to rhodium is clearly seen in the ^{13}C NMR spectrum for **3** which features a distinctive carbene signal at δ = 181.33 ppm (strongly shifted downfield as compared to **2** (δ = 211.86 ppm) as expected), with typical coupling to Rh (doublet, $^1J_{Rh–C}$ = 51 Hz).[21,22] The proposed structure for **3** is confirmed by X-ray crystallography (Figure 1). Consistent with the NMR data, the NHC is bound to Rh in a monodentate fashion and the Rh–C$_{carbene}$ distance [2.068(5) Å] is in the expected range (see Online Supplementary Materials, Table S2). The Rh–C$_{COD}$ bond distances in *trans* position with respect to the NHC ligand [2.180(5) and 2.153(5) Å] are slightly elongated compared to that *trans* to the chloride [2.114(5) and 2.106(5) Å], which is in agreement with the strong sigma donation of the NHC. This *trans* effect is also reflected by the increased olefinic C(3)=C(4) [1.404(7) Å] bond distance *vs.* C(7)=C(8) [1.348(9) Å]. The C$_{NHC}$–Rh–Cl angle [87.5(1)°] is close to the ideal 90° angle for a square planar geometry and the imidazolyl ring plane lies close to perpendicular to the Rh coordination square-plane [84.0(2)°] which is typical in Rh(NHC)(COD)Cl structures.[22,27]

The most striking feature of the solid-state structure for **3** is the unusually large in-plane tilting of the NHC ligand. In the solid state, crystal packing effects can influence molecular geometry.[28–30] We thus examined the intermolecular interactions in the crystal structure of **3**. A weak Cl···H–O hydrogen bond interaction is observed between the chloride ligand and the free hydroxyl pendant group of the bifunctional NHC–OH ligand of an adjacent molecule, as reflected by the short H···Cl separation [2.63(5) Å] and the O–H···Cl angle [160(5)°] which is close to linear. Similar interactions were found in previously reported crystal structures for [Rh(NHC)(COD)Cl] species featuring hydroxyl-functionalized pendent arms,[22,31] without incidence on the metal–NHC binding. In addition, no abnormally short homopolar C–H···H–C contacts or π···π stacking effects have been identified in the crystal structure of **3**, so it is reasonable to think that non-covalent intermolecular interactions are not responsible for the unusual geometry of **3**, although crystal packing effects can never be totally excluded.

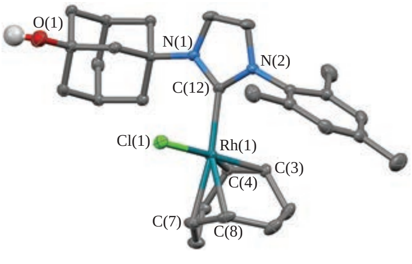


Figure 1 Solid-state molecular structure of **3** (30% probability ellipsoids). Hydrogen atoms, except that of the hydroxyl group have been omitted for clarity. Selected bond distances (Å) and angles (°): Rh(1)–Cl(1) 2.381(1), Rh(1)–C(12) 2.068(5), Rh(1)–C(3) 2.114(5), Rh(1)–C(4) 2.106(5), Rh(1)–C(7) 2.180(5), Rh(1)–C(8) 2.153(5), N(1)–C(12) 1.366(6), N(2)–C(12) 1.358(6); N(1)–C(12)–N(2) 103.9(4), C(12)–Rh(1)–Cl(1) 87.5(1), Rh(1)–C(12)–N(1) 134.2(4), Rh(1)–C(12)–N(2) 120.7(3).

In order to quantify such deformation, Crabtree and coworkers[32] introduced the yaw distortion angle notion, noted θ, which is defined as the ‘rotation of the NHC about the axis normal to the azole plane’ and calculated upon measuring the difference in the two Rh–C–N angles (Figure 2). To the best of our knowledge, complex **3** displays the highest yaw distortion (θ = 6.8°) for a monodentate NHC bound to Rh. This indicates that a peculiar steric profile is imparted by this unsymmetrical substituent {Ad^{OH}, Mes} combination.

To clarify this point, we carried out the systematic analysis of the yaw distortion angle in 85 structurally characterized Rh(NHC)(COD)Cl complexes, since such careful analysis of the bending of the Rh–NHC bond has not been carried out before for monodentate NHCs. The distribution of θ values is shown in Figure 2. Some representative examples are also presented in Table S2 to nurture the discussion.

From this analysis it is clear that small yaw angles (below 3°) are most of the time preferred (Figure 2), and account for 80% of the analyzed structures. Symmetrical NHCs generally display small θ values, even when the wingtips have a large steric profile (Table S2, entries 9–11). A plausible explanation is that the bending of the NHC with respect to the Rh–C bond, on one side or another, does not reduce steric pressure for symmetrically-substituted NHCs.

Unsymmetrical NHCs featuring two non-bulky N-substituents tend to display small θ values as well (Table S2, entries 6–8). In such cases, the steric pressure is small and bending of the NHC is unnecessary. The largest yaw distortion values (θ > 3°) are typically observed for unsymmetrically substituted NHCs featuring one particularly bulky substituent (CF_3 < Bu^t < Ad) in combination with a second substituent of lower steric profile (Table S2, entries 1–5). In the case of compound **3**, the pronounced steric pressure imposed by the adamantyl moiety most likely pushes the mesityl group (which is oriented nearly perpendicular to the imidazolyl ring to diminish its steric profile), to bend over, as is reflected by the Rh(1)–C(12)–N(2) angle [120.7(3)°] which is significantly lower than the Rh(1)–C(12)–N(1) one [134.2(4)°]. Note however that drastically larger (up to 30°) yaw angles values have been observed in chelating bidentate NHC ligands as a result of ring strain.[20,32–34] As shown in Table S2, θ values do not directly correlate with Rh–C$_{carbene}$ bond lengths, the latter being slightly elongated when bulky adamantyl N-substituents are used (Table S2, entries 1 and 9), disregarding of the yaw distortion.

In summary, we have elaborated the straightforward synthesis of a new unsymmetrical NHC ligand featuring two different (3-hydroxyadamantyl and mesityl) N-substituents and shown

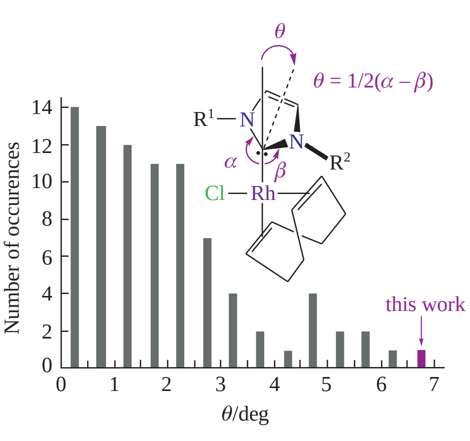


Figure 2 Distribution of yaw distortion angle θ values in structurally characterized Rh(NHC)(COD)Cl complexes. Analysis performed on 85 independent crystal structures. When several complexes are found in the asymmetric unit, the average θ value is considered.

that the steric imbalance between the two NHC wingtips leads to significant bending of the rhodium–carbene bond. The impact of this particular steric profile on reactivity is currently under investigation.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.01.015.

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