

Double C–H Activation in a Rh–NHC Complex Leading to the Isolation of a 14-Electron Rh(III) Complex

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The wide interest in the synthesis of coordinatively unsaturated metal complexes arises from the central role such compounds play as intermediates in many stoichiometric and catalytic processes.¹ In the context of catalytic C–H bond activation and functionalization, d⁶ and d⁸ 14-electron metal complexes are of special importance. Structural characterization of four-coordinate, formally 14-electron complexes of d⁶ iridium,² and ruthenium,³ and of three-coordinate d⁸ rhodium,⁴ palladium,⁵ and platinum,⁶ compounds have been recently reported. However, 14-electron complexes of rhodium(III) have so far eluded isolation.⁷ Because such unsaturated Rh(III) compounds are proposed key intermediates in Rh-catalyzed functionalizations of C–H bonds,⁸ their isolation and characterization remains a highly desirable goal.

The current research effort in the area of *N*-heterocyclic carbene (NHC) complexes of LTMs has originated from the desire to develop highly active, phosphine-free catalysts.⁹ Recent theoretical and experimental work has shown that not only are these ligands more electron-donating than even basic alkylphosphines, but NHC ligands IAd and I'Bu (IAd, *N,N*-di(adamantyl)imidazol-2-ylidene; I'Bu, *N,N*-di(*tert*-butyl)imidazol-2-ylidene) appear to be substantially more bulky than sterically demanding phosphine ligands such as P(*t*Bu)₃.¹⁰ We thus reasoned that reactivity studies involving the bulky and very basic I'Bu with appropriate Rh(I) precursors might allow for the isolation of stable, unsaturated, and high valent rhodium compounds via intramolecular C–H activation.¹¹

As a starting point, we investigated the reactivity of a hexane slurry containing [Rh(COE)₂Cl]₂ with a slight excess of I'Bu (4.16 equiv). Stirring this slurry at room temperature for 4 h affords a limpid yellow solution. Concentration and subsequent addition of pentane leads to the precipitation of a yellow solid in high yield. ¹H NMR data of RhCl(I'Bu)(I'Bu') (**2**, Scheme 1) show the expected hydride peak at –22.93 ppm as a broad singlet. While all signals for the cyclometalated I'Bu' ligand give rise to sharp resonances, the ones associated with the second I'Bu ligand are broad, indicating a fluxional exchange of the *tert*-butyl groups.¹² X-ray quality crystals, grown by slow evaporation of a hexane solution, explain this behavior (Figure 1). In the solid state, this ligand is involved in an agostic interaction of one of the *tert*-butyl groups with the rhodium metal center with distances of 2.073 Å [Rh(1)–H(16A)] and 2.704 Å [Rh(1)–C(16)]. The cyclometalated I'Bu' ligand is trans to it with the metalated CH₂ group cis to the hydride ligand and trans to the chloride.

A significantly different outcome is observed when the reaction is carried out in benzene. In this case, workup of the reaction mixture gives a dark yellow solid in 88% yield, and the ¹H NMR data are consistent with formation of the unusual, doubly cyclometalated complex RhCl(I'Bu')₂ (**3**). Elemental analysis supports this formulation, and, to ascertain the exact structure of complex **3**, X-ray quality crystals were grown from a hexane solution. The unsaturated complex **3** displays a distorted square pyramidal structure around the rhodium center (Figure 1). Analogous to **2**,

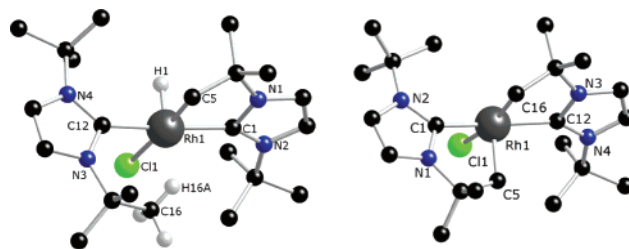
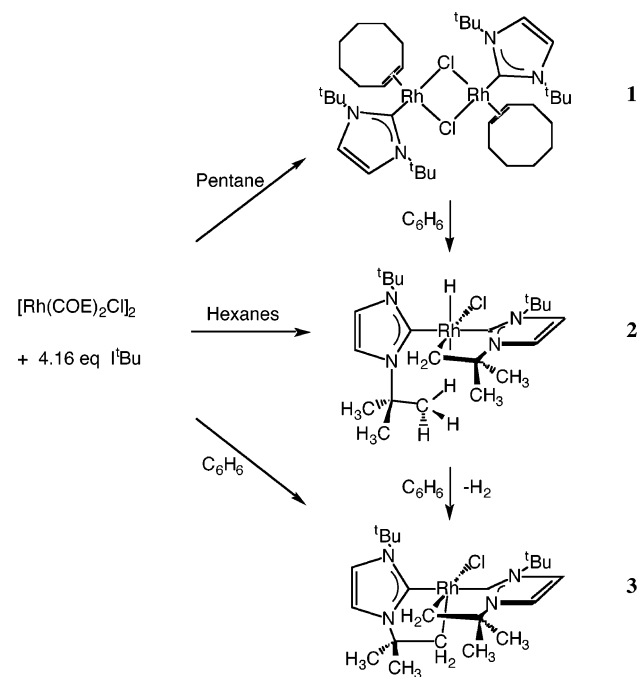


Figure 1. Ball-and-stick views of RhCl(I'Bu)(I'Bu') (**2**, left) and RhCl(I'Bu')₂ (**3**, right).

Scheme 1. Solvent-Dependent Reaction between [Rh(COE)₂Cl]₂ and I'Bu



the two carbenic carbon atoms are disposed trans to each other at an angle of 167.43° with their corresponding cyclometalated CH₂ groups cis with respect to each other (90.58°).

We investigated the formation of **3** by ¹H NMR in a C₆D₆ solution. An initially strong signal for the hydride signal at ca. –23 ppm (for **2**) was followed, after ca. 1 h, by the appearance of a characteristic peak at 4.74 ppm (solubilized H₂) and concomitant formation of the resonances for **3**.¹³ It is worth noting that, while agostic interactions between C–H bonds and metal centers are commonly postulated intermediates en route to C–H bond activation,¹⁴ such species are difficult to detect. To the best of our knowledge, this is the first time that both the immediate precursor (i.e., the agostic complex **2**) and the product of a C–H activation process (**3**) have been characterized by X-ray crystallography.^{15,16}

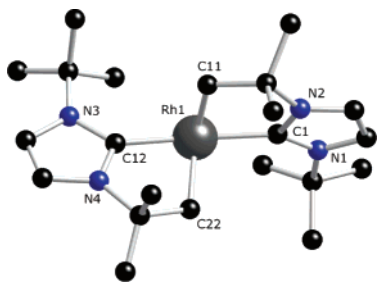
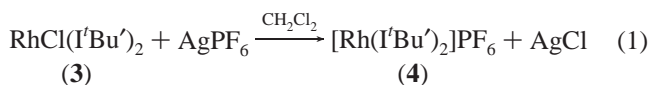


Figure 2. Ball-and-stick representation of $[\text{Rh}(\text{I}'\text{Bu}')_2]\text{PF}_6$ (**4**). Hydrogen atoms and the PF_6^- counterion are omitted for clarity.

In addition, activation of C–H bonds by Rh(III) is extremely uncommon,¹⁷ and double cyclometalations of ligand systems on rhodium are unknown.¹⁸

Yet another outcome for the reaction is observed when pentane is used as solvent. When a dilute pentane slurry of $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ (1 mL/4 mg) was treated with I'Bu (4.16 equiv), initial dissolution was observed (10 min), and, after 30 min, a heavy pale-yellow precipitate formed. Workup and characterization of this solid indicated the formation of the mixed dimer $[\text{Rh}(\text{COE})(\text{I}'\text{Bu})\text{Cl}]_2$ (**1**).¹⁹ When the pentane suspension containing **1** (and additional I'Bu) is treated with benzene and stirred overnight, dissolution of **1** and formation of **3** is observed, while isolated **1** is stable in benzene solution in the absence of additional I'Bu. Complex **1** thus represents a precursor on the way to **2** and **3** and convincingly demonstrates that the presence of only one electron-donating I'Bu ligand is not sufficient to favor intramolecular C–H activation.

Synthesis of a 14-electron Rh(III) complex is achieved by abstraction of the chloride ligand from **3** with AgPF_6 in CH_2Cl_2 (eq 1). Workup yields the cationic complex $[\text{Rh}(\text{I}'\text{Bu}')_2]\text{PF}_6$ (**4**) as a yellow-orange solid. ³¹P and ¹⁹F NMR show the expected resonances for the free PF_6^- counterion. ¹H NMR gives rise to characteristic signals for the metalated CH_2 groups [at 2.39 (dd) and 3.06 (d) ppm], three distinct resonances for the free CH_3 groups (intensity 3:1:1), and two doublets for the protons of the imidazole rings. X-ray quality crystals were obtained by slow evaporation of a $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_5\text{F}$ solution, and the structure of **4** is shown in Figure 2.



This four-coordinate Rh(III) complex adopts a highly distorted, *cis*-divacant octahedral structure. It is especially worth noting that, while 14-electron complexes described in the literature so far are distinguished by having strong agostic interactions,^{2,3a,b,4–6} or by adopting a triplet spin state,^{3c} such stabilization is not observed in **4**.²⁰ We believe that the hard and electron-donating all-carbon-based ligation is at least partly responsible for the unusual stability of this complex.

In conclusion, we describe the solvent-dependent interaction of I'Bu with a Rh(I)–olefin complex leading to the isolation of two precursors en route to a unique double cyclometalation process. Abstraction of the chloride ligand from **3** enables the isolation of a “bare” 14-electron Rh(III) complex. The electronic nature of these unsaturated Rh(III) compounds might allow the isolation of stable Rh(V) species; investigations of the catalytic activity of the complexes as well as direct intermolecular C–H activation using less bulky NHC ligands are underway.

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Supporting Information Available: Experimental procedures, compound characterization, and crystallographic data (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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