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Carbene Ligands

Abnormally Bound N-Heterocyclic Carbene Complexes of Ruthenium: C–H Activation of Both C4 and C5 Positions in the Same Ligand**

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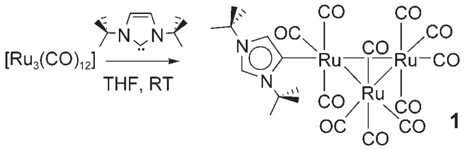
Ruthenium N-heterocyclic carbene (NHC) complexes have been the focus of considerable interest owing to their applications in a range of homogeneous catalytic processes.[1] However, some of these precatalysts have been shown to undergo degradation reactions under quite mild conditions, suggesting that M–NHC bonds may not be as robust as once believed.[2] This is further substantiated by a number of reports detailing Ru–NHC complexes that prove susceptible to intramolecular C–X (X = H, C, N) bond cleavage,[3] migratory insertion,[4] and cyclopropanation/rearrangement.[5]

One mode of reaction hitherto unknown with ruthenium involves the C–H activation of a backbone (C4) position of a carbene (or imidazolium salt) to give an "abnormal" NHC (aNHC) complex. Despite being first reported in 2002, aNHCs remain quite rare among the myriad of reports detailing NHC reactivity.[6] This is unlikely to persist in light of findings such as those recently reported by Lebel, Nolan, and co-workers, who showed that although Pd(NHC)$_2$Cl$_2$, which contains one normal (C2 bound) and one abnormal NHC, successfully catalyzes C–C coupling, the presence of two normally bound ligands renders the complex inactive.[7] Thus, efforts to synthesize and study the reactivity of new aNHC complexes, with catalytically important metals such as ruthenium, is of clear importance. Herein we report that 1,3-di-*tert*-butylimidazol-2-ylidene (I*t*Bu) reacts with [Ru$_3$(CO)$_{12}$] at room temperature to generate the novel Ru–aNHC complex **1**. We believe this to be the first example of aNHC formation from a free monodentate carbene. Subsequent heating of **1** results in an unprecedented activation of the second "abnormal" (C5) site to afford a triruthenium cluster containing an Ru$_3$C$_2$ framework (**2**).

The aNHC complex **1** was isolated in 81 % yield as a red-orange, air-stable solid following the room temperature addition of 1 equivalent of I*t*Bu to a THF solution of [Ru$_3$(CO)$_{12}$], which resulted in the immediate evolution of CO (Scheme 1).[8] The X-ray crystal structure of **1** (Figure 1)[9] showed coordination of abnormally bound I*t*Bu via the C4 position to [Ru$_3$(CO)$_{11}$] and transfer of the activated hydrogen to the available C2 site. The aNHC occupies an equatorial position at the six-coordinate Ru1 atom with an angle of 9.8° between the plane of the Ru$_3$ core and the five-membered heterocyclic ring. Although free I*t*Bu was used from the start of this reaction, it is clear from the solid-state structure that C2 coordination via the carbene lone pair is precluded by the bulky *tert*-butyl substituents. Even with C4 coordination, the N–*t*Bu groups still interfere enough to push the equatorial CO ligand on Ru1 away to enforce a C12-Ru1-C2 angle of 108.1(1)°.[10] The Ru–C12 bond length (2.151(2) Å) is somewhat longer than the Ru–C$_{\mathrm{NHC}}$ distance reported for the "normal" carbene complex [Ru$_3$(CO)$_{11}$(IMe$_2$)] (2.115(4) Å; IMe$_2$ = 1,3-dimethylimidazol-2-ylidene).[8b]



Scheme 1. Formation of the abnormal NHC complex **1**.

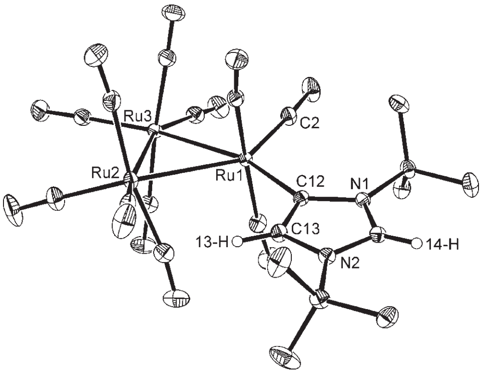


Figure 1. Molecular structure of **1** (ellipsoids at the 30% probability level and all hydrogens, except the C2 and C5 hydrogens, are omitted for clarity). Selected bond lengths [Å]: Ru1–Ru2 2.8835(3), Ru1–Ru3 2.8456(3), Ru2–Ru3 2.8504(3), Ru1–C12 2.151(2).

In solution, ^{1}H NMR spectroscopy revealed two different *tert*-butyl-group environments and two high-frequency signals ($\delta = 6.4$ and 8.4 ppm, doublets with $J_{\mathrm{HH}} = 1.5$ Hz), which were assigned to the protons on C4 (i.e. 13-H in the structure in Figure 1) and C2 (labeled 14-H in Figure 1) on the basis of long-range correlations (^{1}H-^{13}C HMBC) to two ^{13}C resonances at $\delta = 130.5$ and 132.5 ppm, respectively. A one-bond

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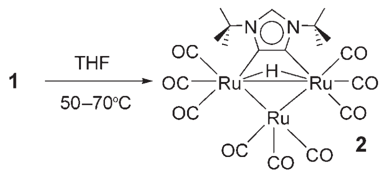
correlation (^1H-^{13}C HMQC) was found between the $\delta =$ 6.4 ppm signal and a quaternary ^{13}C resonance at $\delta =$ 134.1 ppm resulting from the metal-bound C4 atom.

When **1** was heated in $[D_8]$-THF (50–70 °C), the μ_3-η^2-bridging heterocyclic complex **2** was formed through C–H activation of the C5 position (Scheme 2).[11] The remaining C2-bound proton appeared at $\delta = 8.6$ ppm in the ^1H NMR spectrum, whereas the bridging hydride showed a shift of $\delta = -17.9$ ppm. The $^{13}C\{^1H\}$ NMR data for **2** comprised of singlets for the C4/C5 ($\delta = 139.4$ ppm) and C2 ($\delta = 144.0$ ppm) carbon atoms. Two other high-frequency proton resonances, a triplet at $\delta = 8.8$ ppm and a doublet at $\delta = 7.9$ ppm in a 1:2 ratio, indicated the formation of some 1,3-di-*tert*-butylimidazolium-containing species, which is discussed further below.



Scheme 2. Conversion of **1** to the bridged complex **2**.

The X-ray crystal structure of **2** is shown in Figure 2.[12] The doubly activated heterocyclic ring may be viewed as forming a 5c–4e bonding interaction with the Ru_3 core. This is illustrated by the significant ring tilt towards Ru1, which necessarily results in large deviations from the ideal geometry for both Ru2 and Ru3. In particular, the angle between the least-squares plane of the heterocyclic ring and the plane containing the three ruthenium atoms is 73.2°. As expected for an interaction of this type, the Ru2–Ru3 distance is elongated (2.9739(3) Å) relative to the other two Ru–Ru distances (2.7183(3), 2.7235(3) Å).[13] Overall, the 48 e count for the complex is consistent with a zwitterionic description of the structure.

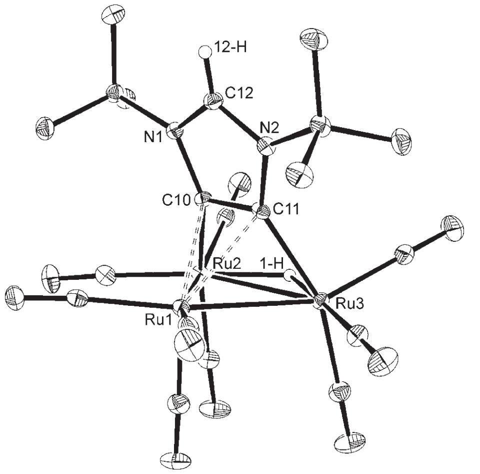


Figure 2. Molecular structure of **2** (ellipsoids at 30% probability level and all hydrogens, except the C2 and Ru–H–Ru hydrogens, are omitted for clarity). Selected bond lengths [Å]: Ru1–Ru2 2.7183(3), Ru1–Ru3 2.7235(3), Ru2–Ru3 2.9739(3), Ru1–C10 2.339(2), Ru1–C11 2.324(3).

When **2** was heated in THF under CO (1 atm, 70 °C, 11 h), no reformation of **1** was observed. However, thermolysis of **2** in the presence of H_2 (1 atm, 50 °C, 17 h) resulted in the formation of more imidazolium (represented by signals at $\delta =$ 8.7 and 7.8 ppm, which were now broad singlets) and the appearance of a new hydride resonance at $\delta = -17.0$ ppm.[14] Prolonged heating (for a total of 40 h) further depleted **2**, although not completely. Although the imidazolium and hydride signals continued to increase, at no stage did they integrate to consistent values. The hydride-containing anionic species was isolated and structurally characterized as the imidazolium salt of the tetraruthenium trihydride anion $[Ru_4(CO)_{12}H_3]^-$ (see the Supporting Information),[15] which results from reaction of **2** with two molecules of H_2. Formation of an Ru_4 anion suggests that other proton silent anions of different nuclearity must be present to account for the variable proton integration of the imidazolium cation.

The overall transformation of free to abnormally bound NHC, C–H activation to afford a bridging heterocycle, and finally, elimination of imidazolium represents an unprecedented set of reactions for a free N-heterocyclic carbene. Our results, in concert with the report by Cabeza et al., detailing a reversible double C–H activation of an NHC N–Me group by $[Ru_3(CO)_{12}]$,[8b] indicate that ruthenium clusters can be used to generate a remarkable range of products when reacted with NHCs. We anticipate that further surprises lie in wait.

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Keywords: C–H activation · cluster compounds · metal–metal bonds · N-heterocyclic carbenes · ruthenium

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[8] $[Ru_3(CO)_{12}]$ reacts with the dimer of 1,3-diethyl-4,5-dihydroimidazol-2-ylidene ($(IEt_2H_2)_2$; hexane, 60°C) to give the "normal" complex $[Ru_3(CO)_{11}(IEt_2H_2)]$. a) M. F. Lappert, P. L. Pye, *J. Chem. Soc. Dalton Trans.* **1977**, 2172–2180. Similarly, $[Ru_3(CO)_{11}(IMe_2)]$ has been isolated, but found to undergo C–H activation of an NMe group at elevated temperature. b) J. A. Cabeza, I. del Río, D. Moguel, M. G. Sánchez-Vega, *Chem. Commun.* **2005**, 3956–3958.

[9] Data for **1**: $C_{22}H_{20}N_2O_{11}Ru_3$, $M_r = 791.61$, crystal dimensions $0.35 \times 0.30 \times 0.30$ mm^3, monoclinic, space group $P2_1/n$, $a = 12.9520(2)$, $b = 13.4390(2)$, $c = 16.7480(2)$ Å, $\beta = 106.861(1)°$, $U = 2789.87(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.885$ Mg m^{-3}, $F(000) = 1544$, $\mu = 1.661$ mm^{-1}, 8154 independent reflections, $R1 = 0.0312$, $wR2 = 0.0677$ for reflections with $I > 2\sigma(I)$.

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[11] A high yield of **2** was produced if an argon purge was maintained during heating to remove the released CO.

[12] Data for **2**: $C_{20}H_{20}N_2O_9Ru_3$, $M_r = 735.59$, crystal dimensions $0.20 \times 0.15 \times 0.12$ mm^3, orthorhombic, space group *Pbca*, $a = 16.8740(1)$, $b = 15.4110(1)$, $c = 19.4920(2)$ Å, $U = 5068.8(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.928$ Mg m^{-3}, $F(000) = 2864$, $\mu = 1.814$ mm^{-1}, 9072 independent reflections, $R1 = 0.0281$, $wR2 = 0.0615$. 1-H located and refined subject to being equidistant from Ru2 and Ru3.

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[15] Data for **3**: $C_{23}H_{24}N_2O_{12}Ru_4$, $M_r = 924.72$, crystal dimensions $0.12 \times 0.12 \times 0.10$ mm^3, monoclinic, space group $P2_1/n$, $a = 13.8140(1)$, $b = 13.9020(1)$, $c = 17.0120(2)$ Å, $\beta = 108.075(1)°$, $U = 3105.80(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.978$ Mg m^{-3}, $F(000) = 1792$, $\mu = 1.966$ mm^{-1}, 9072 independent reflections, $R1 = 0.0536$, $wR2 = 0.0725$ for reflections with $I > 2\sigma(I)$.

[16] CCDC-643194 (**1**), CCDC-643195 (**2**), and CCDC-643196 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.