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Communication

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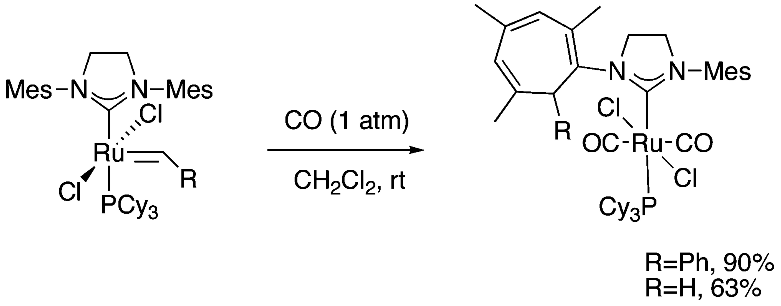

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# Carbon Monoxide-Promoted Carbene Insertion into the Aryl Substituent of an N-Heterocyclic Carbene Ligand: Buchner Reaction in a Ruthenium Carbene Complex

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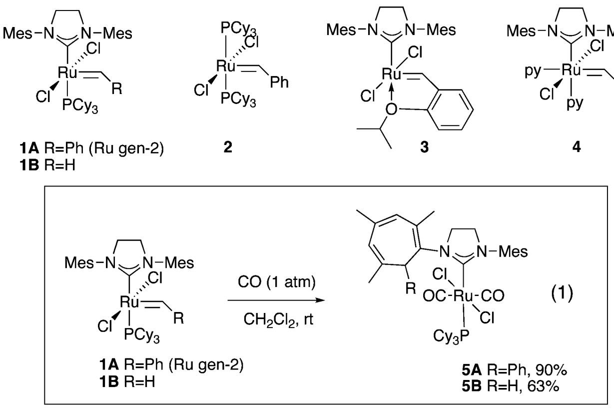
Ruthenium carbenes have had a profound impact in organic and materials synthesis due to their remarkable chemoselectivity in catalysis of the alkene metathesis reaction. The Grubbs group reported a better alkene metathesis catalyst featuring the N-heterocyclic carbene ligand, now known as the "second generation" ruthenium carbene complex **1A**.[1] Generally, the N-heterocyclic carbene ligand plays an important role as a *noninterfering* supporting ligand in metathesis reactions. In this report, we identify a new carbene insertion reaction in the Grubbs' second generation complex promoted by carbon monoxide (eq 1). The reaction pathway of eq 1 represents an unprecedented carbene insertion into the mesityl group on the N-heterocyclic carbene supporting ligand, a Buchner reaction of a ruthenium carbene.

***Scheme 1.*** Unexpected Carbene Insertion Products



**1A** R=Ph (Ru gen-2)
**1B** R=H

**2**

**3**

**4**

**1A** R=Ph (Ru gen-2)
**1B** R=H

**5A** R=Ph, 90%
**5B** R=H, 63%

The net bond insertion from a metathesis-competent carbene complex is fundamentally interesting and important. What defines the remarkable ability of Grubbs' complexes **1**−**4** to promote alkene metathesis over other reactions such as cyclopropanation? Cyclopropanation and bond insertion processes triggered from a metathesis-active carbene are unusual.[2] The tendency toward cyclopropanation depends on both carbene electrophilicity and metal coordination environment. Carbene complexes **1**−**4** give alkene metathesis because they can dissociate a ligand (Cy$_3$P in the case of **1**, **2**). In contrast, coordinatively saturated ruthenium carbenes give cyclopropanation reactions.[3] Carbon monoxide binding serves as a switch toward cyclopropanation reactivity. The close proximity[4a] of the aromatic ring to an electrophilic carbene could lead to reaction between the metal carbene and the aromatic ligand of the N-heterocyclic carbene.[5,6] Carbene insertion into the aromatic $\pi$ system, giving ring expansion, has not been previously observed.

Due to our interest in rapidly quenching metathesis reactions for kinetic studies,[7] we considered using carbon monoxide to block any available coordination sites on the metal carbene, thereby stopping metathesis. The quenching proved to be very efficient and rapidly stopped an enyne metathesis reaction (data not shown). Treatment of complex **1A** with carbon monoxide immediately resulted in a canary yellow solution. On concentration, the solution deposited a yellow solid. An analytical sample was crystallized from dichloromethane/decane at $-20$ °C to afford crystals, mp 143−145 °C, which proved suitable for X-ray structure analysis.

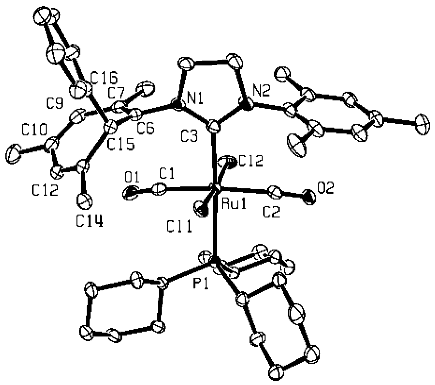


***Figure 1.*** ORTEP drawing of complex **5A** (displacement ellipsoids drawn at 50% probability).

Crystal structure determination[8] revealed that one of the mesityl groups of the N-heterocyclic carbene had been transformed to a seven-membered ring by a net benzylidene insertion (Figure 1). The alternating short (av. 1.35 Å) and long (av. 1.45 Å) C−C bonds of the ring clearly indicate the cycloheptatrienyl substructure. The phenyl substituent is oriented *anti* to the metal center. The plane of the heterocyclic carbene is oriented along the OC−Ru−CO axis rather than the Cl−Ru−Cl axis or bisecting the Cl−Ru−CO bond angle, which might have been assumed on steric grounds. Taking the OC−Ru−CO axis as the *x* axis and the P−Ru−C (heterocyclic carbene) as the *z* axis, the $d_{xz}$ and $d_{xy}$ orbitals have the appropriate symmetry to bond with the $\pi^*$ orbitals of the CO ligands, whereas the $d_{yz}$ orbital has appropriate symmetry to $\pi$-bond to the heterocyclic carbene in the observed orientation. In complexes of type $Ru(CO)_2X_2L_2$ (where X is a halide or pseudo-halide and L is a neutral donor ligand), the most stable coordination geometry is Ru(*cis*-CO)$_2$(*cis*-X)$_2$(*trans*-L)$_2$.[9] The *trans* geometry of the carbonyl ligands suggests that CO addition generates complex **5A** as the kinetic product.

Spectroscopic characterization verified the structure of **5A** in solution. FT-IR in hexanes showed one strong absorption at 1982 cm$^{-1}$. The $^{31}$P NMR spectrum gave a single peak at $\delta$ 16.01 ppm. The cycloheptatrienyl vinylic protons at $\delta$ 5.9 and 5.75 correlated with carbon-13 resonances at 126.7 and 126.3 ppm, respectively (HMQC). The benzyl proton at 4.57 ppm correlated with a methine carbon at $\delta$ 54.58 ppm. These observations support that the 1,3,5-cycloheptatriene tautomer exists in solution at room temperature.

Similarly, the methylidene **1B**[4b] gives a cycloheptatrienyl insertion product **5B** (mp 130−132 °C), analogous to the insertion/rearrangement product observed from complex **1A**. This product

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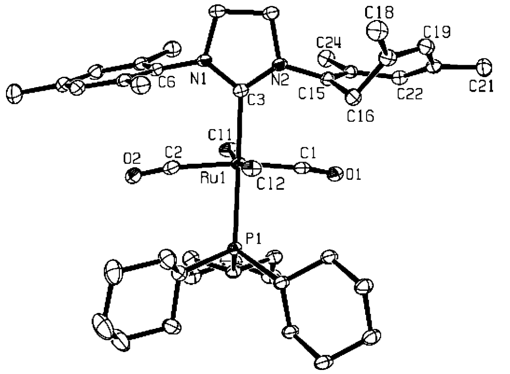


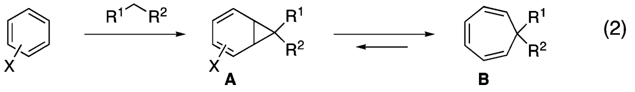
***Figure 2.*** ORTEP drawing of complex **5B** (displacement ellipsoids drawn at 50% probability).

was completely characterized including the X-ray crystal structure (Figure 2). The $^{31}$P spectrum in deuteriobenzene gave a single resonance at $\delta$ 13.44 ppm. FT-IR in hexanes displayed intense bands at 1979 and 1945 cm$^{-1}$ assigned to different carbonyl ligands. The proton and carbon NMR established the presence of the cycloheptatrienyl group, similar to that seen in complex **5A**.[8]

The cyclopropanation/insertion pathway can also be triggered by added isocyanide ligand. For example, complex **1A** reacted with 2.2 equiv of *p*-chlorophenyl isocyanide at room temperature to give a complex (single resonance in the $^{31}$P spectrum, $\delta$ 13.08) that contains the cycloheptatrienyl substructure ($^1$H NMR shows singlets at $\delta$ 5.61, 5.41, and 5.04 ppm). Similar results were observed with *p*-methoxyphenyl isocyanide.[8] Further investigation of the scope of ligand-promoted cyclopropanation is warranted.

The CO-promoted insertion can be carried out after enyne metathesis. Enyne metathesis between propargyl benzoate and ethylene (60 psig) using 4 mol % of **1A** was stopped by perfusion of carbon monoxide. The insertion product **5A** was observed in the crude $^{31}$P spectrum.[8] Interestingly, the methylidene insertion product **5B** was not seen in the crude NMR spectrum.

The structures of complexes **5A** and **5B** reveal an unexpected carbene insertion into a stable aromatic ring of the 1,3-bis(mesityl)-imidazolidine ($H_2$IMes) supporting ligand. This is an unprecedented transformation for a metathesis-active ruthenium carbene.[10] The first step of the Buchner reaction is cyclopropanation of an aromatic ring. The resulting cyclopropane, a norcaradiene **A**, rearranges by 6$\pi$ electrocyclization to furnish the cycloheptatriene **B** (eq 2).



(2)

The carbene substituents $R_1$ and $R_2$ are known to affect the position of the equilibrium; for simple alkyl and aryl groups, the equilibrium favors the triene **B**.[11] In both cases observed in this study, the cycloheptatriene tautomer predominates.

The carbene insertion into the $H_2$IMes ligand is promoted by carbon monoxide binding. On carbon monoxide binding, the carbene cyclopropanates the closest "double bond" of the mesityl group, which is followed by electrocyclic ring opening of the cyclopropane to provide the cycloheptatriene. The absence of regioisomers (resulting from remote cyclopropanation of aromatic $\pi$-bonds) indicates that the carbene is still encumbered to the ruthenium center and is not reacting as a free carbene. The ligand-promoted insertion may be unique to ligands with strong $\pi$-acid properties. CO binding may weaken $\pi$-back-bonding between the ruthenium atom and the carbene ligand, making it more electrophilic and disengaging it from the metal center.

In conclusion, a new carbene insertion into a mesityl group of the second generation Grubbs' carbene complex has been identified. Both carbon monoxide and isocyanides promote the cyclopropanation. Rather than simply occupying open coordination sites, the ligand ushers the ruthenium-bound carbene into a position-selective cyclopropanation/rearrangement reaction manifold giving a cycloheptatriene (Buchner reaction). The insertion may prove useful to identify carbene intermediates in enyne metathesis. Studies along these lines are ongoing in our laboratories.

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**Supporting Information Available:** Detailed experimental procedures for the synthesis and characterization of **5A** and **5B**, and the X-ray crystallographic data for **5A** and **5B** (Tables S1−S8). This material is available free of charge via the Internet at http://pubs.acs.org.

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