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Alkyne *gem*-Hydrogenation: Formation of Pianostool Ruthenium Carbene Complexes and Analysis of Their Chemical Character

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Abstract: Parahydrogen (*p*-H₂) induced polarization (PHIP) NMR spectroscopy showed that [Cp^xRu] complexes with greatly different electronic properties invariably engage propargyl alcohol derivatives into *gem*-hydrogenation with formation of pianostool ruthenium carbenes; in so doing, less electron rich Cp^x rings lower the barriers, stabilize the resulting complexes and hence provide opportunities for harnessing genuine carbene reactivity. The chemical character of the resulting ruthenium complexes was studied by DFT-assisted analysis of the chemical shift tensors determined by solid-state ¹³C NMR spectroscopy. The combined experimental and computational data draw the portrait of a family of ruthenium carbenes that amalgamate purely electrophilic behavior with characteristics more befitting metathesis-active Grubbs-type catalysts.

Transition metal complexes comprising a formal metal-carbon double bond are commonly classified as either "Fischer carbenes" or "Schrock alkylidenes".¹ The former are electrophilic entities which typically incorporate low-valent metal centers with strong-field ancillary ligands; their carbene unit itself usually bears a heteroelement substituent.^{2,3} "Schrock alkylidenes", in contrast, feature a high valent metal center bound to a nucleophilic carbon substituent, often comprised within a weaker-field ligand environment.^{4,5} It is important to recognize, however, that this terminology denotes only

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the extremes of a continuum: it is not necessarily intuitive by looking at the molecular structure to which category a given metal carbene complex may belong. The famous Grubbs catalysts, which have revolutionized the practice of olefin metathesis, may perhaps be cited in this context.^{6,7,8,9,10}



Scheme 1. The interwoven pathways of *trans*- and *gem*-hydrogenation of alkynes; Cp* = pentamethylcyclopentadienyl

Pianostool ruthenium complexes of type **D** are isoelectronic with Grubbs carbenes. Although such species had been invoked as reactive intermediates in a number of different transformations including cyclopropanation,^{11,12} little was known about structure and bonding until very recently. Our current interest was invigorated by the finding that carbenes of this type can be generated by *gem*hydrogenation of ordinary alkynes using $[Cp*RuCl]_4$ as the catalyst.^{13,14} This unorthodox transformation, in which both H-atoms of H₂ are delivered to one and the same C-atom of the triple bond, has no precedent in the classical canon of homogeneous catalysis; it constitutes the early phase of a reaction pathway that allows alkynes to be converted into *E*-alkenes **H** by *trans*-selective

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semi-reduction (Scheme 1).¹³⁻¹⁵ It is important to note that this stepwise process leading from **C** via **D** to **H** competes with a concerted mechanism, which bifurcates at the stage of the metallacyclopropene intermediate **C** initially formed upon transfer of the first H-atom to the alkyne ligand in π -complex **B**. For unbiased substrates, the barriers for either route downstream of **C** were computed to be very similar;¹³ propargylic –OR substituents, however, which are able to engage with an emerging carbene via hydrogen bonding or a Lewis acid/Lewis base interaction, foster the stepwise path by stabilizing the intermediates and exert a pronounced directing effect; in favorable cases have the resulting pianostool ruthenium carbenes of type **D** been isolated in analytically pure form and were fully characterized by spectroscopic and crystallographic means.^{13,14}

This involved overall manifold is of fundamental interest but renders reaction optimization difficult: The concerted step from **C** to **G** is intrinsically selective for the *E*-alkene **H**, whereas a transient carbene **D** opens a gateway to side reactions such as positional alkene isomerization and/or overreduction, which often plaque *trans*-hydrogenation.¹⁵ Experimental and computational data concur in that the conversion of **D** to product as well as to the side products proceeds via an associative mechanism, in which a second H₂ molecule needs to be ligated to the ruthenium center to lower the barriers.¹³ On the other hand, one can envisage that purposeful carbene formation by *gem*-hydrogenation allows alkynes to be used as surrogates for hazardous carbene sources such as diazo derivatives or cyclopropenes. The possible outlook of harnessing genuine carbene chemistry downstream from **D**, however, is contingent on the ability to either fully stop or outperform the evolution of **D** into the *trans*-alkene **H** and/or side products via **F** and **E**, respectively. Moreover, it mandates an answer to the question whether ruthenium complexes of type **D** fall into the realm of Fischer carbenes or Schrock alkylidenes.



Figure 1. Panel of cationic [Cp^XRu] complexes with largely different electronic properties

To address these central issues, a library of $[Cp^{X}Ru(MeCN)_{3}]PF_{6}$ precatalysts (Cp^{X} = substituted cyclopentadienyl)¹⁶ was prepared and their ability to form carbene complexes by *gem*-hydrogenation studied using propargylic ether **10** as the model substrate (Figure 1). Cyclic voltammetry confirmed that all complexes undergo reversible one-electron oxidation at potentials ($E_{1/2}$) ranging from 0.322 V to 0.903 V. This favorably large span of almost 0.6 V should help to unveil if Cp^{X} ligands of different donor capacity exert any noticeable effects on carbene formation and stability.^{17,18,19}

Figure 2 captures the behavior of ten different $[Cp^{x}Ru]$ complexes in the hydrogenation of substrate **10**. The reactions were performed with parahydrogen (*p*-H₂) in order to take advantage of the sensitivity of PHIP-enhanced ¹H NMR spectroscopy (PHIP = *p*-H₂-induced polarization), which allows fleeting intermediates to be monitored even if present in low concentration.^{20,21,22} The characteristic spectral fingerprint of the CH₂-group formed by *gem*-hydrogenation of the triple bond proves the intervention of carbenes **11** in all cases investigated. Moreover, the observed coupling pattern shows that these carbenes invariably reside *distal* to the steering –OMe group; only in the spectrum derived from complex **3** is the regioisomeric carbene present in appreciable concentration (*proximal:distal*, 3:7). The observation that the most crowded Cp^X ligand entails appreciable carbene formation at the more hindered site is counterintuitive and deserves closer inspection.



Figure 2. Catalyst-dependent OPSY-NMR spectra recorded during the hydrogenation of 10

Of arguably greater significance in the present context is the fact that PHIP-enhanced signals of the *E*alkene **12** are detected only in the reactions catalyzed by **1** and **3**, which carry the most electrondonating Cp^{X} ligands. It is important to note that the olefin detectable in the OPSY experiment must have been formed by the concerted mechanism in which both alkene H-atoms derive from the same H₂ molecule.²³ The observation that electron rich cationic catalysts up-regulate this intrinsically selective pathway provides valuable guidance for future studies aiming at an improvement of *trans*hydrogenation by ligand tuning.

The comparison with the *neutral* complexes $[Cp^*RuCl]_4$ and $[Cp^ERuCl]$ (E = COOMe)^{16,24} is equally informative: the former is the only catalyst that leads to notable overreduction with formation of **13**, whereas neither $[Cp^ERuCl]$ nor any of the cationic species does. Since overreduction is known to

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proceed only if the carbene initially formed ligates and activates a second H₂ molecule,¹³ the spectra shown in Figure 2 provide yet another relevant information for reaction optimization. In any case, one can conclude that less electron-rich [Cp^XRu] fragments disfavor associative downstream processes leading to *E*-alkene formation, isomerization and/or overreduction.

Complementary to the information gained from the ¹H PHIP NMR experiments about carbene formation and stability, solid-state ¹³C NMR allows the electronic character of these organometallic intermediates to be assessed.^{25,26,27} While isotropic chemical shifts ($\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$) are obtained by solution NMR, the three principal components of the chemical shift tensor ($\delta_{11} \ge \delta_{22} \ge$ δ_{33}) can be determined by measurements in the solid state. They are directly related to the shielding tensor σ_{ii} ($\delta_{ii} = \sigma_{iso}^{ref} - \sigma_{ii}$) which can be calculated by ab initio methods and de-convoluted into diamagnetic and paramagnetic terms ($\sigma_{ii} = \sigma_{dia} + \sigma_{para}$).²⁸ While σ_{dia} is largely related to core electrons and leads to shielding, the paramagnetic contributions $\sigma_{\mbox{\tiny para}}$ cause deshielding and arise from magnetically induced coupling of the electronic ground state to excited states by action of the angular momentum operator \hat{L}_i . The paramagnetic deshielding is particularly pronounced for an energetically high-lying ground state and low-lying excited states, or in other words frontier molecular orbitals (FMOs). In a pictorial view, a strong deshielding of a given nucleus occurs along a direction *i* if a high-lying occupied orbital on this nucleus can be superimposed onto a low-lying vacant orbital on the same nucleus by rotation along the axis *i*. For example, in a metal carbene the large deshielding of the δ_{11} component is mainly caused by a coupling of the high-lying occupied σ (M-C) orbital with the low-lying vacant π^* (M=C) orbital by the \hat{L}_1 operator (Figure 4a). As the extent of deshielding increases with a decreasing energy gap between these (frontier) orbitals, it is strongly correlated with the nature of the M=C bond. The principal components of the chemical shift tensor hence constitute an experimental probe for relative energy and orientation of frontier orbitals of a given carbene fragment. For instance, the rather low-lying $\pi^*(M=C)$ orbital of a Fischer carbene entails massive deshielding, especially of δ_{11} , while nucleophilic Schrock alkylidenes experience a significant contribution of their high energy π (M=C) orbital to δ_{11} . Based on such patterns, members of these families can *a priori* be distinguished on spectroscopic grounds.²⁵⁻²⁷



Figure 3. Complexes subjected to CST analysis

This powerful analytical tool was applied to complexes **14** - **18** (Figure 3), which correspond to the stationary points **A** - **D** of the reaction coordinate of *gem*-hydrogenation; the computed data were calibrated with the experimental values available for **14**, **17** and **18**. It has previously been noted that the C-atoms of 1-(prop-1-yn-1-yl)cyclohexan-1-ol (δ_{150} = 84/80 ppm) experience large but unequal deshielding upon formation of complex **14** (δ_{150} = 159/130 ppm; Figure 4b).^{29,30} This fact was nicely reproduced by DFT calculations, which indicate that this effect originates from the low lying LUMO essentially composed of a vacant metal d-orbital interacting with the π (C–C) bonding orbital (see the SI for more details). Upon subsequent binding of H₂, the π -ligand in the "loaded" catalysts **15** regains partial alkyne character, however with principal components of the chemical shift tensor that are indicative of significant metal-alkyne interactions (see the SI). This result is in excellent accord with previous NMR studies on ruthenium catalyzed *trans*-addition reactions in solution, which emulated such loaded species by formal replacement of reactive H–E (E = H, SiR₃, SnR₃) by unreactive 2-electron donor ligands (MeCN, pyridine, Me₃P). In all cases investigated were the recorded ¹³C shifts of the coordinated triple bond in complexes analogous to **15** very similar to those of the free alkyne.^{29,30}



Figure 4. a) Typical orientation of the chemical shift (δ) and shielding (σ) tensor in metal carbenes and main orbital couplings leading to the large deshielding of δ_{11}/σ_{11} . b) Calculated chemical shift and shielding tensors of C1 and C2 of the π -complex **14** and corresponding values for the C2 atom of the cyclopropylidene complex **16**. In the 3D plots of the shielding tensors, blue lobes represent shielded regions ($\sigma > 0$) while orange lobes represent deshielded regions ($\sigma < 0$). c) Calculated shielding tensors, simulated NMR spectrum and orbital analysis of the C1 carbon in the ruthenacyclopropene **16** (top), the carbene-carbon in the neutral carbene **17** (middle) and the carbene-carbon in the cationic carbene **18** (bottom). Upon going from **16** to **17** to **18**, the contributions of the σ (M–C) orbital to deshielding increase, while the contributions of the π (M=C) orbital decrease, indicating a more pronounced electrophilic character (due to the lower-lying π^* (M=C) orbital) along this series. All chemical shift and shielding values are reported in ppm.

Transfer of the first H-atom to the π -bond evokes a considerable change in electronic structure. Specifically, the resulting complex **16** shows markedly different CST's at the two carbon atoms: C2, which has accepted this first H-atom, becomes notably shielded, rather isotropic and fairly sp³-like (Figure 4b, right). In stark contrast, C1 is significantly deshielded with a highly anisotropic chemical shift tensor (Figure 4c, top); it actually resembles a true carbone center, indicating a significant double bond character in the Ru–C1 bond (see the SI). This point is nicely illustrated by the comparison of the computed spectra of **16** and **17** shown in Figure 4c (top and middle). Complex **16** is hence best described as a "1-ruthenacyclopropene" rather than a " η^2 -vinylruthenium complex", since the latter term carries the potentially misleading connotation of significant C–C double bond character.³¹

Transfer of the second hydrogen atom to C2 completes the *gem*-hydrogenation event and affords carbene **17**.¹³ Gratifyingly, this complex proved sufficiently stable to allow the low intensity signal of the carbene center to be detected by solid-state NMR (see the SI); the calculated shifts agree with the experimentally obtained values.³² CST analysis shows the expected strong deshielding of δ_{11} perpendicular to the Ru=C bond, as characteristic for metal carbenes (Figure 4c, middle). This deshielding is mainly associated with a strong coupling of the $\sigma(Ru-C)$ bonding orbital with the low-lying $\pi^*(Ru-C)$ orbital. On top, the $\pi(Ru-C)$ orbital shows a significant contribution to δ_{11} , implying that this particular orbital is sufficiently high in energy to couple with the vacant $\sigma^*(Ru-C)$ orbital. This contribution is small for classical Fischer carbenes but had been observed for Grubbs carbenes before.²⁶ Likewise, the orbital contributions to the δ_{22}/σ_{22} components show a pattern reminiscent of Grubbs catalysts,²⁶ because they mostly involve magnetic coupling of the $\sigma(C-C)$ and $\sigma(C-C')$ orbitals to the vacant $\pi^*(Ru-C)$ orbital (see the SI).

To probe the influence of positive charge as well as of a less electron rich Cp^X ligand on the chemical nature of the resulting carbenes, solid-state NMR spectra of the cationic complex **18** were recorded and analyzed, even though the short lifetime of this species even at low temperatures rendered data acquisition difficult (see the SI).³² As expected, all principal components of the chemical shift tensor are even more deshielded than in **17** (Figure 4c, bottom). For δ_{11} , this is mostly due to a more pronounced coupling of the $\sigma(Ru-C)$ orbital with the $\pi^*(Ru-C)$ orbital, evidencing a low-lying and largely C-centered LUMO of $\pi^*(Ru-C)$ character, which in turn implies a strongly electrophilic

character. Along the same line, one can deduce that the contribution of π (Ru–C) to the deshielding of δ_{11} is smaller than in the neutral analogue **17**, which again means that this orbital is lower in energy. Taken together, these features draw the portrait of **18** as a fairly typical Fischer carbene complex, even though it lacks a heteroatom substituent at the carbene center. Moreover, the comparison of **17** and **18** shows that the character of such pianostool ruthenium carbenes can be fine-tuned by modulation of the donor properties of the Cp^x ligands.

We conclude that all tested [Cp^xRu] catalysts were able to engage propargylic alcohol derivatives in *gem*-hydrogenation with formation of ruthenium carbene complexes. Importantly, however, the barriers for this unorthodox transformation can be lowered and the stability of the resulting complexes be notably increased by choosing less electron donating Cp^x rings; this correlation is arguably relevant for applications of reactive intermediates of this type in catalytic applications other than hydrogenation. Their spectroscopic signatures indicate a tunable electrophilic character of the M=C bond with some similarities to classical Grubbs carbenes. One might hence expect such pianostool carbenes to participate either in cyclopropanation or metathesis reactions. As will be shown in the accompanying paper, they can do both, even though a somewhat counterintuitive structure/activity relationship raises interesting mechanistic questions.

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For the Table of Contents



Portrayal: Less electron-donating cyclopentadienyl (Cp^X) ligands lower the barrier for the perplexing *gem*-hydrogenation of alkynes by [Cp^XRu] complexes and kinetically stabilize the resulting pianostool ruthenium carbenes. The chemical shift tensors extracted from solid state ¹³C NMR spectra draw the portrait of electrophilic carbenes of the "Fischer-type" with a certain flavor reminiscent of Grubbs catalysts.

Keywords: Carbenes Complexes · Chemical shift tensors · NMR Spectroscopy · parahydrogen · Ruthenium

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