Organometallics **2001,** *20,* 3845−3847

Novel η^3-Vinylcarbene Complexes Derived from Ruthenium-Based Olefin Metathesis Catalysts

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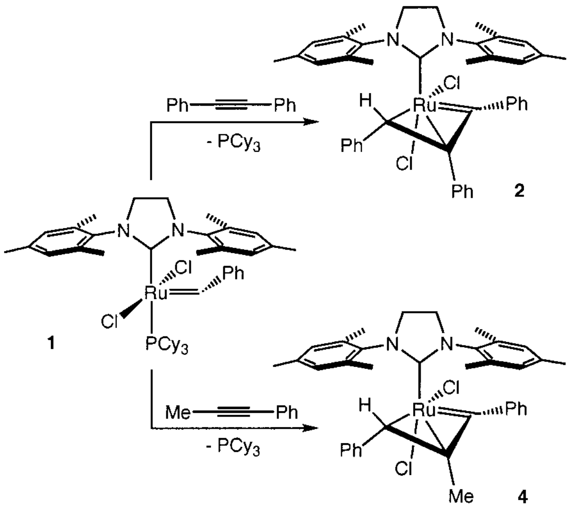
Received April 17, 2001

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on August 9, 2001 on http://pubs.acs.org | doi: 10.1021/om010314a

*Summary: Electron-rich, disubstituted alkynes react with $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**1**; H_2IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) to form phosphine-free η^3-vinylcarbene complexes. An X-ray diffraction study on $(H_2IMes)(Cl)_2Ru[\eta^3$-(CHPh)(CPh)(CPh)] (**2**) confirms the unusual structure. These complexes are relevant to the mechanisms of olefin metathesis and alkyne polymerization.*

The development of well-defined ruthenium catalysts for the olefin metathesis reaction has been accompanied by increasing interest in the mechanism of this process.[1] For example, the popular $L_2X_2Ru{=}CHR$ catalyst family has been studied with a variety of techniques, including kinetic measurements,[2] decomposition studies,[3] computational modeling,[4] mass spectrometry,[5] thermochemistry,[6] and structure−reactivity studies.[7] We are currently interested in metal−olefin adducts because the stereoselectivity of the olefin metathesis reaction is determined by the orientation of olefin binding and subsequent metallacyclobutane formation. One example of a catalytically relevant ruthenium−olefin adduct has been reported by Snapper and co-workers.[8] In this complex, one of the PCy_3 ligands of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ is replaced by an olefin that is tethered to the alkylidene. In a similar vein, Osborn and co-workers have studied tungsten alkylidene−olefin intermediates by low-temperature ^1H and ^{13}C NMR,[9] and Mayr and co-workers have examined the structures of tungsten vinylcarbene and alkylidene−alkyne complexes.[10]

Scheme 1



At this time, we report the synthesis and characterization of ruthenium η^3-vinylcarbene complexes obtained during the course of our investigations. These complexes are not only the first of their kind in ruthenium chemistry but also, as products of one turnover of alkyne polymerization, they are relevant to the olefin metathesis reaction.

The N-heterocyclic carbene-coordinated olefin metathesis catalyst $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**1**; H_2IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene)[11] reacts cleanly with an excess of diphenylacetylene to afford the phosphine-free complex $(H_2IMes)(Cl)_2Ru[\eta^3$-(CHPh)(CPh)(CPh)] (**2**) (Scheme 1). By ^1H NMR, **2** displays a diagnostic signal at δ 4.78 for C*H*Ph, a higher field resonance than is typically exhibited by unbound vinyl fragments.[12] The η^3-vinylcarbene moiety is characterized by a $^{13}C\{^1H\}$ NMR signal at δ 285 for the alkylidene carbon (Ru=*C*Ph), which is diagnostic for ruthenium alkylidenes of this type,[7b,13] and vinyl resonances at δ 67.87 (*C*HPh) and 91.67 (CHPh*C*PhCPh). These vinyl signals also appear at higher field than unbound vinyl

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[12] In comparison, the signals for the terminal protons of the η^1-vinylcarbene complex $(PCy_3)_2(Cl)_2Ru{=}CHCH{=}CH_2$ appear at δ 6.25 and 6.01.[7b]

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10.1021/om010314a CCC: $20.00 © 2001 American Chemical Society
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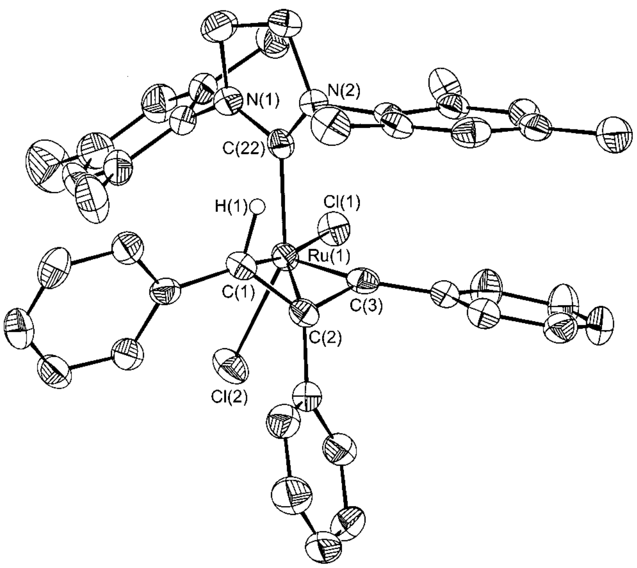
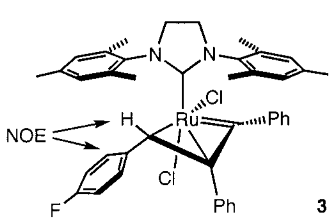


Figure 1. Structure of $(H_2IMes)(Cl)_2Ru[\eta^3\text{-}(CHPh)(CPh)(CPh)]\cdot 3CH_2Cl_2$ (**2**). For clarity, all hydrogen atoms except H(1) and solvent molecules have been omitted. Displacement ellipsoids are drawn at 50% probability; H(1) is drawn at arbitrary scale. Selected bond distances (Å) and angles (deg): Ru(1)–C(1) = 2.356(4), Ru(1)–C(2) = 2.221(4), Ru(1)–C(3) = 1.838(4), Ru(1)–C(22) = 2.045(4), Ru(1)–Cl(1) = 2.369(1), Ru(1)–Cl(2) = 2.364(1), C(1)–C(2) = 1.409(6), C(2)–C(3) = 1.437(6); Cl(1)–Ru(1)–Cl(2) = 86.77(4), C(3)–Ru(1)–C(1) = 69.0(2), C(22)–Ru(1)–Cl(2) = 150.3(1), C(1)–C(2)–C(3) = 116.0(3), C(2)–C(1)–Ru(1) = 66.9(2), C(2)–C(3)–Ru(1) = 84.4(2).

fragments in either organic molecules or η^1-vinylcarbene complexes.[14] We observed no evidence for dissociation of the vinyl group from the metal center at up to 130 °C by ^1H NMR.[15] The mesityl groups of the H_2IMes ligand are characterized by six methyl resonances in both the ^1H and $^{13}C\{^1H\}$ NMR, as well as four distinct meta protons, which is consistent with an asymmetric environment around the metal center and restricted rotation about the N-heterocyclic carbene–ruthenium bond.

The crystal structure of **2** reveals several interesting features (Figure 1).[16] Most importantly, the chlorides are in a cis configuration, with Cl(2) now situated trans to the N-heterocyclic carbene. This position is usually occupied by a phosphine or other donor ligand in $L_2X_2Ru{=}CHR$ complexes. In addition, the mesityl groups of the H_2IMes ligand are twisted with respect to each other by approximately 30°. The ruthenium–alkylidene (Ru=C(3)) bond length of 1.838(4) Å is comparable to d(Ru=C) values for related complexes, such as $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (1.835(2) Å)[17] and $(IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (1.841(11) Å).[13] Whereas the Ru–C(2) distance of 2.221(4) Å is typical for a ruthenium–carbon single bond,[18] the Ru–C(1) distance of 2.356(4) Å is significantly longer, although not unprecedented. Within the vinyl fragment, the C(1)–C(2) distance of 1.409(6) Å is somewhat longer than a typical C=C double bond (~1.35 Å), and the C(2)–C(3) distance of 1.437(6) Å is somewhat shorter than a typical C–C single bond (~1.55 Å).

Reaction of diphenylacetylene with the *p*-fluorobenzylidene derivative of **1** provides $(H_2IMes)(Cl)_2Ru[\eta^3\text{-}(CH(p\text{-}C_6H_4F))(CPh)(CPh)]$ (**3**). ^{19}F coupling in the $p\text{-}C_6H_4F$ ring distinguishes these particular ortho and meta protons from the other aromatic resonances in the ^1H NMR spectrum of **3**, and it is possible to observe an NOE between these protons and the benzylic proton $C\mathit{H}(p\text{-}C_6H_4F)$. This experiment confirms that the benzylidene in the starting material (**1**) becomes the CHPh group in the product (**2**).



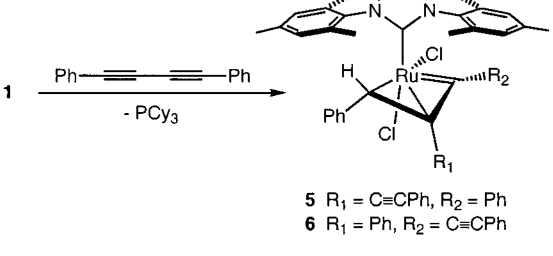
3

The reaction of **1** with 1-phenyl-1-propyne produces exclusively $(H_2IMes)(Cl)_2Ru[\eta^3\text{-}(CHPh)(CMe)(CPh)]$ (**4**) (Scheme 1). The characterization data of **4** are similar to those of **2**, except for the additional methyl resonances at δ 1.79 and 11.49 in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively. In comparison, the methyl group of the ethylidene complex $(PCy_3)_2(Cl)_2Ru{=}CHMe$ appears at δ 2.59 and 49.15.[7b] These differences, especially of the ^{13}C chemical shifts, indicate that the methyl group in **4** is attached to the internal vinyl carbon CHPh*CMe*CPh, rather than the alkylidene carbon (i.e., CHPhCPh*CMe*).

In contrast to the selective formation of **4**, the reaction of **1** with 1,4-diphenylbutadiyne yields a mixture of $(H_2IMes)(Cl)_2Ru[\eta^3\text{-}(CHPh)(CC{\equiv}CPh)(CPh)]$ (**5**) and another isomer, most likely $(H_2IMes)(Cl)_2Ru[\eta^3\text{-}(CHPh)(CPh)(CC{\equiv}CPh)]$ (**6**) (Scheme 2). Unfortunately, it was not possible to confirm the identities of **5** and **6** by $^{13}C\{^1H\}$ NMR because of their poor solubility, but a single crystal selected for X-ray diffraction corresponded to **5**.[19] The overall structure of **5** and the geometrical data for the η^3-vinylcarbene fragment are similar to those of complex **2**.

Four limiting structures for the [Ru(CHR)(CR′)(CR′)] moiety are a metallocyclopropane-carbene complex (A), an η^3-vinylcarbene complex (B), an allyl-type complex (C), and a metallacyclobutene complex (D). On the basis

Scheme 2



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[14] For example, the $^{13}C\{^1H\}$ signals for $(PCy_3)_2(Cl)_2Ru{=}CH\mathit{C}H{=}\mathit{C}H_2$ are δ 116 and 154.[7b]

[15] Mayr has observed dissociation of the vinyl group in $[W(CPhCHCMe_2)(Br)_2(CO)_2(4\text{-picoline})]$.[10a]

[16] Crystallographic data for **2** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. 155016. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

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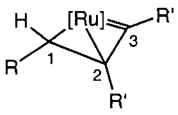

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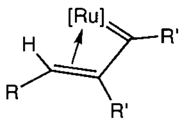

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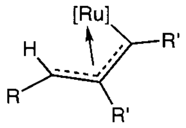

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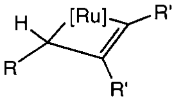


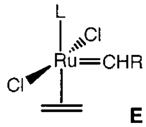
D

of the structural and spectroscopic data, the most accurate bonding description for complexes **2**−**6** appears to be intermediate between A and B. It is neither C nor D, because a double bond is clearly localized on Ru═C(3) rather than on C(2)−C(3). Structure D is also not consistent with the bent geometry of the RuC_3 subunit. In comparison to the vinyl fragment in **2**, the metal-coordinated olefin in Snapper's adduct retains more olefinic character.[8] This is reflected in the C═C distance of 1.347(7) Å, which is typical for a carbon−carbon double bond, as well as the more planar geometry of the olefin and the longer ruthenium−olefin distance (d(Ru−C) = 2.339(5) and 2.362(5) Å).[18]

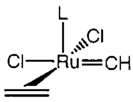
Although η^1-vinylcarbene complexes are common, **2**−**6** are the first examples of η^3-vinylcarbene complexes in ruthenium chemistry. Previously, η^3-vinylcarbene complexes have been isolated in iron, chromium, and tungsten carbonyl systems,[20] and they have been proposed as intermediates in the Dötz reaction.[21] Schrock and co-workers have also reported a tantalum alkylidene that reacts with diphenylacetylene to yield an η^1-vinylcarbene complex.[22]

In the metal carbene catalyzed polymerization of alkynes, an alkylidene reacts with an alkyne to form a metallacyclobutene intermediate, which then rearranges to produce a new alkylidene.[23] If this process continues, a growing polymer chain forms. However, in the case of complexes **2**−**6**, the vinylcarbene intermediate is apparently trapped after the first turnover by coordination of the vinyl group to the metal center. This coordination, which stabilizes the otherwise 14-electron species, must be quite strong, because **2** catalyzes the polymerization of diphenylacetylene only under forcing conditions (1 mol % **2** in molten diphenylacetylene at 80 °C for 20 h).[24] The isolated η^3-vinylcarbene complexes are also not active for ring-closing metathesis.[25]

Nevertheless, this system is relevant to $L_2X_2Ru{=}CHR$ olefin metathesis catalysts, because one proposed intermediate is the phosphine-dissociated, 14-electron species $(L)(X)_2Ru{=}CHR$.[2] The substrate then binds to this intermediate to form the 16-electron olefin adduct $(L)(olefin)(X)_2Ru{=}CHR$. We[1a,2c,d] and others[5] have proposed two conformations for this adduct: E, in which



E



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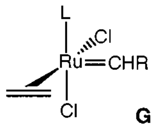

G

the olefin is bound trans to the remaining L ligand, and F, in which the chlorides adopt a cis arrangement in the alkylidene−halide−olefin plane. Although **2**−**6** are not intermediates in the olefin metathesis reaction, the structures of these complexes demonstrate for the first time that it is also possible for the chlorides to adopt a cis arrangement that places one of the chlorides trans to the L ligand, as in G.[26,27]

The reaction of diphenylacetylene with $(IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (IMes = 1,3-dimesitylimidazol-2-ylidene), where the N-heterocyclic carbene contains an unsaturated backbone, yields the IMes analogue to **2**. In contrast, η^3-vinylcarbene complexes are not observed with the bis(phosphine) olefin metathesis catalyst $(PCy_3)_2(Cl)_2Ru{=}CHPh$, which suggests that the more electron-rich metal center in **1** may be important by allowing the initial reaction with a disubstituted alkyne to occur and then in stabilizing the vinyl group. Furthermore, the reaction was not observed with the methylidene $[Ru]{=}CH_2$ or dimethylvinyl carbene $[Ru]{=}CHCH{=}CMe_2$ derivatives of **1**, or with alkynes containing electron-withdrawing substituents, such as dimethyl acetylenedicarboxylate and hexafluoro-2-butyne. Current work is directed toward understanding the selectivity of η^3-vinylcarbene formation, as well as exploring the reactivity of these unusual complexes.

Acknowledgment. This research was supported by the National Science Foundation. T.M.T. also acknowledges the U.S. Department of Defense for an NDSEG graduate fellowship. We thank Lawrence M. Henling (Caltech) for assistance with the crystallography.

Supporting Information Available: Text giving synthesis and characterization data of compounds **2**−**6** and other experimental details and tables giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] For example, d(Ru−C) values for ruthenium−methyl complexes in the Cambridge Structural Database range from 2.09 to 2.24 Å. Allen, F. H.; Kennard, O. CSD Version 5.20. 3D Search and Research Using the Cambridge Structural Database. *Chem. Des. Automation News* **1993**, *8*, 1, 31−37.

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[24] Catalyst **1** also polymerizes diphenylacetylene under the same conditions. At the end of this reaction, **2** is present in the reaction mixture.

[25] In contrast, Snapper's ruthenium−olefin adduct is active for further RCM and ROMP reactions.[8]

[26] Interestingly, calculations by Chen and co-workers indicate that the $(PH_3)(Cl)_2Ru[\eta^2\text{-}(CH_2CH_2CH_2)]$ metallacyclobutane intermediate with chlorides in a cis arrangement (as in G) is a lower energy conformation than when they are trans (as in E).[5a]

[27] In related systems, ruthenium alkylidene complexes with chelating bis(phosphine) ligands and cis chlorides have been reported: (a) Nieczypor, P.; van Leeuwen, P. W. N. M.; Mol, J. C.; Lutz, M.; Spek, A. L. *J. Organomet. Chem.* **2001**, *625*, 58−66. (b) Hansen, S. M.; Rominger, F.; Metz, M.; Hofmann, P. *Chem. Eur. J.* **1999**, *5*, 557−566.