Communications

Electrophilic Attack on [Cp*Cl(PPh$_3$)Ru(CCHR)]: Carbyne Formation vs Chloride Abstraction

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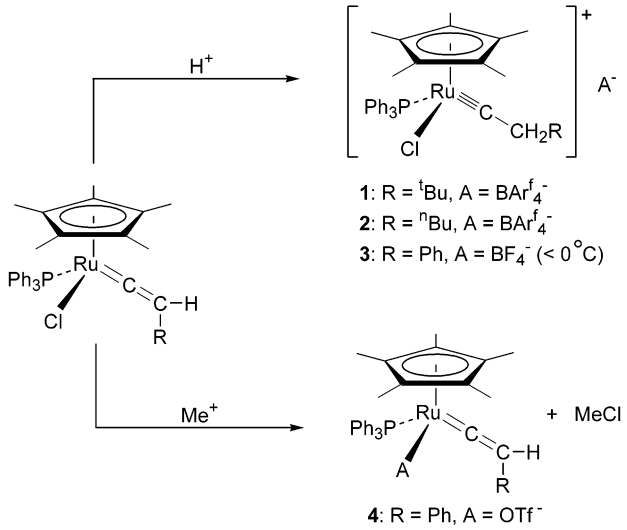
*Summary: The course of electrophilic addition to the ruthenium(II) chloro vinylidenes [Cp*Cl(PPh$_3$)Ru(CCHR)] is influenced by the steric properties of the electrophile and ruthenium complex. Thus, H$^+$ selectively adds to C$_\beta$ of the vinylidene ligand to yield the ruthenium(IV) carbynes [Cp*Cl(PPh$_3$)Ru(CCH$_2$R)][A] (A = BF$_4^-$, BAr$^f_4^-$), while the comparably larger Me$^+$ (from MeOTf) abstracts Cl$^-$ to yield, after anion coordination, [Cp*(OTf)(PPh$_3$)-Ru(CCHR)] and MeCl.*

Recent reports describing electrophilic addition reactions of E$^+$ (from EA) to the ruthenium vinylidenes [Ru(X)(Y)(CCHR)(PR$_3$)$_2$] (X, Y = hydride, chloride, carboxylate) revealed the outcome was dependent upon several factors, including the nature of the counteranion A$^-$ of EA and the ancillary ligands on the metal.[1] Remarkably, despite the presence of hydride, halide, and/or pseudohalide ligands (i.e., ligands with lone pairs on the α-ligand atom) and a coordinatively unsaturated ruthenium center, selective electrophilic addition to C$_\beta$ of the vinylidene ligand[2] occurred, establishing it as the more Brønsted basic site in the complexes studied.[3] Thus, depending upon the conditions, ruthenium carbenes,[1a] carbynes,[1b,d] or carbene−carbyne equilibria[1c,d] were observed. Intrigued by these results, we decided to explore further electrophilic additions to ruthenium vinylidenes, and especially those factors which control the site selectivity of electrophilic attack. We now report a different consequence of electrophilic addition to ruthenium chloro vinylidenes, which reveals that steric factors can influence the selectivity of the reaction.

The neutral ruthenium(II) vinylidenes [Cp*Cl(PPh$_3$)-Ru(CCHR)],[4] when treated with a diethyl ether solution of HBF$_4$ (2 equiv) at −78 °C, selectively add H$^+$ to C$_\beta$ of the vinylidene ligand to afford, after anion metathesis with NaBAr$^f_4$ (Ar^f = 3,5-(CF$_3$)$_2$C$_6$H$_3$), the orange ruthenium(IV) carbynes[5] [Cp*Cl(PPh$_3$)Ru(CCH$_2$R)][BAr$^f_4$], (R = ^{t}Bu, **1**; R = ^{n}Bu, **2**) in good yields (Scheme 1). The instantaneous formation of the cations of **1** and **2** upon adding HBF$_4$ to the ruthenium vinylidene precursor, even at −78 °C (as observed by NMR spectroscopy), frustrated our attempts to detect any possible intermediates. Hence, it is unclear whether the cations are formed via direct attack of H$^+$ at C$_\beta$ of the vinylidene ligand[6] or through some other mechanism involving either initial attack at the metal[7] or other ligand (i.e.,

Scheme 1



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(3) Selective electrophilic attack has been observed on metal hydride halides: Kuhlman, R. *Coord. Chem. Rev.* **1997**, *167*, 205 and references therein.

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(5) Other ruthenium carbynes: (a) Bustelo, E.; Jiménez-Tenorio, M.; Mereiter, K.; Puerta, M. C.; Valerga, P. *Organometallics* **2002**, *21*, 1903. (b) Jung, S.; Brandt, C. D.; Werner, H. *New J. Chem.* **2001**, *25*, 1101. (c) Coalter, J. N., III; Bollinger, J. C.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2000**, *24*, 925. (d) Amoroso, D.; Snelgrove, J. L.; Conrad, J. C.; Drouin, S. D.; Yap, G. P. A.; Fogg, D. E. *Adv. Synth. Catal.* **2002**, *344*, 757. (e) Roper, W. R. *J. Organomet. Chem.* **1986**, *300*, 167.

(6) Reactions between the vinylidene complex [RuHCl(CCH$_2$)(PCy$_3$)$_2$] and D$^+$ revealed only exclusive attack at C$_\beta$ of the vinylidene, as determined by ^{2}H NMR spectroscopy.[1b]

(7) At least one example involving initial protonation at the metal of a coordinatively saturated neutral d^6 metal vinylidene complex followed by rearrangement to the isomeric metal carbyne has been reported: Carvalho, M. F. N. N.; Henderson, R. A.; Pombeiro, A. J. L.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1796.

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chloride) on the metal, followed by hydrogen migration to C_β. Both solids and solutions of **1** show exceptional stability at room temperature under nitrogen even over several days, while **2** proved to be somewhat less stable under similar conditions. The substantial electron-donating properties of the Cp* ligand[8] likely contribute to the stabilization of the strongly π-acidic carbyne ligand and formal Ru(IV) center. Decomposition of **1** and **2** in solution occurs very slowly, yielding mainly Ph_3PH^+ as the only phosphorus-containing species, as determined by $^{31}P\{^1H\}$ NMR.

Room-temperature NMR spectroscopy provides important structural information which supports the formation of a carbyne ligand and oxidized ruthenium in **1** and **2**. The $^{13}C\{^1H\}$ NMR spectra of **1** and **2** reveal a number of important resonances, most notably the downfield-shifted carbyne C_α carbon resonances (δ 348.3 for **1**; δ 347.0 for **2**), which appear as doublets due to coupling with PPh_3 ($^2J_{PC}$ = 15.7 Hz for **1**; $^2J_{PC}$ = 17.1 Hz for **2**). These couplings are lower compared to the $^2J_{PC}$ couplings observed for the ruthenium(II) vinylidene precursors ($^2J_{PC}$ ca. 24 Hz),[4] which is consistent with a lengthening of the Ru−PPh_3 bond as a result of diminished back-bonding with Ru(IV) vs Ru(II).[9] The Cp* signals of **1** and **2** in the $^{13}C\{^1H\}$ NMR spectra are shifted downfield vs [Cp*Cl(PPh_3)Ru(CCHR)],[4] which also points to an increase in oxidation state of the ruthenium center.[9b,10] The room-temperature ^1H NMR spectra of **1** and **2** are particularly interesting and clearly show a separate signal for each of the two C_β methylene protons of the carbyne ligand (for **1**, δ 2.51 and 1.76, both doublets, $^2J_{HH}$ = 20.3 Hz; for **2**, δ 2.35 and 1.86, both multiplets, $^2J_{HH}$ = 20.5 Hz). These observations are consistent with restricted rotation about the C_α−C_β bond of the carbyne ligands,[11] which causes the two protons on C_β to become inequivalent. The cumulative steric effects of the Cp*, PPh_3, and carbyne R groups likely contribute to this rotational barrier. Coalescence of the C_β methylene proton signals was not observed at higher temperatures (C_6D_6, 70 °C) for **1**, while complex **2** proved to be unstable at elevated temperatures and decomposed to a number of unidentified phosphorus-containing species.

The R group of the vinylidene ligand in [Cp*Cl(PPh_3)Ru(CCHR)] appears to influence the stability of the resulting carbyne complex, but not the selectivity of H^+ addition. For example, extending these reactions to include [Cp*Cl(PPh_3)Ru(CCHPh)][4a] (i.e., decreasing the nucleophilicity of C_β by replacing electron-donating alkyl with electron-withdrawing phenyl) yields only unappealing mixtures of products (which typically include ca. 30−60% Ph_3PH^+) *after* warming to room temperature, as evidenced by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. However, monitoring the reaction at low temperatures (−75 °C) using NMR spectroscopy (CD_2Cl_2) immediately after adding HBF_4 at −78 °C reveals rapid and quantitative formation of the carbyne [Cp*Cl(PPh_3)Ru(CCH_2Ph)][BF_4] (**3**). No other species are detected under these conditions. At −75 °C complex **3** exhibits spectroscopic features similar to those observed for **1** and **2** (see Supporting Information), including two inequivalent C_β methylene protons (δ 4.05 and 3.52, both doublets, $^2J_{HH}$ = 20.5 Hz), which again can be ascribed to restricted rotation about the C_α−C_β bond of the carbyne ligand. The NMR spectra of **3** remain essentially unchanged upon warming the solution to 0 °C, although ^1H NMR spectroscopy reveals the C_β methylene protons show an unusual temperature dependence within this temperature range (the separation between doublets *increases* by ca. 0.5 ppm as the temperature approaches 0 °C). Rapid (minutes) decomposition to many products occurs above 0 °C, with Ph_3PH^+ representing the main (>50%) decomposition product (the remaining products could not be confidently identified). Coalescence of the C_β methylene proton signals of **3** was also not observed under these conditions.

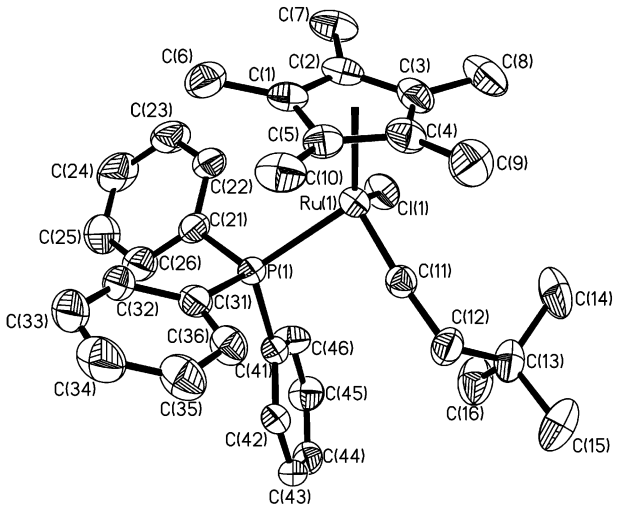

Figure 1. Molecular structure of the cation of **1**·CH_2Cl_2 (the hydrogen atoms, $BAr^f{}_4^-$ counterion, and CH_2Cl_2 solvate have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru(1)−C(11) = 1.710(3), Ru(1)−P(1) = 2.3641(9), Ru(1)−Cl(1) = 2.3715(9), Ru(1)−C(1) = 2.393-(3), Ru(1)−C(2) = 2.391(3), Ru(1)−C(3) = 2.255(3), Ru(1)−C(4) = 2.232(3), Ru(1)−C(5) = 2.240(3); C(11)−Ru(1)−Cl(1) = 101.4(1), C(11)−Ru(1)−P(1) = 90.0(1), P(1)−Ru(1)−Cl-(1) = 90.22(3), C(11)−C(12)−C(13) = 114.4(3), C(12)−C(11)−Ru(1) = 174.1(3).

The solution structures of the cations of **1**−**3** are supported by an X-ray crystallographic study on complex **1**[12] (Figure 1). The ruthenium center in the structure of complex **1** possesses a distorted three-legged piano-stool coordination geometry. A notable feature of **1** is the relatively short ruthenium−C_α carbyne bond

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(11) Rotation about the metal−C_α bond is also possible, since MO calculations reveal the rotational barrier around the metal−carbon triple bond in metal carbynes is quite low: Kostić, N. M.; Fenske, R. F. *J. Am. Chem. Soc.* **1982**, *104*, 3879.

(12) Crystallographic data for $C_{67}H_{55}BCl_3F_{24}PRu$ (**1**·CH_2Cl_2): a = 17.730(1) Å, b = 19.077(1) Å, c = 20.365(1) Å, α = 90°, β = 94.349(1)°, γ = 90°, Z = 4 in space group $P2_1/n$, R1 = 0.0871 (all data), wR2 = 0.1690 (all data), 15 419 reflections, 1098 refined parameters.

distance of 1.710(3) Å, which is shorter when compared to the structurally characterized vinylidenes [Cp*Cl(PPh$_3$)Ru(CCHR)] (range ca. 1.80−1.85 Å).[4a] Equally notable are the slightly longer Ru−P bond (2.3641(9) Å) and slightly shorter Ru−Cl bond (2.3715(9) Å) in the cation of **1** (vs Ru−P = ca. 2.305−2.315 Å and Ru−Cl = ca. 2.395−2.408 Å in [Cp*Cl(PPh$_3$)Ru(CCHR)][4a]), both of which are consistent with an increase in oxidation state of the ruthenium (vide supra). The Ru−C$_\alpha$−C$_\beta$ linkage is bent only slightly (174.1(3)°), possibly because of steric crowding among Cp*, PPh$_3$, and the ^{t}Bu group on C$_\beta$ of the carbyne ligand.

While H$^+$ addition selectively yields the carbynes [Cp*Cl(PPh$_3$)Ru(CCH$_2$R)]$^+$ from the vinylidenes [Cp*Cl(PPh$_3$)Ru(CCHR)], the electrophile Me$^+$ follows a much different reaction course. For example, adding excess (3 equiv) MeOTf to a room-temperature solution of [Cp*Cl(PPh$_3$)Ru(CCHPh)] results in the complete consumption of the vinylidene complex and slowly but cleanly yields [Cp*(OTf)(PPh$_3$)Ru(CCHPh)], **4** (Scheme 1), along with 1 equiv (based on ^{1}H NMR integrations) of MeCl within 30 min of mixing, as determined by NMR spectroscopy. A stoichiometric amount of MeOTf yields similar results under the same conditions but requires several hours for completion. Mechanistically, this reaction *might* proceed initially via direct attack at the metal, or through electrophilic attack at C$_\beta$,[13] followed by methyl migration to the metal. In either case (i.e., ion oxidative addition), reductive elimination would subsequently yield MeCl and **4**. Despite the relatively slow production of **4** under the conditions studied, we see no direct spectroscopic evidence supporting either initial electrophilic attack on the vinylidene or the formation of ruthenium methyl species (the carbene [Cp*Cl(PPh$_3$)Ru(C(OTf)(CH(Me)Ph))] is not observed to form[1a]). Unfortunately, extending these reactions to include [Cp*Cl(PPh$_3$)Ru(CCHR)] (R = ^{t}Bu, ^{n}Bu) only resulted in much poorer selectivity and the rapid production of many unidentified products (as observed by NMR), although MeCl was detected by ^{1}H NMR spectroscopy. These results should not be surprising, since steric factors (especially Cp*[14a] and, to a lesser extent, PPh$_3$[14b]) likely inhibit access of the comparably larger CH$_3^+$ (vs H$^+$) to either the vinylidene or the coordinatively saturated metal. Alternatively, complex **4** may be formed via a mechanism involving direct electrophilic attack of CH$_3^+$ on the chloride ligand of [Cp*Cl(PPh$_3$)Ru(CCHPh)].[15] Halide abstraction involving nonmetal electrophiles are thought to proceed through direct attack at the halide.[16] This is certainly reasonable, considering the greater accessibility of the chloride lone pairs. Furthermore, filled−filled ruthenium d orbital−chloride lone pair repulsions likely enhance the basicity of the chloride ligand.[17]

In summary, we have described an interesting site selectivity in electrophilic addition reactions to ruthenium chloro vinylidenes. The observed selectivity emphasizes how easily the site of electrophilic attack can be diverted from vinylidene to halide just by changing the properties of the electrophile (H$^+$ vs CH$_3^+$). Thus, steric factors should be considered when there is direct competition between different sites for an electrophile, since selectivity can be influenced by the relative accessibility of these sites. Current efforts in our laboratory are directed toward expanding upon the work presented herein.

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Supporting Information Available: Text describing full synthetic procedures and spectroscopic data, along with text and tables giving crystallographic details for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) (a) Kitajima, N.; Tolman, B. W. *Prog. Inorg. Chem.* **1995**, *43*, 419. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(15) The tendency for the chloride of [Cp*Cl(PPh$_3$)Ru(CCHPh)] to ionize in methylene chloride (the solvent used in the reactions studied) most likely would be marginal.

(16) For example, see: (a) Eaborn, C.; Farrel, N.; Murphy, J. L.; Pidock, A. *J. Chem. Soc., Dalton Trans.* **1976**, 58. (b) Eaborn, C.; Farrel, N.; Pidock, A. *J. Chem. Soc., Dalton Trans.* **1976**, 289. (c) Connor, J. A.; Hudson, G. A. *J. Organomet. Chem.* **1974**, *73*, 351. (d) Druce, P. M.; Lappert, M. F.; Riley, P. N. K. *J. Chem. Soc. D* **1967**, 486. (e) Aizenberg, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1994**, 411. (f) Huang, D.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Angew. Chem., Int. Ed.* **1997**, *36*, 2004. (g) Kuhlman, R.; Streib, W. E.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1996**, *118*, 6934.

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