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Reactivity of Cp^*Ru^+ with Acyclic Unsaturated Hydrocarbons: A Novel Catalytic Carbon–Carbon Bond Activation Reaction

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Summary: The versatile reactivity of the electrophilic fragment Cp^*Ru^+ toward unsaturated acyclic hydrocarbons is described: stoichiometric cyclization with 1,3,5-hexatriene and metathesis with 1,7-octadiene as well as catalytic isomerization and/or oligomerization with 1,4-pentadiene, 1,5-hexadiene, 1-hexene, and neohexene. In the case of neohexene, a novel reaction catalytically producing CH_4 and C_{11} and C_{17} hydrocarbons is reported.

Electrophilic metal centers display a high reactivity related to their high Lewis acidic character.[1] Recent examples of this involve C–H bond activation, polymerization, and oligomerization, using early transition metals and lanthanides (d^0 metal centers),[1–4] as well as cationic derivatives of late transition metals.[1,5–7] This reactivity, however, has only rarely been extended to carbon–carbon bond activation. Examples concern the field of hydrocarbon isomerization (pentadiene or neohexene) using scandium or dicationic palladium derivatives.[4c,5]

In related studies, we have shown that the electrophilic fragment Cp^*Ru^+ exhibits a high activity for aromatization of C_6 rings, implying C–H, C–O, C–Cl, and even C–C bond activation.[8] We have now extended our studies to acyclic dienes and olefins for which we anticipated a variety of reactions, including oligomerization, dehydrogenation, and possibly cyclization. This communication describes our preliminary results with trienes, dienes, and olefins which include a novel and unexpected carbon–carbon bond activation reaction.

All the reactions described hereafter were carried out under catalytic conditions using a 100:1 ratio of substrate to ruthenium.[9] The reaction of Cp^*Ru^+ (**1**), generated in situ through protonation of $[Cp^*Ru(OMe)]_2$ by CF_3SO_3H, with 1,3,5-hexatriene leads cleanly at room temperature to the benzene derivative $[Cp^*Ru(\eta^6\text{-}C_6H_6)](CF_3SO_3)$ (**2**) and H_2. This is a stoichiometric reaction, the remaining hexatriene not being transformed.[10]

The reaction of **1** with dienes is highly dependent upon the chain length. Thus, with 1,4-pentadiene we observe a catalytic dimerization producing $C_{10}H_{16}$ isomers.[11] The organometallic derivative $[Cp^*Ru(\eta^6\text{-}C_{10}H_{16})](CF_3SO_3)$ (**3**) is the main complex detected in solution at all stages of the reaction. **3** is formally a Ru(IV) bis(π-allyl) complex resulting from a branched pentadiene dimer (isolated yield 33%).[12] Isolated samples of **3** are shown to be active for the dimerization of pentadiene under the same conditions as above, thus further implicating **3** in the catalytic cycle.

The reaction with 1,5-hexadiene produces C_6H_{10} isomers,

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(9) All operations were carried out under argon using standard Schlenk-tube techniques. Activation experiments were carried out in closed Fischer–Porter bottles equipped with Swagelok fittings which can connect directly to an injection valve of an IGC 16 Intersmat GC. The reactions were followed by GC analysis of the gas phase and/or of the solution. Separations of H_2, CH_4, C_2H_6, and Ar were performed on a $^1/_8$ in. column (molecular sieve 5 Å (2 m), temperature 100 °C); C_2–C_4 compounds were separated on a Porapak Q column at 100 °C. Higher molecular weight derivatives were separated with an SE 30 column using appropriate temperature programs (detector FID or TCD when necessary; sample loop 0.3 mL). The peaks were identified by GC/MS coupling using either a Delsi-Nermag apparatus equipped with a 0.25-μm DB1, 15-m column or an HP 5890 chromatograph equipped with an HP1 15-m column connected to an HP 59970C MS station. Only the final composition of the solutions and/or demonstrative examples are reported hereafter. A typical reaction was carried out by the following procedure: to a mixture of Cp^*Ru^+ (prepared from $[Cp^*Ru(OMe)]_2$ (190 mg, 0.36 mmol) and CF_3SO_3H (0.71 mmol, 63 μL)) in CH_2Cl_2 (5 mL) was added 1,5-pentadiene (0.7 mL, 7.1 mmol). The resulting solution was transferred into a Fischer–Porter bottle and heated for up to 88 h at 120 °C. After the reaction mixture was cooled, the gases were analyzed; the solution was transferred to a Schlenk tube, analyzed by GLC, and then evaporated to dryness. The residue was washed with diethyl ether and pentane and recrystallized from acetone/diethyl ether. Similar procedures were used for all reactions; however, ca. 0.1 mmol of **1** was used when only identification of the organic products was planned. Interestingly, no reaction was ever observed between **1** and CH_2Cl_2 (producing clusters as previously described)[8a,d] in any of these systems because of the higher affinity of **1** for the unsaturated compounds present in the medium. Blank experiments were carried out in each case, using all components of reactions mixtures including CF_3SO_3H but with the absence of $[Cp^*Ru(OMe)]_2$. NMR spectra were recorded on Bruker WM250 or AC200 instruments. The complex ^1H spectra of **3** and **4** were assigned using selective decoupling and COSY $\delta\delta$ techniques.

(10) This type of cyclization has been found to be general with polyunsaturated species and to lead to aromatic compounds through H_2 or H_2O elimination (e.g. hexadienal and hexadienol into benzene, citral into *p*-cymene). Results will be submitted for publication.

(11) After 16 h at 100 °C: "C_5", 12%; "C_{10}", 84%; higher oligomers, 4%.

(12) $[Cp^*Ru(\eta^6\text{-}C_{10}H_{16})](CF_3SO_3)$ (**3**): Anal. Calcd for $C_{21}H_{31}F_3O_3SRu$: C, 48.37; H, 5.95. Found, C, 48.52; H, 5.95. ^{13}C NMR ($(CD_3)_2CO$, δ (ppm)): 8.1 (q, $C_5(CH_3)_5$, $^1J_{C-H}$ = 128 Hz), 17.6 (q, C^{10}, $^1J_{C-H}$ = 147 Hz), 20.6 (q, C^1, $^1J_{C-H}$ = 147 Hz), 34.6 (d, C^6, $^1J_{C-H}$ = 130 Hz), 45.6 (t, C^5, $^1J_{C-H}$ = 128 Hz), 57.1 (dt, C^9, $^1J_{C-H}$ = 161, $^3J_{C-H}$ = 8 Hz), 73.8 (d, $C^{4\text{ or }7}$, $^1J_{C-H}$ = 153 Hz), 76.8 (d, $C^{7\text{ or }4}$, $^1J_{C-H}$ = 153 Hz), 90.4 (d, C^2, $^1J_{C-H}$ = 161 Hz), 92.9 (d, $C^{3\text{ or }8}$, $^1J_{C-H}$ = 158 Hz), 98.2 (d, $C^{8\text{ or }3}$, $^1J_{C-H}$ = 158 Hz), 102.5 (s, $C_5(CH_3)_5$). ^1H NMR ($(CD_3)_2CO$, δ (ppm)): 1.25 (d, $C^{10}H_3$, $^3J_{H-H}$ = 6 Hz, 3 H), 1.91 (s, $C_5(CH_3)_5$, 15 H), 1.8 (m, C^6H), 2.10 (d, C^1H_3, J_{H-H} = 6 Hz), 2.6 (m, C^5H), 2.83 (dd, C^9H), 3.21 (dd, C^9H), 3.31 (m, C^2H), 3.49 (m, C^4H), 3.50 (m, C^8H), 4.07 (t, C^3H), 4.31 (dd, C^7H).

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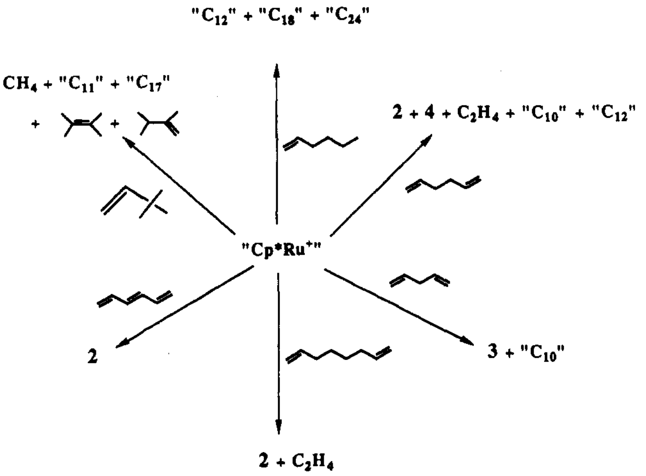
Scheme I. Reactions of Cp^*Ru^+ (1) with Various Acyclic Unsaturated Hydrocarbons[a]



[a] Only the major products of the reactions are given.

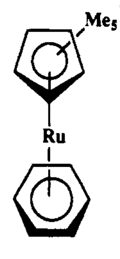
dimers, ethylene, and $C_{10}H_{16}$. The activity of the catalyst is difficult to evaluate in this case, since all the primary products described above are further transformed into higher oligomers.[13] Two organometallic complexes were isolated from the reaction mixture: $[Cp^*Ru(\eta^6\text{-}C_6H_6)](CF_3SO_3)$ (2) and $[Cp^*Ru(\eta^6\text{-}C_{12}H_{20})](CF_3SO_3)$ (4). 4 is a ruthenium(II) complex containing a coordinated linear dodecatriene ligand.[14] 2 is probably produced by dehydrogenation of hexadiene into hexatriene and cyclization. The interesting point here is the observation of $C_{10}H_{16}$ species and ethylene, which suggests metathesis activity. No metathesis reactions were found for acyclic olefins (vide infra), but ring-opening polymerization of norbornene was observed in the presence of 1.

Furthermore, the reaction of 1 with 1,7-octadiene leads cleanly but stoichiometrically to 2 and C_2H_4. Octadiene is known to yield ethylene and cyclohexene upon metathesis, the latter of which in turn is known to be rapidly dehydrogenated to give 2 in the presence of 1.[8b]

The reactions with olefins were anticipated to be more simple. Thus, the reaction of 1-hexene with 1 leads to $C_{12}H_{24}$, $C_{18}H_{36}$, and higher oligomers, the trimers being the most abundant.[15] This is classical behavior for the oligomerization of 1-hexene in the presence of Lewis acids.

However, when the reaction was carried out with neohexene, three different classes of products were formed: (i) neohexene oligomers (ca. 2% of starting neohexene), (ii) 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene resulting from isomerization of neohexene through methyl migration (92%), and (iii) methane (ca. 4%) together with the dienes $C_{11}H_{20}$ (ca. 1%) and $C_{17}H_{32}$ (ca. 1.6%).[16]

Chart I. Proposed Structures for Compounds 2–4



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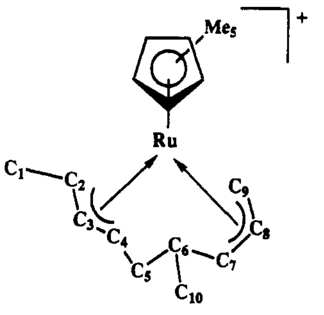

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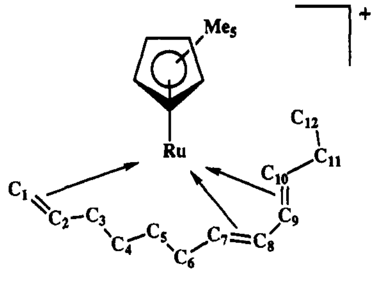

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Process i is a classical oligomerization as described for 1-hexene. Process ii has already been observed and mechanistically studied by Sen et al. This isomerization is due to the formation of a carbocationic center which leads to methyl migration. However, process iii has, to the best of our knowledge, no precedent. It is nevertheless possible that process iii results from a combination of processes i and ii. Steric congestion around the metal center can be such in the case of coordinated dimers and trimers that methyl migration can no longer be operative. Carbocationic rearrangement would then lead to the elimination of a methyl cation which through hydride abstraction would produce methane together with C_{11} and C_{17} hydrocarbons.

As a whole, Cp^*Ru^+ shows a versatile reactivity toward acyclic unsaturated hydrocarbons. The thermodynamic stability of the ruthenium–arene bond in $[Cp^*Ru(\eta^6\text{-}arene)]^+$ responsible for the previously described C–C bond activation reactions is probably also the driving force for the cyclization reactions which will be described in detail elsewhere, whereas the strong Lewis acidic character of this fragment can explain the oligomerization reactions, the methyl migrations, and also the "cracking" reaction. This acidic character is comparable to that of Pd^{2+} previously shown to be able to activate methane.[5] Further studies in this field, in particular mechanistic studies, are presently under way.

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(13) After 7 h at 100 °C: conversion, 16%; C_6H_{10} isomers, 13%; $C_{10}H_{16}$, 2%; $C_{12}H_{20}$, 1%. After 23 h at 100 °C: conversion, 42%; "C_6" isomers, 18%; "C_{10}", 1%; "C_{12}", 2%; higher oligomers and polymers.

(14) $[Cp^*Ru(\eta^6\text{-}C_{12}H_{20})](CF_3SO_3)$ (4): Anal. Calcd for $C_{23}H_{35}F_3O_3SRu$: C, 50.27; H, 6.38. Found, C, 50.16; H, 6.34. ^{13}C NMR ($(CD_3)_2CO$, δ (ppm)): 8.1 (q, $C_5(CH_3)_5$, $^1J_{C-H}$ = 128 Hz), 13.6 (q, C^{12}, $^1J_{C-H}$ = 125 Hz), 22.3 (t, C^{11}, $^1J_{C-H}$ = 126 Hz), 27.0, 33.0, 35.1, 38.2 (4 × t, C^{3-6}, $^1J_{C-H}$ = 129, 128, 129, 129 Hz), 56.4 (dt, C^1, $^1J_{C-H}$ = 128 Hz, $^3J_{C-H}$ = 8 Hz), 78.2 (d, C^2, $^1J_{C-H}$ = 154 Hz), 82.8, 88.5, 91.4, 96.4 (d, C^{7-10}, $^1J_{C-H}$ = 154, 145, 160, 163 Hz), 102.4 (s, $C_5(CH_3)_5$). ^1H NMR ($(CD_3)_2CO$, δ (ppm)): 1.05 (t, $C^{12}H_3$, J_{H-H} = 7 Hz, 3 H), 1.92 (s, $C^{13}H_3$, 15 H), 1.3 (m, C^5H_2, 1 H), 1.5 (m, $C^{11}H_2$, 1 H), 1.45 (m, C^4H_2, 1 H), 1.55 (m, C^6H_2, 1 H), 1.65 (m, C^5H_2, 1 H), 1.75 (m, C^4H_2, 1 H), 2.0 (m, $C^{11}H_2$, 1 H), 2.2 (m, C^6H_2, 1 H), 2.45 (m, C^3H_2, 1 H), 2.68 (m, C^3H_2, 1 H), 2.82 (m, C^9H, 1 H) 3.14 (m, C^2H, 1 H), 3.22 (m, $C^{10}H$, 1 H), 3.55 (m, C^8H, 1 H), 3.74 (m, C^1H_2, 1 H), 3.86 (dd, C^1H_2, $^2J_{gem(H-H)} = {}^3J_{trans(H-H)}$ = 10 Hz, 1 H), 4.69 (m, C^7H, 1 H).

(15) After 168 h at 100 °C (no more evolution): total conversion 30% into $C_{12}H_{24}$, $C_{18}H_{36}$, and some higher oligomers; "C_{12}":"C_{18}" = 10:90, numerous isomers detected, 9 for $C_{12}H_{24}$, 20 for $C_{18}H_{36}$. Monitoring the reaction shows the intermediate formation of "C_{12}" prior to transformation into "C_{18}".

(16) After 12 h at 100 °C: conversion 100%; "C_6" isomers, 92%; "C_{11}", 1%; "C_{17}", 1.6%; "C_{12}", "C_{18}", "C_{24}", and heavier hydrocarbons (over 56 species in the liquid phase). Gas-phase analysis: CH_4, ca. 4%.