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Communications

Five-Membered 2-Methylene-2,3-dihydro Heterocycles from Ruthenium Butatrienylidene Intermediates and 2-(Dimethylamino)methyl-Substituted Furans, Thiophenes, and Selenophenes

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Summary: Trapping of the primary butatrienylidene intermediate $\text{trans-[Cl(dppm)}_2\text{Ru=C=C=C=CH}_2\text{)]}^+$ with five-membered 2-(dimethylamino)methyl-substituted heterocycles provides an easy and efficient route to aminoallenylidene complexes with appended 2-methylene-2,3-dihydrofuran, -thiophene, or -selenophene moieties. Upon warming or acid catalysis isomerization to the aromatic 2-methylated isomers is observed.

Allenylidene complexes have recently emerged as highly useful starting compounds for the construction of metal-bonded heterocycles. The synthetic procedures involve their reactions with difunctional nucleophiles^{1–4} or unsaturated nucleophiles containing a C=C,⁵ C≡C,^{6,7}

C=N,^{8,9} or C=O bond.^{10,11} In all these instances nucleophilic addition to either the metal-bonded carbon atom C_α or the remote carbon atom C_γ precedes the final ring closure step. Similar reactions of butatrienylidene complexes are less well represented. The only examples reported thus far involve ethynylquinoline derivatives of the Cp(PPh₃)₂ entity formed by treatment of the [Cp-(PPh₃)₂Ru=C=C=C=CH₂]⁺ intermediate with donor-substituted aromatic imines.^{12,13} We describe here the transformation of simple (dimethylamino)methyl-substituted heterocycles by a ruthenium butatrienylidene intermediate to give rare examples of five-membered 2-methylene-2,3-dihydro heterocycles attached to an aminoallenylidene ligand, including two representative furans, a thiophene, and a unique selenophene deriva-

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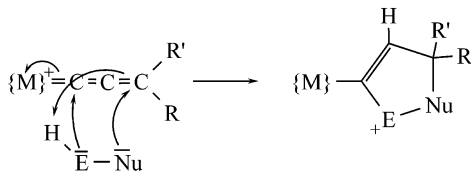
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Scheme 1. Generalized Cyclization Reaction between a Cationic Allenylidene Complex and a Difunctional Protic Nucleophile

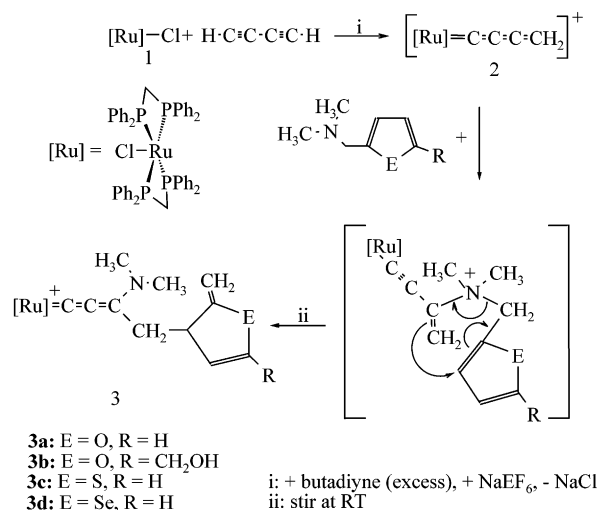


tive. Thermally induced or acid-catalyzed isomerizations to the more stable aromatic methyl-substituted tautomers are also described.

We have recently reported on the trapping of $[\text{Cl}(\text{L}_2)_2\text{-Ru}=\text{C}=\text{C}=\text{C}=\text{CH}_2]^+$ intermediates ($\text{L}_2 = \text{dppm}, \text{dppe}, \text{depe}$) with aprotic allyl- or propargyl-substituted nitrogen,^{14,15} sulfur,¹⁶ and selenium¹⁷ nucleophiles. Butenylnyl adducts are initially formed from regioselective addition of the heteroatom to the carbon atom C_γ of the unsaturated ligand. These rearrange readily to heteroatom-substituted allenylidene complexes, providing rare examples of a Hetero-Cope or Claisen type [3,3] sigmatropic rearrangement occurring within the coordination sphere of a transition metal.¹⁸ We then wondered whether the allylic double bond can also be part of an aromatic π -system. Such behavior would be in contrast with the classical Claisen rearrangement of allyl ethers or amines, where the intracyclic double bond always constitutes the vinyl and not the allyl component.^{19,20} Our first attempts focused on benzylamines, $\text{Me}_2\text{NCH}_2\text{Ar}$. However, the resulting adducts $\text{trans}[\text{Cl}(\text{dppm})_2\text{Ru}=\text{C}=\text{C}(\text{=CH}_2)(\text{NMe}_2\text{CH}_2\text{Ar})]^+$ ($\text{Ar} = \text{Ph}, 3\text{-OMeC}_6\text{H}_4$)²¹ gave intractable mixtures of products when heated to 85 °C in chlorobenzene.

We then turned our attention to (dimethylamino)-methyl-substituted five-membered aromatic heterocycles with smaller resonance energies.²² The intense green solution obtained from $\text{cis-RuCl}_2(\text{dppm})_2$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$), NaSbF_6 as halide abstracting agent, and excess butadiyne smoothly reacts with 2-(dimethylamino)methylthiophene. After 1 h a sharp IR absorption band at 2031 cm^{-1} is detected, which is characteristic of a 2-ammonio-substituted butenylnyl complex.^{21,23} Within the next few hours another much broader IR band at ca. 1990 cm^{-1} grows in at the expense of the initial alkynyl type absorption and develops into a highly intense band over 2–3 days. The position and intensity are indicative of the formation of an aminoallenylidene complex. The purified product from this reaction indeed reveals characteristic downfield reso-

Scheme 2



nance signals at δ 203.1, 153.4, and 119.0 ppm in the ^{13}C NMR spectrum, which are assigned as the C_α , C_γ , and C_β carbon atoms of the cumulated ligand by virtue of the PC coupling constants of 13.7, 1.0, and 1.8 Hz.²⁴ The phosphorus atoms of the two dppm ligands give rise to an AA'BB' splitting pattern, thus indicating the presence of a chiral center within the ligand backbone. Carbon atoms of the heterocycle appear at 148.9 (quaternary), 125.1 and 123.7 (=CH), 107.4 (=CH₂), and 51.5 (CH) ppm, the assignments being aided by a DEPT-135 experiment. Seven individual resonance signals integrated as one proton each appear in the ^1H NMR spectrum. Most characteristic are signals at 1.37 and 1.81 ppm (dd each) for the diastereotopic protons of a CH₂ unit and olefinic resonances at 4.86, 6.07 (heterocycle), 4.52 and 4.96 ppm (=CH₂). The splitting pattern and the observed couplings indicate the presence of a 2,3-dimethylene-3-yl-2,3-dihydrothiophene subunit, which is bonded to the terminal carbon atom of the allenylidene ligand, as is shown as structure **3c** in Scheme 2. **3c** is the product expected from an addition/rearrangement sequence as outlined above and can be isolated in 67% yield after chromatographic workup on silica.

Furan and selenophene derivatives behave in the same manner, giving complexes **3a, b** and **3d** with a 2,3-dimethylene-3-yl-2,3-dihydrofuran or -selenophene substituent attached to the side chain of the aminoallenylidene ligand (Scheme 2). The heterocyclic subunit of the latter compound seems to be unparalleled in organic chemistry. Five-membered 2-methylene-2,3-dihydrofurans^{25–33} or -thiophenes^{31–34} still constitute a

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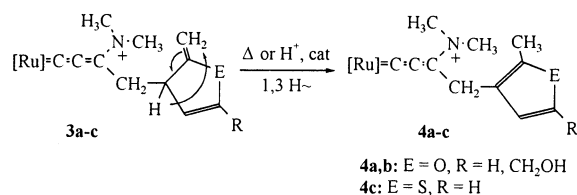
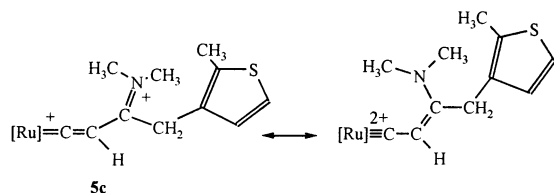
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Scheme 3. Thermal- or Acid-Induced Rearrangement of Complexes 3a–c

Chart 1


rather rare class of heterocycles with considerable synthetic potential. Their synthesis usually requires rather elaborate starting materials, available only from multistep procedures, and sometimes less convenient reaction conditions such as prolonged UV irradiation. If not stabilized by benzanulation, by unsaturated C=E functionalities in resonance with the intracyclic double bond, or by 2-fold substitution at the 4-position, they are highly prone to dimerization,^{32,35} oligomerization,³⁶ or rearrangement to their aromatic 5-methylated isomers,^{25,30,32,35} which often decreases the yield and purity of isolated samples. This is especially true for thiophenes.^{32,37}

In the solid state, complexes **3** display long-term stability under aerobic conditions and are stable toward rearomatization under the conditions of chromatographic workup. In solution complexes **3a–c** isomerize slowly at ambient temperature but notably faster upon heating to 85 °C, as is conveniently monitored by ³¹P NMR spectroscopy of a 1,2-*C*₂D₂Cl₄ solution. As an example, the complex AA'BB' multiplet associated with **3c** is cleanly replaced by the single resonance line of its achiral isomer **4c**. ¹H NMR spectra reveal the disappearance of the two olefinic methylene protons in favor of a methyl singlet and an appreciable shift of the doublet resonances of the heterocyclic protons to lower field. Thus, **4a–c** are obtained from the reactions of *cis*-[RuCl₂(dppm)₂], butadiyne, and the respective amine at 80 °C in chlorobenzene. As is observed for the purely heterocyclic counterparts of **3a–c**, proton migration from the 3-position to the neighboring methylene group is also catalyzed by acids. Addition of small quantities of a 40% solution of HBF₄ in Et₂O to a **3a–c** induces quantitative isomerization to **4a–c** (Scheme 3). When an excess of HBF₄/Et₂O is added to **3c** dissolved in CD₂-Cl₂ and the ³¹P NMR spectrum recorded, only one singlet resonance at δ -16.9 ppm is observed. Upon prolonged standing this signal is gradually replaced by the resonance line of **4c** at δ -7.7 ppm. In the presence of substoichiometric amounts of HBF₄, a mixture of this new species and of **4c** is obtained. We attribute this new

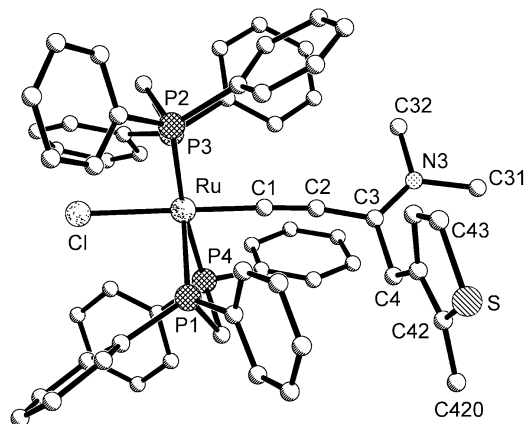


Figure 1. Plot of the cation in the thiophene-substituted allenylidene complex **4c** with the atom numbering. Selected bond lengths (Å) and angles (deg): Ru–C1 = 1.942(9), Ru–C1 = 2.477(2), C1–C2 = 1.228(11), C2–C3 = 1.405(12), C3–N3 = 1.309(12), C3–C4 = 1.508(14), N3–C31 = 1.477(11), N3–C32 = 1.456(13), C41–C42 = 1.342(15), C41–C44 = 1.447(16), C43–C44 = 1.340(16), C43–S = 1.748(14), C42–S = 1.715(12); C1–Ru–C1 = 171.8(3), Ru–C1–C2 = 174.1(8), C1–C2–C3 = 170.1(11).

signal to the protonated dicationic iminium-substituted vinylidene (or aminovinylcarbyne) complex *trans*-[Cl-(dppm)₂RuCCHC(NMe₂)CH₂R]²⁺ (**5c**; Chart 1). Characteristic NMR resonance signals include that of the =CH proton attached to C_β at δ 3.39 ppm (broad) and a broad feature at δ 2.57 ppm for the methylene protons in the ¹H NMR spectrum as well as the resonance signals for the carbon atoms of the C₃ chain at δ 328.4 (C_α), 172.9 (C_γ), and 107.6 ppm (C_β). We note that similar dicationic species have recently been obtained from the protonation of allenylidene complexes [Cp*-(dippe)Ru=C=C=CPhR]⁺ (R = H, Ph).³⁸

The thiophene derivative **4c** was also characterized by X-ray crystallography (Figure 1).³⁹ The bond lengths and angles along the unsaturated RuC₃N chain closely resemble those in other aminoallenylidene complexes.^{15,24,40} Thus, the ClRuC₃ axis is close to linear with some higher degree of bending at C2. The Ru–C1 bond of 1.942(9) Å is considerably shorter than those encountered in alkynyl complexes of the same metal fragment (1.994–2.078 Å). The C1–C2 bond length (1.228(11) Å) still falls within the range of a C≡C triple bond.⁴¹ Other structural features worthy of note are the rather long C2–C3 and the short C3–N3 bond and the planar environment of the nitrogen atom (angle sum 359.9°). This provides strong evidence for an appreciable contribution of the iminium alkynyl resonance form [Ru]C≡CC(R')=NR₂⁺. The appended thiophene substituent is nearly parallel to one of the arene rings (the

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angle between the normals of these planes is 14°). The bond parameters within the heterocycle appear to be normal and require no further comment.⁴²

In conclusion, we have found an efficient access route to aminoallenylidene complexes of ruthenium with rare or even unprecedented five-membered 2-methylene-2,3-dihydro heterocycles as appended substituents. These are assembled in one-pot reactions from simple, readily available starting materials. Noteworthy in these reactions are the participation of an intracyclic double bond of a heteroaromatic entity as the allylic component in a [3,3]-sigmatropic rearrangement and the mild reaction conditions under which this process and the concomitant dearomatization of the heterocycle are achieved. Upon warming or acid catalysis tautomerization to their aromatic counterparts readily occurs. In addition, the protonated form of the thiophene derivative **3c** has been obtained and characterized by NMR spectroscopy.

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Supporting Information Available: Text giving experimental details and spectroscopic and analytical data for complexes **3a–d**, **4a–d**, and **5c** and tables giving crystal data and details of the structure determination, positional and thermal parameters, and bond distances and angles for **4c**. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data have been deposited at the Cambridge Structure Data Centre (CCDC 154230). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, <http://www.ccdc.cam.ac.uk>).

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