Facile C−C Bond Formation between Terminal Acetylenes and Olefines Leading to η^3-Butadienyl and η^2-Butadiene Complexes. A New Reaction Pathway for Metallacyclobutane Complexes

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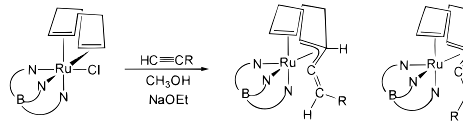
Transition metal vinylidene complexes have been shown to be involved in various C−C coupling reactions such as the migratory insertion of alkyl, aryl, vinyl, and alkynyl ligands onto the electrophilic α-carbon of the vinylidene moiety.[1] A rather rare example of C−C bond formation within a vinylidene complex is the cycloaddition of alkynes and olefines to the M=C bond giving, respectively, metallacyclobutene and metallacyclobutane intermediates which then polymerize through ring opening.[2] Although the underlying process is characteristic of early transition metals, we here give a preliminary account of a facile C−C coupling reaction between olefines and terminal acetylenes proceeding via a ruthenacyclobutane[3] intermediate finally converting into either η^3-butadienyl or η^2-butadiene complexes.[1c,4] To the best of our knowledge, this type of conversion is a novel one.

Treatment of RuTp(COD)Cl (**1**)[5] (Tp = tripyrazolylborate) with terminal acetylenes HC≡CR (R = Ph, C_6H_9, ferrocenyl, CH_2Ph, *n*-Bu) in MeOH in the presence of NaOEt (1 equiv) at 65 °C for 24 h afforded the η^3-butadienyl complexes **3** and **4** in high yields (Table 1, Scheme 1). This process is not restricted to COD complexes. Thus, in similar fashion, RuTp(η^3-(P,C,C)-$Ph_2PCH=CH(Ph)=CH_2$)Cl (**2**)[6] was found to react with HC≡CR (R = Ph, C_6H_9) to give the η^3-butadienyl complexes **5a**,**b** (Scheme 2). In addition to full spectroscopic and analytical characterizations of the products, the solid-state structures of **3a** and **5b** were determined by single-crystal X-ray diffraction.[7] ORTEP diagrams of **3a** and **5b** are included in Schemes 1 and 2 (For clarity, only the coordinated nitrogen atoms of Tp are shown). The most notable feature is the distorted *s-trans* structure of the butadienyl moiety. Since the two allyl carbons, C-1, C-2, are noticeably more apart from the Ru center than is the enynyl carbon C-3, a major resonance contribution from the vinyl−alkene structure is indicated. Furthermore, the relatively uniform bond distances for the three allyl carbons point to substantial π-electron delocalization.[1c,4]

Table 1. Conversion and Product Distribution of the Reaction of **1** with Terminal Acetylenes

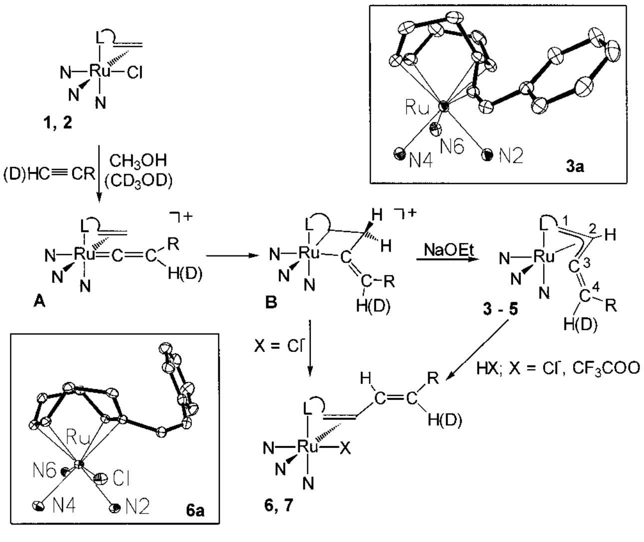


1 3 4

entry	R	% conversion[a]	products,[a] yield % of *Z*	products,[a] yield % of *E*
1	Ph	100	**3a**, 98	
2	C_6H_9	100	**3b**, 24	**4b**, 76
3	ferrocenyl	100		**4c**, 97
4	CH_2Ph	97	**3d**, 94	**4d**, 6
5	*n*-Bu	93	**3e**, 66	**4e**, 33

[a] Conversions and product distributions have been determined by ^1H NMR spectroscopy.

Scheme 1



The reaction mechanism shown in Scheme 1 represents our initial working hypothesis for providing the η^3-butadienyl product. For the first step, the formation of the cationic vinylidene complex **A** via a 1,2 hydrogen shift is a now well-established process.[8]

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(7) Crystal data for **3a**: monoclinic space group $P2_1/n$ (No.14), $a = 8.180(2)$ Å, $b = 11.252(3)$ Å, $c = 25.335(6)$ Å, $\beta = 98.85(1)°$, $V = 2304(1)$ Å^3, $Z = 4$, $R_1 = 0.032$ ($I \geq 2\sigma(I)$), $R_1 = 0.057$ (all data), $wR_2 = 0.064$ (all data), no. of reflections 5029, no. of refined parameters 307. Crystal data for **5b**: monoclinic space group $P21/n$ (No. 14), $a = 9.647(2)$ Å, $b = 15.155(3)$ Å, $c = 24.373(6)$ Å, $\beta = 95.19(1)°$, $V = 3549(1)$ Å^3, $Z = 4$, $R_1 = 0.031$ ($I \geq 2\sigma(I)$), $R_1 = 0.046$ (all data), $wR_2 = 0.070$ (all data), no. of reflections 6265, no. of refined parameters 453. Crystal data for **6a**: triclinic space group $P1$ (No. 2), $a = 8.191(1)$ Å, $b = 9.852(1)$ Å, $c = 16.335(2)$ Å, $\alpha = 103.53(1)°$, $\beta = 93.55(1)°$, $\gamma = 109.04(1)°$, $V = 1197.7(2)$ Å^3, $Z = 2$, $R_1 = 0.024$ ($I \geq 2\sigma(I)$), $R_1 = 0.029$ (all data), $wR_2 = 0.056$ (all data), no. of reflections 6815, no. of refined parameters 317.

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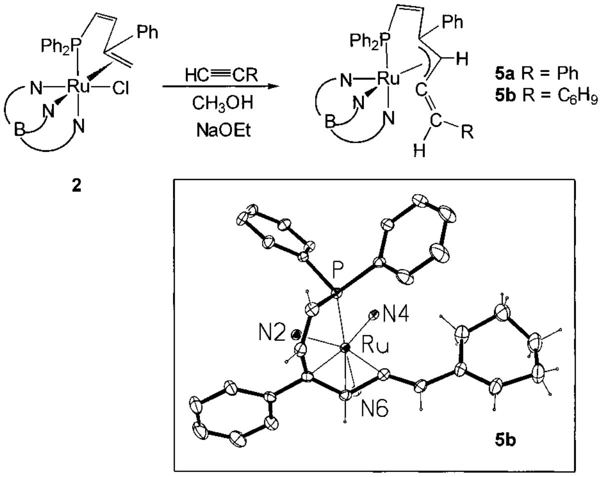
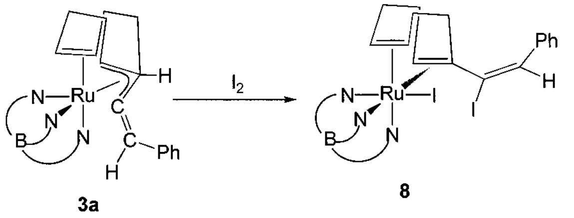
Scheme 2



We[6] and others[9] have already shown that protic solvents favor cationic vinylidene complexes. Subsequently, the metallacyclobutane complex **B** is formed via a [2 + 2] cycloaddition, followed by deprotonation of one of the β-hydrogen atoms of **B** yielding the stable η^3-butadienyl complex.

The following observations may be taken to support this mechanism. (i) The occurrence of a vinylidene intermediate could be verified by a labeling experiment. Thus, the η^3-butadienyl product **3a-*d*$_1$** of the reaction of deuterium-labeled phenylacetylene DC≡CPh and **1** contains deuterium exclusively at the olefinic carbon C-4 of the butadienyl moiety (Scheme 1). On the other hand, the η^3-butadienyl complex **3a** did not incorporate deuterium to give **3a-*d*$_1$** under reflux in CD_3OD in the presence of NaOEt. (ii) The formation of RuTp(COD)H that might occur by chloride replacement from **1** with MeOH followed by β elimination was not observed. Beyond that, when RuTp(COD)H[10] was used as the starting material in place of **1**, under otherwise identical conditions, only small amounts (<20%) of η^3-butadienyl products were obtained in addition to polyacetylenes as the main products. (iii) In the absence of base only polyacetylenes[11] were obtained with decomposition of the Ru complex to intractable materials. (iv) When in place of NaOEt an excess of KCl is added, **B** rearranges presumably via a β-hydrogen elimination/reductive elimination sequence (equivalent to a 1,2 hydrogen shift) to the neutral η^2-butadiene complex **6a** (structure included in Scheme 1). The vacant coordination site of the resulting 16-electron intermediate is occupied by the incoming chloride.

Scheme 3



The stereochemistry of **3** and **4**, difficult to determine by NMR methods, is established by the products formed from the reaction with HCl or CF_3COOH at room temperature given by the olefine complexes **6** (*Z* isomers) and **7** (*E* isomers) with the vinyl side chain (Scheme 1). Under this experimental condition no isomerization takes place and the stereochemistry of the butadienyl fragment is readily apparent from the vicinal coupling constant $^3J_{HH}$ of the vinyl moiety being about 11 and 16 Hz in case of a cis and trans arrangement, respectively. This result implies that the C-3 carbon of η^3-butadienyl complexes is nucleophilic, which offers the possibility of further functionalization by treating them with electrophiles, e.g. **3a** has been reacted with I_2 to yield complex **8** in essentially quantitative yield (Scheme 3).

In conclusion, it is shown that selective coupling of olefines and terminal acetylenes is feasible in the coordination sphere of Ru(II). Although the coupling in the present case is particularly assisted by the intramolecular mode with favorable stereochemical conditions brought about by the anchoring group L, an extension to the intermolecular mode should in principle be conceivable. The deprotonation pathway for the onward reaction of the metallacyclobutane complex has yet not been considered.[12] The butadienyl fragment is nucleophilic at C-3 and is capable of reacting with electrophiles such as H^+ and I_2 to give the 1,3-diene unit. We believe this work may initiate a systematic search of coupling olefines with acteylenes into functionalized 1,3-dienes in a synthetically useful fashion.

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Supporting Information Available: Text giving full experimental details and analytical data for complexes **3**–**8** and tables of X-ray structural data, including data collection parameters, positional and thermal parameters, and bond distances and angles for complexes **3a**, **5b**, and **6a** (27 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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