

Allyl/Alkyne Coupling Reactions Mediated by Neutral Ruthenium(II). Isolation and Characterization of Ruthenium(II) η^3 -Allyl η^2 -Alkyne Complexes

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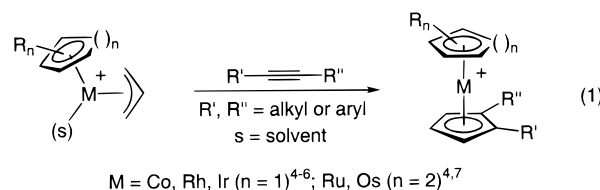
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Summary: In contrast to the cyclization products obtained from allyl/alkyne coupling reactions in the isostructural cationic series, neutral complexes of the form $(C_5Me_5)Ru(\eta^3\text{-allyl})(\eta^2\text{-alkyne})$ react to give acyclic η^5 -pentadienyl complexes in high yield.

Investigations of transition-metal-mediated allyl/alkyne coupling reactions have revealed a variety of synthetically valuable or potentially exploitable reactivity patterns.^{1–8} In particular, metal-mediated allyl/alkyne cycloaddition reactions using cationic late-transition-metal complexes of the form $[(C_nR_n)M(\eta^3\text{-allyl})(\eta^2\text{-alkyne})]^+$ (eq 1) have been used to prepare

substituted η^5 -cyclopentadienyl complexes^{4–7} and, more recently, η^5 -cycloheptadienyl complexes.⁸ To probe the effects of reducing the electrophilicity of the metal without substantially altering the molecular orbitals involved, we have investigated the chemistry of the isostructural but neutral $(C_5Me_5)Ru^{II}$ template. In this communication, we report the synthesis of a range of isolable $(C_5Me_5)Ru(\eta^3\text{-allyl})(\eta^2\text{-alkyne})$ complexes, which undergo allyl/alkyne coupling to yield acyclic η^5 -pentadienyl complexes rather than cycloadducts.



Despite the kinetic lability of most allyl alkyne complexes, $(C_5Me_5)Ru(\eta^3\text{-allyl})(\eta^2\text{-PhC}\equiv\text{CPh})$ (**3a**) can be synthesized by simply treating a THF solution of $(C_5Me_5)Ru(\eta^3\text{-allyl})X_2$ ($X = Br, Cl$)⁹ **1** with Rieke zinc¹⁰ (10–12 equiv) in the presence of diphenylacetylene (eq 2).¹¹ Complex **3a** was isolated as an air-stable orange material by trituration of the crude residue into pentane. Analytically pure complex **3a** was obtained by recrystallization from cold pentane (76%).¹² The *exo* orientation of the allyl ligand in complex **3a** was confirmed both by difference NOE spectroscopy and by X-ray crystallography (vide infra). While this complex is quite stable in the solid state, slow conversion to the *endo* isomer is observed upon standing in benzene solution at room temperature (ca. 30% conversion after 24 h).

The corresponding 2-butyne complex $(C_5Me_5)Ru(\eta^3\text{-allyl})(\eta^2\text{-MeC}\equiv\text{CMe})$ (**3b**) can be prepared in a similar manner, although it is thermally more labile than diphenylacetylene complex **3a**. Prolonged exposure of **3b** at room temperature to either vacuum or the atmosphere results in decomposition to unidentifiable products, yet this complex is indefinitely stable in the

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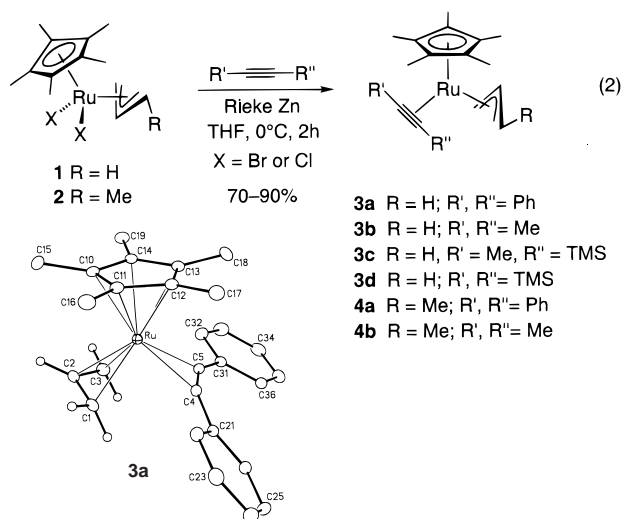
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(11) Freshly acid-washed zinc powder also reduces $(C_5Me_5)Ru(\eta^3\text{-allyl})X_2$, but the reaction proceeds much more slowly.

(12) Complete experimental and characterization data are provided as Supporting Information.



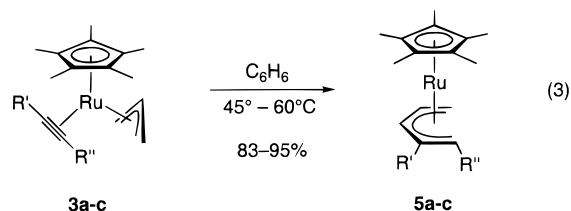
solid state when maintained below -20°C , even under air. Reduction of $(\text{C}_5\text{Me}_5)\text{Ru}(\eta^3\text{-allyl})\text{X}_2$ in the presence of either 1-(trimethylsilyl)propyne or bis(trimethylsilyl)acetylene (BTMSA) also leads to the corresponding isolable alkyne complex **3c** or **3d**, respectively. In addition, the η^3 -crotyl alkyne derivatives **4a** and **4b** were prepared analogously by reduction of $(\text{C}_5\text{Me}_5)\text{Ru}(\eta^3\text{-crotyl})\text{Br}_2$ (**2**).⁹

The spectroscopic data^{12,13} for complexes **3** and **4** are consistent with the η^3 -allyl η^2 -alkyne formulation, although the two-electron-donor alkyne ligands exhibit ^{13}C NMR chemical shifts minimally perturbed from those of the free alkynes.¹⁴ Rather than an indication of weak coordination, we attribute the small chemical shift differences to a balance of anisotropic shielding by the metal and the deshielding resulting from the reduction of the alkyne π -bond order, which increases its olefinic character. The metal–alkyne interaction can be further assessed with the aid of the X-ray crystal structure of complex **3a**, the first structurally characterized η^3 -allyl η^2 -alkyne complex.¹⁵ The alkyne bond length is 1.261(3) Å, midway between the typical values for C–C double and triple bonds. The deviation from linearity observed for the substituents on the alkyne ligand, 29.3(2) and 29.2(2)°, confirms the significant back-bonding interaction from the metal to the alkyne.

Isolable complexes incorporating an allyl and one or more alkyne ligands are very rare.^{3a,8a} The bonding of the alkyne to the $(\text{C}_5\text{Me}_5)\text{Ru}(\eta^3\text{-C}_3\text{H}_5)$ fragment results in the close proximity of the orthogonal alkyne π -bonding orbital to a filled metal-based orbital, making the relative stability of these compounds particularly sur-

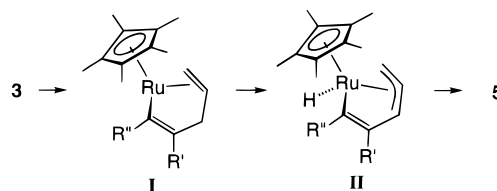
prising. Such four-electron repulsive interactions have been invoked to rationalize both the structure and high reactivity of other two-electron alkyne complexes.¹⁶ However, the significantly increased kinetic lability of the electron-rich 2-butyne ligand in complex **3b** relative to the π -acidic diphenylacetylene ligand of **3a** is consistent with this rationalization.

Although $(\text{C}_5\text{Me}_5)\text{Ru}(\eta^3\text{-allyl})(\eta^2\text{-PhC}\equiv\text{CPh})$ (**3a**) is stable at room temperature, allyl/alkyne coupling is induced upon heating, resulting in the near-quantitative formation of the acyclic η^5 -pentadienyl complex **5a** (eq 3).¹⁷ The structure of air-stable **5a** is established on the



basis of spectroscopic analysis¹² and by comparison to previously reported $(\text{C}_5\text{Me}_5)\text{Ru}(\eta^5\text{-pentadienyl})$ complexes prepared from intact pentadienyl precursors.¹⁸ Spectroscopic analysis reveals that the alkyne-derived phenyl groups are oriented *cis* in the final product. The formation of 1,2-disubstituted η^5 -pentadienyl ligands via the coupling of alkyne and allyl ligands has also been reported for rhenium^{3d} and chromium^{3e} templates. The reaction presumably proceeds via migratory coupling to give the unsaturated σ,π -vinyl olefin intermediate **I** (Scheme 1),¹⁹ as demonstrated in related systems.^{3a,e,1}

Scheme 1



We propose that the unsaturated ruthenium center then activates an allylic hydrogen atom, generating the Ru(IV) hydride intermediate **II**, which subsequently undergoes reductive elimination to yield the η^5 -pentadienyl product.

With the exception of BTMSA complex **3d**,²⁰ the formation of 1,2-disubstituted η^5 -pentadienyl complexes **5** from η^3 -allyl alkyne complexes **3** is general for alkyl- and aryl-substituted alkynes. However, the temperature

(13) Selected NMR spectroscopic data (C_6D_6) for **3a**: ^1H NMR (300 MHz) δ 8.01 (dt, $J = 8.2, 1.5$ Hz, 4H, H_{Ph}), 7.29 (t, $J = 8.4$ Hz, 4H, H_{Ph}), 7.10 (tt, $J = 6.9, 1.5$ Hz, 2H, H_{Ph}), 3.12 (tt, $J = 9.5, 6.4$ Hz, 1H, $\text{H}_{\text{central}}$), 2.85 (d, $J = 6.4$ Hz, 2H, H_{syn}), 1.47 (s, 15 H, C_5Me_5), 0.44 (d, $J = 9.5$ Hz, 2H, H_{anti}); ^{13}C { ^1H } NMR (75 MHz) δ 132.5, 132.3, 128.3, 126.3, 98.1, 94.1, 79.6, 44.8, 9.7.

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(15) Crystal data for complex **3a** ($\text{C}_{27}\text{H}_{30}\text{Ru}$, -80°C): monoclinic, $P2_1/c$, $a = 7.3502(3)$ Å, $b = 18.5243(9)$ Å, $c = 16.0368(8)$ Å, $\beta = 94.2041(10)^\circ$, $V = 2177.65(18)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.390$ g cm⁻³, $\mu = 0.729$ mm⁻¹, $R_1 = 0.0260$, $wR_2 = 0.0699$ ($F_o^2 > -3\sigma(F_o^2)$).¹²

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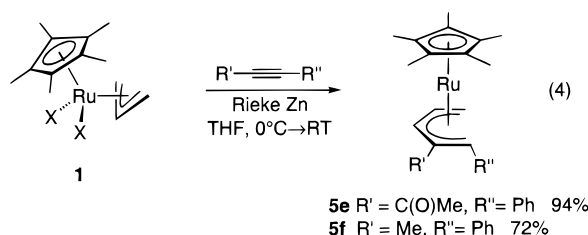
(17) For most disubstituted alkynes, the presence of excess alkyne has no significant effect on the course of the reaction. However, the reactions of acetylene, dimethyl acetylenedicarboxylate, and ethyl 2-butyrate under these conditions proceed via alternative reactivity patterns. These reactions will be discussed in a separate account: Older, C. M.; Stryker, J. M. Manuscript in preparation.

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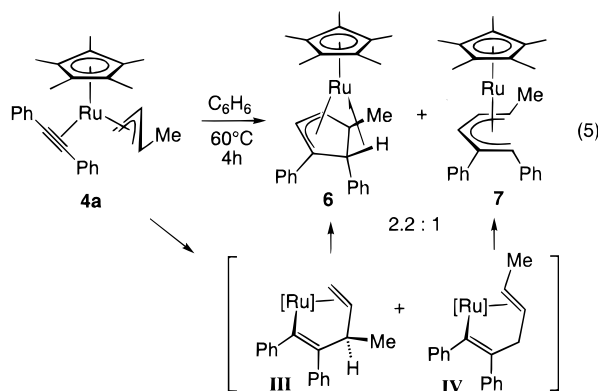
(19) For both complexes **3a** and **3b**, the vinyl olefin intermediate can be trapped upon addition of carbon monoxide.

(20) Thermolysis of $(\text{C}_5\text{Me}_5)\text{Ru}(\eta^3\text{-allyl})(\eta^2\text{-TMSC}\equiv\text{CTMS})$ (**3d**) results in the formation of several unidentified products.

required to induce allyl/alkyne coupling is dependent on the alkyne: while the diphenylacetylene complex **3a** requires temperatures above 50 °C to effect coupling, the 2-butyne derivative **3b** undergoes insertion slowly at room temperature.¹² Thermolysis of the unsymmetric alkyne complex **3c** at 55 °C results in the regioselective formation of a single η^5 -pentadienyl product, **5c**, with the large trimethylsilyl substituent located at the terminus of the pentadienyl ligand. This implies that the initial migratory allyl/alkyne coupling occurs at the sterically less hindered end of the alkyne ligand. The coupling of some alkynes is particularly facile: addition of either 1-phenylpropyne or 4-phenyl-3-butyne-2-one to complex **1** and zinc yields the η^5 -pentadienyl complexes **5e** and **5f** directly (eq 4).²¹



The presence of an alkyl substituent on the η^3 -allyl ligand complicates the allyl/alkyne reactivity manifold. Thermolysis of $(C_5Me_5)Ru(\eta^3\text{-crotyl})(\eta^2\text{-PhC}\equiv\text{CPh})$ (**4a**) in benzene results in the formation of an inseparable 2.2:1 mixture of two products, isolated as a yellow powder in 84% yield (eq 5). The structure of the minor



product, acyclic η^5 -pentadienyl complex **7**, is assigned on the basis of spectroscopic comparison to the diphenylacetylene adduct **5a**.¹² The major product is provision-

ally assigned as the agostic η^3 -cyclopentenyl complex **6**, on the basis of spectroscopic similarity to several closely related, well-characterized complexes of this structural class.^{22,23} These data also indicate that the methyl substituent on the cyclopentenyl ring is located *endo* to the ruthenium center, suggesting that the two regioisomeric products may arise from partitioning at the coupling stage, producing a mixture of vinyl olefin intermediates **III** and **IV** (eq 5). Only intermediate **IV** can undergo facile allylic activation; intermediate **III** instead undergoes competitive migratory cyclization, as observed in the more electrophilic systems.⁴⁻⁷ By comparison, attempts to induce coupling in $(C_5Me_5)Ru(\eta^3\text{-crotyl})(\eta^2\text{-MeC}\equiv\text{CMe})$ (**4b**) lead only to decomposition.

Thus, mild thermolysis of neutral ruthenium allyl/alkyne complexes provides acyclic pentadienyl products, in sharp contrast to the cycloaddition products obtained from isostructural, but cationic, late transition metal complexes. This difference in reactivity is presumably due to the more electron-rich $(C_5Me_5)Ru$ template inhibiting the rate of migratory cyclization and increasing the accessibility of the $Ru(IV)$ oxidation state. These effects combine to promote the allylic activation pathway responsible for the formation of η^5 -pentadienyl complexes. By modulating the electron density of the metal template, it is thus possible to control the partitioning between cyclization and C-H bond activation pathways.

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Supporting Information Available: Text giving experimental procedures and complete spectroscopic and analytical data for all new compounds and text and tables giving details of the crystal structure determination for complex **3a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(21) The use of cyclooctyne and 2,8-decadiyne also leads to products tentatively formulated as η^5 -pentadienyl complexes.

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(23) ¹H NMR spectroscopic data for complex **6** (360 MHz, C₆D₆): δ 7.27–7.67 (m, 10H, H_{Ph}), 4.67 (d, J = 3.5 Hz, 1H, H₂), 3.74 (dq, J = 11.8, 5.9 Hz, 1H, H_{4exo}), 2.94 (d, J = 3.7 Hz, 1H, H₃), 1.59 (s, 15H, C₅Me₅), 1.31 (d, J = 5.9 Hz, 3H, CH₃), –4.89 (d, J = 11.9 Hz, 1H, H_{agostic}).