10396 *J. Am. Chem. Soc.* **1993,** *115,* 10396-10397

Coupling of Propargyl Alcohols via Allenylidene–Alkynyl or Vinylvinylidene–Alkynyl Combination on a Thiolate-Bridged Diruthenium Center. Syntheses and Crystal Structures of Diruthenacyclopentanone and Diruthenacyclopentenone Complexes

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Received June 8, 1993

Interaction of organic and organometallic propargyl derivatives with transition metals has given entry into a variety of propargyl, allenyl, and allenylidene complexes[1] which have attracted increasing attention due to their intriguing structural features and reactivities.[2] In our continuing studies on thiolate-bridged dinuclear Cp*Ru (Cp* = η^5-C_5Me_5) compounds,[3,4] we recently reported that treatment of a paramagnetic complex Cp*Ru(μ_2-SPr^i)$_3$RuCp*, **1**, with terminal alkynes gives a series of dinuclear terminal dialkynyl complexes Cp*Ru(C≡CR)(μ_2-SPr^i)$_2$Ru(C≡CR)Cp* (**2**, R = Tol, Ph, Bu^t, cyclohexenyl).[5] This prompted us to investigate if complex **1** incorporates propargyl alcohols in a similar fashion. However, as reported herein, dialkynyl complexes like **2** were not produced upon treatment of **1** with HC≡CC(OH)R$_2$ (R = Ph, Tol, Me), but instead unusual coupling of the propargyl alcohols on the diruthenium site readily proceeded to yield new types of dinuclear metallacycles **3** (**3a**, R = Ph; **3b**, R = Tol) and **4** (Scheme I).

Complex **1** smoothly reacted with HC≡CC(OH)R$_2$ (5 equiv per **1**; R = Ph, Tol) in THF at room temperature. Subsequent workup resulted in isolation of **3** as dark brown microcrystalline solids which have been spectroscopically characterized;[6] **3a** was further defined by X-ray crystallography.[7] Figure 1 shows an ORTEP drawing of **3a** having the dinuclear structure in which the two alkyne molecules form a diarylmethylene/diarylvinylidene-substituted diruthenacyclopentanone framework with Ru(1) and Ru(2). The five-membered metallacycle is essentially planar, and the molecule has a noncrystallographic symmetry plane which includes a Ru–Ru vector.

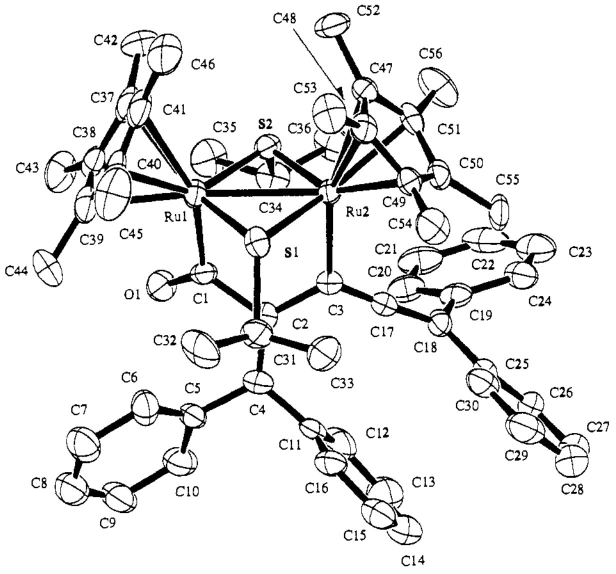
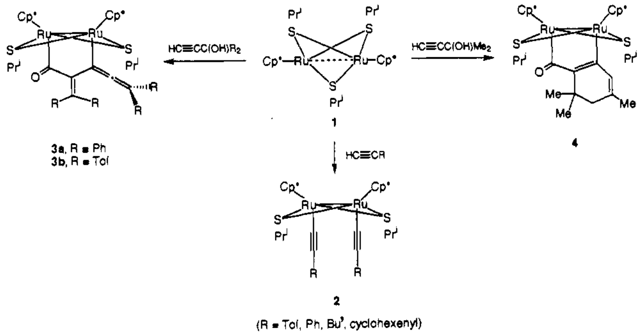


Figure 1. ORTEP drawing of complex **3a**. A solvated benzene molecule is omitted.

Scheme I



The most surprising feature of this structure is the diruthenacyclopentanone unit with both diarylmethylene and diarylvinylidene substituents, produced by coupling of the two alkyne molecules on the diruthenium site in **1** accompanied by a pseduo-1,3-shift of an oxygen atom. To the best of our knowledge, this is the first example of any type of transformation in which propargyl alcohols are converted in such a manner on metal centers.[8]

Similar treatment of **1** with HC≡CC(OH)Me$_2$ did not give the methyl analogue of **3** but yielded a diruthenacyclopentenone

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[6] **3a**: yield, 46%; IR (KBr) ν(C=C=C) 1847(w), ν(C=O) 1597(s); ^{1}H NMR (CDCl$_3$) δ 7.6–6.2 (m, 20H, Ph), 3.87 (sep, 2H, *J* = 6.6 Hz, SC*H*Me$_2$), 1.70, 1.48 (s, 15H each, Cp*), 1.42, 1.14 (d, 6H each, *J* = 6.6 Hz, SCH*Me*$_2$). **3b**: Yield, 42%; IR (KBr) ν(C=C=C) 1855(w), ν(C=O) 1592(s); ^{1}H NMR (CDCl$_3$) δ 6.92, 6.84 (d, 4H each, *J* = 8.2 Hz, aryl), 6.78, 6.66, 6.56, 6.24 (d, 2H each, *J* = 8.0 Hz, aryl), 3.87 (sep, 2H, *J* = 6.6 Hz, SC*H*Me$_2$), 2.27 (s, 6H, C$_6$H$_4$*Me*), 2.16, 1.67 (s, 3H each, C$_6$H$_4$*Me*), 1.71, 1.48 (s, 15H each, Cp*), 1.42, 1.09 (d, 6H each, *J* = 6.6 Hz, SCH*Me*$_2$).

[7] $P\bar{1}$ (triclinic), a = 11.971(2) Å, b = 20.501(3) Å, c = 11.418(2) Å, α = 94.46(1)°, β = 113.02(1)°, γ = 99.29(1)°, V = 2514.6(8) Å^3, Z = 2, $R(R_w)$ = 0.053(0.058). Bond lengths: Ru(1)–Ru(2), 2.7616(8); Ru(1)–C(1), 2.039(7); Ru(2)–C(3), 2.178(7); C(1)–C(2), 1.529(9); C(2)–C(3), 1.513(9); C(2)–C(4), 1.371(9); C(3)–C(17), 1.296(9); and C(17)–C(18), 1.334(9) Å. Bond angles: Ru(2)–Ru(1)–C(1), 88.1(2); Ru(1)–Ru(2)–C(3), 87.0(2); Ru(1)–C(1)–C(2), 122.2(5); C(1)–C(2)–C(3), 116.9(6); Ru(2)–C(3)–C(2), 119.2(5); and C(3)–C(17)–C(18), 175.8(8)°.

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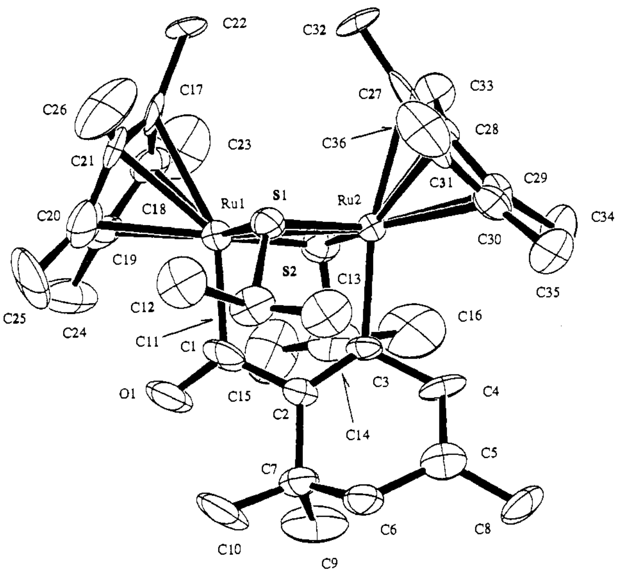
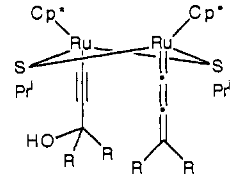


Figure 2. ORTEP drawing of complex **4**.

complex **4**.[9] The structure of **4** determined by X-ray diffraction analysis is depicted in Figure 2,[10] which clearly demonstrates that another type of coupling of propargyl alcohol has proceeded to form the fused ring system. The five-membered metallacycle is essentially planar, and pseudo-1,3-shift of an oxygen atom was also observed.

One possible pathway for the formation of **3** and **4** could involve intramolecular C–C bond formation between alkynyl/allenylidene or alkynyl/vinylvinylidene ligands in intermediates **5** and **6**, respectively,[11,12] although we must await further investigation to elucidate the detailed reaction mechanisms. The direct GC analysis of the reaction mixture indicated that almost stoichiometric amount of Pr^{i}SH and 20–30% of H$_2$ per **3** or **4** were formed during these transformations.



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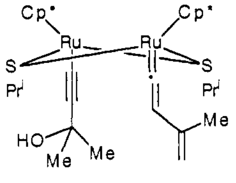
R = Ph, Tol



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Previously we reported that upon treatment with HBF$_4$ and I$_2$, two alkynyl ligands in the dialkynyl complex **2** (R = Tol, Ph) readily coupled to form diruthenacyclopentadienoindan complexes and 1,4-disubstituted-1,3-diynes, respectively. These transformations were understood to proceed via a vinylidene–alkynyl combination pathway.[5] The present study offers a related but quite different type of activation and transformation of alkynes on the thiolate-bridged diruthenium template. We believe that this work lays the foundation for future investigation into developing the allenylidene–alkynyl and vinylvinylidene–alkynyl couplings into synthetically useful reactions. Further studies are in progress aimed at inducing additional transformations of **3** and **4** with organic, inorganic, and organometallic reagents.

Acknowledgment. The Ministry of Education, Science and Culture, Japan is gratefully acknowledged for support of this research.

Supplementary Material Available: Experimental details including results of elemental analysis for **3** and **4**; for **3a** and **4**, tables of crystal and data collection parameters, atomic coordinates, anisotropic thermal parameters, and complete bond distances and angles (15 pages); listings of observed and calculated structure factors for **3a** and **4** (38 pages). Ordering information is given on any current masthead page.

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(8) Recently, Carty reported the zwitterionic diruthenacyclopentane and diruthenacyclopentene derivatives obtained by treatment of Ru$_2$(CO)$_6$(μ_2-η^1:η^2-PhC=C=CH$_2$)(μ_2-PPh$_2$) with Et$_2$NH or Bu^{t}NC.[2i] Allenyl/alkyne coupling at a dimetal center has been reported by Dixneuf et al.[2h]

(9) **4**: yield, 52%; IR (KBr) ν(C=O) 1624(s); ^{1}H NMR (CDCl$_3$) δ 6.17 (s, 1H, vinyl), 3.40 (sep, 2H, J = 6.7 Hz, SC*H*Me$_2$), 1.73, 1.70 (s, 15H each, Cp*), 1.64 (s, 3H, Me), 1.45 (S, 2H, CH$_2$), 1.24, 1.05 (d, 6H each, J = 6.6 Hz, SCH*Me*$_2$), 0.79 (s, 6H, Me).

(10) $P2_1/n$ (monoclinic), a = 10.789(2) Å, b = 18.633(3) Å, c = 17.941(2) Å, β = 93.48(1)°, V = 3600.1(9) Å^3, Z = 4, $R(R_w)$ = 0.067(0.048). Bond lengths: Ru(1)–Ru(2), 2.727(2); Ru(1)–C(1), 2.08(1); Ru(2)–C(3), 2.09(1); C(1)–C(2), 1.52(1); C(2)–C(3), 1.32(1); C(3)–C(4), 1.51(2); and C(4)–C(5), 1.38(1) Å. Bond angles: Ru(2)–Ru(1)–C(1), 87.8(4); Ru(1)–Ru(2)–C(3), 84.4(3); Ru(1)–C(1)–C(2), 119.8(9); C(1)–C(2)–C(3), 118(1); and Ru(2)–C(3)–C(2), 127.5(10)°.

(11) Propargyl alcohols of the form HC≡CC(OH)R$_2$ have been converted to allenylidene (for R = aryl) and vinylvinylidene (for R = alkyl) ligands on several transition metals.[1] Indeed, the related terminal allenylidene complex [Cp*Ru(Cl)(μ_2-SPr^i)$_2$Ru(=C=C=CTol$_2$)Cp*][OTf] (OTf = OSO$_2$CF$_3$) has been independently prepared from [Cp*Ru(μ_2-SPr^i)$_2$(μ_2-Cl)RuCp*][OTf] and structurally characterized.[12] In addition, complex **1** has been shown to react with terminal alkynes to afford dialkynyl complexes **2**.[5]

(12) Matsuzaka, H.; Takagi, Y.; Hidai, M., submitted for publication.