Unprecedented Rhodium-Mediated Tetramerization of Bulky Terminal Alkynes Leading to Hydropentalenylrhodium Complexes

Hiroaki Komatsu, Yasunobu Suzuki, and Hiroshi Yamazaki*
Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, Kasuga, Bunkyo-ku, Tokyo 112-8551

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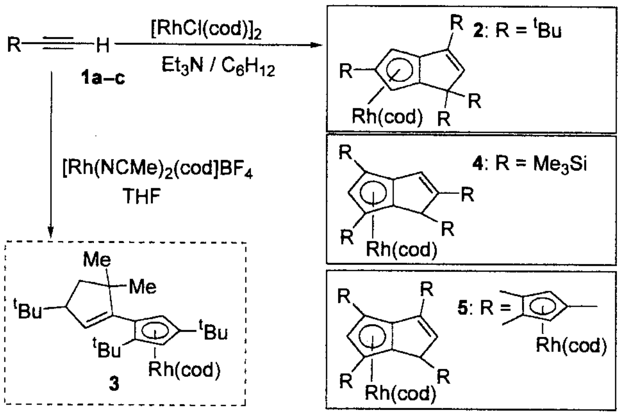
The reactions of bulky terminal alkynes, $RC\equiv CH$ [R= ^{t}Bu, **1a**; Me_3Si, **1b**; (cod)Rh(η^5-$Me_2C_5H_2$), **1c**] with $[RhCl(cod)]_2$ in the presence of Et_3N have been found to provide novel hydropentalenylrhodium complexes, (cod)Rh(η^5-$R_4C_8H_3$) (**2**, **4** and **5**). The structures have been determined by a single-crystal X-ray diffraction analysis. A mechanism involving the migration of an α-*tert*-butyl group or an α-hydrogen atom of the metal–vinyl intermediates is proposed.

Oligomerization of the terminal alkynes by various transition metal complexes has been extensively studied.[1] The formation of linear dimer and cyclic trimer are very common but the selective formation of a higher oligomer is rather scarce.[2] Recently, we and others reported the highly selective synthesis of butatrienes from bulky terminal alkynes by ruthenium, osmium and iridium complex catalysts.[3] As a continuation of our study, we now report the rhodium-mediated tetramerization of bulky terminal alkynes, $RC\equiv CH$ [R= ^{t}Bu, (**1a**); Me_3Si, (**1b**); (cod)Rh(η^5-$Me_2C_5H_2$), (**1c**)] by $[(cod)RhCl]_2$, leading to hydropentalenylrhodium complexes, (cod)Rh(η^5-$R_4C_8H_3$) (Scheme 1).



Scheme 1.

tert-Butylacetylene **1a** (0.096 g, 1.17 mmol) was kept at room temperature for one day in the presence of $[RhCl(cod)]_2$ (0.014 g, 0.028 mmol) and Et_3N (0.182 g, 1.80 mmol) in cyclohexane. No oligomers of **1a** were detected in the reaction mixture. After removal of the solvent, the residue was chromatographed on alumina. The yellow-orange eluate by hexane was evacuated and the residue was crystallized from ethanol to produce orange-yellow crystals (**2**) (0.004 g, 13% yield). The ^{1}H NMR spectrum of **2** (in $CDCl_3$) showed four singlet peaks ascribed to ^{t}Bu groups (δ = 0.83, 1.08, 1.31, 1.40). The reaction of $[Rh(NCMe)_2(cod)][BF_4]$ with ^{t}Bu$C\equiv CH$ in THF has been known to give a cyclic tetramer-rhodium complex (**3**) which exhibits a different NMR spectrum from **2**.[4] The X-ray structure determination of **2** revealed it to be the novel hydropentalenylrhodium complex (Figure 1).[5] It is noteworthy that two of the four ^{t}Bu groups in **2** are accommodated on the same carbon atom suggesting the involvement of a ^{t}Bu group migration during the reaction. There are some reports on the formation of hydropentalenyl and pentalenyl metal complexes from the corresponding hydropentalene anion, pentalene dianion and cyclooctatetraene dianion.[6] As far as we know, this is a first example of the direct formation of the hydropentalenyl-metal complex from terminal alkynes, although there is a precedent for the palladium mediated formation of dihydropentalene itself.[7]

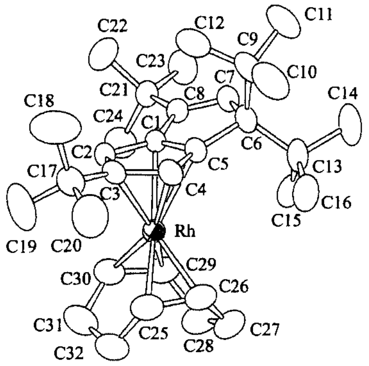


Figure 1. ORTEP view of **2**.

Treatment of $[RhCl(cod)]_2/Et_3N$ with excess amount of **1b** and **1c** provided **4** (orange crystals, 50% yield) and **5** (yellow crystals, 74% yield), having the same empirical formula, (cod)Rh($R_4C_8H_3$). The ^{1}H NMR spectrum of **4** shows four singlets ascribed to four different Me_3Si groups (δ = –0.05, 0.16, 0.27, 0.36) and that of **5** reveals eight singlets ascribed to eight different methyl groups on the cyclopentadienyl groups (δ = 1.70, 1.72, 1.76, 1.81, 1.84, 1.87, 1.93, 1.99), suggesting a low symmetry for the molecules. The structures of **4** and **5** were determined by a single-crystal X-ray diffraction analysis.[8] The ORTEP view of **4** is shown in Figure 2. They have the same

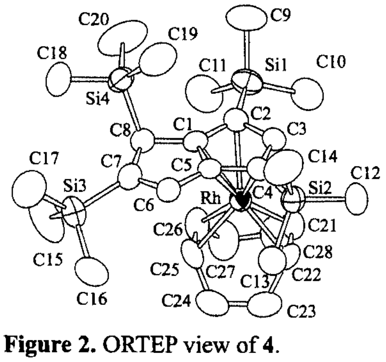
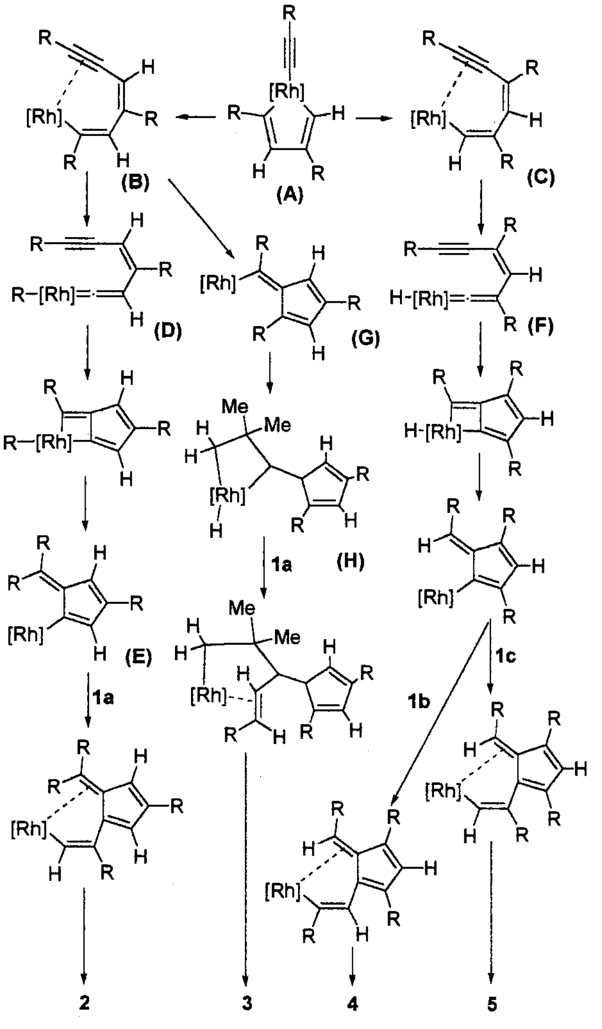


Figure 2. ORTEP view of **4**.

hydropentalenyl skeletons as **2**. No migration of the R groups was observed in these cases. They differ from one another with respect to their regio- and stereochemistries. A more bulky alkyne, (cod)Rh(η^5-$Me_4C_5C{\equiv}CH$), resulted in the recovery of the starting alkyne. Under similar reaction conditions mentioned above, mesitylacetylene afforded a dinuclear acetylide-rhodium complex [(μ-η^1:η^2-$Me_3C_6H_2C{\equiv}C$)Rh(cod)]$_2$ (**6**) (30% yield); the structure was determined by X-ray analysis.[9] Simple phenylacetylene provided an insoluble polymer.[10]

For the present rhodium mediated tetramerization of terminal alkynes, we tentatively suggest the mechanism summarized in Scheme 2. The first step may be the formation of alkynylrhodiacyclopentadienes (**A**). Reductive coupling of **A** occurs in two ways, giving **B** and **C**. It is necessary to consider the migration of a ^{t}Bu group from the parent carbon during the formation of **2**. We assume the formation of a vinylidene intermediate (**D**) from **B** by the migration of an α-^{t}Bu group of the vinyl to the rhodium metal. Intramolecular addition of the acetylene moiety to the rhodium–carbon double bond followed by reductive coupling may provide **E**. Insertion of the fourth *tert*-butylacetylene into the rhodium–carbon bond in **E** and the subsequent intramolecular cyclization may result in **2**. There is a precedent for the formation of a metal vinylidene complex by migration of an α-hydrogen of a vinyl to the metal.[11] A similar α-hydrogen migration step (from **C** to **F**) may be involved during the formation of **4** and **5**. The subsequent steps are similar to those for **2** although the regioselectivity of the insertion step of the fourth alkyne is dependent on the employed alkyne. The mechanism including an sp^3 C–H bond activation as an important step was proposed by Green et al. for the formation of **3** as depicted together in Scheme 2. We were not successful in detecting **3** under our reaction conditions.



Scheme 2.

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5 Crystallographic data. **2**: $C_{32}H_{51}Rh$, fw = 538.66; triclinic, space group $P\bar{1}$ (No.2); a = 11.077(2) Å, b = 15.651(3) Å, c = 9.017(2) Å, α = 94.85(2)°, β = 107.02(2)°, γ = 73.21(1)°, V = 1431.5(5) Å^3; Z = 2; D_{calc} = 1.250 g·cm^{-3}; R = 0.031, R_w = 0.029.
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8 Crystallographic data. **4**: $C_{28}H_{51}Si_4Rh$, fw = 602.96, orthorhombic, space group $Pca2_1$(No.29); a = 11.045(3) Å, b = 16.239(3) Å, c = 18.456(3) Å , V = 3310(1) Å^3; Z = 4; D_{calc} = 1.210 g·cm^{-3} ; R = 0.033, R_w = 0.046. Crystallographic data. **5**: $C_{72}H_{96}Rh_5$, fw = 1476.08; triclinic, space group $P\bar{1}$ (No.2); a = 16.762(3) Å, b = 23.884(4) Å, c = 8.881(3) Å, α = 100.59(2)°, β = 95.39(2)°, γ = 93.97(1)°, V = 3465(1); Z = 2; D_{calc} = 1.414 g·cm^{-3}; R = 0.055, R_w = 0.056.
9 **6**: FT-IR (KBr); ν(C≡C) 2005 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.24 (s, Me, 6H), 2.45 (s, Me_2, 12H), 6.83 (s, Ph, 4H), 4.48 (br, cod, 8H), 2.34 (m, cod, 8H), 2.02 (pseudo-q, cod, 8H). Crystallographic data. $C_{38}H_{46}Rh_2$, fw = 708.59; monoclinic, space group Cc(No.9); a = 10.108(2) Å, b = 13.722(4) Å, c = 23.804(2) Å, β = 98.007(19), V = 3269(1) Å^3; Z = 4; D_{calc} = 1.439 g·cm^{-3}; R = 0.030, R_w = 0.025.
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