

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

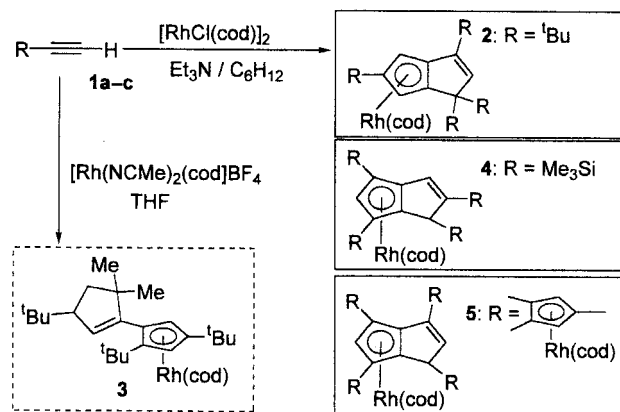
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The reactions of bulky terminal alkynes, $\text{RC}\equiv\text{CH}$ [$\text{R} = \text{'Bu}$, **1a**; Me_3Si , **1b**; $(\text{cod})\text{Rh}(\eta^5\text{-Me}_2\text{C}_5\text{H}_2)$, **1c**] with $[\text{RhCl}(\text{cod})]_2$ in the presence of Et_3N have been found to provide novel hydropentalenylrhodium complexes, $(\text{cod})\text{Rh}(\eta^5\text{-R}_4\text{C}_8\text{H}_3)$ (**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, $\text{RC}\equiv\text{CH}$ [$\text{R} = \text{'Bu}$, (**1a**); Me_3Si , (**1b**); $(\text{cod})\text{Rh}(\eta^5\text{-Me}_2\text{C}_5\text{H}_2)$, (**1c**)] by $[(\text{cod})\text{RhCl}]_2$, leading to hydropentalenylrhodium complexes, $(\text{cod})\text{Rh}(\eta^5\text{-R}_4\text{C}_8\text{H}_3)$ (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 $[\text{RhCl}(\text{cod})]_2$ (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 ^1H NMR spectrum of **2** (in CDCl_3) showed four singlet peaks ascribed to *t*Bu groups ($\delta = 0.83, 1.08, 1.31, 1.40$). The reaction of $[\text{Rh}(\text{NCMe})_2(\text{cod})][\text{BF}_4]$ with $\text{'BuC}\equiv\text{CH}$ in THF has been known to give a cyclic tetramer-rhodium complex (**3**) which

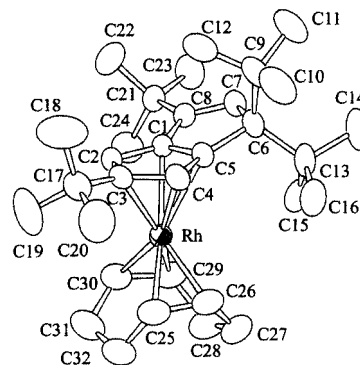


Figure 1. ORTEP view of **2**.

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

Treatment of $[\text{RhCl}(\text{cod})]_2/\text{Et}_3\text{N}$ with excess amount of **1b** and **1c** provided **4** (orange crystals, 50% yield) and **5** (yellow crystals, 74% yield), having the same empirical formula, $(\text{cod})\text{Rh}(\text{R}_4\text{C}_8\text{H}_3)$. The ^1H NMR spectrum of **4** shows four singlets ascribed to four different Me_3Si groups ($\delta = -0.05, 0.16, 0.27, 0.36$) and that of **5** reveals eight singlets ascribed to eight different methyl groups on the cyclopentadienyl groups ($\delta = 1.70, 1.72, 1.76, 1.81, 1.84, 1.87, 1.93, 1.99$), 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

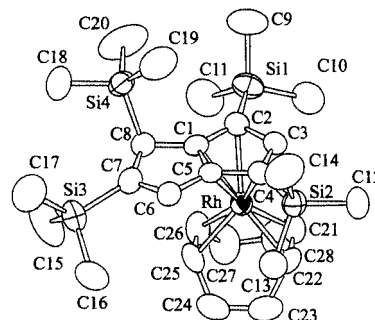


Figure 2. ORTEP view of **4**.

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^3 -Me₄C₅C≡CH), resulted in the recovery of the starting alkyne. Under similar reaction conditions mentioned above, mesitylacetylene afforded a dinuclear acetylido-rhodium complex [(μ - η^1 : η^2 -Me₃C₆H₂C≡C)Rh(cod)]₂ (**6**) (30% yield); the structure was determined by X-ray analysis.⁹ Simple phenylacetylene provided an insoluble polymer.¹⁰

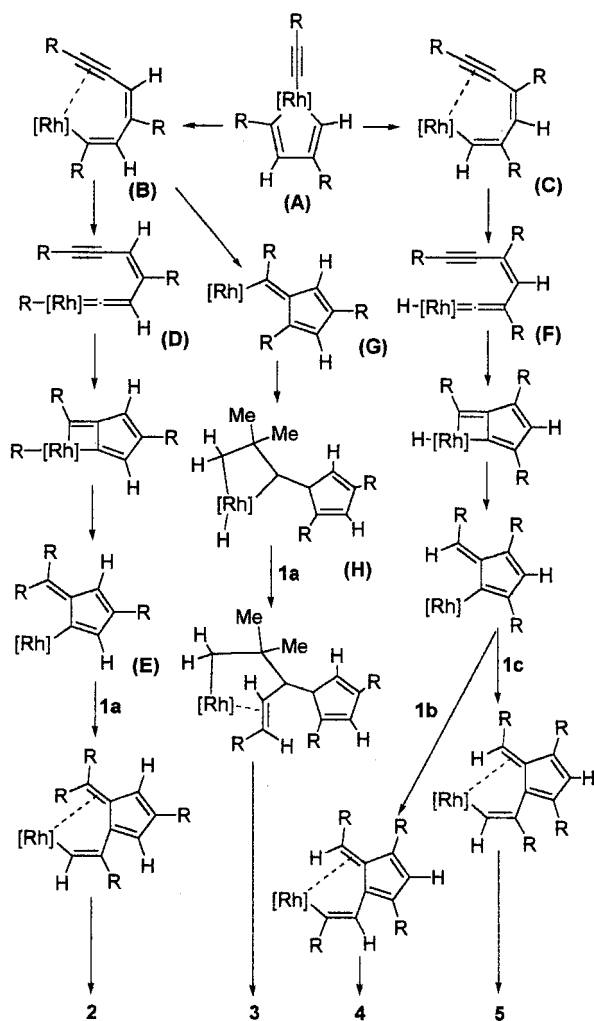
For the present rhodium mediated tetramerization of terminal alkynes, we tentatively suggest the mechanism summarized in Scheme 2. The first step may be the formation of alkynyl-rhodiacyclopentadienes (**A**). Reductive coupling of **A** occurs in two ways, giving **B** and **C**. It is necessary to consider the migration of a ^tBu 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 -^tBu 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 sp³ 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.

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References and Notes

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- 5 Crystallographic data. **2**: C₃₂H₅₁Rh, fw = 538.66; triclinic, space group P1 (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) Å³; *Z* = 2; *D*_{calc} = 1.250 g·cm⁻³; *R* = 0.031, *R*_w = 0.029.
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- 8 Crystallographic data. **4**: C₂₈H₅₁Si₄Rh, fw = 602.96, orthorhombic, space group Pca2₁(No.29); *a* = 11.045(3) Å, *b* = 16.239(3) Å, *c* = 18.456(3) Å, *V* = 3310(1) Å³; *Z* = 4; *D*_{calc} = 1.210 g·cm⁻³; *R* = 0.033, *R*_w = 0.046. Crystallographic data. **5**: C₇₂H₉₆Rh₅, fw = 1476.08; triclinic, space group P1 (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. ¹H NMR (CDCl₃) δ 2.24 (s, Me, 6H), 2.45 (s, Me₂, 12H), 6.83 (s, Ph, 4H), 4.48 (br, cod, 8H), 2.34 (m, cod, 8H), 2.02 (pseudo-q, cod, 8H). Crystallographic data. C₃₈H₄₆Rh₂, 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) Å³; *Z* = 4; *D*_{calc} = 1.439 g·cm⁻³; *R* = 0.030, *R*_w = 0.025.
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Scheme 2.