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Preliminary Communication

Unusual rhodium promoted reaction of a vinylcyclopropene to give a cyclobutadiene ligand. Formation of (η^5-pentamethylcyclopentadienyl)-[η^4-tri-t-butyl(methyl)cyclobutadiene]rhodium *

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Abstract

In contrast to its cyclopentadienyl and indenyl analogues **5** and **6**, the pentamethylcyclopentadienyl-rhodium complex **8** undergoes a thermal reaction to give the η^4-cyclobutadiene complex **9**, which has been characterized by ^{1}H and ^{13}C NMR spectroscopy and microanalysis. A mechanism is proposed for the H-shift and ring closure pathway.

Key words: Rhodium; Cyclobutadiene; Carbon–carbon bonds; Vinylcyclopropene; Mechanism; Rearrangement

η^4-Cyclobutadiene complexes of rhodium are quite rare. The simplest example **1**, containing the parent cyclobutadiene ligand, has been prepared as white crystals by the reaction of [Rh(η^5-C_5H_5)(CO)$_2$] with photo-α-pyrone [1]. A more common synthetic method involves cyclodimerization of two alkyne molecules to give a variety of substituted and polycyclic ligands containing the cyclobutadiene nucleus [2–10]. Here we report a novel method for construction of a substituted cyclobutadiene ligand by a ring opening of a vinylcyclopropene, followed by a hydrogen shift and ring closure.

We have previously reported the reaction of 1,2,3-tri-t-butyl-3-vinyl-1-cyclopropene **2** with [RhCl(C_2H_4)$_2$]$_2$ to give the crystallographically characterized dimeric complex **3**, in which the cyclopropene ring has undergone oxidative addition to the metal center to give a pentadienediyl ligand [11]. On standing, the pentadienediyl ligand in this 16-electron complex undergoes a sequential ring-closure and hydrogen shift on the *endo*-face of the resultant cyclopentadiene ligand to give complex **4**, the cyclopentadienyl derivative of which was crystallographically characterized [12]. In contrast, the 18-electron cyclopentadienyl derivative **5** is thermally unreactive towards ring closure at 120°C [11], and the corresponding indenyl analogue **6** undergoes thermal ring closure to give the cyclopentadiene complex **7** without any subsequent hydrogen shift [13].

Reaction of **3** with pentamethylcyclopentadienyllithium affords the corresponding derivative **8** as an orange solid in 95% yield. The pentadienediyl ligand in this compound exhibits a ^{1}H NMR spectrum similar to those observed for **3**, **5**, and **6**. ** The ^{13}C{^{1}H} NMR spectrum of **8** is also consistent with the illustrated structure. ** In contrast to its precursor **3** and its relatives **5** and **6**, complex **8** reacts on warming in $CHCl_3$ solution at 50°C to give the cyclobutadiene complex **9** (50%) along with the known complex [$RhCl_2(C_5Me_5)]_2$ (36%). The latter product was identi-

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* Dedicated to Professor Helmut Werner on the occasion of his 60th birthday.

** Complex **8**: ^{1}H NMR (C_6D_6) δ 1.21 (s, 9 H, ^{t}Bu), 1.36 (s, 9 H, ^{t}Bu), 1.46 (s, 9 H, ^{t}Bu), 1.66 (s, 15 H, $C_5(CH_3)_5$), 1.71 (dd, 1H, H_3, $J_{1,3}$ = 10, J_{RhH} = 2), 2.13 (dd, 1H, H_2, $J_{1,2}$ = 6, J_{RhH} = 1), 3.80 (ddd, 1H H_1, $J_{1,3}$ = 10, $J_{1,2}$ = 6, J_{RhH} = 2). ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9 H, ^{t}Bu), 1.22 (s, 9 H, ^{t}Bu), 1.26 (s, 9 H, ^{t}Bu), 1.77 (s, 15 H, $C_5(CH_3)_5$), 1.47 (dd, 1H, H_3, $J_{1,3}$ = 10, J_{RhH} = 2), 2.09 (d, 1H, H_2, $J_{1,2}$ = 6), 3.86 (ddd, 1H, H_1, $J_{1,3}$ = 10, $J_{1,2}$ = 6, J_{RhH} = 2). ^{13}C{^{1}H} NMR (C_6D_6) δ 11.97 [s, $C_5(CH_3)_5$], 32.58 [br s, $C(CH_3)_3$], 32.98 [s, $C(CH_3)_3$], 33.62 [s, $C(CH_3)_3$], 35.91 [s, $C(CH_3)_3$], 37.11 [s, $C(CH_3)_3$], 38.12 [s, $C(CH_3)_3$], 46.93 (d, $^1J_{RhC}$ = 16, CH_2), 88.40 (d, $^1J_{RhC}$ = 4, Rh–C(^{t}Bu)–C^{t}Bu), 89.34 (d, $^1J_{RhC}$ = 9, CH), 98.09 [d, $C_5(CH_3)_5$, $^1J_{RhC}$ = 4], 129.45 [d, $^2J_{RhC}$ = 4, Rh–C(^{t}Bu)=C(^{t}Bu), 158.32 (d, $^1J_{RhC}$ = 29, Rh–C(^{t}Bu)=C(^{t}Bu)]. Even though the complex is spectroscopically pure, we have been unable to obtain satisfactory microanalysis results. Its derivative **9** does analyze correctly, *** and we feel confident of the structure and elemental composition of **8**.

*** Complex **9**: m.p. 150°C (with decomposition): ^{1}H NMR (C_6D_6) δ 1.25 (s, 18 H, ^tBu_A), 1.29 (s, 9H, ^tBu_B), 1.66 (s, 3H, CH_3), 1.98 (d, 15H, $C_5(CH_3)_5$, J_{RhH} = 0.6); ^{1}H NMR ($CDCl_3$) δ 1.16 (s, 9H, ^tBu_B), 1.17 (s, 18H, ^tBu_A), 1.65 (s, 3H, CH_3), 1.97 (d, 15H, $C_5(CH_3)_5$, $^3J_{RhH}$ = 0.6 Hz): ^{13}C NMR ($CDCl_3$) δ 11.68 (q, $^1J_{CH}$ = 125, $C_5(CH_3)_5$, 14.51 (q, $^1J_{CH}$ = 126, CH_3), 30.94 (m, $C_B(CH_3)_3$), 32.43 (quartet of septets, $^1J_{CH}$ = 125, $^3J_{CH}$ = 5, $C_A(CH_3)_3$), 32.48 (m, $C_A(CH_3)_3$), 33.17 (quartet of septets, $^1J_{CH}$ = 125, $^3J_{CH}$ = 5, $C_B(CH_3)_3$), 71.30 (q, $^2J_{CH}$ = 6, CCH_3), 88.42 (m, $CC_B(CH_3)_3$), 90.69 (m, $CC_A(CH_3)_3$), 95.51 (m, $C_5(CH_3)_5$). Anal. Calcd. for $C_{27}H_{45}Rh$: C, 68.62; H, 9.59. Found: C, 68.71; H 9.48%.

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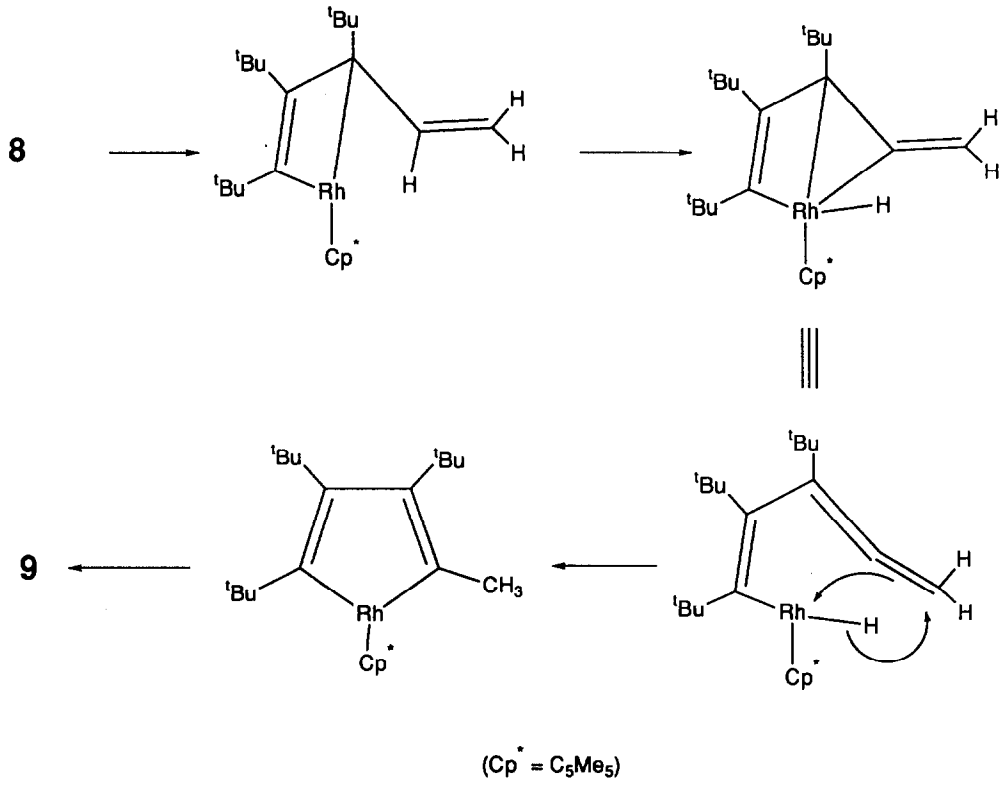
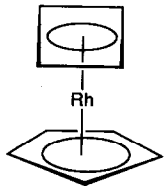


Scheme 1.

fied by comparison of its NMR spectrum with that of an authentic sample [14,15]. Complex **9** was produced as an air-stable cream solid and was unambiguously



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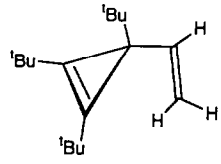

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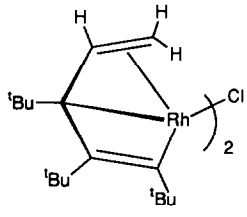

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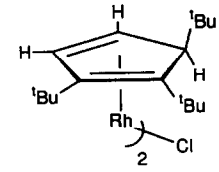

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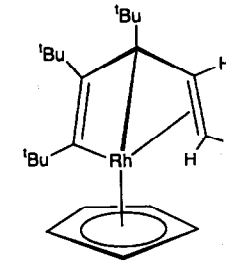

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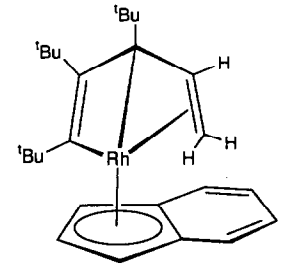

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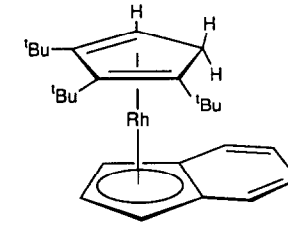

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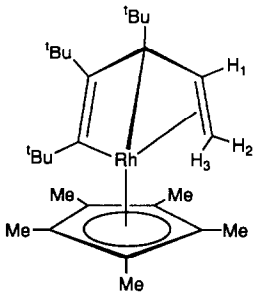

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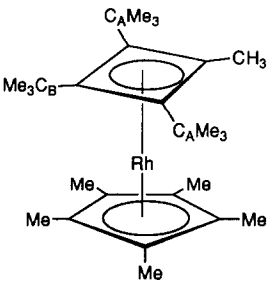

9

identified by its NMR spectra and microanalysis. *** The ^{1}H NMR and ^{13}C NMR spectra each show resonances for two different t-butyl groups, in a ratio of 2:1, and it clear that the three hydrogens originally present in the vinyl group of **8** have been transformed into a methyl group in **9**. The ^{13}C NMR spectrum clearly shows the three expected resonances for the carbon atoms of the cyclobutadiene ring, that for the methyl substituted carbon (δ 71.30 ppm) being readily identified by its quartet coupling ($^{2}J_{CH} = 6$ Hz) to the methyl protons.

The differences in thermal reactivity of **5**, **6**, and **8** are remarkable. Formation of **9** from **8** clearly requires a hydrogen shift, and a suggested mechanism for formation of **9** is shown in Scheme 1. It seems clear that the shift of a hydrogen atom from the internal to the terminal vinylic carbon center must occur prior to ring formation. Compared to the cyclopentadienyl and indenyl analogues **5** and **6**, the pentamethylcyclopentadienyl ligand in **8** should render the metal center more electron rich and may thereby facilitate the required vinylic C–H activation reaction via a β-elimination pathway. Increased steric crowding at the metal center in **8** relative to **5** or **6** may also facilitate dissociation of the olefin prior to C–H activation. Readdition of H to the terminal carbon of the resultant allene ligand affords a metallacyclopentadiene that can close to the observed cyclobutadiene in a step reminiscent of that proposed for cyclo-coupling of two alkynes [2–10].

Complex **9** was thermally stable under the reaction conditions under which it was generated, and hence is not the source of the observed $[RhCl_2(C_5Me_5)]_2$. This product is possibly formed by partial decomposition of **8** by elimination of **2**, to give a $[Rh(C_5Me_5)]$ fragment that is subsequently oxidized by the $CHCl_3$ solvent. While elimination of **2** might appear to be unfavorable due to formation of a strained cyclopropene ring, the steric relaxation afforded by allowing adjacent t-butyl groups to move further away from each other in a smaller three membered ring may compensate for that increased strain energy. Precedent for elimination of **2** exists in the reaction of **3** with PMe_3 [11].

Further studies of the effects of steric crowding on reactivity patterns in pentadienediyl complexes are in progress.

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