

Intramolecular Hydroalkylation as a Route to Strained Dicationic Bis(arene) [3]Ruthenocyclophanes

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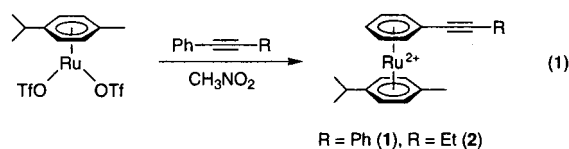
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Summary: Base-promoted intramolecular hydroalkylation of the carbon–carbon triple bond in the ruthenium bis(arene) complexes [(*p*-cymene)Ru(η^6 -C₆H₅C≡CR)]-[OTf]₂ (**1**, R = Et; **2**, R = Ph; OTf = O₃SCF₃) generates the strained [3]ruthenocyclophane complexes **3** and **4**, in which a propenyl (–CH₂CR=CH–) group bridges the two arene ligands. The presence of the propenyl bridge results in a bent-metallocene structure for the [3]ruthenocyclophane cation in **4**, with an angle of 11.8° between the arene ligands.

Metallocenophanes have emerged as an extremely important class of compounds in organometallic chemistry.¹ Significant progress has been made in exploiting the differences in reactivity observed for metallocenophanes caused by the ansa bridge(s); metallocenophanes have been utilized as highly specific catalysts for olefin polymerizations² and as precursors for metal-containing polymers.^{3,4} Although not as heavily investigated as metallocenophanes, *metallocyclophanes*,⁵ in which two neutral aromatic ligands are linked, have also been used to modify the reactivity of bis(arene) metal complexes,⁶ most notably by Elschenbroich for the early transition metals chromium and vanadium.^{5,7–10} There have only been a handful of reports, however, on late-transition-metal metallocyclophane complexes.^{11–13} We communicate here the synthesis of two new dicationic bis(arene) [3]ruthenocyclophanes that are generated by an intriguing base-promoted intramolecular hydroalkylation reaction.^{14–17}

Coordination of an aromatic compound with a dicationic metal fragment such as [(arene)Ru]²⁺ or [Cp*Ir]²⁺ dramatically activates the arenes toward nucleophilic attack.^{18–20} We have been investigating whether this strong electrophilic activation extends to the substituent groups on the arene ligands. In the course of this work, we synthesized the first examples of dicationic bis(arene) ruthenium complexes with acetylenic substituents. Reaction of [(*p*-cymene)Ru(OTf)₂] (OTf = O₃SCF₃)²¹ with diphenylacetylene or 1-phenyl-1-butyne in nitromethane leads to the rapid (<10 min) formation of the bis(arene) ruthenium complexes [(*p*-cymene)Ru(C₆H₅-C≡CR)]²⁺[OTf]₂ (**1**, R = Et; **2**, R = Ph) in excellent (>70%) yield (eq 1).²² The use of nitromethane is absolutely



critical to the success of these reactions; when other solvents are employed (CH₂Cl₂, CHCl₃, CF₃COOH, propylene carbonate), the reactions are much slower and do not cleanly generate **1** and **2**. The kinetic acceleration of bis(arene) ruthenium complex formation in nitromethane may provide new synthetic opportunities in cationic late-metal–arene chemistry, especially for complexes that contain electron-deficient benzene derivatives.

While investigating the reactivity of **1** and **2**, we serendipitously discovered that treatment of these complexes with excess alkoxide base in alcohol results in a carbon–carbon bond-forming reaction involving substituents on both arene ligands. Quenching the reaction with acid allowed for the isolation of the new [3]ruthenocyclophane complexes **3** and **4**, in which a propenyl (–CH=CRCH₂–) group bridges the two arene ligands. Although the synthesis of **3** and **4** can be performed in almost any basic alcohol solution, it is most conveniently accomplished through the reaction of **1** and **2** with excess K₂CO₃ in methanol, followed by acidifica-

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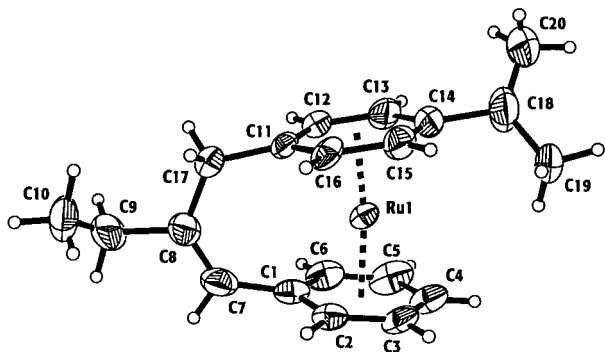
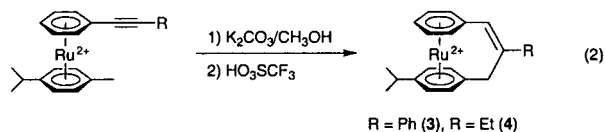


Figure 1. Molecular structure of one of the two unique ruthenocyclophane cations in $4[\text{BPh}_4]_2$. Selected bond lengths (Å) and angles (deg): Ru(1)–C(1), 2.154(4); Ru(1)–C(2), 2.186(4); Ru(1)–C(3), 2.234(4); Ru(1)–C(4), 2.244(4); Ru(1)–C(5), 2.233(4); Ru(1)–C(6), 2.191(4); Ru(1)–C(11), 2.189(4); Ru(1)–C(12), 2.193(4); Ru(1)–C(13), 2.229(5); Ru(1)–C(14), 2.274(5); Ru(1)–C(15), 2.221(4); Ru(1)–C(16), 2.200(4); C(7)–C(8), 1.322(7); C(1)–C(7)–C(8), 129.5(4); C(7)–C(8)–C(17), 128.5(4); C(8)–C(17)–C(11), 121.7(2).

tion with triflic acid (eq 2).²³ Monitoring the reaction

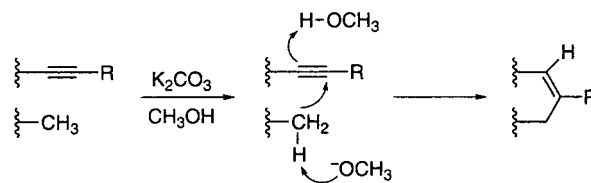


by NMR spectroscopy (see below) reveals that it is essentially quantitative; however, isolated yields of analytically pure **3** and **4** are modest (30–50%), due to product loss incurred during the removal of the KOTf byproduct. The identity of **3** and **4** as propenyl-bridged [3]ruthenocyclophanes¹¹ was determined by NMR and IR spectroscopy and later confirmed by X-ray crystallography of **4** (Figure 1).

The conversion of **1** and **2** into the [3]ruthenocyclophanes **3** and **4** is formally a base-promoted intramolecular hydroalkylation reaction^{15–17} in which a methyl C–H bond of the *p*-cymene ligand is added across the carbon–carbon triple bond of the phenylacetylene ligand. The likely sequence of steps in the hydroalkylation reaction are deprotonation of the *p*-cymene methyl group by methoxide^{24–26} and nucleophilic addition of the resulting benzyl anion to the β -carbon of the acetylene substituent, followed by protonation of the vinyl anion by the methanol solvent (Scheme 1). Base-promoted

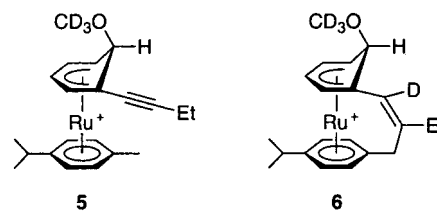
(23) Preparation of **3**: An Erlenmeyer flask was charged with **1** (0.10 g, 0.14 mmol), K_2CO_3 (50 mg, 0.36 mmol), and CH_3OH (10 mL). This mixture was vigorously stirred for 3 h, during which time most of the K_2CO_3 dissolved and the solution turned brown. The reaction mixture was then made acidic (pH 4) with HO_3SCF_3 and filtered through Celite. Subsequent addition of Et_2O (50 mL) generated an off-white precipitate, which was isolated by filtration, washed with water (2×5 mL) and Et_2O (2×10 mL), and then dried under vacuum. Recrystallization of this material from $\text{CH}_3\text{NO}_2/\text{Et}_2\text{O}$ at -20°C gave **3** as white needles in 49% yield (49 mg, 0.069 mmol). Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{RuO}_6\text{F}_6\text{S}_2$: C, 43.88; H, 3.40. Found: C, 43.37; H, 3.12. ^1H NMR (CD_3NO_2): δ 7.63 (m, 2H, *o*-Ph *H*), 7.49 (m, 3H, *m*, *p*-Ph *H*), 7.27 (app t, $J = 6.1$ Hz, 1H, *p*-Ar *H*), 7.07–7.10 (overlapping m, 4H, *p*-cymene Ar *H* and *m*-Ar *H*), 7.03 (app d, $J = 6.6$ Hz, 2H, *p*-cymene Ar *H*), 7.00 (app d, $J = 6.1$ Hz, 2H, *o*-Ar *H*), 6.83 (t, $J = 2.5$ Hz, 1H, bridge CH), 3.96 (d, $J = 2.5$ Hz, 2H, bridge CH_2), 3.12 (septet, $J = 7.0$ Hz, 1H, $-\text{CH}(\text{CH}_3)_2$), 1.41 (d, $J = 7.0$ Hz, 6H, $-\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (CD_3NO_2): δ 154.0 (bridge CPh), 140.0 (Ph C–R), 128.6 (Ph CH), 128.1 (Ph CH), 126.8 (Ar C–Pr), 126.2 (Ph CH), 114.4 (bridge CH), 107.8 (Ar C–CH), 107.7 (Ar C–CH₂), 96.1 (Ar CH), 94.9 (Ar CH), 94.7 (Ar CH), 94.1 (Ar CH), 93.7 (Ar CH), 31.2 ($-\text{CH}(\text{CH}_3)_2$), 30.4 (bridge CH_2), 21.2 ($-\text{CH}(\text{CH}_3)_2$). IR (KBr, cm^{-1}): 1265 (vs, S–O, free $-\text{OTf}$).

Scheme 1



intramolecular hydroalkylation reactions previously reported by Bennett¹⁵ and Nelson^{16,17} involved conjugate addition at relatively accessible vinyl substituents to give unstrained chelating ligands. In contrast, formation of **3** and **4** occurs readily—despite the geometrical constraints associated with the linear acetylene group and the strained nature of the resulting propenyl bridge (see below). This intramolecular hydroalkylation also represents the first known instance of a conjugate addition reaction at a metal-complexed phenylacetylene ligand.²⁷

Monitoring the reaction of **2** with K_2CO_3 in CD_3OD by NMR spectroscopy revealed a rapid (<5 min) conversion of **2** into the cyclohexadienyl complex **5**, formed by regioselective nucleophilic addition of $[\text{OCD}_3]^-$ ortho to the electron-withdrawing butynyl substituent.²⁸ In the



presence of excess base, **5** then undergoes intramolecular hydroalkylation to give the bridged cyclohexadienyl complex **6**. Addition of triflic acid to **6** leads to removal of the exo- OCD_3 group to give **4-d**.²⁹ Consistent with Scheme 1, the use of CD_3OD as the solvent results in deuterium incorporation at the vinylic position of the bridge in **4-d** and **6**. Remarkably, deuterium is not incorporated into the methylene position of the bridge during the formation of **4-d**, which indicates that the initially formed benzyl anion is irreversibly trapped by the acetylene before it can be protonated by CD_3OD .³⁰

We were able to obtain a crystal structure of **4** as the tetraphenylborate salt, $4[\text{BPh}_4]_2$; an ORTEP drawing of one of the two independent but nearly identical [3]-ruthenocyclophane cations in the asymmetric unit is given in Figure 1.³¹ Because the propenyl bridge is not long enough to span the distance between the arenes, the structure of $4[\text{BPh}_4]_2$ is significantly distorted from that normally seen for a bis(arene)ruthenium complex.

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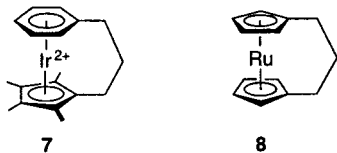
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The arene ligands in $4[\text{BPh}_4]_2$ are significantly bent, with an the angle (α) of 11.8° between the least-squares planes of the benzene rings. In fact, this is the first reported structure of a dicationic bis(arene) ruthenium complex that does not have essentially parallel benzene rings. Similar bent structures are observed in the propyl-bridged [3]iridocyclophane complex **7** ($\alpha = 11^\circ$),¹² and in the parent [3]ruthenocyclophane **8** ($\alpha = 14^\circ$).³²



The average Ru(1)–C(ring) bond length of 2.21(1) Å in $4[\text{BPh}_4]_2$ is typical for a [(arene)₂Ru]²⁺ complex,^{33,34} however, the ruthenium is displaced away from symmetrical coordination of the arene ligands toward the propenyl bridge. This results in a wide range of Ru(1)–C(ring) distances—from 2.154(4) Å for Ru(1)–C(1) to 2.274(5) Å for Ru–C(14). The Ru(1)–C(1) distance of 2.154(4) Å is especially short for a bis(arene)ruthenium complex. Noticeable structural deviations are also seen in the propenyl bridge of $4[\text{BPh}_4]_2$, in that the internal bond angles (C(1)–C(7)–C(8) = $129.5(4)^\circ$, C(7)–C(8)–C(17) = $128.5(4)^\circ$, and C(8)–C(17)–C(11) = $121.7(2)^\circ$) are all significantly larger than expected.

Previously reported propenyl-bridged [3]metallo-cyclophanes possess structural features ($\alpha \approx 10\text{--}14^\circ$, large internal bond angles in the bridge) very similar to those observed for $4[\text{BPh}_4]_2$.^{35–38} However, the lack of consensus as to how much ring strain is present in these complexes produces descriptions varying from essentially unstrained³⁸ to dramatically strained.³⁷ The

(31) $4[\text{BPh}_4]_2$ was synthesized by the reaction of **4** with excess Na[BPh₄] in ethanol. Crystals of $4[\text{BPh}_4]_2$ suitable for X-ray crystallography were grown from acetone/Et₂O. Crystal data for $4[\text{BPh}_4]_2 \cdot \frac{1}{2}\text{Me}_2\text{CO}$: C_{69.5}H₆₇RuB₂O_{0.5}, monoclinic, space group *Pc*, *a* = 17.565(5) Å, *b* = 17.415(4) Å, *c* = 17.565(5) Å, α = $90.000(4)^\circ$, β = $90.765(4)^\circ$, γ = $90.000(4)^\circ$, *V* = 5355(2) Å³, *Z* = 4, *D*_{calcd} = 1.292 Mg/m³, *F*(000) = 2168. A total of 39 949 measured reflections and 18 573 independent reflections (*R*_{int} = 0.0248) were collected on a Siemens SMART Platform CCD at 173(2) K using Mo K α radiation (λ = 0.710 73 Å). The structure was solved by direct methods and refined on *F*² to *R*1 = 0.0328 and *wR*2 = 0.0894 for 17 422 reflections with *I* > 2 σ (*I*) and *R*1 = 0.0369 and *wR*2 = 0.0968 for all data, with a goodness of fit on *F*² of 1.089. The intensity data were corrected for absorption (SADABS). Since the lattice parameters seem to indicate higher symmetry, the structure was carefully checked for that possibility as well as for pseudosymmetry, both of which were not found. An ORTEP drawing (Figure S1) of the second unique [3]ruthenocyclophane cation is given in the Supporting Information.

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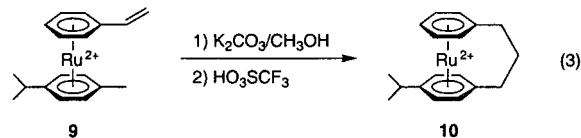
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presence of significant ring strain in **3** and **4** can be independently demonstrated by the fact that the arene ligands in these complexes are more susceptible to dissociation than in unbridged bis(arene)ruthenium complexes. For example, clean displacement of *both* arenes occurs on heating DMSO solutions of **3** and **4** at 60 °C for 60 h, giving [Ru(DMSO)₆]²⁺ and the free organic species. The half-life for the disappearance of **3** and **4** (through initial displacement of one arene ligand) in DMSO at 60 °C is 8 h. At 100 °C, substitution of both arene ligands by DMSO is complete after only 20 min. In contrast, the disappearance of the unbridged bis(arene) ruthenium complex [(*p*-cymene)Ru(C₆H₆)](OTf)₂ in DMSO at 60 °C occurs with an apparent half-life of 15 days, and removal of both arene ligands requires over 12 h at 100 °C. The favorable arene dissociation reactions of **3** and **4** suggest a potential application for strained ruthenocyclophanes as precursors for the generation of highly reactive ruthenium catalysts under mild conditions.^{40,41}

Initial investigations aimed at extending the scope of the intramolecular hydroalkylation route to ruthenocyclophanes indicate that this reaction is likely to be general for bis(arene) ruthenium complexes with unsaturated substituents. For example, the ruthenium styrene complex **9**²² undergoes intramolecular hydroalkylation on treatment with excess alkoxide to give the propyl-bridged [3]ruthenocyclophane **10** (eq 3). On the



basis of these encouraging results, we are currently exploring the use of intramolecular hydroalkylation for the synthesis of additional strained bis(arene) ruthenocyclophanes and other late-transition-metal metallocyclophanes.

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Supporting Information Available: Text giving full experimental procedures and characterization data for the reported complexes, tables giving details of data collection, structure solution, and refinement, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for $4[\text{BPh}_4]_2$, and an ORTEP diagram of the second ruthenocyclophane cation in the asymmetric unit of $4[\text{BPh}_4]_2$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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