

normally preferred reactivity pattern.

The [3 + 3] annulation strategy described herein represents a promising new approach to highly functionalized six-membered ring carbocycles. Good to excellent stereochemical control can be achieved at multiple stereocenters in a predictable fashion, and products can be readily accessed in chiral, nonracemic form.

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**Supplementary Material Available:** General synthetic procedure and complete spectral data for all compounds synthesized (8 pages). Ordering information is given on any current masthead page.

### Formation of 2,3-Dehydro-1,2-dihydro-1,1-dimethylnaphthalene, an "Isoaromatic" Molecule

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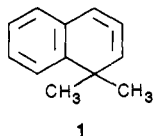
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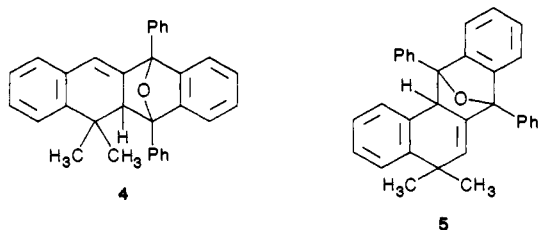
Compounds containing 1,3,5-cyclohexatriene rings ("aromatic compounds") are well-known. In contrast, compounds containing 1,2,4-cyclohexatriene rings ("isoaromatic compounds") have never previously been observed even as transient intermediates.

We now report evidence for the formation and trapping of 2,3-dehydro-1,2-dihydro-1,1-dimethylnaphthalene (**1**), the first example of a molecule containing a 1,2,4-cyclohexatriene ring.



Hydrocarbon **1** was formed by dehydrobromination of **2** (or its isomer **3**).<sup>1</sup> Bromo olefins **2** and **3** were prepared in ca. 3:1 ratio from 1,1-dimethyl-2-tetralone as shown in Scheme I. The major isomer, **2**, could be rapidly and quantitatively converted to **3** by treatment with potassium *tert*-butoxide solutions at room temperature (Scheme I).

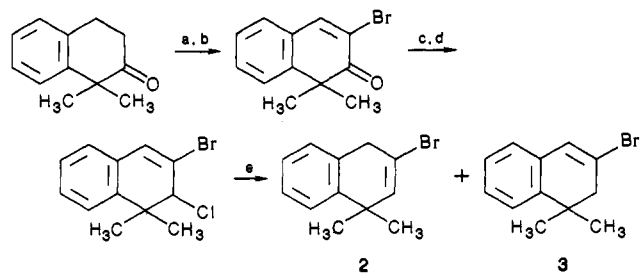
When potassium *tert*-butoxide was added to a THF solution containing equimolar amounts of **2** and 1,3-diphenylisobenzofuran at 50 °C, adducts **4** (mp 192–194 °C) and **5** (mp 171–173 °C) were obtained in a 3:2 ratio. (After chromatography on silica gel, the combined yield of **4** and **5** was 20%.) The structures of the two adducts were demonstrated by their elemental analyses and spectra.<sup>2</sup>



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(1) 1,2-Cyclohexadienes have similarly been prepared by dehydrobromination of 1-bromocyclohexenes: Wittig, G.; Fritze, P. *Justus Liebigs Ann. Chem.* **1968**, *711*, 82. Bottini, A. T.; Corson, F. P.; Fitzgerald, R.; Frost, K. A., II. *Tetrahedron* **1972**, *28*, 4881. Bottini, A. T.; Hilton, L. L.; Plott, J. *Ibid.* **1975**, *31*, 1997. Balci, M.; Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*, 7607; **1981**, *103*, 2874.

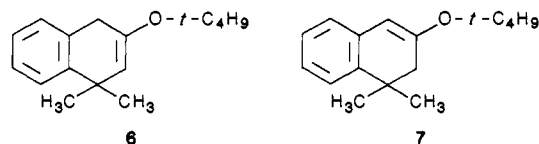
### Scheme I<sup>a</sup>



<sup>a</sup> (a) 2Br<sub>2</sub>; (b) quinoline, 120 °C; (c) NaBH<sub>4</sub>, CeCl<sub>3</sub>; (d) HCl, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C; (e) NaBH<sub>4</sub> in aqueous diglyme.

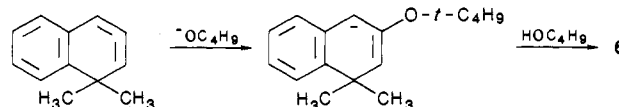
Formation of adducts **4** and **5** can only reasonably result from Diels–Alder condensation reactions of the reactive intermediate **1**.

Reaction of either **2** or **3** with potassium *tert*-butoxide at 50 °C in the absence of hydrocarbons yielded, in addition to a mixture of hydrocarbons from which no single compound could be isolated, the vinyl ether **6**, identified by its elemental



analysis and spectra<sup>3</sup> and its conversion to 3,3-dimethyl-2-tetralone on reaction with dilute acid. (Ether **6** can also be isolated in small amounts from reaction mixtures including 1,3-diphenylisobenzofuran.)

Most of the plausible routes for displacement of bromide in reaction of **2** or **3** with potassium *tert*-butoxide (e.g., addition–elimination of *tert*-butoxide to **3** or initial dehydrobromination of **3** to form a benzocyclohexyne) should yield the conjugated ether **7** rather than **6**.<sup>4</sup> However, no evidence for formation of **7** could be detected. It is improbable that **7** would isomerize completely to **6** under the reaction conditions, since **7** should be the more stable isomer<sup>5</sup> and since we observed that 2-methoxy-1,4-dihydronaphthalene does not undergo isomerization to its conjugated isomer even at much longer reaction times under similar reaction conditions. We therefore suggest that **6** is formed by reaction of potassium *tert*-butoxide with **1**, with the resulting anion undergoing kinetically controlled protonation at the central carbon:



(2) Compound **4**: <sup>1</sup>H NMR (300 MHz) δ 0.18 (s, 3 H), 1.44 (s, 3 H), 3.76 (d, *J* = 2.7 Hz, 1 H), 6.52 (d, *J* = 2.7 Hz, 1 H), 7.06–7.26 (m, 6 H), 7.39–7.55 (m, 7 H), 7.65 (d, *J* = 7.7, 1 H), 7.86 (d, *J* = 7.3, 2 H), 7.97 (d, *J* = 9.0, 2 H); <sup>13</sup>C NMR δ 22.72, 26.35, 38.32, 55.60, 88.86, 90.81, 116.98, 119.64, 122.56, 123.92, 125.97, 126.19, 127.06, 127.22, 127.44, 127.65, 128.30, 128.52, 128.68, 133.61, 135.02, 136.75, 144.77, 145.48, 145.75, 147.26. Anal. C, H. Compound **5**: <sup>1</sup>H NMR δ 1.36 (s, 3 H), 1.43 (s, 3 H), 4.65 (d, *J* = 2.7 Hz, 1 H), 5.85 (d, *J* = 2.7 Hz, 1 H), 1.04–1.25 (m, 7 H), 7.43–7.55 (m, 7 H), 7.82–7.95 (m, 4 H); <sup>13</sup>C NMR δ 28.89, 29.49, 38.75, 47.48, 89.51, 90.98, 118.49, 123.16, 123.75, 125.00, 125.76, 125.97, 126.24, 127.11, 128.14, 128.57, 129.28, 129.93, 134.91, 135.43, 135.75, 144.77, 144.18, 147.32.

(3) <sup>1</sup>H NMR δ 1.26 (s, 6 H), 1.43 (s, 9 H), 2.22 (d, *J* = 1.3 Hz, 2 H), 5.28 (t, *J* = 1.3 Hz, 1 H), 6.9–7.3 (m, 4 H). Anal. C, H.

(4) Formation of an ether from **2** rather than **3** seems unlikely, both because of the very low concentration of **2** in equilibrium with **3** and because both addition of bases to **2** and elimination of HBr from **2** should be much slower than similar reactions of **3**.

(5) 1-Methoxy-1,3-cyclohexadiene has been shown to be the most stable of the methoxycyclohexadiene isomers (Taskinen, E.; Nummelin, K. *J. Org. Chem.* **1985**, *50*, 4844).

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**Registry No. 1,** 105282-83-5; **2,** 105282-78-8; **3,** 105282-79-9; **4,** 105282-80-2; **5,** 105282-81-3; **6,** 105282-82-4; 1,1-dimethyl-2-tetralone, 20027-76-3; 3-bromo-1,1-dimethyl-2-naphthalenone, 105282-76-6; 3-bromo-2-chloro-1,1-dimethyl-1,2-dihydronaphthalene, 105282-77-7; 1,3-diphenylisobenzofuran, 5471-63-6; 4,4-dimethyl-2-tetralone, 83810-57-5.

## Methylidene Migratory Insertion into an Ru-H Bond

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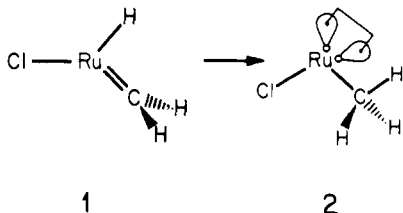
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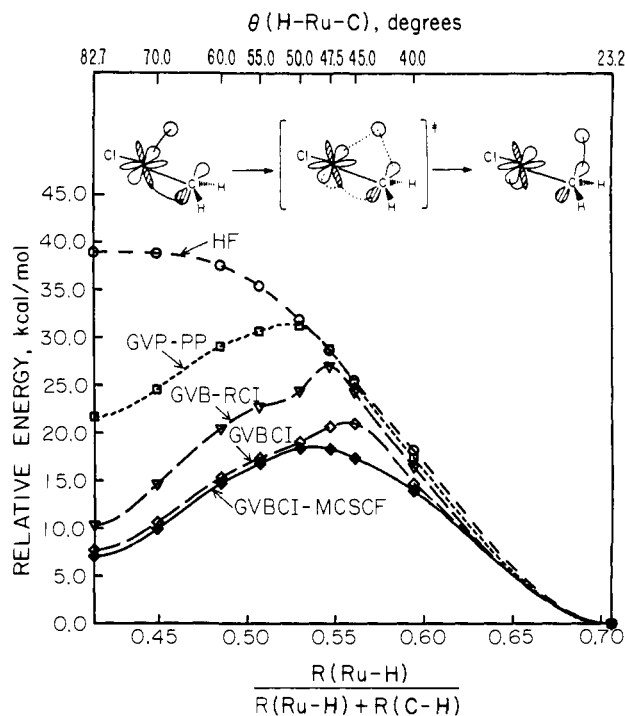
The migratory insertions of  $\text{CH}_x$  fragments into transition-metal-hydrogen and transition-metal-alkyl bonds have long been proposed as chain initiation and propagation steps in the Fischer-Tropsch synthesis of hydrocarbons.<sup>1</sup> Particularly for ruthenium, an effective heterogeneous catalyst for the production of high molecular weight polymethylenes,<sup>2</sup> there is strong indirect evidence that the chain growth mechanism involves methylidene insertion into growing alkyl chains.<sup>1,3</sup> Several experiments on homogeneous systems point to the facility of direct  $\text{CH}_2$  insertions into both M-H and M-R bonds.<sup>4</sup> Thorn and Tulip<sup>5a</sup> proposed that acidification of a hydrido hydroxymethyliridium complex proceeds via a hydridomethyleneiridium intermediate which undergoes  $\text{CH}_2$  insertion into the Ir-H bond to yield an iridium methyl complex. Upon hydrogen abstraction from mononuclear metal dimethyl complexes, Thorn and Tulip,<sup>5b</sup> as well as Cooper,<sup>6</sup> Maitlis,<sup>7</sup> and Werner,<sup>8</sup> have postulated the intermediacy of methyl methylidene metal complexes which insert  $\text{CH}_2$  into M-CH<sub>3</sub> and then  $\beta$ -hydride eliminate en route to the formation of ethylene hydride complexes. Thus these studies suggest that both the chain initiation and propagation steps in Fischer-Tropsch synthesis may be facile even at a single metal center.

As a model for these important elementary reactions, we have used ab initio quantum mechanical techniques to investigate the migratory insertion of  $\text{CH}_2$  into an adjacent Ru-H bond. To our knowledge, these calculations provide the first quantitative description of the energetics of such a reaction, including evaluations of both the activation barrier to insertion as well as the relative stabilities of the reactant and product. The reaction pathway is depicted below



where **1** is a model for 18-electron complexes such as  $(\text{C}_5\text{H}_5)_2$

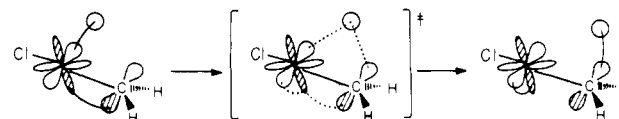
- (1) Biloen, P.; Sachtler, W. M. H. *Adv. Catal.* **1981**, *30*, 165.  
 (2) (a) Anderson, R. B. In *Catalysis*; Emmett, P. H., Ed.; Reinhold: New York, 1956; Vol. IV, pp 237-242. (b) Pichler, H.; Buffleb, H. *Brennstoff-Chem.* **1940**, *21*, 257, 273, 285.  
 (3) (a) Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181. (b) *Ibid.* **1981**, *103*, 1287. (c) Baker, J. A.; Bell, A. T. *J. Catal.* **1982**, *78*, 165-181.  
 (4) The first observation of general alkylidene insertions into M-R bonds was by: Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43.  
 (5) (a) Thorn, D. L.; Tulip, T. H. *Organometallics* **1982**, *1*, 1580. (b) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984.  
 (6) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648.  
 (7) Isobe, K.; Andrews, D. G.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 809.  
 (8) Kletzin, H.; Werner, H.; Serhadli, O.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 46.



**Figure 1.** Reaction coordinate for the insertion of  $\text{CH}_2$  into Ru-H in **1** to form  $\text{ClRu}(\text{CH}_3)$  (**2**) at the HF, GVB-PP(3/6), GVB-RCI(3/6), GVB-RCI(3/6), and GVB-RCI(3/6)-MCSCF levels. Energy (kcal/mol) is plotted relative to the total energy for **2** vs.  $R(\text{Ru-H})/[R(\text{Ru-H}) + R(\text{C-H})]$  (normalized reaction coordinate). Also shown at the top are the corresponding H-Ru-C angles (deg). The full GVB-RCI-MCSCF leads simultaneously to a proper description of both the reactant-like and product-like configurations important at the transition state and hence to a smooth potential curve. Some lower level calculations lead to a less smooth transition, the wave function being less capable of simultaneous description of both reactant and product channels.

$(\text{PPh}_3)_2\text{Ru}(\text{R})(\text{CH}_2)$  (**3**) or  $[(\text{C}_6\text{Me}_6)(\text{PPh}_3)_2\text{Ru}(\text{CH}_3)(\text{CH}_2)]^+$  (**4**), the intermediate postulated by Werner.<sup>8</sup> As discussed previously,<sup>9</sup> **1** conforms to the valence bond (VB) view of oxidation states in which electronegative ligands may remove no more than two units of charge from the metal (the easily ionized s-electrons), leaving the other ligands to form covalent bonds to unpaired d-electrons (or to form donor bonds into empty metal valence orbitals). Thus ligands with large electron affinities<sup>10</sup> such as Cp ( $\eta^5\text{-C}_5\text{H}_5$ ) and Cl form rather ionic bonds with the metal valence electrons, while neutral  $\pi$ -donor ligands (e.g.,  $\pi$ -aryls) and phosphines require empty metal valence orbitals. Finally, ligands with unpaired electrons (and small electron affinities, e.g.,  $\text{CH}_2$ ,  $\text{CH}_3$ , H, NO, etc.) require unpaired metal d-electrons with which to form covalent bonds. As a result, we believe the singlet state of **1** is a good model for **3** and **4**, since all three complexes have a metal VB oxidation state of +1. Ru(I) is  $d^7$ , with three unpaired d-electrons to form covalent bonds to R and  $\text{CH}_2$  in **1**, **3**, and **4**.

Consider the process of inserting the  $\text{CH}_2$  ligand into the Ru-H bond to form an Ru- $\text{CH}_3$  species. We begin with an Ru-H bond and two Ru-C in-plane bonds (one  $\sigma$  and one  $\pi$ ) which are converted to a C-H bond, one Ru-C bond and an Ru d lone pair. Notice that the presence of the in-plane  $\pi$ -bond<sup>11</sup> suggests a



- (9) Carter, E. A.; Goddard, W. A., III *J. Am. Chem. Soc.* **1986**, *108*, 2180.  
 (10) The electron affinities of Cp and Cl are 2.2 eV (Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, 736-772) and 3.62 eV (Hotop, H.; Lineberger, W. C. *J. Chem. Phys. Ref. Data* **1975**, *4*, 539-576), respectively.  
 (11) This conformation is the lowest energy orientation for **1**: Carter, E. A.; Goddard, W. A., III, manuscript in preparation.