ORGANIC LETTERS

2001
Vol. 3, No. 1
65−66

Reactions of Cycloproparenes with Metal Carbenes

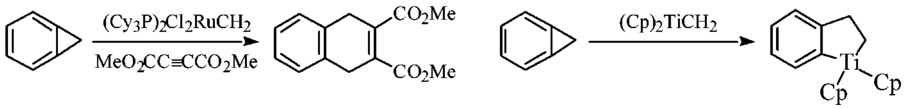
**Vladislav A. Litosh, Rajesh K. Saini, Ilsa Y. Guzman-Jimenez,
Kenton H. Whitmire, and W. E. Billups***

Department of Chemistry, Rice University, Houston, Texas 77005-1892

billups@rice.edu

Received October 25, 2000

ABSTRACT



Benzocyclopropene and cyclopropa[*b*]naphthalene react with dichloro-bis(tricyclohexylphosphine)methylideneruthenium, incorporating the metallacarbene to form unstable 3-ruthenacyclopentenes, which decompose to give *o*-xylylenes that can be trapped as Diels–Alder adducts by dimethyl acetylenedicarboxylate. In contrast, bis(η^5-cyclopentadienyl)methylidenetitanium forms moderately stable 2- and 3-titanacyclopentene complexes.

The high strain energy of the cycloproparenes[1] brings about extraordinary reactivity toward organometallic reagents. Studies include the reactions of benzocyclopropene **1**[2] with coordinated *n* and π ligands of nickel(0)[3] and palladium(II)[4] and the oxidative addition of platinum(0) and palladium(0) complexes to cyclopropa[*b*]naphthalene **2**,[5] forming metallacyclic compounds.[6] Wilkinson's catalyst was found to exhibit the same behavior.[6,7] We report here a study of the reactions of benzocyclopropene **1** and cyclopropa[*b*]naphthalene **2** with dichloro-bis(tricyclohexylphosphine)methylideneruthenium **3**[8] and bis(η^5-cyclopentadienyl)methylidenetitanium **4**.[9]

Our initial study focused on the reaction of dichloro-bis(tricyclohexylphosphine)benzylideneruthenium (Grubbs catalyst)[8] with cycloproparenes. However, this complex proved to be unreactive, and the more reactive complex **3** was synthesized by stirring a solution of the benzylidene derivative[8] in methylene chloride under an atmosphere of ethylene for 15 min. When **1** was treated with an equimolar amount of **3**, a polymeric material was formed. A trace of [2*n*]-cyclophane(1,3) **5**[10] and styrene (yield < 2%) were also isolated by preparative TLC and GC, respectively. The formation of **5**, a dimer of *o*-xylylene **6**,[11] strongly suggests that the tetraene is the source of the polymeric material. Indeed, the intermediate *o*-xylylene could be trapped when dimethyl acetylenedicarboxylate was added to the reaction mixture. The Diels−Alder adduct **7** was isolated by preparative thin-layer chromatography in 45% yield and identified by comparison with previously reported NMR spectroscopic data.[12] These results are summarized in Scheme 1.

Mechanistic insight into the initial cycloaddition reaction leading to intermediates **8** and **9** is not obvious. A concerted cycloaddition of the Ru═C bond to the strained C−C σ bond

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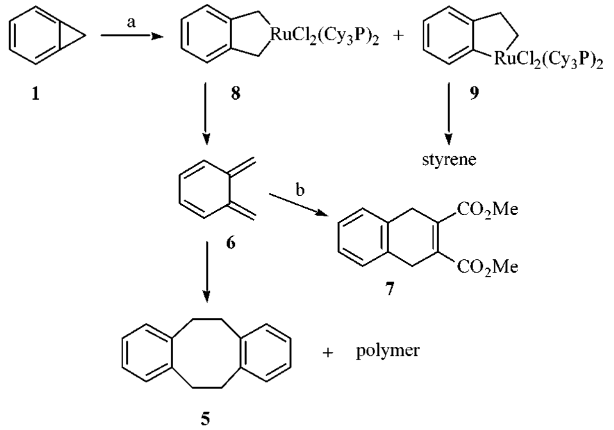
10.1021/ol0067787 CCC: $20.00

Scheme 1[a]

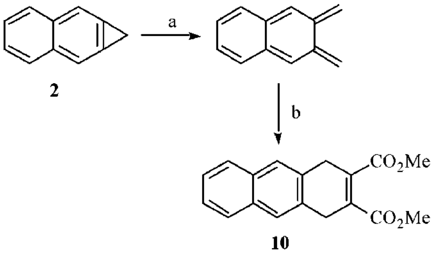


[a]Reagents and conditions: (a) $(Cy_3P)_2Cl_2RuCH_2$ (**3**), 25 °C. (b) $MeO_2CC{\equiv}CCO_2Me$.

cannot be eliminated and has analogy in previously reported work using Pt(IV) complexes.[13] Reductive elimination from intermediates **8** and **9** would release the hydrocarbons *o*-xylylene and styrene, respectively. 2-Ruthenacyclopentenes have been observed previously[14] and found to undergo β-hydride elimination followed by reductive elimination.

Treatment of naphtho[*b*]cyclopropene **2** with **3** in the presence of dimethyl acetylenedicarboxylate yields the Diels−Alder adduct **10**, which was isolated in 14% yield by preparative TLC and identified by NMR spectroscopy (Scheme 2).[12]

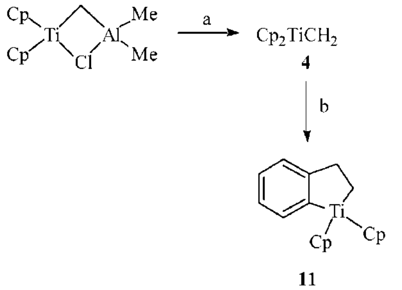
Scheme 2[a]



[a]Reagents and conditions: (a) $(Cy_3P)_2Cl_2RuCH_2$ (**3**), 25 °C. (b) $MeO_2CC{\equiv}CCO_2Me$.

The intermediates that are formed in the reactions with titanium reagents proved to be more stable. Thus benzocyclopropene was found to react at −30 °C with **4**,[9] generated in situ by treating Tebbe's reagent with 4-(dimethylamino)pyridine (DMAP),[15] to give the titanabenzocyclopentene **11** in 60% crude yield (Scheme 3). Acidolysis of the crude product using aqueous HCl gave only ethylbenzene, demonstrating the regiospecificity of the reaction.

Scheme 3[a]



[a]Reagents and conditions: (a) 4-(Dimethylamino)pyridine (DMAP), 25 °C. (b) Benzocyclopropene.

Although **11** decomposes slowly at room temperature, low temperature crystallization from hexane gave a reddish powder that could be characterized spectroscopically by ^{1}H NMR spectroscopy. Signals were observed at δ 3.31 (t, 2H, $J = 8.8$ Hz), 4.59 (t, 2H $J = 8.8$ Hz), 6.58 (s, 10H), 6.84 (m, 2H), 7.10 (m, 1H), and 7.24 (d, 1H, $J = 1.3$ Hz). ^{13}C NMR signals ($CDCl_3$) were observed at 254.58, 128.15, 127.53, 125.29, 120.63, 120.58, 109.44, 74.45, and 30.07 ppm. EI HRMS M^+ calcd 282.0890, found 282.0884.

The reaction of **4** with cyclopropa[*b*]naphthalene **2** did not follow the regiospecific route observed for benzocyclopropene. Thus acidolysis of the crude product formed when **2** was reacted with **4** yielded 2-ethylnaphthalene (44%) and 2,3-dimethylnaphtlene (17%). These hydrocarbons were identified by comparison of their spectral properties with authentic samples. In this case the intermediate titanacycles could not be isolated.

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundation (CHE-9710042) and the Robert A. Welch Foundation. We thank Professor Andrew Barron for helpful discussions.

OL0067787

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