Reactions of Cycloproparenes with Metal Carbene

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ABSTRACT

Benzocyclopropene and cyclopropa[b]naphthalene react with dichloro-bis(tricyclohexylphosphine)methylideneruthenium, incorporating the metallacarbone to form unstable 3-ruthenacyclopentenes, which decompose to give o-xylene that can be trapped as Diels–Alder adducts by dimethyl acetylenedicarboxylate. In contrast, bis(η5-cyclopentadienyl)methylidene-titanium forms moderately stable 2- and 3-titanacyclopentene complexes.

The high strain energy of the cycloproparenes1 brings about extraordinary reactivity toward organometallic reagents. Studies include the reactions of benzocyclopropene 1 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 forming metallocyclic compounds.5 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 and bis(η5-cyclopentadienyl)methylidene-titanium 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 derivative8 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 [2n]-cyclophane(1,3)510 and styrene (yield < 2%) were also isolated by preparative TLC and GC, respectively. The formation of 5, a dimer of o-xylene 6,11 strongly suggests that the tetraene is the source of the polymeric material. Indeed, the intermediate o-xylene 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=CC bond to the strained C–C σ bond

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

Treatment of naphth[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).

The intermediates that are formed in the reactions with titanium reagents proved to be more stable. Thus benzylocyclopropene was found to react at $-30^\circ$C with 4,9 generated in situ by treating Tebbe’s reagent with 4-(dimethylamino)pyridine (DMAP), 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.

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 $\delta$ 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 cycloprop[b]naphthalene 2 did not follow the regiospecfic route observed for benzocyclopropene. Thus acidolysis of the crude product formed when 2 was reacted with 4 yielded 2-ethynaphthalene (44%) and 2,3-dimethylnaphthalene (17%). These hydrocarbons were identified by comparison of their spectral properties with authentic samples. In this case the intermediate titanacycles could not be isolated.

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