A novel catalytic route to 2-bicyclo[2.2.1]hept-2-ylidenebicyclo[2.2.1]-heptane involving C–H bond activation of bicyclo[2.2.1]hept-2-ene

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Abstract

The tungsten(II) carbonyl compound $(CO)_4W(\mu\text{-Cl})_3W(SnCl_3)(CO)_3$ has been found to be a very effective catalyst for dimerization reaction of bicyclo[2.2.1]hept-2-ene to 2-bicyclo[2.2.1]hept-2-ylidenebicyclo[2.2.1]-heptane conducted in dichloromethane solution at room temperature. A very labile η^2-norbornene complex of tungsten(II) has been shown to be formed on the pathway to the catalytically active species. A mechanism involving C—H bond activation of the η^2-norbornene ligand and the formation of metallacarbene is proposed to explain those results. In addition, it has been determined that other products, such as cyclotrimers and the ring opening metathesis polymerization (ROMP) polymer of norbornene can be formed in amounts depending upon the catalyst-to-norbornene molar ratio. The reaction products are identified by means of chromatography (GC–MS) and ^1H and ^{13}C NMR spectroscopy.
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1. Introduction

Although transition metal-catalyzed dimerization and oligomerization of olefins have been investigated extensively for many years [1], the topic remains of great interest, both academic and industrial. One of these reactions is [2 + 2] dimerization of cyclic olefins such as bicyclo[2.2.1]hept-2-ene (norbornene, NBE), bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD), and their derivatives [2]. Catalysts containing Cu [2a], Co [2a], Fe [2d], Mo [2e], Ru [2g,h], Pd [2i], and, most commonly, Ni [2a,b,c,f], have been demonstrated to be involved in the [2 + 2] dimerization reaction. However, although many transition metal systems have been examined, dimerization reactions involving group 6 metals still remain very rare. Moreover, the dimerization of NBE and the formation of 2-bicyclo[2.2.1]hept-2-ylidenebicyclo[2.2.1]-heptane (2,2′-binorbornylidene) (**1**) is unprecedented in the above

catalytic systems. Nevertheless, compound **1** was detected in small amounts during the ring opening metathesis polymerization (ROMP) of NBE catalyzed by transition metal halides such as WCl_6, $MoCl_5$, and $ReCl_5$ [3]. Similarly, the recently reported ROMP reaction of NBE catalyzed by tungsten(II) (**2**) and molybdenum(II) (**3**) compounds of the type $(CO)_4M(\mu\text{-Cl})_3M(SnCl_3)(CO)_3$ is accompanied by the formation of oligomers as a step preceding the initiation of the ROMP reaction [4]. In the latter studies we have also found that the coordination of cyclic olefin to the transition metal atom is a very important step in the ROMP reaction. An η^2-olefin ligand such as NBE or NBD can rearrange to give a carbene species initiating the catalytic ROMP reaction [4,5].

Numerous studies on stoichiometric reactions of carbene complexes have shown that the coupling of two carbene ligands leads to the formation of a carbon–carbon double bond, i.e. a new olefin or, to put it differently, a carbene dimer [6]. However, nobody has yet demonstrated that transition metal complexes can be used as catalysts in such a specific dimerization reaction of olefins giving **1**.
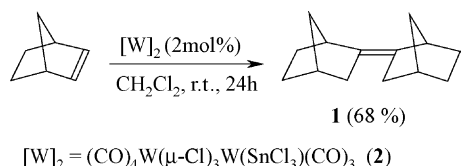
Scheme 1.

To date, the McMurry and Fleming procedure for reductive dimerization of ketones [7] has been applied for the synthesis of compound **1** [3,8]. Using this method, Nelsen and Reinhardt obtained from 2-norbornanone the four possible stereoisomers (*syn-trans*, *anti-trans*, *syn-cis*, and *anti-cis*) of compound **1** in 20% yield [8]. From the latter mixture the pure *syn-trans* isomer of **1** was separated by preparative TLC and characterized by NMR spectroscopy. Thus, there is a strong need for a simple and straightforward synthesis of **1** using norbornene as a cheaper starting material. We report here that the binuclear tungsten(II) compound $(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3$ (**2**) [9] can be used as a catalyst for clean conversion of norbornene to compound **1** in fairly good, 68% yield. The overall one-pot synthesis of **1** is illustrated in Scheme 1.

2. Experimental

2.1. Reaction procedure

A dichloromethane solution ($10\,cm^3$) of NBE (0.24 g, 2.5 mmol) and *n*-heptane ($0.3\,cm^3$ as internal chromatographic standard) was added under an atmosphere of nitrogen to a $50\,cm^3$ Schlenk tube containing compound **2** (0.045 g, 0.05 mmol). The reaction mixture was stirred at room temperature until completion (ca. 24 h, GC-FID monitoring). The solvent was evaporated in vacuum and the crude reaction product extracted with *n*-heptane. Analysis by GC–MS showed 68% of **1**, 5% of hydroxyl-2,2′-binorbornyl, and 27% of norbornene cyclotrimers. Fractional distillation at 65 °C under reduced pressure gave pure **1** as colorless oil. GC–MS for the four stereoisomers of **1** ($C_{14}H_{20}$, $M_r = 188.32$) appearing as three signals at retention time 11.48 min (43.2%), 11.53 min (23.3%), and 11.63 (33.5%), *m/z* (relative intensity): 41(14), 67(22), 79(39), 91(33), 105(11), 131(18), 159(100), 188(35).

2.2. NMR characteristics of the four steroisomers of **1**

^1H NMR (δ, $CDCl_3$) – *anti-cis*: 2.79 (s, 2H[1]), 2.32 (s, 2H[4]), 1.94 (d, $J_{H–H} = 15\,Hz$, 2H[3]), ca. 1.6 (2H[3′]), 1.54 (m, 4H[5,6]), 1.27 (m, 2H[7]), 1.22 (m, 6H[5,6,7]); *syn-cis*: 2.76 (s, 2H[1]), 2.32 (s, 2H[4], 1.94 (d, $J_{H–H} = 15\,Hz$, 2H[3]), ca. 1.6, 2H[3′]), 1.54 (m, 4H[5,6]), 1.27 (m, 2H[7]), 1.22 (m, 6H[5,6,7]); *anti-trans*: 2.58 (s, 2H, H[1]), 2.32 (s, 2H[4], 2.03 (d, $J_{H–H} = 15\,Hz$, 2H[3]), 1.80 (d, $J_{H–H} = 15\,Hz$, 2H[3′]), 1.54 (m, 4H[5,6]), 1.27 (m, 2H[7]), 1.22 (m, 6H[5,6,7]); *syn-trans* [8]: 2.54 (s, 2H[1]), 2.32 (s, 2H[4], 2.12 (d,

$J_{H–H} = 15\,Hz$, 2H[3]), 1.71 (d, $J_{H–H} = 15\,Hz$, 2H[3′]), 1.54 (m, 4H[5,6]), 1.27 (m, 2H[7]), 1.22 (m, 6H[5,6,7]). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$) – *anti-cis*: 131.84 (C^2), 41.87 (C^1), 39.69 (C^7), 37.01 (C^3), 36.59 (C^4), 29.73 (C^5), 28.72 (C^6); *syn-cis*: 131.95 (C^2), 41.82 (C^1), 39.89 (C^7), 37.04 (C^3), 36.64 (C^4), 28.93 (C^5), 28.67 (C^6); *anti-trans*: 131.43 (C^2), 41.37 (C^1), 39.26 (C^7), 37.08 (C^3), 36.70 (C^4), 29.77 (C^5), 28.55 (C^6); *syn-trans* [8]: 131.53 (C^2), 41.01 (C^1), 39.03 (C^7), 37.16 (C^3), 36.78 (C^4), 29.07 (C^5), 28.59 (C^6).

3. Results and discussion

Two reaction procedures were used in synthesis of **1**. In the procedure presented in Scheme 1, compound **2** and norbornene (1:50 molar ratio) in dichloromethane solution ($10\,cm^3$) were stirred at room temperature and conversion of NBE (ca. 50% after 1 h and 90% after 24 h) was confirmed by the GC–FID method. Analysis of the crude product by the GC–MS method showed the formation of compound **1** ($m/z = 188$) in 68% yield. Other products, such as hydroxyl-2,2′-binorbornyl ($m/z = 206$; 5%), and cyclotrimers of norbornene (several signals with $m/z = 282$; 27%), were also detected. To avoid the formation of ROMP polymers, a solution of NBE was added to the solution of the catalyst in five portions over a period of 5 h. Conversion of each portion of NBE reached ca. 80% within 10 min. In such a procedure 90% conversion of NBE was achieved within a short time (5 h), but the overall yield of **1** decreased drastically, while yield of cyclotrimers was much higher.

Monitoring the reaction of NBE in the presence of **2** or **3** [10] by ^1H NMR spectroscopy in $CDCl_3$ or CD_2Cl_2 solution allowed us to observe the coordination of NBE to the metal centre in the step preceding the formation of **1**. Two of the six characteristic proton signals for an η^2-norbornene ligand coordinated to tungsten(II) [5] were detected at δ 5.05 and -0.72; other signals were obscured by the NBE and compound **1** signals. However, such an interaction of NBE with the metal atom can be observed only during the first few minutes of reaction preceding the appearance and increase in intensity of signals at δ 2.80, 2.77, 2.59, and 2.53 due to the methine protons (H[1]) of *anti-cis*, *syn-cis*, *anti-trans*, and *syn-trans* steroisomers of **1**, respectively. The integral ratio of the latter signals made it possible to calculate the molecular ratio of the four isomers: 1:0.65:0.57:0.61, respectively. The isomer ratio calculated from NMR spectra is in a good agreement with that obtained from GC–MS analysis, with one exception: the *anti-trans* and *syn-trans* isomers, which have the lowest retention time (11.48 min), are not separated. The retention time for the *anti-cis* and *syn-cis* isomers is 11.53 and 11.63 min, respectively. Prolonged reaction in the NMR tube allowed us to observe the formation of ROMP polymers due to characteristic olefinic proton signals at δ 5.32 (*trans*) and 5.20 (*cis*) [4].

Although different mechanism pathways may account for the dimerization reaction of cyclic olefins, a mechanism
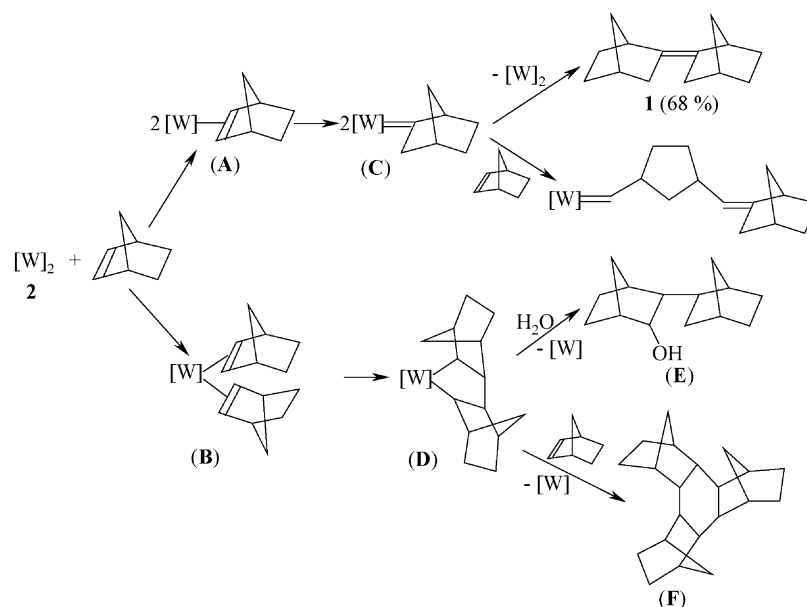
Scheme 2.

rationale based on the observed results, involving coordination of norbornene to the metal atom and its transformation to a carbene species is depicted in Scheme 2.

The splitting of chlorine bridges in **2** or **3** by NBE is accompanied by its coordination to the transition metal atom and the formation of a monoolefin (**A**) or bisolefin (**B**) complex. The 1,2-hydrogen shift gives the metallacarbene complex **C**. The similar rearrangement of the η^2-cyclohexene to cyclohexylidene ligand was recently observed by Wolczanski and co-workers [11]. A bimolecular coupling of two carbene ligands derived from complex **C** leads to the formation of **1** and regenerates the binuclear complex of tungsten. An analogous dimerization of alkylidene complexes was earlier observed by Schrock and co-workers [12]. In the presence of an excess of NBE the carbene species **C** initiates the ROMP reaction. Additionally, reductive dimerization and cyclotrimerization of NBE take place. This indicates an alternative route involving the coupling of two mutually *cis* η^2-olefin ligands in compound **B** and the formation of metallacyclopentane (**D**) as an intermediate species. As a result of hydrolysis of **D** by H_2O the hydroxyl-2,2′-binorbornyl (**E**) is formed. The insertion of an NBE molecule into the metal–carbon bond of metallacyclopentane **D**, followed by reductive elimination, affords a mixture of several isomers of cyclotrimer (**F**). Although the reaction course is analogous for tungsten (**2**) and molybdenum (**3**) catalysts, cyclotrimer yield in the presence of **3** is much higher, exceeding twice the yield of **1**. During the conversion of NBE in the presence of **2** or **3** monitored by NMR in CDCl$_3$ or CD$_2$Cl$_2$ solution, at the beginning of the reaction the appearance of a small amount of chloronorbornane [5] (<1% of **1** by NMR) is always observed. The latter compound is probably formed as a result of the hydrolysis of the carbene species **C** by HCl derived from the solvent.

4. Conclusions

In summary, we have developed a new and straightforward synthesis of 2,2′-binorbornylidene (**1**) from norbornene using a tungsten(II) carbonyl complex as a catalyst.

Also, it is worth pointing out that the formation of **1** gives direct evidence for the formation of norbornylidene from η^2-norbornene ligand of tungsten(II) complex.

Studies on the application of compounds **2** and **3** as the catalyst in such a specific dimerization of other cyclic and acyclic olefins are in progress.

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