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Grubbs and Hoveyda-Type Ruthenium Complexes Bearing a Cyclic Bent-Allene

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Abstract

Stable cyclic bent-allene **1** displaces the chelating ether linkage of the Hoveyda-Grubbs-type ruthenium complex **2** bearing triphenylphosphine. The resulting complex **3** features an unusual cis-arrangement of the phosphine and the cyclic bent-allene, while retaining a distorted square pyramidal geometry around the ruthenium center. Monitoring by ^{31}P NMR spectroscopy the reaction of cyclic bent-allene **1** with the indenylidene bis(triphenylphosphine)ruthenium dichloride complex **4** allowed for the observation of dissociated triphenylphosphine, and the formation of a ruthenium complex featuring **1** and triphenylphosphine in the desired trans-configuration. However, continued reaction times saw the disappearance of this complex, and after workup complex **5** featuring a cis-arrangement was isolated.

Keywords

ruthenium; olefin metathesis; carbon-based ligands; bent-allenes; carbenes

The olefin metathesis reaction has proven to be an exceptionally powerful tool for creating new carbon-carbon bonds [1]. At the end of the 90s, it has been found that the replacement of one phosphine of the Grubbs and Hoveyda-Grubbs first generation catalysts **A** [2] and **B** [3], respectively, by an imidazol-2-ylidene [4], and even better by the saturated N-heterocyclic carbene (NHC) analogue (**C** [5], and **D** [6]), afforded catalysts that exhibit levels of performance which were previously only possible with the most active early metal systems [7], but with significantly broader and better functional group tolerance (Scheme 1). The increased activity of the second generation ruthenium olefin metathesis catalysts **C** and **D** is largely attributed to the strong electron-donating properties of the NHC ligand, which stabilizes the 14-electron alkylidene intermediate, and causes preferential binding of the π -acidic olefin over reassociation of the phosphine ligand [8]. Recently, we have shown that complexes of type **E**, bearing cyclic (alkyl)(amino)carbenes (CAACs), which are stronger σ -donor but also stronger π -acceptor ligands than NHCs [9], feature excellent catalytic activity in ring-closing metathesis reactions for the formation of di- and tri-substituted olefins [10]. Relative to most NHC-substituted complexes, CAAC-substituted catalysts **E** exhibit lower *E/Z* ratios (3:1 at 70% conversion) in the cross-metathesis of *cis*-1,4-diacetoxy-2-butene with allylbenzene [11]. Complexes of type **E** also demonstrate good selectivity for the formation of terminal olefins versus internal olefins in the ethenolysis of methyl oleate with

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excellent activity; complex **E**₁ achieved 35 000 TONs, the highest recorded to our knowledge [12].

From these results, electron-rich carbon based ligands seem very appropriate for building powerful ruthenium olefin metathesis catalysts. We have recently isolated bent-allene derivatives such as **F** [13], also coined carbo(dicarbenes) [14], which are not only stronger σ -donors but also less π -acceptor ligands than CAACs and NHCs [15,16]. Indeed, they feature a carbon center formally possessing two lone pairs, as shown by resonance structures **F'** and **F''** (Scheme 1). Here we report the preparation of Hoveyda-Grubbs-type complexes bearing cyclic bent-allenes as the ancillary ligand [17,18].

The most straightforward preparation of new ruthenium based olefin metathesis catalysts is the substitution of a tricyclohexylphosphine on complexes **A** or **B** by a suitable donor ligand [1]. Reaction of the stable cyclic bent-allene **1** (obtained by deprotonation of the corresponding pyrazolium salt) with both complexes **A** and **B** resulted in complex mixtures. Attempts at separation by silica gel chromatography led only to decomposition, despite the fact that the Grubbs pre-catalysts are stable under the same conditions, one of their many exemplary attributes. Then, we turned our attention to complex **2** bearing a smaller triphenylphosphine ligand, which we believed might be easier to substitute than the bulky tricyclohexylphosphine of the commercial catalyst **B**. Reaction of one equivalent of allene **1** with **2** at 40 °C (no substitution reaction was observed at room temperature) in benzene resulted in the formation of a single product, **3** (Scheme 2). ¹H NMR shows a signal at δ = 17.9 ppm, in the range expected for the benzylidene proton (**2**: δ = 16.7 ppm). However, ³¹P NMR spectroscopy indicated that the triphenylphosphine ligand was still coordinated to the ruthenium (**3**: $\delta^{31}\text{P}$ = 53.0 ppm; **2**: 61.1 ppm). In addition, the ¹H NMR spectrum indicated that the chelating ether atom was no longer interacting with the metal center, as inferred by the upfield shift of the isopropyl CH (**3**: δ = 4.3 ppm; **2**: 5.4 ppm). An X-ray crystallographic study of **3** (Fig. 1, left) corroborated our NMR assignments, although the arrangement of the ligands around the metal was surprising. The ruthenium complex features a cis-arrangement of the phosphine and **1**, while retaining a distorted square pyramidal geometry around the ruthenium center. Although this cis-configuration is not unprecedented [19], it is very rare with non-chelating ligands [20]. Another interesting structural feature of **3** is the previously unobserved bending back of the O-Ar groups of the bent-allene ligand away from the metal [21], probably due to increased steric congestion around the metal center.

Unfortunately complex **3** is inactive in the prototypical test for ring closing metathesis of diethyldiallyl malonate at 30 °C [22]. Increased temperatures and reaction times (12 hours, 60 °C) did not allow for the observation of any metathesis product. Note that low catalytic activity had also been observed for NHC ruthenium complexes with cis donor ligands [19,20]. Attempts were made to remove the triphenylphosphine, using various oxidizing agents, to encourage the chelation of the alkoxy group. No change in the NMR spectrum was observed upon prolonged exposure to oxygen and sulfur, probably due to the absence of a trans ligand favoring triphenylphosphine dissociation. When the Lewis acidic copper(I) chloride was added, rapid decomposition was observed, most likely due to the availability of a second pair of electrons at the allene carbon.

We then investigated the possibility of preparing indenylidene ruthenium complexes derived from **4**. The latter is readily available from tris(triphenylphosphine)ruthenium dichloride and diphenyl propargyl alcohol, and Nolan [23] and Fürstner [24] have both shown that a simple ligand exchange led to catalytically active tricyclohexylphosphine and NHC complexes. Monitoring by ³¹P NMR spectroscopy the reaction of cyclic bent-allene **1** with **4** allowed for the observation of dissociated triphenylphosphine, the starting material ($\delta^{31}\text{P}$ = 29 ppm), and two new signals at $\delta^{31}\text{P}$ = 38 and 50 ppm. Continued reaction times saw the disappearance

of the high field signals, leaving only the peak at 50 ppm along with that of the free triphenylphosphine. The final product was unambiguously identified by a single crystal X-ray diffraction study as complex **5** (Scheme 3; Fig. 2, right). Unfortunately, this complex also featured a cis-arrangement of the phosphine and bent-allene **1**. We postulate that the upfield ^{31}P signal observed at $\delta = 38$ ppm belongs to a ruthenium complex containing the bent-allene and triphenylphosphine in the desired trans-configuration, but that **5** is the more thermodynamically favored isomer [19b].

Complexes **3** and **5** are new examples of ruthenium complexes with an unusual cis-configuration of the phosphine and the second L ligand. In contrast to most of the previously reported complexes of this type, **3** and **5** do not feature a chelating ligand. To favor the trans-arrangement, which seems to be a requirement for catalytic applications, more sterically demanding and rigid bent-allene ligands are highly desirable; their preparation is currently under investigation.

Experimental Section

All reactions were performed under an atmosphere of argon and solvents were dried over Na metal or CaH_2 . Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. ^1H NMR (300 MHz) and $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz) spectra were obtained with a Bruker Avance 300 spectrometer at 298 K. ^1H and ^{13}C chemical shifts (δ) are reported in parts per million (ppm) relative to TMS, and were referenced to the residual solvent peak. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept. = septet, m = multiplet, br = broad signal. Coupling constants (J) are reported in hertz (Hz). Melting points were measured with a Mel-Temp melting point apparatus system. Ruthenium complexes **2** [3] and **4** [24a] were prepared according to the literature.

Cyclic bent-allene **1**

This compound was prepared in two steps as follows. 2,6-diisopropylphenol (33 mL, 176 mmol) and triethylamine (33 mL, 235 mmol) were added to a dichloromethane slurry of 3,5-dichloro-1,2-diphenylpyrazolium tetrafluoroborate [25] (22.1 g, 59 mmol). The reaction mixture was stirred overnight. Water was added and the organic layer was separated, washed with water, and dried with magnesium sulfate. The solvent was evaporated and the residue was washed with ether, affording 3,5-bis(2,6-diisopropylphenoxy)-1,2-diphenylpyrazolium tetrafluoroborate as a white solid (34.2 g, 88 % yield); ^1H NMR (300 MHz, CDCl_3) δ 7.84-7.82 (m, 4 H), 7.53-7.42 (m, 6 H), 7.30-7.25 (m, 2 H), 7.18-7.16 (m, 4 H), 4.69 (s, 1 H), 3.07 (sept, $J = 7$ Hz, 4 H), 1.15 (s, 24 H); ^{13}C NMR (75 MHz, CDCl_3) δ 158.99, 147.86, 140.57, 131.95, 130.35, 129.55, 129.33, 128.50, 125.23, 75.01, 27.37, 23.79. Potassium bis(trimethylsilyl)amide (315 mg, 1.58 mmol) and 3,5-bis(2,6-diisopropylphenoxy)-1,2-diphenylpyrazolium tetrafluoroborate (1.045 g, 1.58 mmol) were cooled to -78°C in a dry ice/acetone bath under an atmosphere of argon. Diethyl ether (20 mL) was slowly added to the solids and let to sit for 5 minutes before stirring. The reaction was stirred at low temperature for 30 minutes, then the cold bath was removed, and the reaction mixture was brought to room temperature and stirred an additional 30 minutes. The volatiles were evaporated and the residue was extracted with diethyl ether via cannula filtration. The yellow solution was evaporated to give the cyclic bent-allene **1** as a light yellow solid (770 mg, 85 % yield); m.p.: 110°C ; ^1H NMR (300 MHz, C_6D_6) δ 7.54 (d, $J = 7.6$ Hz, 4 H), 7.11-7.04 (m, 10 H), 6.90-6.88 (m, 2 H), 3.42 (t, $J = 6.9$ Hz, 4 H), 1.31 (s, br, 24 H); ^{13}C NMR (75 MHz, C_6D_6) δ 176.45, 150.52, 141.10, 137.69, 129.67, 127.41, 126.79, 124.95, 124.43, 116.21, 28.26, 23.73.

Cyclic bent-allene ruthenium complex 3

Cyclic bent-allene **1** (34.4 mg, 0.06 mmol) and dichloro(*o*-isopropoxyphenylmethylene) (triphenylphosphine)ruthenium **2** (35 mg, 0.06 mmol) were loaded into a Schlenk tube in the glove box. Benzene (3 mL) was added and the reaction was heated at 40 °C overnight. The reaction was cooled to room temperature and the solvent was evaporated affording a green solid. A concentrated dichloromethane solution was layered with pentane and cooled to −20 °C, affording green single crystals of **3** (40.5 mg, 58 % yield); m.p.: 176 °C; ¹H NMR (300 MHz, CDCl₃) δ 17.95 (d, *J* = 23 Hz, 1 H), 11.02-10.99 (m, 1 H), 8.64 (br, 2 H), 8.28 (br, 4 H), 7.97-7.81 (m, 4 H), 7.58-7.41 (m, 6 H), 7.18-6.65 (m, 14 H), 6.58-6.31 (m, 4 H), 4.26 (sept, *J* = 7 Hz, 1 H), 3.93 (sept, *J* = 7 Hz, 1 H), 3.83 (br, 1 H), 3.60 (sept, *J* = 7 Hz, 1 H), 3.40 (sept, *J* = 7 Hz, 1 H), 1.83 (d, *J* = 7 Hz, 6 H), 1.46 (d, *J* = 7 Hz, 6 H), 1.34 (d, *J* = 7 Hz, 6 H), 1.32 (br, 6 H), 1.23 (d, *J* = 7 Hz, 6 H); ³¹P NMR (121.5 MHz, CDCl₃) δ = 53.0 ppm.

Cyclic bent-allene ruthenium complex 5

Cyclic bent-allene **1** (280 mg, 0.49 mmol) and dichloro(3-phenyl-1H-indene-1-ylidene) (bistriphenylphosphine)ruthenium **4** (217 mg, 0.25 mmol) were loaded into a Schlenk tube in the glovebox, and benzene was added. The reaction was stirred overnight at room temperature. The solvent was evaporated and the dark red residue was washed with pentane. Single crystals of **5** were grown by layering a dichloromethane solution with pentane and placing in a −20 °C freezer overnight (176 mg, 59 % yield); m. p. = 180 °C; ¹H NMR (300 MHz, CDCl₃) δ 9.39 (d, *J* = 7 Hz, 1 H), 8.11-8.05 (m, 2 H), 7.70-7.64 (m, 3 H), 7.61-7.55 (m, 3 H), 7.51-7.46 (m, 2 H), 7.24-6.92 (m, 16 H), 6.87-6.78 (m, 4 H), 6.73-6.67 (m, 3 H), 6.64-6.56 (m, 3 H), 6.36 (s, 1 H), 6.29-6.26 (m, 1 H), 5.88-5.85 (m, 2 H), 3.73-3.62 (m, 1 H), 2.94-2.84 (m, 1 H), 2.75-2.65 (m, 1 H), 2.25-2.21 (m, 1 H), 1.35 (d, *J* = 7 Hz, 3 H), 1.01 (d, *J* = 7 Hz, 3 H), 0.94 (d, *J* = 7 Hz, 3 H), 0.81 (d, *J* = 7 Hz, 3 H), 0.74 (d, *J* = 7 Hz, 3 H), 0.55 (d, *J* = 7 Hz, 3 H), 0.27-0.22 (m, 6 H); ³¹P NMR (121.5 MHz, CDCl₃) δ = 50.12.

Crystal structure determination of complexes 3 and 5

A Bruker X8-APEX X-ray diffraction instrument with Mo-radiation was used for data collection. All data frames were collected at low temperatures (*T* = 100 K) using an ω, φ-scan mode (0.5° ω-scan width, hemisphere of reflections) and integrated using a Bruker SAINTPLUS software package. The intensity data were corrected for Lorentzian polarization. Absorption corrections were performed using the SADABS program. The SIR97 was used for direct methods of phase determination, and Bruker SHELXTL software package for structure refinement and difference Fourier maps. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of compounds were refined by means of a full matrix least-squares procedure on *F*². All H-atoms were included in the refinement in calculated positions riding on the C atoms. Drawings of molecules were performed using Ortep 3. **Crystal and structure parameters of 3:** size 0.32 × 0.17 × 0.10 mm³, triclinic, space group P-1, *a* = 13.0054(19) Å, *b* = 22.590(3) Å, *c* = 23.269(3) Å, α = 78.651(2)°, β = 75.723(2)°, γ = 73.746(2)°, *V* = 6300.1(16) Å³, ρ_{calcd} = 1.218 g/cm³, Mo-radiation (λ = 0.71073 Å), *T* = 100(2) K, reflections collected = 23202, independent reflections = 13378 (*R*_{int} = 0.0517), absorption coefficient μ = 0.404 mm^{−1}; max/min transmission = 0.9607 and 0.8817, 1390 parameters were refined and converged at *R*₁ = 0.0604, *wR*₂ = 0.1378, with intensity *I* > 2σ(*I*). **Crystal and structure parameters of 5:** size 0.32 × 0.17 × 0.10 mm³, triclinic, space group P-1, *a* = 11.0065(13) Å, *b* = 13.7273(17) Å, *c* = 13.7273(17) Å, α = 74.765(2)°, β = 78.541(2)°, γ = 68.002(2)°, *V* = 3426.4(7) Å³, ρ_{calcd} = 1.259 g/cm³, Mo-radiation (λ = 0.71073 Å), *T* = 100(2) K, reflections collected = 38731, independent reflections = 15174 (*R*_{int} = 0.0391), absorption coefficient μ = 0.472 mm^{−1}; max/min transmission = 0.9543 and 0.8636, 1390 parameters were refined and converged at *R*₁ = 0.0482, *wR*₂ = 0.1216, with intensity *I* > 2σ(*I*). Compounds **3** and **5** have been

deposited in the Cambridge Crystallographic Data Center under CCDC 813596 and 813597, and can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. X-ray crystal structures for complexes **3** (left) and **5** (right). Hydrogen atoms are omitted for clarity. Bond lengths and angles are given in the supplementary material.

Scheme 1.

First (**A** and **B**) and second generation (**C** and **D**) of ruthenium olefin metathesis catalysts; Hoveyda-Grubbs-type catalysts bearing a cyclic (alkyl)(amino)carbene (CAAC) as ancillary ligand (**E**); Cyclic bent-allenes **F** and their resonance forms **F'** and **F''**.

Scheme 2.
Synthesis of cyclic bent-allene ruthenium complex **3**.

Scheme 3.
Synthesis of cyclic bent-allene ruthenium complex **5**.