

Short Note

4,5-Di-*tert*-butyl-1,3,6,8-tetraphenyl-4,5,8a,8b-tetrahydro-as-indacene

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Abstract: Reaction of triplet O₂ with the bridged dipotassium dicyclopentadienyl salt, *ansa*-[(CHBu^t)₂(Ph₂C₅H₂)₂]K₂(THF)₃ **1**, in dry MeCN facilitated an intramolecular cyclopentadienyl ring-C to ring-C bond formation and the precipitation of the crude product 4,5-di-*tert*-butyl-1,3,6,8-tetraphenyl-4,5,8a,8b-tetrahydro-as-indacene **2** as an off-white solid in a 73% yield (>95% pure, ¹H NMR). Characterization of **2** was carried out using multinuclear NMR spectroscopy (¹H and ¹³C), single-crystal X-ray crystallography, FTIR spectroscopy, and thermal analytical techniques (SDT, DSC). The molecular structure consisted of a rigid, C₂-symmetric six-membered ring in a chair conformation with four of the ring-C atoms fused to 1,3-diphenylcyclopentadiene rings and the other two ring-C atoms substituted with trans di-axial Bu^t groups.

Keywords: tetrahydro-as-indacene; cyclopentadienyl ring oxidation; intramolecular C-C bond formation; ring-fused dicyclopentadiene; dicyclopentadienyl salt; superoxide radical



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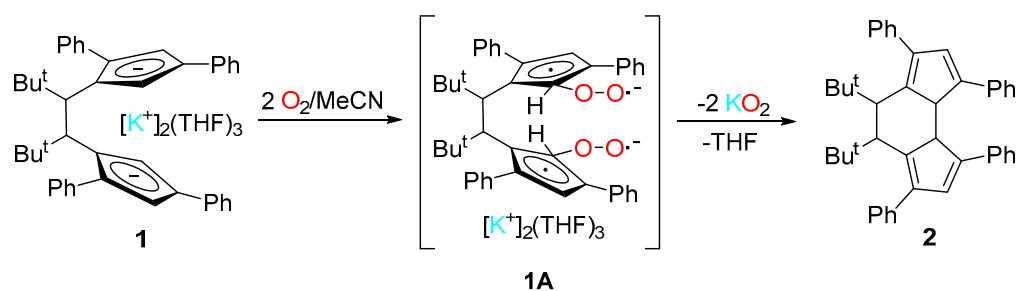
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1. Introduction

The direct reaction of triplet O₂ with cyclopentadienyl rings has not been a frequently used tool in synthesis, aside from the construction of the important cyclopentadienone ligand from highly substituted cyclopentadienyl precursors [1]. Scattered reports from the literature describe the interaction of triplet O₂ with cyclopentadienyl-M and mixed (cyclopentadienyl)(arene)-M compounds to give substituted π-(cyclopentadiene)M(η-cyclopentadienyl) complexes [2], as well as both stable and unstable metal cyclopentadienyl [3] and metal arene peroxidic dimers [4–6]. The formation of a peroxide bridge between the exocyclic C atoms of coordinated diphenylfulvene (dpf) ligands by exposure of [Rh(dpf)₂]⁺ to O₂ has also been observed [7]. In one noteworthy case, the O₂-induced dimerization of substituted η⁵-cyclopentadienyliron(I) η⁶-arene complexes in pentane occurred via the intermolecular formation of a C-C bond between the arene rings [4]. In our investigation of the oxidation of the 2C-atom-bridged dicyclopentadienyl K⁺ salt, *ansa*-[(CHBu^t)₂(Ph₂C₅H₂)₂]K₂(THF)₃ **1** [8], we observed an intramolecular cyclopentadienyl ring C- to ring-C bond formation, resulting in the formation of 4,5-di-*tert*-butyl-1,3,6,8-tetraphenyl-4,5,8a,8b-tetrahydro-as-indacene (**2**, Scheme 1). Herein, we report the synthesis and molecular structure of **2**, obtained by single-crystal X-ray crystallography. To our knowledge, this is the first example of the triplet O₂-mediated intramolecular C-C bond formation between cyclopentadienyl rings to give a substituted tetrahydro-as-indacene molecule.



Scheme 1. Synthesis of **2** from **1** and triplet O_2 .

2. Results and Discussion

Exposure of yellow-colored and rapidly stirred MeCN solutions of the dicyclopentadienyl dipotassium salt complex *ansa*- $[(\text{CHBu}^t)_2(\text{Ph}_2\text{C}_5\text{H}_2)_2]\text{K}_2(\text{THF})_3$ **1** [8] to pure O_2 (1 atm) resulted in a rapid color change to an intense green with the deposition of a white solid within 2 min. With continued stirring over 17 hrs, the intense green color faded to a dark brown with lighter colored solids in the reaction mixture. Isolation of **2** from the reaction mixture was carried out by filtration of the light-brown-colored solids, followed by extraction of the solids with toluene under N_2 . Removal of toluene from the extract under vacuum left 4,5-di-*tert*-butyl-1,3,6,8-tetraphenyl-4,5,8a,8b-tetrahydro-as-indacene **2** as an off-white crude solid product in a 73% yield (Scheme 1). The ^1H NMR spectrum of crude **2** showed the exclusive formation of one product with well-resolved PhH resonances, a pair of sharp singlet peaks for the tetrahydro-as-indacene core protons CHBu^t and CHC (2 H each, δ 3.31 and 3.66), one singlet peak for two cyclopentadienyl ring H 's (2H, δ 6.95), and one peak for the Bu^t group (18H, δ 0.87) and revealed the C_2 -symmetric structure of **2**. The extraction of **2** into toluene left an orange-colored solid by-product trapped in celite. The by-product was identified as KO_2 contaminated with unidentified organics due to the observed reactivity of the by-product with water, its paramagnetism, and comparison of the FTIR spectrum of the by-product to an authentic sample of KO_2 (Figures S6 and S7, Supplementary Materials). Based upon the identification of KO_2 in the by-product, we suggest that this reaction proceeds via a bridged diradical (bis)superoxo intermediate (**1A**, Scheme 1). The intermediate **1A** forms by dioxygen-mediated one-electron oxidations of each of the diphenyl cyclopentadienyl rings, and subsequently collapses to the product **2** by loss of KO_2 and radical coupling between the rings (Scheme 1). A single-crystal X-ray diffraction study of **2** was carried out (Figures S13–S19, Tables S1–S6, Supplementary Materials) and revealed the tetrahydro-as-indacene structure resulting from the formation of a new C–C bond (Figure 1, C8A–C8B 1.568(2) Å) between the two formerly 1,3-diphenylcyclopentadienyl radicals of intermediate **1A** (Scheme 1). Each resulting diphenylcyclopentadiene ring is fused to a central six-membered ring locked into a chair conformation via double bonds at C3A (C3–C3A 1.357(2) Å) and C6A (C6–C6A 1.360(2) Å) and single bonds at C8B (C1–C8B 1.523(2) Å) and C8A (C8–C8A 1.518(2) Å) (Figure 1). The trigonal planar bond angles around C3A and C6A as well as the tetrahedral angles around C4, C5, C8A, and C8B are consistent with those expected for a tetrahydro-as-indacene core (Figure 1). Crystalline **2** obtained from both *i*PrOH and 2-butanol exhibits ambient light fluorescence and obvious green fluorescence under long-wave UV light (Figures S3 and S4, Supplementary Materials). Although the color of the ambient light fluorescence of **2** obtained from *i*PrOH and **2** obtained from 2-butanol appears slightly different (Figures S3 and S4, Supplementary Materials), a separate single-crystal X-ray diffraction study of a crystal of **2** grown from 2-butanol (Figure S23 and Table S7, Supplementary Materials) showed the same structure as the crystal obtained from *i*PrOH (vide infra), with no changes in molecular parameters or packing arrangement (Figures S20–S22, Supplementary Materials). The crystal structure data indicates that differences in ambient light fluorescence between crystalline **2** obtained from *i*PrOH compared to 2-butanol are not due to the solid-state molecular structure or packing effects, but more likely due to differences in crystallite size in the bulk samples. Thermal analysis of crystalline **2** (from *i*PrOH) gave SDT and DSC thermograms that showed an

exotherm (onset 189.72 °C) followed by a melting transition (257.91 °C) and decomposition (Figures S8 and S9, Supplementary Materials). Visual inspection of the residue in the DSC pan after controlled pyrolysis to 220 °C showed a color change to yellow. Analysis of the yellow residue by ^1H NMR (CDCl_3) showed the presence of a small amount of unreacted **2** along with more significant peaks in chemical shift regions consistent with the conversion of **2**, presumably via Diels–Alder chemistry (Figures S10 and S11, Supplementary Materials). More detailed investigations of the photophysical and thermal properties of **2** as well as the chemistry of **2** as a ligand for bimetallic complexes are the subject of ongoing research in our lab.

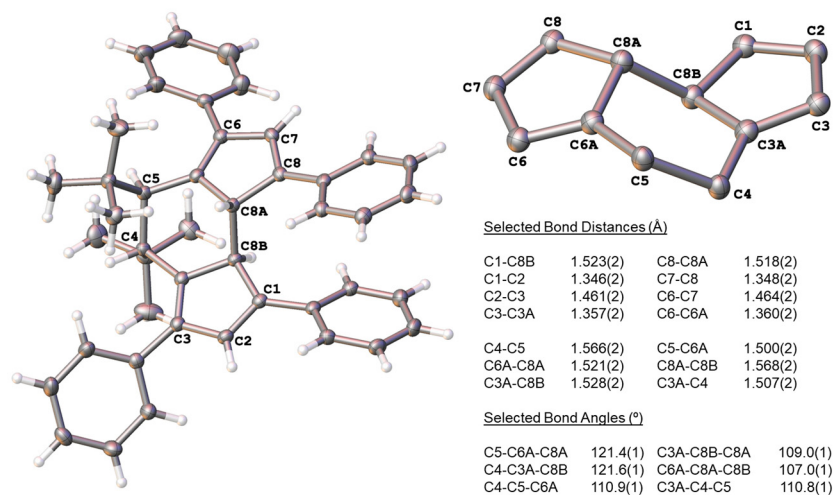


Figure 1. Thermal ellipsoid view of the molecular structure of **2** (left) with a depiction of the tetrahydro-as-indacene core framework (right) and selected bond distances and angles. Thermal ellipsoids are shown at the 50% probability level.

3. Materials and Methods

Chemicals and solvents were purchased as reagent-grade through commercial suppliers. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Jeol 500 MHz spectrometer. Chemical shifts were reported in parts per million (ppm), and the solvent peaks were used as internal references: proton (residual CHCl_3 δ 7.26), and carbon (CDCl_3 , $\text{C}\{\text{D}\}$ triplet, δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet), integration, and assignment. Infrared spectra were recorded using a Thermo Scientific Nicolet iS50 FTIR spectrometer in ATR mode. The determination of the paramagnetism of **2** was carried out at room temperature using a benchtop Sherwood Scientific Mark 1 magnetic susceptibility balance. Simultaneous differential thermal analysis (SDT) was carried out using a TA Instruments SDT650 instrument. Differential scanning calorimetry (DSC) thermograms were obtained using a TA Instruments DSC2500 instrument. The single-crystal X-ray diffraction study of **2** was carried out at 100.01(12) K using $\text{Cu K}\alpha$ radiation (1.54184 Å) on a Rigaku Synergy-i dual source (Mo, Cu) diffractometer, equipped with a Bantam HyPix-3000 direct photon counting detector. The data were integrated using the CrysAlisPro software program (Rigaku Oxford Diffraction, 2020, 1.171.42.49) [9] and scaled using an empirical absorption correction implemented in the SCALE 3 AB-SPACK software program as well as a numerical absorption correction based on Gaussian integration over a multifaceted crystal model. Structure solution and refinement were carried out in Olex2 (version 1.5) [10] using direct methods (SHELXT-2014/5) [11] and full-matrix least-squares (SHELXL-2016/6) [12]. All non-hydrogen atoms were refined anisotropically, and all carbon-bonded hydrogen atoms were placed using a riding model with their positions constrained relative to their parent atom using the appropriate HFIX command in SHELXL.

Synthesis of 4,5-Di-tert-butyl-1,3,6,8-tetraphenyl-4,5,8a,8b-tetrahydro-as-indacene 2

To a yellow-colored and vigorously stirred solution of **1** (2.23 g, 2.57 mmol) in dry MeCN (30 mL) under vacuum, pure O₂ was admitted at 1 atm pressure using a Hg bubbler system. The color faded from yellow to brown and then to an intense green color within 2 min as white solids began precipitating from the reaction mixture. The O₂ pressure was maintained at 1 atm for 1 h, then isolated from the bubbler and left to stir for 17 h, producing a dark-brown-colored reaction mixture containing lighter-colored solids. The reaction mixture was filtered under N₂ using a medium-porosity glass frit and gave a light brown filter cake and a dark-brown-colored filtrate. The filter cake was washed with dry MeCN (20 mL) and vacuum-dried to give a light brown solid (1.45 g). Extraction of the light brown solid with toluene (20 mL) under N₂, followed by filtration of insoluble salts over celite, evaporation of the toluene, and vacuum drying, gave the crude product **2** as an off-white-colored solid (1.07 g, 73%), which was >95% pure (¹H NMR). ¹H NMR (CDCl₃): δ 0.87 (s, 18 H, Bu^t); 3.31, 3.66 (s, 4H, CHCPh and CHBu^t); 6.95 (s, 2H, cyclopentadiene ring CH); 6.76, 6.83, 7.31, 7.43 (t, 12H, Ph ring meta- and para-H); 7.10, 7.59 (d, 8H, Ph ring ortho-H). ¹³C NMR (CDCl₃): δ 29.5, 36.9, 44.4, 57.6 (C(Me)₃, C(Me)₃, CHBu^t, CHCPh); 125.6, 125.8, 126.6, 127.8, 128.1, 128.4, 135.0, 137.1, 138.1, 139.4, 146.6, 149.4 (6-membered ring C, cyclopentadiene ring CH and CPh, PhC and PhCH). FTIR (ATR, cm⁻¹): 3078, 3055, 3023 (Ph ring and cyclopentadiene ring ν-CH); 2960, 2945, 2901, 2864 (aliphatic ν-CH); 1597, 1575, 1544, 1493, 1471, 1442 (overlapping, Ph ring and cyclopentadiene ring ν-CC); 1394, 1366, 1354, 1319, 1298, 1215, 1184, 1155, 1146, 1076, 1031, 1021, 1001, 967, 920, 909, 902, 894, 882, 871, 841, 774, 767, 754, 717, 692, 667, 661, 650, 638, 618, 577, 562, 541, 491. Crystalline **2** was obtained from hot iPrOH and 2-butanol by slow cooling and evaporation as well as from 50/50 THF/MeOH or from the 50/50 THF/MeOH MeCN layer (Figure S12, Supporting Information). CAUTION! The paramagnetic, orange-colored by-product that is left over after extraction of **2** into toluene consists of a mixture of KO₂, celite, and unidentified organics (Figures S6 and S7, Supplementary Materials) and is extremely reactive and shock-sensitive. It is imperative that this material be handled with extreme care in order to avoid exposure to heat, shock, or friction. The best post-synthetic protocol is to carry out the controlled hydrolysis of the by-product followed by disposal of the residue in accordance with local hazardous waste regulations.

Supplementary Materials: For compound **2**: ¹H, ¹³C NMR spectra (Figures S1–S4), FTIR (ATR) spectrum (Figures S5 and S5A), photos of the physical appearance of crystalline **2** as well as fluorescence of **2** under long-wave UV (Figures S3 and S4), SDT, and DSC thermograms (Figures S8–S10), physical appearance and ¹H NMR spectrum of possible Diel-Alder adduct of **2** (Figure S11), microscopic images of crystal samples of **2** (Figure S12), and full details of the single-crystal X-ray diffraction study of **2** (for **2** obtained from both iPrOH (Figures S13–S19, Tables S1–S6) and 2-butanol (Figures S20–S23, Table S7). Separate crystallographic information files for **2** obtained from iPrOH and 2-butanol. For the by-product: comparison of the FTIR spectrum of the by-product with KO₂ and celite, and magnetic susceptibility balance data for the by-product (Figures S6 and S7).

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Data Availability Statement: Crystallographic data for **2** were deposited in the Cambridge Crystallographic Data Center (CCDC) as deposition number 2263159. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (accessed on 15 May 2023) or by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: +44-1223-336033.

Conflicts of Interest: The authors declare no conflict of interest.

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