

RESEARCH ARTICLE

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A cobalt complex of a microbial arene oxidation product

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Abstract

We report the first synthesis of a cobalt Cp diene complex wherein the diene is derived by microbial dearomatising dihydroxylation of an aromatic ring. The complex has been characterised crystallographically and its structure is compared to that of an uncomplexed diene precursor.

Background

The dearomatising dihydroxylation of an aromatic substrate by a microorganism was first reported by Gibson in 1968 [1]. The production and utilisation of these arene-derived diols in synthesis has since become established methodology, not least because in most instances the oxidation of substituted arenes gives enantiopure diols. The field has been the subject of several extensive reviews [2-8]. To date, over 400 arene *cis*-diols have been reported. The great majority of these are produced by organisms expressing toluene dioxygenase (TDO), naphthalene dioxygenase (NDO) and biphenyl dioxygenase (BPDO) enzymes. These oxidise substituted arenes in a regio- and stereoselective fashion. A robust predictive model has been developed by Boyd *et al.* for these transformations [9] and the sense of enantioinduction is conserved across organisms and substrates (Scheme 1 (a), *ortho-meta* oxygenation). However, organisms that express benzoate dioxygenase (BZDO) enzymes oxidise benzoic acids in a process that exhibits not only different regioselectivity, but also the opposite absolute sense of enantioinduction. For example, *R. eutrophus* B9 [10], *P. putida* U103 [11] and *P. putida* KTSY01 (pSYM01) [12] oxidise benzoic acid to benzoate 1,2-*cis* dihydrodiol **4** (Scheme 1(b), *ipso-ortho* oxygenation). Substituted benzoic acids can also be oxidised by BZDO [13-17].

Diol acid **4** and its derivatives have been employed in several synthetic contexts. Widdowson was the first to establish the absolute configuration of **4** and employ it

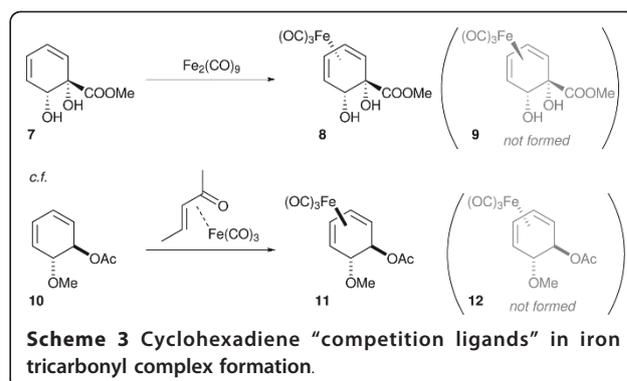
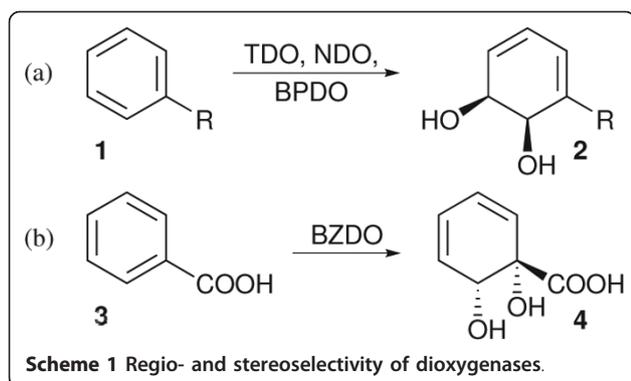
in [4+2] cycloadditions [18] and Mihovilovic subsequently reported tethered cycloadditions [19,20]. Applications of **4** in carbohydrate chemistry have been reported by Parker [21] and by us [22]. Myers has reported the synthesis of a useful library of chirons from **4** [23] and their application in the total synthesis of tetracyclines [24,25]. The Hudlický route to idesolide [26] and our route to grandifloracin [27] also employ **4** as a chiral pool starting material for total synthesis.

Apart from isolated uses of organotin derivatives in cross-coupling [28-30] and formation of a zinc metal-organic framework [31], the organometallic chemistry of microbial arene dihydrodiols has been dominated by iron complexes. The more common *ortho-meta* diols of type **2** have been employed by Stephenson [32-39], Pearson [40], Suemune [41] and Mombrú [42] in the formation of tricarbonyliron(0) diene complexes. These complexes have proven to be useful in synthesis [43,44]. As shown in Scheme 2, the *endo* isomer (that in which the metal is complexed to the ligand face bearing the hydroxyl groups) is the only diastereoisomer obtained in each instance. This may be rationalised due to the Lewis basic nature of the hydroxyl groups, which serve to coordinate the incoming metal fragment, thus directing it to the same face of the diene.

We have recently explored iron diene complexation in the context of *ipso-ortho* arene dihydrodiol **4** and its derivatives and found that complexation of a tricarbonyliron fragment to methyl ester **7** affords solely the isomer in which the hydroxyls are *endo* and the ester is *exo* (**8**, Scheme 3) [45]. This result is noteworthy, since in contrast to **5**, ligand **7** presents Lewis basic functionality on both sides of the ring. Accordingly, we have

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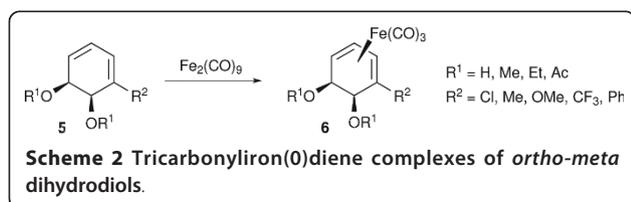


termed **7** a "competition ligand" and concluded from the exclusive formation of **8** that a diol is a much more effective directing group than a methyl ester. Literature precedent for cyclohexadiene ligands able to act as competition ligands in tricarbonyliron complexation was limited to a single report from Berchtold [46]. It was reported that complexation of **10** gave **11** as the sole product, implying that the acetoxy functionality is a markedly better site of coordination for the incoming iron fragment than the methyl ether.

Encouraged by the uses of arene dihydrodiols in iron complexation described above, we sought to explore the chemistry of group **9** complexes of these ligands. Specifically, a cobalt cyclopentadienyl complex of an arene dihydrodiol would be isolobal with the corresponding tricarbonyliron complex [47], yet display distinct reactivities in certain cases. Such group **9** complexes of arene dihydrodiols have not been reported previously. Vollhardt has reported cobalt complex **13** [49] and Maitlis has reported iridium complex **14** [49] (Figure 1), yet these were not accessed by direct complexation of a cyclohexadiene diol; rather, they derive from double nucleophilic additions of methoxide anion to the corresponding dicationic η^6 complexes of benzene.

Results

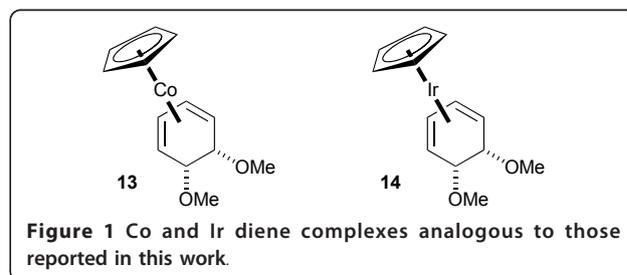
Four compounds were considered as potential ligands for cobalt (Scheme 4). Acetonide methyl ester **16** may be synthesised by two reported routes which differ in the order of events [15,18,23]. Formation of the methyl ester first gives **7**, the diol of which may then be protected to give **16**. Alternatively, formation of the acetonide gives **15**, which may then be readily esterified to **16**

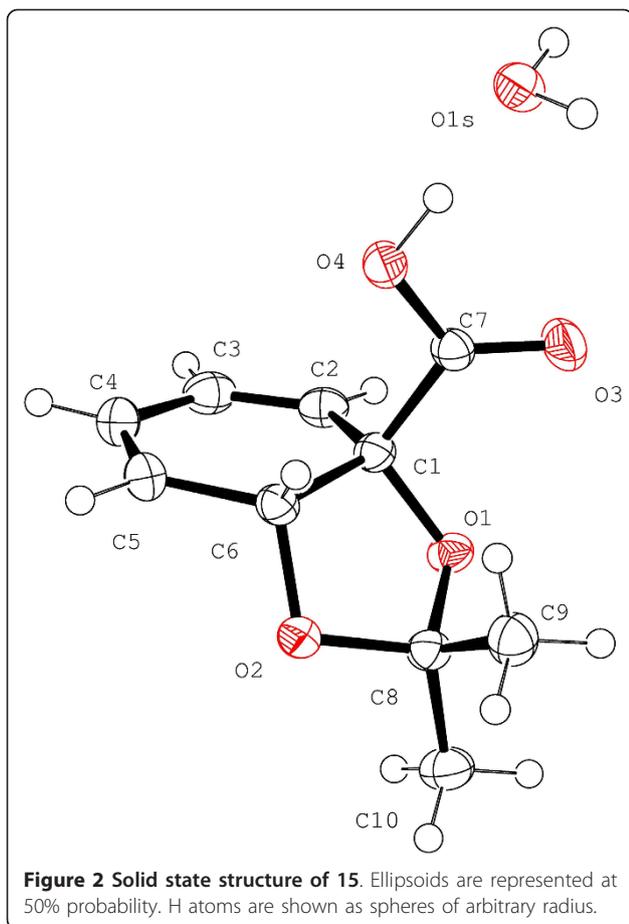


(Scheme 4). Either route affords **16** in near-quantitative yield. We were able to crystallise **15** as its monohydrate and determine its molecular structure by single crystal x-ray diffraction (Figure 2, Table 1 Additional file 1).

Dienes **4**, **7**, **15** and **16** are all viable ligands for CpCo complex formation. Our primary focus was acetonide ester **16**, for two reasons. Firstly, we had previously observed free acid **4** to form an intractable mixture when we attempted the synthesis of its iron tricarbonyl complex, with methyl esters proving more amenable to complexation. Secondly, we wished to ascertain whether the presence of the acetonide in **16** would favour complexation on the upper ligand face, in contrast to **8** [51]. Furthermore, it should be noted that diene rearrangements upon complexation have been described for analogous cobalt complexes; Vollhardt has proposed the intermediacy of η^5 cyclohexadienyl cobalt complexes to account for the rearrangement of tethered amines [52] and enol ethers [53], further developing this chemistry to effect a concise total synthesis of strychnine [54,55].

Our initial attempts at forming diene complexes involved CpCo(CO)₂ as a precursor, which was exposed to UV light in the presence of diene ligand, in order to effect photodissociation of the carbonyl ligands. This approach did not furnish any products, however, and an approach employing ClCo(PPh₃)₃ and NaCp as precursors was similarly unsuccessful. We then turned to use of Jonas' reagent, CpCo(C₂H₄)₂ (**17**), which is able to undergo ligand exchange with dienes and loss of two molar equivalents of ethylene [56]. Reaction of **16** and





17 in toluene at room temperature afforded novel cobalt complex **18**, in which the metal was indeed complexed to the upper ligand face, but no alkene isomerisation had occurred (Scheme 5). Crystallisation of **18** from hexane afforded crystals suitable for X-ray structure determination (Figure 3, Table 1).

Discussion

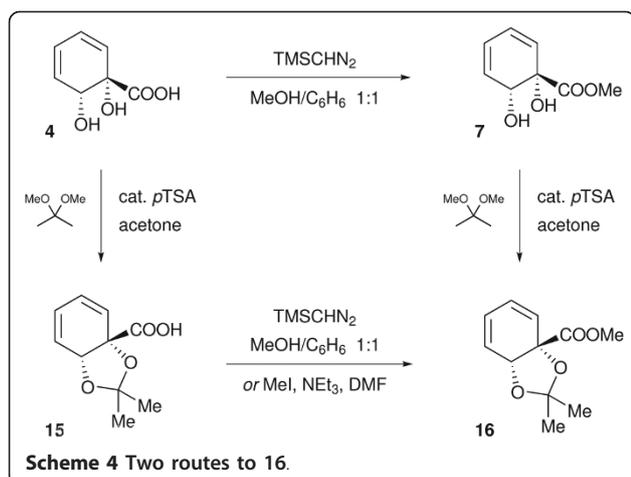
With structures in hand for both uncomplexed and complexed dienes **15** and **18** we are able to compare the two. To our knowledge, this is the first time a direct comparison of a CpCo cyclohexadiene complex and an uncomplexed diene precursor has been made, since for other reported CpCo cyclohexadiene crystal structures, no structures of their precursors are available.

It is immediately evident that complexation to Co effects a major change in the conformation of the cyclohexadiene ring. Whereas the uncomplexed ligand **15** possesses a near-planar cyclohexadiene ring, in **18** this ring adopts a boat conformation. Specifically, the C2-C3-C4-C5 diene motif remains near-coplanar (dihedral angle of 2.7(3)° in **18** and -6.5(2)° in **15**), but the two sp^3 hybridised atoms (C1 and C6) are significantly out

Table 1 Crystal data and structure refinement for compounds **15** and **18**

Compound	15	18
CCDC Number	838051	838052
Empirical formula	C ₁₀ H ₁₄ O ₅	C ₁₆ H ₁₉ CoO ₄
Formula weight	214.21	334.24
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	8.1060(1)	7.3050(1)
<i>b</i> /Å	10.241(3)	8.6650(1)
<i>c</i> /Å	12.952(4)	23.568(3)
α /°	90	90
β /°	90	90
γ /°	90	90
<i>U</i> /Å ³	1075.19(5)	1491.80(3)
<i>Z</i>	4	4
<i>D_c</i> /gcm ⁻³	1.323	1.488
μ /mm ⁻¹	0.106	1.163
<i>F</i> (000)	456	696
Crystal size/mm	0.20 × 0.15 × 0.10	0.24 × 0.20 × 0.12
Theta min., max for data collection	3.98, 30.51	7.88, 30.53
Index ranges	-9 ≤ <i>h</i> ≤ 11; -14 ≤ <i>k</i> ≤ 14; -18 ≤ <i>l</i> ≤ 18	-10 ≤ <i>h</i> ≤ 10; -12 ≤ <i>k</i> ≤ 12; -31 ≤ <i>l</i> ≤ 33
Reflections collected	19801	27485
Independent reflections, <i>R</i> _{int}	3116, 0.0380	4488, 0.0474
Completeness	$\theta = 30.51^\circ$, 96.4%	$\theta = 30.53^\circ$, 97.5%
Max., min. transmission	0.9894, 0.9790	0.8731, 0.7678
Data/restraints/parameters	3116/0/151	4488/0/267
Goodness-of-fit on <i>F</i> ²	1.031	1.203
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0322, 0.0712	0.0299, 0.0654
Final <i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0419, 0.0754	0.0333, 0.0663
Absolute structure parameter [50]	0.1(7)	-0.007(12)
Largest diff. peak, hole/eÅ ⁻³	0.185, -0.172	0.353, -0.268

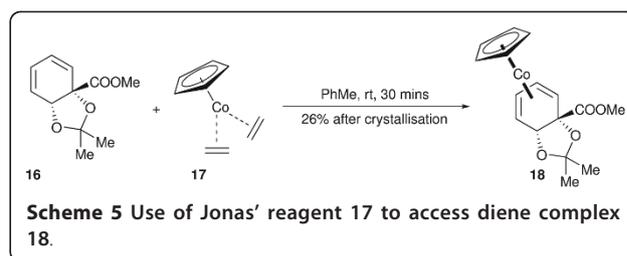
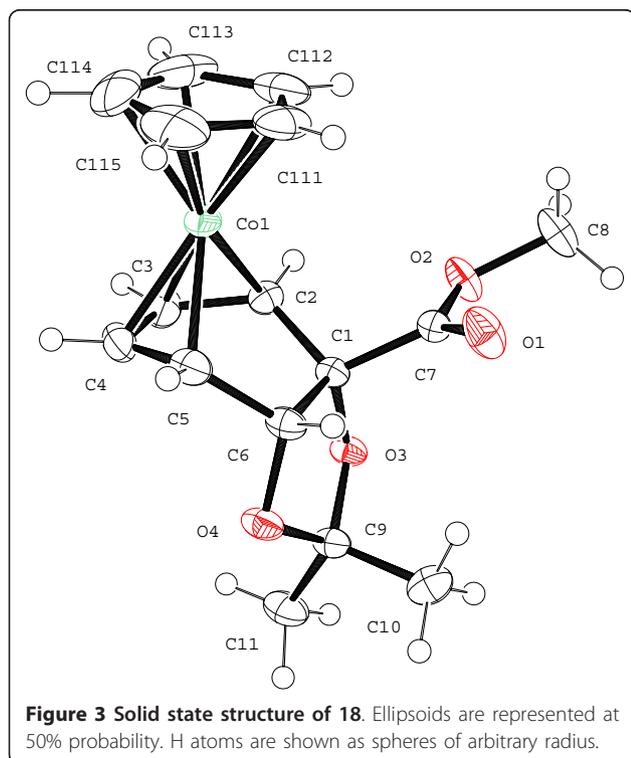
of plane in **18** (dihedral angles of 41.8(2)° for C1-C2-C3-C4 and 42.9(3)° for C3-C4-C5-C6 in **18**, compared with 1.7(2)° and 4.0(2)° in **15**). A consequence of this is that in complex **18** the lower face of the cyclohexadiene ring is subject to additional steric hindrance due to the acetamide *endo* methyl group. This is evidenced by the shorter distance between this carbon and C3 or C4 (**18** has C3-C11 4.572(3) Å and C4-C11 4.709(3) Å, whereas in **15** the corresponding distances are 5.160(2) Å and 5.296(2) Å). The effect on Co complexation on the C-C bond order in the cyclohexadiene ring is also clearly visible. In uncomplexed **15**, C2-C3 and C4-C5 are both 1.327(2) Å, whereas the formally single C3-C4 bond is appreciably longer at 1.463(2) Å. In contrast, in complex



18, bond lengths are 1.424(3) Å for C2-C3 and C3-C4 and 1.418(3) for C4-C5, *i.e.* equivalent within 3σ , as is preceded [47]. It should also be noted that in complex **18**, the η^5 -cyclopentadienyl and η^4 -diene ligands are not coplanar. Rather, the angle between the C2-C5 and C111-C115 planes is 8.40°.

Conclusions

We have prepared the first organocobalt complex derived from a product of microbial arene dihydroxylation and characterised it by crystallographic and other means. We are currently investigating synthetic applications of this complex and our results will be reported in due course.



Experimental

Synthesis of (+)- η^5 -Cyclopentadienyl(η^4 -(3aS,4S,7aS)-methyl 2,2-dimethyl-3a,7a-dihydrobenzo[d][1,3]dioxole-3a-carboxylate)cobalt(I) **18**

Diene **16** (301 mg, 1.43 mmol, 1 equiv) was dissolved in dry, degassed toluene (10 mL) in a side-armed Schlenk that had been purged and refilled with argon three times. The resulting solution was added *via* cannula to η^5 -cyclopentadienylbis(ethylene)cobalt **17** (258 mg, 1.43 mmol, 1 equiv) and the mixture was stirred for 30 min at room temperature until the evolution of ethylene had ceased. The solvent was removed *in vacuo* and the solid residue was redissolved in a minimal amount of hexane and left to crystallise at -28°C for 48 h. Complex **18** was isolated as red-orange crystals (124 mg, 26%); m. pt. 118–120°C; $[\alpha]_D +42$ ($c = 1$, CH_2Cl_2); $^1\text{H-NMR}$ (300 MHz, C_6D_6 , Additional file 2) δ 5.44 (1H, d, $J = 5.0$ Hz, O-CH-), 5.09–5.04 (2H, m, $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$), 4.41 (5H, s, Cp-H), 3.53 (3H, s, O- CH_3), 3.14 (1H, dd, $J = 5.5, 1.0$ Hz, $-\text{CH}-\text{C}-\text{COOCH}_3$), 2.82 (1H, td, $J = 5.0, 2.0$ Hz, $-\text{O}-\text{CH}-\text{CH}-$), 1.42 (3H, s, C- CH_3), 1.28 (3H, s, C- CH_3) ppm; $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , Additional file 2) δ 174.9, 113.9, 82.1, 80.8, 79.8, 74.6, 51.6, 48.9, 48.6, 27.1, 25.6 ppm; ν_{max} (film) 2986, 2937, 1732, 1436, 1370, 1307, 1259, 1229, 1206, 1166, 1109, 1064, 1009, 888, 821, 762 cm^{-1} ; HRMS (+ve ESI-TOF) m/z calcd for $(\text{C}_{15}\text{H}_{20}\text{CoO}_4+\text{H})^+$, 335.0688, found 335.0694. Found: C, 57.58; H, 5.76. $\text{C}_{15}\text{H}_{20}\text{CoO}_4$ requires C, 57.49; H, 5.73%.

Methods

Reactions were carried out under an atmosphere of argon. Solvents were dried and degassed by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system. All reagents were purchased from the Sigma-Aldrich Chemical Co. or Fisher Scientific Ltd. and were used without further purification. IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT IR spectrometer with universal ATR sampling accessory, with absorbances quoted as ν in cm^{-1} . NMR spectra were run on a Bruker Avance 300 instrument at 298 K. Mass spectra were recorded with a micrOTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Bruker Daltonik). Specific rotations were recorded on an Optical

Activity AA-10 Automatic polarimeter with a path length of 1 dm. Concentrations (c) are quoted in g/100 mL.

Additional material

Additional file 1: Crystallographic data. Crystallographic data in CIF format for **15** and **18**.

Additional file 2: NMR Spectra. ¹H, ¹³C and 2D NMR spectra for complex **18**.

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Authors' contributions

SEL, ALJ and AJWS conceived the experiments. DvdW, TP and MAK synthesised all reported compounds. ALJ performed crystallographic studies. SEL wrote the manuscript. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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