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[5]Trovacenol, (η^7-C_7H_7)V(η^5-C_5H_4OH): Synthesis and Structural Characterization[†,1]

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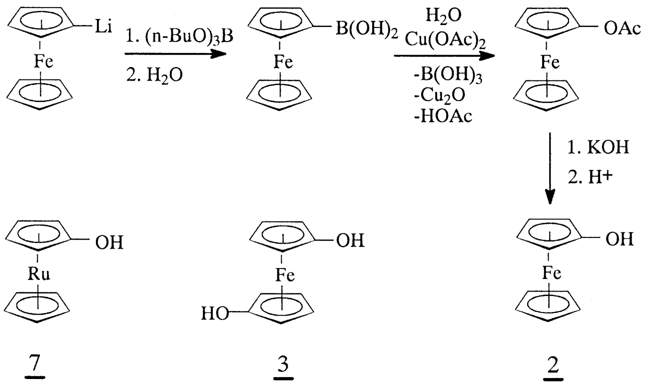
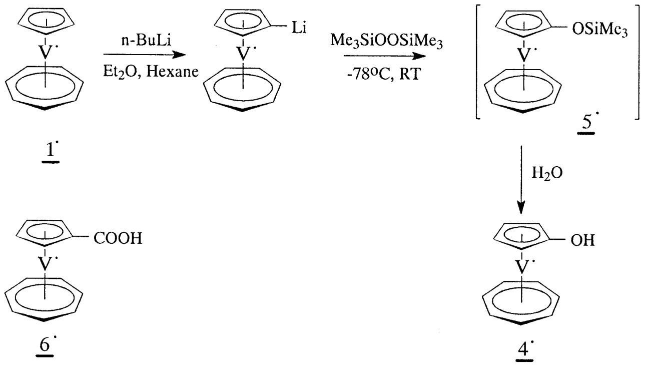
*Summary: [5]Trovacenol (**4**$^\bullet$) prepared according to the sequence (C_7H_7)V(C_5H_5) (**1**$^\bullet$)→ (C_7H_7)V($C_5H_4OSiMe_3$) (**5**$^\bullet$) → (C_7H_7)V(C_5H_4OH) (**4**$^\bullet$) in the crystal adopts a sheet structure. The sheets consist of parallel chains of hydrogen bonds, graph set C(4), to which the [5]trovacenyl groups are connected, forming double layers. Packing of the trovacene units on both sides of the (···O−H···O−H···)$_n$ spines displays a herringbone pattern. In this way O−H···O as well as (C_7H_7)H···π(C_5H_5) hydrogen bonding is optimized. This study represents the first full structural characterization of a metallocenol.*

Exploring the chemistry of a class of organometallic compounds, in our case that of (η^7-C_7H_7)V(η^5-C_5H_5) (trovacene; **1**$^\bullet$)[1] calls for the preparation of fundamental functional derivatives to be used in follow-up reactions. For ferrocene this has given rise to an immense number of organic compounds containing one or several ferrocenyl moieties. Interestingly, ferrocenol, (η^5-C_5H_5)Fe(η^5-C_5H_4OH) (**2**), although first prepared by Nesmeyanov in 1959,[2] has not been used that much over the years. However, as Herberhold[3] has demonstrated not too long ago, ferrocenol (**2**) and 1,1′-ferrocenediol (**3**) may serve as starting materials for a large variety of interesting products. Our occupation with oligonuclear trovacenes has therefore led us to attempt the synthesis of [5]trovacenol, (η^7-C_7H_7)V(η^5-C_5H_4OH) (**4**$^\bullet$), to be used as a reagent to generate terminal trovacenyl units in spacered [5.5]bi- and [5.5.5]tertrovacenes. Apart from its potential use as an educt, [5]trovacenol (**4**$^\bullet$) is also of interest in view of its hydrogen-bonding characteristics, which should govern the crystal structure.[4] Furthermore, hydrogen bonding may give rise to a monomer ⇌ dimer equilibrium in fluid solution with attendant exchange coupling of the two paramagnetic centers, as exhibited by [5]trovacenecarboxylic acid, (η^7-C_5H_7)V(η^5-C_5H_4COOH).[5] We here report on the low-yield synthesis of **4**$^\bullet$, which permits answering the latter type of questions.

Scheme 1



Scheme 2



Results and Discussion. Synthesis and Redox Properties. It became clear immediately that the Nesmeyanov route to ferrocenols (Scheme 1), air-sensitive compounds of low thermal stability, fails in the case of trovacene. Most likely, Cu^{II}, introduced in the form of the reagent Cu(OAc)$_2$, and V^0 in (η^7-C_7H_7)V(η^5-C_5H_5) (**1**$^\bullet$) are incompatible. This was not too surprising in view of the redox potentials, $E_{1/2}[(C_5H_5)_2Fe^{+/0}] = 0.49$ V and $E_{1/2}[(C_5H_5)V(C_7H_7)^{+/0}] = 0.26$ V vs SCE, which should render trovacenols even more vulnerable than ferrocenols. An alternative path to ferrocenols consists of the reaction of ferrocenyllithium with bis(trimethylsilyl)peroxide[3] and subsequent desilylation. Application of this protocol to trovacene (**1**$^\bullet$) afforded [5]trovacenol (**4**$^\bullet$),, albeit in very low yield (Scheme 2). As yet we have been unable to reproducibly isolate the intermediate [5]-trimethylsiloxytrovacene (**5**$^\bullet$). The new complex **4**$^\bullet$ is a red-violet solid which can be recrystallized from benzene/pentane at 8 °C to yield violet air-sensitive platelets suitable for X-ray diffraction analysis. Even in the

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[†] Dedicated to Max Herberhold on the occasion of his retirement from the University of Bayreuth.

(1) Trovacene Chemistry. 5. Part 4: Elschenbroich, C.; Wolf, M.; Schiemann, O.; Harms, K.; Burghaus, O.; Pebler, J. Submitted for publication in *Organometallics*. The number in brackets indicates the site of peripheral substitution: [5]trovacenyl derivatives are functionalized at the cyclopentadienyl ligand and [7]trovacenyl derivatives at the cycloheptatrienyl ligand.

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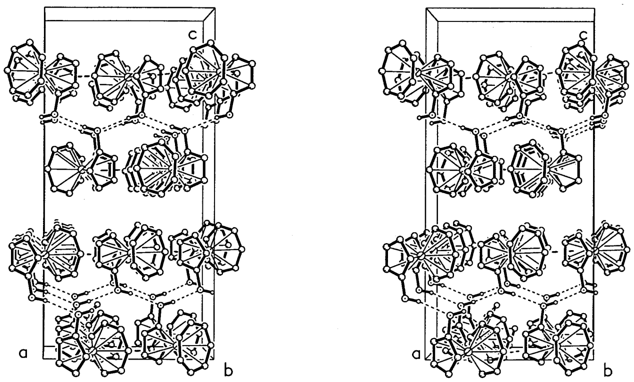

Figure 1. Stereoplot of the unit cell of [5]trovacenol ($\mathbf{4^•}$) (SHELXTL drawing).

absence of oxygen, solutions of $\mathbf{5^•}$ decompose at room temperature within days, depositing a pale yellow material. Interestingly, in the EI-MS the peaks for $C_7H_7V^+$ and $C_5H_4OH^+$ appear with similar intensity, whereas in sandwich complexes containing ligands of different size the larger perimeter ligands are usually eliminated preferentially.[6] This indicates that substitution of H for OH considerably weakens the V−Cp bond, which is in line with the lability of [5]trovacenol. Cyclic voltammetry performed on $\mathbf{4^•}$ points to reversible oxidation, the potential $E_{1/2}(\mathbf{4}^{+/0}) = 0.11$ V signifying a 150 mV cathodic shift relative to parent $\mathbf{1^•}$ (vs SCE, in DME, (n-Bu)$_4$NClO$_4$ at −40 °C, $v = 100$ mV/s). The latter may explain the low yield of $\mathbf{4^•}$ in that the intermediate $\mathbf{5^•}$ suffers oxidative decomposition, competing with Li/OSiMe$_3$ exchange. Reduction of $\mathbf{4^•}$ is irreversible; the cathodic peak appears at $E_{p,c}(\mathbf{4}^{0/-}) = -2.20$ V. Possibly, discharge of the slightly acidic proton of the OH group renders the reduction chemically irreversible. Electrochemical data for the ferrocenols, which would be interesting for comparison, have not been reported as yet.

X-ray Diffraction. Figure 1 presents the packing of $\mathbf{4^•}$ in the unit cell. In Figure 2 intermolecular interactions are detailed and the numbering scheme is given; important bond distances and angles are provided in the caption. Not surprisingly, in view of the platelike habit of the material, a sheet structure is adopted by $\mathbf{4^•}$. The crystal structure of [5]trovacenol therefore differs fundamentally from that of [5]trovacenecarboxylic acid ($\mathbf{6^•}$),[5] where hydrogen-bonded dimers are encountered in the crystal, as well as from that of parent trovacene, which is governed by close packing.[7] The individual sheets in $\mathbf{4^•}$ consist of double layers of trovacenyl units which are held together by parallel zigzag chains of hydrogen bonds, the latter conforming to the C(4) graph set in the Etter terminology.[8] In this way, corrugated layers of hydrogen bonds are created. Trovacenyl groups on the same side of the $(\cdots O-H\cdots O-H\cdots)_n$ chain are arranged according to a herringbone pattern, typical for the packing of small aromatic hydrocarbons;[9] pairs of trovacenyl groups on opposite sides of the chain alternate between syn and gauche conformations. Consequently, two differing hydrogen bond lengths are observed, a shorter one, O(1)−H(1)···O(1′A) = 2.89 Å, which links gauche-oriented trovacene pairs and a longer one, O(1′)−H(1′)···O(1) = 2.96 Å, which applies to syn-oriented trovacene couples. Both values are fairly large compared to the prototypical parameter for hydrogen bonding in phenol, which amounts to O−H···O = 2.70 Å.[10] The fact that two different lengths are present in the structure of $\mathbf{4^•}$ suggests, however, that they do not represent the inherent strength of the hydrogen bond in this system; rather, other factors which govern the mutual approach of the trovacene units along the chain must also be considered. As depicted in Figure 2, the herringbone type of packing permits or is even caused by interactions of slightly positively charged hydrogen atoms of a η^7-C_7H_7 ligand with the electron-rich π-electron system of an adjacent η^5-C_5H_5 ligand. The actual packing within a chain therefore reflects the simultaneous optimization of the hydrogen-bonding variants O−H···O and C−H···π-(C_5H_5). To evaluate the strength of the C−H···π(C_5H_5) interaction in the present case, it is instructive to

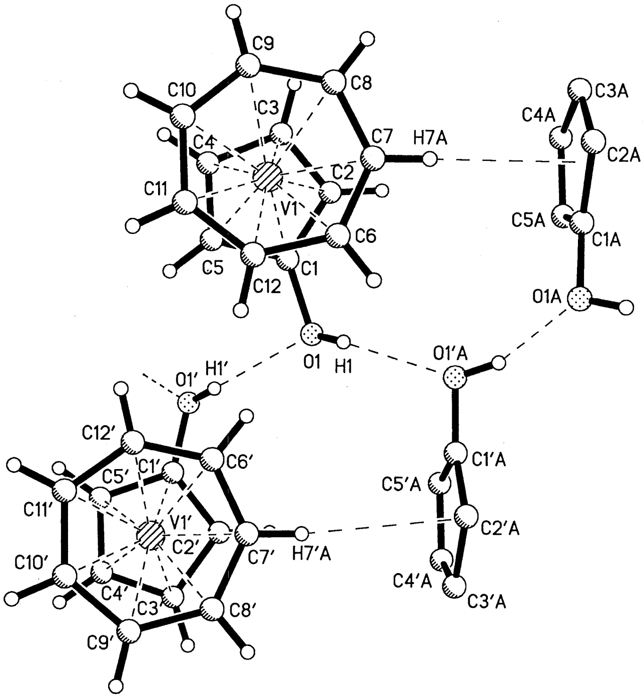

Figure 2. Excerpt from one of the strings of hydrogen-bonded [5]trovacenol units which comprise a double layer. The different kinds of intermolecular interactions are indicated, and the numbering scheme is given. Selected bond lengths (Å): C−C(Cp, mean), 1.394(15); C−C(Tr, mean), 1.400(15); V(1)−C_7, 2.151(14)−2.208(11); V(1)−C_5, 2.246(10)−2.281(9); C_7(centroid)−V(1), 1.457(1); C_5(centroid)−V(1), 1.927(4); C′−C′(Cp, mean), 1.397(15); C′−C′(Tr, mean), 1.394(17); V(1′)-C'_7, 2.128(11)−2.237(11); V(1′)-C'_5, 2.228(9)−2.280(8); C'_7(centroid)−V(1′), 1.467(1); C'_5(centroid)−V(1′), 1.916(5); Intermolecular parameters (Å): O(1′)−H(1′)···O(1), 2.955(13); O(1)−H(1)···O(1′A), 2.889(13); C(7)−C_5A(centroid), 3.607(10); H(7A)···C_5A(centroid), 2.700; C(7′)-C'_5A(centroid), 3.696(11); H(7′A)···C'_5A(centroid), 2.790.

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consult a Cambridge Structural Database (CSD) search performed for X−H···π (X = O, N, C) hydrogen bonds in organometallic crystals.[11] From this search it is seen that the C−H···π(C_5H_5) bond encountered in crystalline **4**$^\bullet$ may be placed in the stronger bracket, values between 2.5 Å (very few examples) and 3.0 Å (highest abundance) being listed. In the same compilation, the angles that the vector H···π(C_5H_5, centroid) makes with the plane of the aromatic system cluster around 80°. It is seen from Figure 2 that **4**$^\bullet$ complies with these values. The relative strength of the C−H···π(C_5H_5) interaction in **4**$^\bullet$ may reflect some "charge assistance" under the reasonable assumption that η^5-C_5H_5 bears a negative partial charge.[12]

Attempts to put these considerations into perspective suffer from the scarcity of structural information on hydroxymetallocenes; the only reported example in which an OH group directly bonds to a π-perimeter ligand is hydroxyruthenocene, (η^5-C_5H_5)Ru(η^5-C_5H_4OH) (**7**).[13] In contrast to **4**$^\bullet$ and **1**$^\bullet$, the crystal structure of **7** resembles that of parent ruthenocene; disorder which consists of a statistical distribution of the OH group over two half-occupied sites prevented an analysis of hydrogen bonding, however. For ferrocenol no X-ray structural study has been forthcoming. However, α-ferrocenyl alcohols, in which the OH group is separated from the Cp ring by an sp^3 carbon atom, show intra- and intermolecular hydrogen bonding as well as O−H···π-(C_5H_5) interactions.[14]

EPR Spectroscopy. The abundance of hydrogen bonds in crystalline **4**$^\bullet$ inspired us to seek for monomer ··· oligomer equilibria in fluid solution. As demonstrated previously for the case of [5]trovacenecarboxylic acid, (η^7-C_7H_7)V(η^5-C_5H_4COOH) (**6**$^\bullet$),[5] the hyperfine pattern of the EPR spectrum should provide hints in that it would be modified by electron−electron spin−spin exchange interaction. However, EPR performed on scrupulously aprotic solutions of **4**$^\bullet$ failed to reveal any deviation from the spectrum expected for monomeric **4**$^\bullet$. Therefore, either hydrogen bonding is too weak to generate the dimer (**4**$^\bullet$)$_2$ in a concentration detectable by EPR or the lifetime of (**4**$^\bullet$)$_2$ is short on the $a(^{51}V)$ hyperfine time scale. The EPR parameters for **4**$^\bullet$ (fluid solution, $g = 1.983$, $a(^{51}V) = -7.06$ mT; rigid solution, $g_x = 1.973$, $g_y = 1.975$, $g_z = 1.996$, $A_x(^{51}V) = -10.00$ mT, $A_y(^{51}V) = -10.06$ mT, $A_z(^{51}V) = -1.22$ mT) deviate only marginally from those of the parent [5]trovacene (**1**$^\bullet$). Apparently, the +M and −I effects of the peripheral OH substituents cancel, thereby leaving the electronic structure of trovacene virtually unperturbed.

Future work will entail the synthesis of the [5]-trovacenol precursor [5]trimethylsiloxytrovacene (**5**$^\bullet$) by the method of Plenio,[15] starting from cyclopent-2-enone in order to hopefully increase the yield of the target molecule **4**$^\bullet$.

Experimental Section. Chemical manipulations and physical measurements were carried out using techniques and instruments specified previously.[16] Trovacene was prepared from $C_5H_5V(CO)_4$[17b] according to the original procedure.[17a] Bis(trimethylsilyl)peroxide was synthesized as described previously.[18]

[5]Trovacenol, (η^7-C_7H_7)V(η^5-C_5H_4OH) (4$^\bullet$). To a solution of trovacene (**1**$^\bullet$; 390 mg, 1,88 mmol) in 120 mL of diethyl ether was added at room temperature 1.2 mL of a solution (1.55 M) of *n*-butyllithium in hexane. After the mixture was stirred for 14 h and cooled to −78 °C, bis(trimethylsilyl)peroxide (0.5 mL, 2.3 mmol) was added dropwise over 2 h. The mixture was warmed to room temperature and was stirred overnight. Water (2 mL) was added, and after 1 h the organic phase was separated and dried over $MgSO_4$. Filtration over Celite afforded a violet solution, which was brougth to dryness in vacuo. The residue was dissolved in 8 mL of hot toluene and subjected to column chromatography (Al_2O_3, 2 × 30 cm). Elution with petroleum ether/toluene followed by diethyl ether yielded the first violet band, containing unreacted **1**$^\bullet$. Elution with tetrahydrofuran generated a second pale yellow band of unknown nature. Elution with ethanol furnished a third purple band of the product [5]trovacenol. Recrystallization from benzene/petroleum ether at 8 °C afforded 20 mg (4% yield) of **4**$^\bullet$ as violet platelets. MS (EI, 70 eV): *m/z* (relative intensity) 223 (M^+, 100), 142 ($C_7H_7V^+$, 8), 132 (C_5H_4-OH^+, 11), 129 (C_6H_6+, 10), 116 ($C_5H_5V^+$, 4). Anal. Calcd for $C_{12}H_{12}OV$ (223.06): C, 64.61; H, 5.38. Found: C, 64.11; H, 5.98. For EPR and CV data, see text.

X-ray Crystallographic Study of 4$^\bullet$. The crystal analyzed proved to be a racemic twin; refinement led to the twin ratio 0.54(8). Positional disorder of both types of hydroxy groups is present such that a minor fraction (16% and 8% occupancy) is bonded to C(5) and C(5′), respectively. All hydrogen atoms have been refined on calculated positions using a riding model where the parameters C−H = 0.93 and O−H = 0.84 Å were adopted. The choice of the O−H orientation has been based on the criterion of forming the best hydrogen bond.

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Supporting Information Available: Tables giving crystal data and details of the structure determinations, positional and thermal parameters, and all bond distances and angles for **4**$^\bullet$. This material is available free of charge via the Internet at http://pubs.acs.org.

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