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Synthesis, characterisation and molecular structure of [Rh(COE)$_2$(acac)] (COE = cyclooctene, η^2-C_8H_{14}), an important starting material for the preparation of rhodium catalyst precursors

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Dedicated to Professor Martin A. Bennett on the occasion of his 65th birthday

Abstract

The compound [Rh(COE)$_2$(acac)] (**1**) is a catalyst precursor in its own right, and a starting material for the preparation of other catalyst precursors for use in a variety of reactions such as hydroboration, diboration and the addition of arylboronic acids to aldehydes. Although a preparation using Tl(acac) and [Rh(COE)$_2$(μ-Cl)]$_2$ is in the literature, it would appear that it is not widely known and we have received several requests for our synthetic protocol for **1**, which does not use any thallium salts. We present herein a synthesis of **1** from [Rh(COE)$_2$(μ-Cl)]$_2$ and Na(acac), along with its full spectroscopic and structural characterisation. The single crystal X-ray structure of **1** indicates approximate square-planar geometry at Rh, with the two olefinic C=C bonds lying perpendicular to the square plane.

Keywords: Rhodium; Catalyst; Olefin; Acetylacetonate; Boronic acid; Hydroboration

1. Introduction

Complexes of the form [Rh(β-diketonate)L$_2$], where L = alkene, phosphine, or phosphite and β-diketonate = acetylacetonate (acac), trifluoroacetylacetonate (tfacac) and hexafluoroacetylacetonate (hfacac), have received considerable attention as catalyst precursors[2] or starting materials for the synthesis of catalyst precursors for a variety of reactions including, for example, alkene hydroboration [1,2] and diboration [3–5], CO_2 hydrogenation [6–8], hydroformylation [9], and the addition of arylboronic acids to aldehydes [10], or in stoichiometric and structural studies [11,12]. Often, the [Rh(CO)$_2$(acac)] [9,11,12] or [Rh(η^4-COD)(β-diketonate)] (COD = 1,5-yclooctadiene, C_8H_{12}) [14,15] complexes are used as precursors to the [Rh(R$_3$P)$_2$-(β-diketonate)] reagents, and formation of [Rh(R$_3$P)$_4$]$^+$ [(β-diketonate)]$^-$ can be a significant side reaction with the latter.[3] One of the problems stems from the competing lability of the bidentate COD and β-diketonate ligands. With [Rh(CO)$_2$(acac)] the limited lability of the second CO ligand can cause problems.

For some time, we have employed [Rh(η^2-COE)$_2$(acac)] (**1**) (COE = cyclooctene = C_8H_{14}) both as

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[2] A 'catalyst precursor' is the compound added to a reaction mixture that forms the 'active catalyst' under the reaction conditions.

[3] Note added in proof: A recent paper describing the displacement of both hfacac and COD from [Rh(COD)(hfacac)] by bidentate phosphines has now appeared [38].

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a catalyst precursor in its own right [2] and as an extremely efficient means by which to prepare $[Rh(PR_3)_2(acac)]$ systems which we have shown can be converted cleanly to zwitterionic $[Rh(PR_3)_2(\eta^6\text{-catBcat})]$ (cat = 1,2-$O_2C_6H_4$) catalyst systems by treatment with B_2cat_3 or excess HBcat [1–5,16].

Quite recently, Ueda and Miyaura demonstrated [10] the efficiency of a catalyst for the addition of $ArB(OH)_2$ to RCHO, which was prepared in situ by addition of one equivalent of $^t Bu_3P$ to **1**.

Addition of excess phosphine inhibits the reaction, and thus the active species is presumably a mono-phosphine rhodium complex suggesting the importance of having monodentate labile ligands such as COE, in contrast to COD.

In 1985, Bennett and Mitchell reported [17] the use of **1** in a reaction with a secondary phosphite yet in this paper they reported only an outline of the synthesis and provided no characterisation of **1** itself. In 1996, Esteruelas et al. [13] used **1** synthesised by the published procedure [18] for $[Ir(\eta^2\text{-COE})_2(acac)]$, which uses $[Ir(COE)_2(\mu\text{-Cl})]_2$ and Tl(acac), and yet again no details were provided. In fact, a procedure [19] for synthesising **1** using Tl(acac) was reported by Bennet and Patmore in 1971, along with some characterisation data. It would appear, however, that this original report is not widely known, and an alternative procedure avoiding the use of thallium salts would certainly be desirable for pharmaceutical applications. Indeed, we received several requests for information on our synthetic protocol for **1**. This prompted us to report herein a detailed and reliable procedure for preparing **1** without the use of thallium salts, along with its full spectroscopic and structural characterisation.

2. Experimental

2.1. General procedures

All reactions were carried out in a nitrogen atmosphere using Schlenk techniques or an Innovative Technology, Inc. System 1 glove box. Glassware was oven dried before transfer into the glove box. NMR spectra were recorded on Varian Inova 500 (^1H, HSQC) and Varian VXR 400 (^{13}C, DEPT) instruments. Proton and ^{13}C-NMR spectra were referenced to external $SiMe_4$ via residual protons in the deuterated solvents or solvent resonances, respectively. Elemental analyses were conducted in the Department of Chemistry at the University of Durham using an Exeter Analytical Inc. CE-440 Elemental Analyzer. The $[Rh(COE)_2(\mu\text{-Cl})]_2$ was prepared using published procedures [20], whereas the NaH (60% dispersion in mineral oil), and acetylacetone were used as purchased from Lancaster Synthesis and Aldrich Chemical Company, respectively. Toluene was dried and deoxygenated by passage through columns of activated alumina and BASF-R311 catalyst under Ar pressure using a locally modified version of the Innovative Technology, Inc. SPS-400 solvent purification system [21]. C_6D_6 and hexane were dried over potassium and sodium, respectively, and were distilled under nitrogen before use.

2.2. Synthesis of Na(acac)

A suspension of NaH, 60% in mineral oil, (1.63 g, 0.041 mol) was degassed and then added to hexane (150 ml) and cooled to −78 °C with stirring. A solution of acetylacetone (4.10 g, 0.041 mol) in hexane (50 ml) was added dropwise over a period of 10 min, to allow for the evolution of H_2, giving a white precipitate. The reaction mixture was then allowed to warm to room temperature and was stirred for 1 h after which the reaction mixture was filtered, washed with hexane, and the precipitate then dried in vacuo to yield 4.98 g (99.6%) of Na(acac) as a fine white powder. ^1H-NMR (CD_3CN): δ 4.99 (1H, CH), 1.69 (6H, CH_3). IR (Nujol, cm^{-1}): ν(acac) 1582, 1518. Found: C = 48.97, H = 5.94%. $C_5H_7O_2Na$ requires C = 49.18, H = 5.78%. N.B. This simple procedure yields rigorously dry Na(acac). Although hydrated Na(acac) is commercially available, and may be suitable for use in the preparation of **1**, a source of any moisture is undesirable for many catalytic reactions.

2.3. Synthesis of $[Rh(\eta^2\text{-COE})_2(acac)]$ (1)

To a mixture of $[Rh(COE)_2(\mu\text{-Cl})]_2$ (0.276 g, 0.385 mmol) and Na(acac) (0.094 g, 0.770 mmol) was added toluene (20 ml) and the reaction was warmed to 40 °C with stirring under N_2 for 3 h. The reaction mixture was filtered via filter cannula, to remove NaCl, and the toluene was removed in vacuo. The product was extracted into hexane, filtered through a thin pad of Celite®, and isolated by removal of the hexane in vacuo, yielding 0.263 g (81%) of **1** as a yellow powder. Single crystals suitable for X-ray diffraction were grown from hexane at −30 °C. ^1H-NMR (C_6D_6): δ 5.04 (s, acac CH), 2.51 (4H, olefin COE), 2.47 (4H, COE), 2.42 (4H, COE), 1.69 (6H, acac CH_3 + 4H, COE), 1.56 (4H, COE), 1.41 (8H, COE); $^{13}C\{^1H\}$-NMR: δ 185.3 (s, acac C=O), 99.1 (s, acac CH), 78.3 (d, J_{C-Rh} = 13 Hz, olefinic COE), 30.5 (s, COE), 28.2 (s, COE), 27.3 (s, acac CH_3), 27.0 (s, COE). IR (Nujol, cm^{-1}): ν(acac) 1620, 1510. Found: C = 59.10, H = 8.34%. $RhC_{21}H_{35}O_2$ requires C = 59.71, H = 8.35%.

2.4. Crystal structure determination

$C_{21}H_{35}O_2Rh$, $M = 442.40$, orthorhombic, $a = 17.736(3)$ Å, $b = 11.041(2)$ Å, $c = 20.520(3)$ Å, $V =$

4018(1) Å^3, $T = 150$ K, space group *Pbca* (No. 61), $Z = 8$, μ(Mo–K$_\alpha$) = 0.860 mm^{-1}, 28 186 reflections measured, 5767 unique ($R_{int} = 0.0219$) which were used in all calculations and 4801 greater than $2\sigma(I)$. The final $R(F)$ was 0.0295 ($I > 2\sigma(I)$ data) and the $wR(F^2)$ was 0.0745 (all data). A yellow crystal of dimensions $0.38 \times 0.32 \times 0.20$ mm^3 was used for the single crystal structure determination of **1**. Data were collected using graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$) on a Bruker SMART-CCD 1K detector diffractometer equipped with a Cryostream N_2 flow cooling device [22]. Series of narrow ω-scans (0.3°) were performed at several ϕ-settings in such a way as to cover a hemisphere of data to a maximum resolution of 0.70 Å. Cell parameters were determined and refined using the SMART software [23] from the centroid values of 946 reflections with 2θ values between 27 and 46°. Raw frame data were integrated using the SAINT program [24]. The structure was solved using Direct Methods and refined by full-matrix least-squares on F^2 using SHELXTL [25]. The reflection intensities were corrected by numerical integration based on measurements and indexing of the crystal faces, $T_{max} = 0.851$, $T_{min} = 0.770$. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters (adps). Hydrogen atoms were geometrically placed and allowed to ride on their parent C atom with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl hydrogens and $U_{iso}(H) = 1.2U_{eq}(C)$ for all others. Idealized C–H distances were fixed at 0.95 Å for the aromatic C–H, 0.98 Å for methyl groups, 0.99 Å for secondary –CH_2– groups and at 1.00 Å for tertiary C–H groups.

3. Results and discussion

Complex **1** was obtained in high yield by the reaction of Na(acac) and [Rh(η^2-COE)$_2$(μ-Cl)]$_2$ (**2**) in toluene with gentle heating at 40 °C for 3 h. Shorter times can result in incomplete reaction, whereas extending the reaction period often results in dark precipitates due to some decomposition of **2**, but these are easily removed by filtration through Celite®. Extraction into hexane followed by the removal of solvent yields **1** as a yellow–orange powder. The compound is stable in the solid state at ambient temperature, but there is evidence of decomposition after 24 h when in solution. Assignment of the ^{13}C{^{1}H}-NMR spectrum was aided by a DEPT [26] experiment, and showed singlets at δ 185.3 due to the C=O carbons on the acac group, a singlet at δ 99.1 due to the central carbon of the acac group, a doublet at δ 78.3 ($^1J_{C-Rh} = 13$ Hz) due to the olefin carbons of the COE ligands, singlets at δ 30.5, 28.2 and 27.0 due to aliphatic COE carbons, and a singlet at δ 27.3 for the acac methyl groups. The proton NMR spectrum shows a sharp peak at δ 5.04 due to the methyne proton on the acac group, but broad resonances at δ 2.51, 2.47, 2.42, 1.69, 1.56 and 1.41 due to the aliphatic and coordinated olefin COE and acac-CH_3 protons. A ^{1}H–^{13}C HSQC [27] experiment (Fig. 1) showed that the ^{1}H resonance at δ 5.04 is connected to the ^{13}C resonance at δ 99.1, for the central acac carbon atom, and the ^{1}H resonance at δ 2.51 is due to the coordinated olefin moiety, as it is connected to the ^{13}C doublet at δ 78.3, from the olefinic carbons. The ^{1}H resonances at δ 2.47 and 2.42 are both connected to the

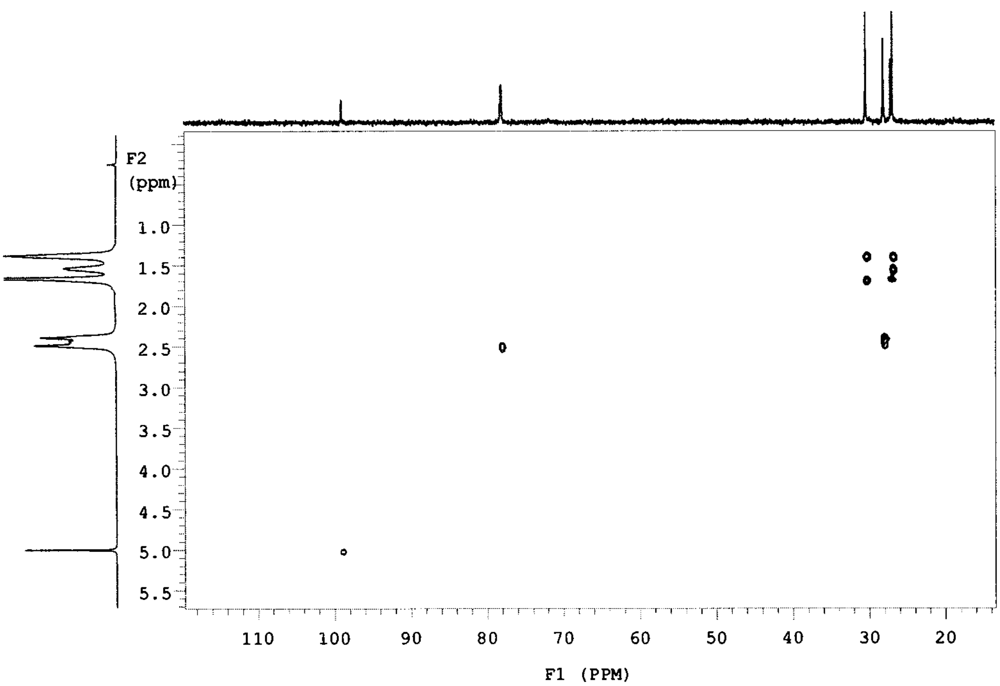

Fig. 1. The ^{1}H–^{13}C HSQC spectrum of **1**.

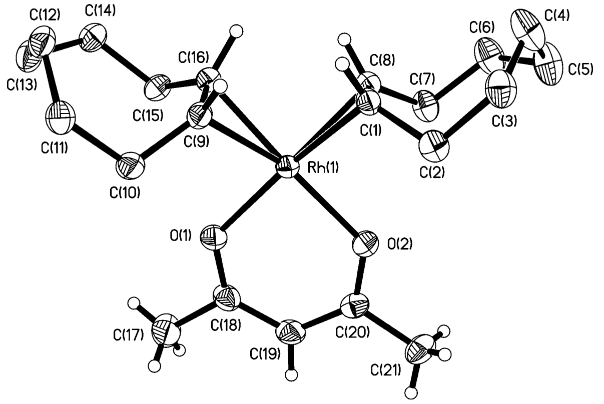

Fig. 2. ORTEP diagram for [Rh(COE)$_2$(acac)] (**1**), showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level for heavy atoms with selected hydrogens being represented by circles of arbitrary radius. Methylene hydrogen atoms on the COE ligands have been omitted for clarity. X(1A) and X(1B) are the mid-points of C(1)–C(8) and C(9)–C(16), respectively. Selected bond lengths (Å) and angles (°): C(1)–Rh(1) = 2.1325(18); C(8)–Rh(1) = 2.1347(19); C(9)–R(1) = 2.1298(19); C(16)–Rh(1) = 2.1417(18); X(1A)–Rh(1) = 2.005(13); X(1B)–Rh(1) = 2.009(14); O(1)–Rh(1) = 2.0624(14); O(2)–Rh(1) = 2.0652(13); X(1A)–Rh(1)–X(1B) = 93.4(6); X(1A)–Rh(1)–O(1) = 171.1(4); X(1B)–Rh(1)–O(1) = 90.1(4); X(1A)–Rh(1)–O(2) = 90.0(4); X(1B)–Rh(1)–O(2) = 171.7(4); O(1)–Rh(1)–O(2) = 87.69(9).

^{13}C resonance at δ 28.2, due to two sets of inequivalent (axial and equatorial) aliphatic COE protons. Next, the ^{1}H resonance at δ 1.69, integrating for a total of ten protons, is connected to ^{13}C resonances at δ 30.5 (four methylene COE protons) and δ 27.3 (six acac-CH_3 protons). Finally the ^{1}H resonance at δ 1.56 (four protons) is connected to the methylene ^{13}C resonance at δ 27.0, and the ^{1}H resonance at δ 1.41 (eight protons) is connected to methylene ^{13}C resonances at δ 30.5 and δ 27.0. The complicated nature of the ^{1}H-NMR spectrum is a result of coincidental overlap of various relatively broad resonances.

Compound **1** crystallises in the orthorhombic space group *Pbca*. The eight molecules in the unit cell are arranged in pairs related by an inversion centre, placing the bulky cyclooctene groups as far away from each other as possible.

The geometry around rhodium is approximately square-planar (Fig. 2), with angles X(1A)–Rh(1)–X(1B) = 93.6°, X(1A)–Rh(1)–O(2) = 89.4°, X(1B)–Rh–O(1) = 90.2° and O(1)–Rh–O(2) = 87.69(9)° (X(1A) = mid-point of C(1)–C(8), X(1B) = mid-point of C(9)–C(16), C(1), C(8), C(9), and C(16) being the olefinic carbons of the COE ligands). The planes defined by O(1)–Rh(1)–O(2) and X(1A)–Rh(1)–X(1B) are at an angle of 10.6° to each other. The distances from the rhodium atom to the centre of the C–C double bonds are 2.015 Å (Rh–X(1A)) and 2.017 Å (Rh–X(1B)). The deviations of the atoms from the plane defined by Rh(1), O(1), O(2), X(1A) and X(1B) are Rh(1): −0.0054 Å; O(1): 0.1342 Å; O(2): −0.1376 Å; X(1A): 0.1312 Å; X(1B): −0.1332 Å. The olefinic C=C bonds of the COE moieties are nearly perpendicular to this 'square plane': C(1)=C(8) is at 91.2° and C(9)=C(16) is at 91.1°.

A search of the Cambridge Structural Database [28] revealed that although there are 419 known examples with Rh–C_8-rings, only eleven of these are Rh–COE compounds. Of these, only nine [29–37] contain simple, unsubstituted COE ligands. The only bis(COE) compound [33], [Rh(COE)$_2$(η^5-*N*-methylpiperidin-4-yl-Cp)], has an X–Rh–X angle of 92.7°, with Rh–(C=C)-centroid distances of 2.013 and 2.023 Å, all of which are similar to compound **1**. The Rh–(C=C)-centroid distances for the other Rh–COE compounds range from 1.959 [34] to 2.069 Å [30].

In this paper, we have provided full details of the synthesis and characterisation of **1** which are expected to increase the availability of this useful compound for synthetic and catalytic applications.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 170713 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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