www.elsevier.nl/locate/jorganchem
Journal of Organometallic Chemistry 593–594 (2000) 494–496

Journal of Organo metallic Chemistry

Communication

Synthesis and X-ray crystal structure of decamethylrhodocenium hexafluorophosphate

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Received 2 September 1999; accepted 6 October 1999

Dedicated to Professor Fausto Calderazzo.

Abstract

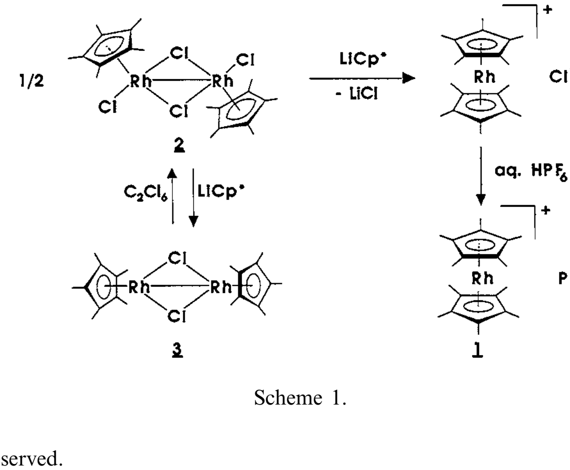
Decamethylrhodocenium hexafluorophosphate has been synthesized from $[RhCp^*Cl_2]_2$ and LiCp* ($Cp^* = \eta^5\text{-}C_5Me_5$), and its X-ray crystal structure shows a star-shaped, perfectly staggered geometry. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Metallocene; Decamethylmetallocene; Rhodocenium; Decamethylrhodocenium

1. Introduction

Since the discovery of transition-metal sandwich complexes [1], it has been understood that the use of permethylated ligands brings about considerable stabilization [2–7], especially for paramagnetic states [3–7]. However, although a number of first-row decamethylmetallocenes $[MCp^*_2]$ are known [2–7], second-row decamethylmetallocene chemistry is still poor [6–8]. In particular, no rhodocenium sandwich complex is known. We report here a new synthesis of decamethylrhodocenium [8] and the X-ray crystal structure determination of decamethylrhodocenium hexafluorophosphate (**1**).

The complex **1** was synthesized in THF by reaction of $[RhCp^*Cl_2]_2$ (**2**) [9], with LiCp* in 42% yield after metathesis using aqueous HPF_6 and recrystallization from acetone–ethanol. A side reaction is the reduction of **2** by LiCp* giving $[RhCp^*Cl]_2$, (**3**) [10]. However, **3** can be oxidized by C_2Cl_6 back to **2**, which can then be re-used (Scheme 1). This synthesis parallels that of decamethylbirhodocenium [11]. Suitable crystals for X-ray crystal structure analysis were obtained for the air and moisture stable complex **1** (see Section 2). Compound **1** has crystallographic inversion symmetry leading to a ‘star-shaped’ geometry (Fig. 1, top). Thus, the two Cp* rings are parallel and twisted by 36°, corresponding to a regular staggering. The Rh(III) center lies at a crystallographic center of symmetry, and it therefore occupies a position exactly in the middle of the axes connecting the centers of the planar rings. The distance from the rhodium to the rings is 1.81 Å. The



Scheme 1.

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PII: S0022-328X(99)00605-1

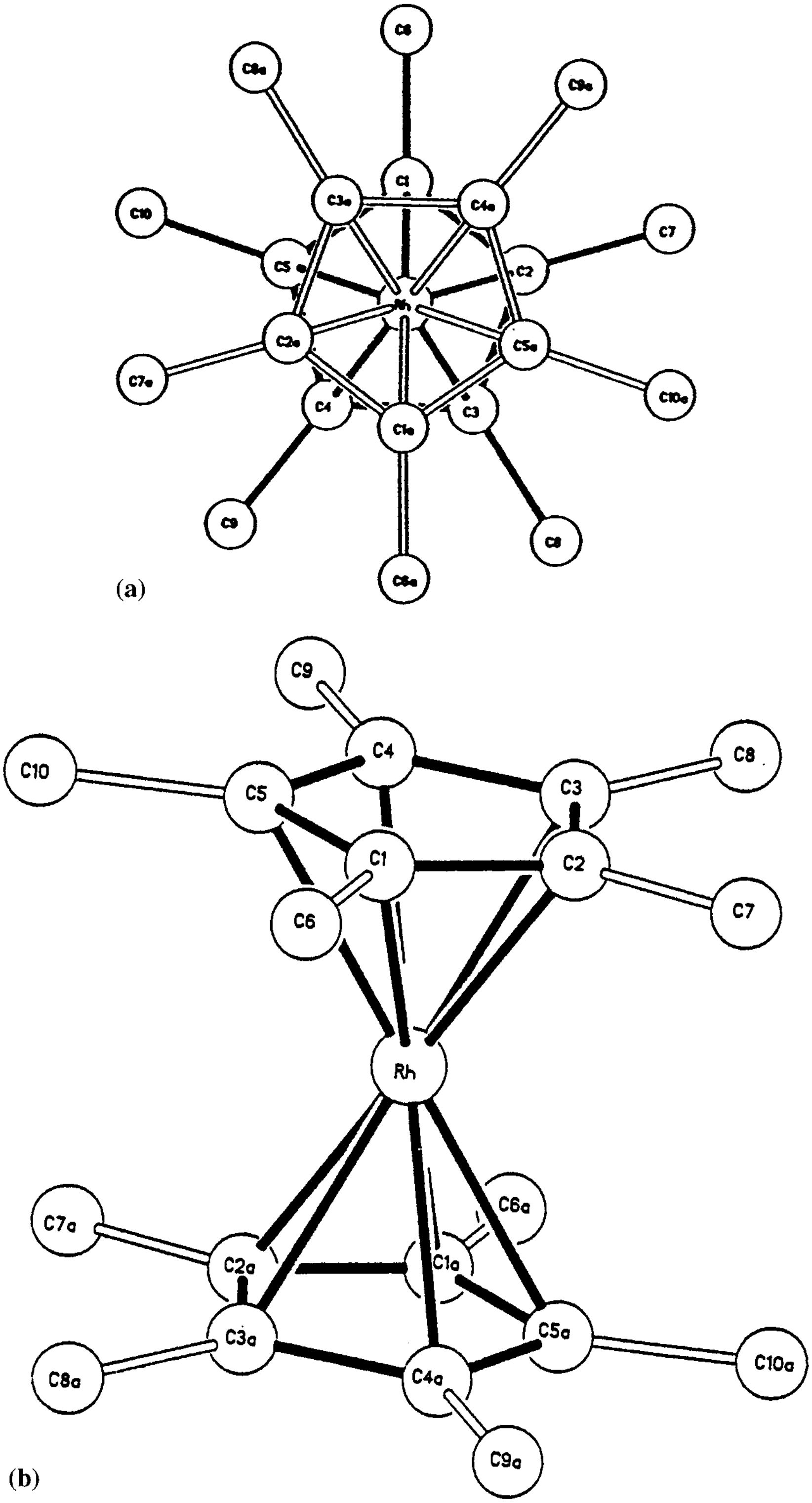

Fig. 1. X-ray crystal structure of [RhCp$^*_2$][PF$_6$] (**1**). (a) Top view: the twist angle between the two parallel Cp* rings is 36°, according to a perfectly staggered geometry. (b) Side view: mean Rh–C ring bond 2.180(0.005) Å; Rh-ring (centroid) distance: 1.81 Å. The mean angle between the Cp* ring and the exocyclic C–C bonds slightly bent away from the metal is 1.6°. The atom designator C_{ia} refers to a carbon atom that is related to carbon atom C_i by the crystallographic inversion symmetry.

methyl substituents on the rings are bent away from the metal. The mean angle formed by the carbons is 1.6° (Fig. 1).

The complex **1** is the starting point en route toward starburst reactions involving multiple C–C bond formation for the synthesis of dendritic cores [12]. It should also stimulate studies challenged by the instability of rhodocene [13–15].

2. Experimental

2.1. General data

All reactions of air and moisture-sensitive compounds were performed under an argon atmosphere employing Schlenk techniques and/or a Vacuum Atmosphere drylab. Reagent-grade tetrahydrofuran (THF), diethyl ether and pentane were predried over Na foil and distilled from sodium benzophenone ketyl under argon immediately prior to use. Hydrated rhodium chloride was used as received from Johnson–Mathey. $[RhCp^*Cl_2]_2$ was synthesized according to Moseley et al. [9]. ^{1}H-NMR spectra were recorded with a Brucker AC 200 (200 MHz) spectrometer. ^{13}C-NMR spectra were recorded in a pulsed Fourier transform mode at 50.327 MHz with a Brucker AC 200 spectrometer.

2.2. Synthesis of $[RhCp^*_2][PF_6]$

In a Schlenk flask, 0.35 g (0.64 mmol) of $[RhCp^*Cl_2]_2$ (**2**) and 30 ml of THF were introduced under argon. The solution was cooled to −10°C, then 0.182 g (1.28 mmol) of LiCp* was added, and this reaction mixture was stirred for 3 h at −10°C, then overnight at room temperature. The solvent was removed under reduced pressure. The ^{1}H-NMR spectrum in THF-d^8 shows the presence of both **1** and $[RhCp^*Cl]_2$ (**3**) in the ratio 1:1. Work up was achieved using 30 ml water, and addition of aqueous HPF_6 (1.3 mmol) provoked the precipitation of **1**. Filtration and recrystallization from acetone–ethanol provided 0.278 g (0.53 mmol, 42% yield) of **1** as colorless crystals. When C_2Cl_6 (64 mg, 0.27 mmol) was added to the reaction mixture in THF before work up, **3** was quantitatively oxidized back to **2** after 1 h at room temperature as indicated by the disappearance of **3** and the appearance of **2** in the ^{1}H-NMR spectrum [10]. Addition of LiCp* again (0.077 g, 0.054 mmol) at −10°C in THF followed by the procedure indicated above provided overall 0.384 g (0.73 mmol, 58% yield) of **3** after recrystallization from acetone/ethanol. ^{1}H-NMR (δ in ppm vs. $SiMe_4$, CD_3COCD_3): 1.84 ppm. ^{13}C-NMR (δ in ppm vs. $SiMe_4$, CD_3COCD_3): 9.5 (s, CH_3), 80.0 (d, ring C; $^1J_{^{103}Rh-^{13}C} = 8$ Hz).

2.3. X-ray crystal structure determination

The air-stable yellow X-ray quality crystals of **1** were obtained by crystallization from acetone–water. Crystal data: monoclinic $P2_1/n$ $a = 10.024$ (5) Å, $b = 8.425$ (6) Å, $c = 12.885$ (9) Å; $\beta = 90.33(5)°$; $V = 1088(1)$ Å^3; $Z = 2$; $T = 213$ K; Mo–K$_\alpha$; $R_1 = 0.036$, $R_2 = 0.037$ for 1250 observed reflections. Data collection on a Siemens (Nicolet, Syntex) R3m/V diffractometer at 223 K (see also Fig. 1 and Section 3).

3. Supplementary material

Tables of atomic, positional and thermal parameters, bond angles and general temperature factor expressions, tables of calculated and observed structure factors. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC 116611 for compound **2** and CCDC 116612 for compound **3**. 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; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We are grateful to DFG for a post-doctoral grant to DB and to Johnson–Matthey for the loan of $RhCl_3$ hydrate.

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