### Journal of Organometallic Chemistry 824 (2016) 166-171

Contents lists available at ScienceDirect

# Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

# Confirmation of the pentadienyl/alkyne [5 + 2] cycloaddition reactivity of the Cp\*Co( $\eta^5$ -1,2,5-trimethylpentadienyl)<sup>+</sup> complex

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# ARTICLE INFO

Article history: Received 8 August 2016 Received in revised form 5 October 2016 Accepted 6 October 2016 Available online 8 October 2016

Keywords: Cobalt Pentadienyl [5 + 2] cycloaddition Seven-membered ring

# 1. Introduction

Cycloaddition chemistry has found widespread application in organic synthesis, with continuous growth observed since the first reports of the [4 + 2] Diels-Alder reaction [1]. The modern development of metal-mediated cycloaddition mechanisms has permitted the creation of new reaction pathways that circumvent orbital symmetry restrictions limiting the application of classic pericyclic motifs. One example of such a mechanism is the metalmediated [5 + 2] cycloaddition reaction for synthesis of sevenmembered carbocycles [1e]. We have previously reported the pentadienyl/alkyne [5 + 2] cycloaddition reaction of half-sandwich Cp\*Co( $\eta^5$ -pentadienyl) cations **1** to yield  $\eta^2$ , $\eta^3$ -cycloheptadienyl complexes 2 under kinetic control (Scheme 1) [2,3]. Nonconjugated  $\eta^2$ ,  $\eta^3$ -cycloheptadienyl intermediates wherein  $R^1 = H$ isomerize to the thermodynamically favoured conjugated  $\eta^5$ cycloheptadienyl complexes 3 at elevated temperature. This isomerization is believed to occur via dissociation of the  $\eta^2$ -alkene with concomitant formation of an agostic hydride complex;  $\beta$ -hydride elimination and reinsertion complete isomerization [4]. When R<sup>1</sup> and  $R^2 \neq H$ ,  $\beta$ -hydride elimination is blocked, rendering the  $\eta^2$ ,  $\eta^3$ cycloheptadienyl complexes thermally stable [2b]. A wide range of

# ABSTRACT

The [5 + 2] cycloaddition reactivity of the Cp\*Co( $\eta^{5}$ -1,2,5-trimethylpentadienyl)<sup>+</sup> complex and ethyne has been demonstrated. This reactivity was predicted computationally and runs against previous synthetic observations of decreasing reactivity with increasing substitution. The pentadienyl complex and the resulting Cp\*Co( $\eta^{2}$ , $\eta^{3}$ -1,2,5-trimethylcycloheptadienyl)<sup>+</sup> species have been characterized spectroscopically and crystallographically. The X-ray structure of the pentadienyl complex has a dihedral angle between the two  $\eta^{5}$ -bound planes that falls within the range expected for reactivity (3.1(8)°), providing strong support for our computationally proposed structure/reactivity relationship.

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 $n^{5}$ -pentadienyl substitution patterns have been prepared [5a] and their [5+2] cycloaddition reactivity evaluated with both acetylene and 2-butyne [2]. The cycloaddition reactivity of cobalt- $\eta^5$ -pentadienyl complexes is highly dependent on the substitution pattern of the  $\eta^5$ -pentadienyl complex. Experimentally, it was observed that only substituents at the C1- and C5-positions are tolerated; all other substitution patterns tested (1,2-, 1,3-, and 1,4-disubstituted, and 1,2,4-trisubsituted) all proved unreactive [2]. Additionally, a substituent in the 1-position is mandatory, with the unsubstituted parent pentadienyl complex proving unreactive [2]. This structure/ reactivity relationship is believed to arise from a combination of  $\eta^5$ pentadienyl complex distortion and transition state strain. A dihedral angle between the two  $\eta^5$ -bound planes of less than *ca*. 7.6° is required for reactivity, with substituents in both the 1- and 5-positions producing the greatest effect by enforcing angles of less than 4° [4]. With the common theme in the synthetic studies being an observed decrease in reactivity with increasing substitution, we were surprised to find that density functional theory predicted  $Cp^*Co(\eta^5-1,2,5-trimethylpentadienyl)^+$  (**1a**) to be highly reactive towards acetylene [4]. Both the calculated transition state barrier for rate-limiting alkyne capture (23.9 kcal/mol) and the dihedral angle between the  $\eta^5$ -planes (3.67°) were in the predicted range for effective reactivity. Here we report our synthesis of Cp\*Co( $\eta^5$ -1,2,5trimethylpentadienyl)<sup>+</sup> complex **1a** and its reactivity with alkynes, providing strong support for our mechanistic proposal and structure/reactivity model.







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**Scheme 1.**  $\eta^5$ -Pentadienyl/alkyne [5 + 2] cycloaddition.

## 2. Results and discussion

We have previously reported the HBF<sub>4</sub>·OEt<sub>2</sub>-mediated synthesis of Cp\*Co( $\eta^5$ -pentadienyl)<sup>+</sup>-type complexes **1** from Cp\*Co(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> **4** with both nonconjugated (Scheme 2, Route A) and conjugated pentadienols (5 and 6) [5a,6]. We first explored the preparation of  $Cp^*Co(\eta^5-1,2,5-trimethylpentadienyl)^+$  **1a** from the nonconjugated (2E,5E)-3-methylhepta-2,5-dien-4-ol (5). As a trial synthesis we prepared 2-bromo-2-butenyl magnesium bromide from a 1:1 mixture of 2-bromo-2-butene stereoisomers and subsequently quenched with (E)-but-2-enal (Scheme 3). The resulting 3methylhepta-2,5-dien-4-ol product was formed as a 4:1 mixture of stereoisomers favouring the undesired (2Z,5E)-3-methylhepta-2,5-dien-4-ol. During Grignard reagent formation it is likely that a radical intermediate isomerized to the less sterically hindered vinyl magnesium halide product, which was subsequently trapped with the aldehyde [7]. The enrichment with the undesired isomer suggests that a stereochemically pure starting material (i.e., (E)-2bromobut-2-ene) will prove equally problematic, and we therefore turned our attention to preparation of the conjugated (3E.5E)-5-methylhepta-3,5-dien-2-ol (6) (Scheme 4). Sodium hydridemediated Horner-Emmons-Wadsworth reaction between triethylphosphonoacetate and tiglic aldehyde in THF first gave (2E,4E)ethyl 4-methylhexa-2,4-dienoate (7) [8]. Unexpectedly, the use of NaH as a suspension in mineral oil is essential for clean reactivity; if the suspension is first washed with hexane, as is commonly done, the reaction yields a complex mixture of unidentified products. Subsequent LiAlH<sub>4</sub> reduction yielded alcohol **8**, which was then oxidized with activated MnO<sub>2</sub> on carbon to provide aldehyde 9 [9,10]; addition of methyl magnesium bromide produces alcohol 6, completing the synthetic sequence.

Our original protocol for the preparation of  $Cp^*Co(\eta^5-$  pentadienyl)<sup>+</sup> complexes from conjugated pentadienol substrates



**Scheme 2.** Two routes for  $[Cp^*Co(\eta^5-1,2,5-trimethylpentadienyl)]BF<sub>4</sub> (1a) preparation.$ 



Scheme 3. Preparation of nonconjugated pentadienol 5 as a mixture of stereoisomers.



Scheme 4. Preparation of conjugated pentadienol 6.

entailed olefin exchange at elevated temperature, followed by HBF<sub>4</sub>·OEt<sub>2</sub> protonation at -78 °C. This procedure was intended to improve the yield of heavily substituted  $\eta^5$ -pentadienyl substrates, but little difference was observed [5a]. Therefore, to reduce procedural complexity, we chose to investigate pentadienyl synthesis analogous to Route A with conjugated dienols (Scheme 2, Route B). We were pleased to find that the reaction proceeds smoothly, giving a 78% yield of pentadienyl complex **1a**, which is in line with yields obtained for related complexes (the corresponding reaction from the pentadienol mixture 5 gave a poor yield of 20%). Crystallization via slow diffusion of diethyl ether into methylene chloride resulted in crystals suitable for X-ray diffraction. The solid state structure agrees well with that proposed computationally, with the key dihedral angle indicating a higher degree of co-planarity than predicted, measuring 3.1(8)° compared to a calculated value of 3.67° (Fig. 2) [4].

With the requisite pentadienyl complex in hand we turned our efforts towards its [5 + 2] cycloaddition reactivity (Scheme 5). Pentadienyl complex **1a** was dissolved in methylene chloride in a test tube and acetylene gas was bubbled through the system until saturation. The tube was sealed with a septum and allowed to react overnight. Removal of solvent and benchtop chromatography provided the  $\eta^2$ , $\eta^3$ -cycloheptadienyl complex **2a** in 87% yield as evidenced by NMR spectroscopy and X-ray crystallography. Cycloheptadienyl complex **2a** is stable at moderately elevated temperature (60–70 °C), similar to the analogous Cp\*Co( $\eta^2$ , $\eta^3$ -1,5-cycloheptadienyl)<sup>+</sup> complex previously reported [2b]. We also



**Scheme 5.** Preparation of  $[Cp^*Co(\eta^2, \eta^3-1, 2, 5-trimethylcycloheptadienyl)]BF<sub>4</sub> ($ **2a**).

investigated [5 + 2] cycloaddition with 2-butyne. Upon addition of 2-butyne and heating, we were surprised to find that the expected  $\eta^2$ , $\eta^3$ -cycloheptadienyl complex was not obtained, but rather conversion to an unidentified product mixture had occurred. This product instability is likely due to the high steric bulk of the  $\eta^2$ , $\eta^3$ -pentamethylcycloheptadienyl intermediate favouring ligand dissociation; similar difficulty occurs with the 2-butyne adduct of the Cp\*Co( $\eta^5$ -1,5-dimethylpentadienyl)<sup>+</sup> complex, with slow decomposition being observed in solution at room temperature [2b].

# 3. Crystallography

Pentadienyl complex **1a** was obtained as dark red rectangular needles through two-chambered liquid diffusion of  $Et_2O$  into a  $CH_2Cl_2$  solution (Fig. 1). Crystallographic details are compiled in Table 1. The crystal was multiply twinned and the  $BF_4^-$  ion was disordered. After the final refinement, residual electron density peaks were observed near the two carbon termini of the open pentadienyl ligand. These were each about 1 Å from the carbon atom and 0.3–0.4 eÅ<sup>-3</sup> in height. They appeared to be significant (though weaker than the main H peaks) yet a model could not be found to properly account for them. Whether the hydrogen atoms at the carbon termini were geometrically placed or refined, the same Fourier peaks were still observed.

The Cp\*Co( $\eta^2$ , $\eta^3$ -1,2,5-trimethylcycloheptadienyl)<sup>+</sup> complex **2a** was obtained as deep red plates through two-chambered liquid diffusion of Et<sub>2</sub>O into a CH<sub>2</sub>Cl<sub>2</sub> solution (Fig. 2). The structure was significantly disordered, with the BF<sub>4</sub> anion and the  $\eta^2$ , $\eta^3$ -cycloheptadienyl ligand being involved. The boron atoms of both anions are located on special positions. In one anion, the disorder was best described as an equal contribution from two orientations, while in the second anion refinement of the occupancy factor gave a 73/27 ratio of the two possible orientations. The seven-membered ring of the ligand was also modelled with a two-fold disorder. Refinement of the occupancy gave a 70/30 ratio of the two configurations. The ring can be coordinated to the cobalt through its two opposing faces, such that each orientation is numbered counter clockwise to the other (Fig. 3) [11].



**Fig. 1.** X-ray crystal structure of  $[Cp^*Co(\eta^{5}-1,2,5-trimethylpentadienyl)][BF<sub>4</sub>] ($ **1a** $) with non-hydrogen atoms represented by thermal ellipsoids drawn at the 20% probability level. Hydrogen atoms and the disordered <math>[BF_4]$  anion have been omitted for clarity. Final residuals: R1 = 0.0452, wR2 = 0.1093. Selected interatomic distances (Å): Co-C1, 2.160(3); Co-C2, 2.097(3); Co-C3, 2.047(3); Co-C4, 2.052(3); Co-C5, 2.219(3); C1-C2, 1.397(5); C2-C3, 1.403(5); C3-C4, 1.445(5); C4-C5, 1.381(5); C1-C6, 1.518(4); C2-C7, 1.522(4); C5-C8, 1.506(4). Selected angles (°): C1-C2-C3, 121.8(3); C2-C3-C4, 125.5(3); C3-C4-C5, 127.9(3).



**Fig. 2.** X-ray crystal structure of  $[Cp^*Co(\eta^2, \eta^3-1, 2, 5-trimethylcycloheptadienyl)][BF<sub>4</sub>] ($ **2a** $) with non-hydrogen atoms represented by thermal ellipsoids drawn at the 20% probability level. Hydrogen atoms, the disordered <math>[BF_4]$  anions, and the minor component of the disorder in the trimethylcycloheptadienyl ligand have been omitted for clarity. Final residuals: R1 = 0.0509, wR2 = 0.1559. Selected interatomic distances (Å): Co-C12, 2.115(10); Co-C13, 2.106(9); Co-C15, 2.199(13); Co-C16, 2.057(16); Co-C17, 2.198(11); C11-C12, 1.487(15); C12-C13, 1.346(16); C13-C14, 1.539(19); C14-C15, 1.518(18); C15-C16, 1.394(17); C16-C17, 1.371(15); C11-C17, 1.481(13); C11-C18, 1.493(14); C14-C20, 1.497(16); C15-C19, 11.530(19). Selected angles (°):C11-C12-C13, 127.5(12); C12-C13-C14, 120.0(12); C13-C14-C15, 102.1(9); C14-C15-C16, 124.8(13); C15-C16-C17, 126.0(14); C11-C17-C16, 129.2(12).

Table	1	
X-rav	crystallographic	details.

	1a	2a
formula	C <sub>18</sub> H <sub>28</sub> BCoF <sub>4</sub>	C <sub>20</sub> H <sub>30</sub> BCoF <sub>4</sub>
fw	390.14	416.18
Cryst. dimens. (mm)	$0.280\times0.070\times0.040$	$0.350\times0.200\times0.190$
Cryst. system	monoclinic	orthorhombic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	Pnn2 (No. 34)
unit cell param.		
a (Å)	7.6504(13)	14.720(2)
b (Å)	15.127(3)	15.047(2)
c (Å)	15.958(3)	8.9487(13)
$\beta$ (deg)	96.843(2)	
$V(Å^3)$	1833.7(5)	1982.1(5)
Ζ	4	4
$\rho_{calcd}$ (Mg m <sup>-3</sup> )	1.413	1.395
$\mu$ (mm <sup>-1</sup> )	0.970	0.902
total data	21243	23192
no. indep. reflns.	4470	4929
no. obsd. reflns.	3403	3223
goodness-of-fit (S)	1.033	1.018
final R indices		
$R_1$	0.0452	0.0509
wR <sub>2</sub>	0.1093	0.1559
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	0.437, -0.395	0.451, -0.215

# 4. Conclusion

We have demonstrated the [5 + 2] cycloaddition reactivity of Cp\*Co( $\eta^{5}$ -1,2,5-trimethylpentadienyl)<sup>+</sup> **1a** with acetylene, a computational prediction that ran against experimental observations of decreased reactivity with increased pentadienyl substitution. While cycloaddition with acetylene proceeded as expected to yield the Cp\*Co( $\eta^{2}$ , $\eta^{3}$ -1,2,5-trimethylcycloheptadienyl)<sup>+</sup> complex, reaction with 2-butyne led to an unidentified product mixture, possibly due to decomposition of the sterically hindered putative Cp\*Co( $\eta^{2}$ , $\eta^{3}$ -1,2,3,4,5-pentamethylcycloheptadienyl)<sup>+</sup> intermediate.



**Fig. 3.** X-ray crystal structure of  $[Cp^*Co(\eta^2, \eta^3-1, 2, 5-trimethylcycloheptadienyl)][BF_4]$  (**2a**) drawn to show the contributions of the two different ligand conformations. On the left is the major conformer (70%) on the right is the minor (30%). Thermal ellipsoids of the non-hydrogen atoms are drawn at the 20% probability level.

# 5. Experimental

Reagents and Methods. All manipulations on air and moisture sensitive compounds were performed under nitrogen atmosphere using standard Schlenk techniques or in a glovebox. Acetone was dried over boric oxide, degassed via three freeze-pump-thaw cycles, vacuum-transferred and stored under nitrogen. Diethyl ether was dried by passing through activated Al<sub>2</sub>O<sub>3</sub> (mBraun SPS). All other reagents were used without further purification. Flash column chromatography was performed with silica gel ( $40-63 \mu m$ ). IR spectra were recorded on a Brüker Platinum ATR with diamond crystal. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance300 (<sup>1</sup>H, 300 MHz; <sup>13</sup>C, 75 MHz) spectrometer. <sup>1</sup>H NMR chemical shifts are reported relative to residual protiated solvent. <sup>13</sup>C NMR chemical shifts are reported relative to the deuterated solvent. High-resolution mass spectra, performed by Mr. Xiao Feng of the DalChem Mass Spectrometry Laboratory at Dalhousie University, were obtained on a Brüker microTOF Focus Mass Spectrometer. Elemental analysis was performed by the Centre for Environmental Analysis and Remediation at Saint Mary's University using a Perkin Elmer 2400 Series II CHN Analyzer. Activated MnO<sub>2</sub> [10], (2E,4E)-4-methylhexa-2,4-dien-1-ol (8) [9], (2E,4E)-4methylhexa-2,4-dienal (9) [9], and  $Cp^*Co(C_2H_4)_2$  (4) [12] were prepared according to literature procedures. (2E,4E)-Ethyl 4methylhexa-2,4-dienoate (7) was prepared using a modification to a literature procedure by substituting unwashed 60% NaH suspension in mineral oil for KOtBu and purifying by silica gel chromatography using a gradient column of hexane, 1% EtOAC/hexanes, then 2% EtOAc/hexanes to ensure removal of the mineral oil, otherwise all procedural details were identical [8].

(3*E*,5*E*)-5-methylhepta-3,5-dien-2-ol (6). In a Schlenk flask under nitrogen, (2*E*,4*E*)-4-methylhexa-2,4-dienal (9) (1.05 g, 8.6 mmol) was dissolved in THF (50 mL) and cooled to -78 °C in a dry ice/acetone bath. To this solution, 3.0 M methyl magnesium bromide (3.45 mL, 10.3 mmol) was added via syringe. The solution was stirred for 30 min at -78 °C, then allowed to warm to room temperature. The reaction was quenched with saturated NH<sub>4</sub>Cl solution, extracted with diethyl ether, washed with brine, and dried over MgSO<sub>4</sub>. The solvent was removed under vacuum and the crude material purified by silica gel column chromatography with 20% EtOAC/hexane as eluent to yield 650 mg (54%) of product as a pale yellow oil. IR (neat, cm<sup>-1</sup>): 3347, 2970, 2922, 2861, 1650, 1448, 1394, 1379, 1367, 1350, 1331, 1300, 1146, 1082, 1056, 1027, 962, 940, 870, 853, 843, 797. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  6.23 (d, *J* = 15.7 Hz, 1H), 5.61 (dd, J = 15.7, 6.6 Hz, 1H), 5.58 (q, J = 6.6 Hz, 1H), 4.37 (quint, J = 6.4 Hz, 1H), 1.75 (s, 3H), 1.74 (d, 3H, obscured by other signal), 1.63 (br. s, 1H), 1.31 (d, J = 6.4 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  134.6, 133.8, 130.1, 127.3, 69.2, 23.5, 13.8, 12.0. Electrospray MS m/z calculated for C<sub>8</sub>H<sub>15</sub>O (M + H<sup>+</sup>): 127.1123; found: 127.0375.

 $[Cp^*Co(\eta^5-1,2,5-trimethylpentadienyl)]^+BF_4^-$  (1a). A Schlenk tube was charged with a solution of  $Cp^*Co(C_2H_4)_2$  (135 mg, 0.54 mmol) in acetone (~5 mL) in a glove box and equipped with a stir-bar and septum. The solution was removed to a Schlenk line, placed under a nitrogen atmosphere, and cooled to -78 °C. Tetrafluoroboric acid (54% in diethyl ether, 74 µL, 0.54 mmol) was added by syringe and the reaction was stirred at -78 °C for 10 min. A solution of (3E,5E)-5-Methylhepta-3,5-dien-2-ol (6) (68 mg, 0.54 mmol) in acetone (1 mL) was then added and the reaction was allowed to warm gradually to room temperature overnight (~16 h). The solvent was removed in vacuo and the crude product was purified by silica gel chromatography, eluting with a 3% methanol in dichloromethane mixture. Removal of solvent in vacuo afforded 1a as a red solid (165 mg, 78%) that was of suitable purity for use in subsequent reactions. Crystals suitable for diffraction analysis were grown via two-chambered liquid diffusion (Et<sub>2</sub>O into CH<sub>2</sub>Cl<sub>2</sub>). Compound **1a** decomposes slowly in solution, therefore only spectroscopic characterization was obtained. IR (filmcast,  $cm^{-1}$ ): 2967 (w), 2915 (w), 1474 (w), 1455 (w), 1429 (w), 1386 (m), 1092 (m), 1048 (s), 1031 (s), <sup>1</sup>H NMR (300 MHz, acetone- $d_6$ ):  $\delta$  6.41 (d, J = 7.24 Hz, 1H), 5.14 (dd, J = 12.7, 7.0 Hz, 1H), 2.78 (dq, J = 12.7, 6.4 Hz, 1H), 2.20 (s, 3H), 1.87 (s, 15H), 1.52 (d, J = 6.3 Hz, 3H), 1.42 (d, J = 6.4 Hz, 3H), 1.26 (m, 1H). <sup>1</sup>H-<sup>1</sup>H COSY (300 MHz, acetone- $d_6$ ):  $\delta$  6.41  $\leftrightarrow$   $\delta$  5.14;  $\delta$  5.14  $\leftrightarrow$   $\delta$  2.78;  $\delta$  2.78  $\leftrightarrow$   $\delta$  1.42;  $\delta$  1.52  $\leftrightarrow$   $\delta$  1.26. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 110.4, 99.1, 96.5, 94.1, 87.2, 73.7, 19.1, 17.4, 14.8, 9.2. Electrospray MS *m*/*z* calculated for C<sub>18</sub>H<sub>28</sub>Co (M<sup>+</sup>): 303.1523; found: 303.1504.

**[Cp\*Co**( $\eta^2$ , $\eta^3$ -**1**,**2**,**5**-trimethylcycloheptadienyl)]<sup>+</sup>BF<sub>4</sub> (2a). [Cp\*Co( $\eta^5$ -1,2,5-trimethylpentadienyl)]<sup>+</sup>BF<sub>4</sub> (**1a**) (165 mg, 0.42 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) in a test tube. Acetylene gas was then bubbled through the solution for 15 min in order to ensure saturation. The tube was sealed with a rubber septum and allowed to stand at room temperature overnight. The solvent was then removed *in vacuo* and the product purified by silica gel chromatography using 3% methanol in dichloromethane. The red fraction was collected and dried providing 153 mg (87%) of product as a thick, red oil. Crystals suitable for diffraction analysis were grown via two-chambered liquid diffusion (Et<sub>2</sub>O into CH<sub>2</sub>Cl<sub>2</sub>). IR (filmcast, cm-1): 2964 (w), 2918 (w), 2876 (w), 1456 (w), 1431 (w),

1384 (w), 1281 (w), 1260 (w), 1090 (m), 1045 (s), 1026 (s), 865 (w), 800 (m). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  3.53 (dd, I = 7.8, 3.3 Hz, 1H), 3.36 (d, J = 7.8 Hz, 1H), 2.45–2.25 (m, 4H), 1.81 (s, 18H, overlapping Cp\* and Me peaks), 1.50 (d, *J* = 6.6 Hz, 3H), 1.39 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 97.0, 90.4, 67.2, 54.3, 52.5, 50.1, 30.8, 27.3, 19.9, 19.2, 16.8, 9.6. Electrospray MS *m*/*z* calculated for C<sub>20</sub>H<sub>30</sub>Co (M<sup>+</sup>): 329.1680; found: 329.1676. Analysis calculated for C<sub>20</sub>H<sub>30</sub>CoBF<sub>4</sub>: C, 57.72; H, 7.27; found: C, 57.41; H, 7.16.

Crystallographic Experimental Details. X-ray structure measurements were made on a Bruker APEXII CCD equipped diffractometer (30 mA, 50 kV) using monochromated Mo Ka radiation  $(\lambda = 0.71073 \text{ Å})$  at 125 K [13]. The crystal chosen for each analysis was attached to the tip of a 400 µm MicroLoop with paratone-N oil. For each determination, the initial orientation and unit cell were indexed using a least-squares analysis of a random set of reflections collected from three series of  $0.5^{\circ}$   $\omega$ -scans, 15 s per frame and 12 frames per series, that were well distributed in reciprocal space. For data collection, four  $\omega$ -scan frame series were collected with 0.5° wide scans, 30 s frames and 366 frames per series at varying  $\varphi$ angles ( $\phi = 0^{\circ}$ , 90°, 180°, 270°). The crystal to detector distance was set to 6 cm and a complete sphere of data was collected. Cell refinement and data reduction were performed with the Bruker SAINT [14] software, which corrects for beam inhomogeneity, possible crystal decay, Lorentz, and polarisation effects. A multiscan absorption correction was applied (SADABS [15]). The structures were solved using SHELXS-2014 [16] (1a) or SHELXT-2014 [16] (2b) and were refined using a full-matrix least-squares method on  $F^2$  with SHELXL-2014 [16]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were included at geometrically idealized positions and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at  $1.2U_{eq}$  of the parent carbon atom ( $1.5U_{eq}$  was used for methyl hydrogens). All diagrams were prepared using the programs POV-Ray 3.7 [17] via Diamond 3.2 [18] or Mercury CSD 3.7 [19]. **Compound 1a**: The crystal chosen for data collection was found to be multiply twinned during the data processing and refinement. The original unit cell chosen was orthorhombic C-centred, however, there was no space group that matched the observed systematic absences. If instead a primitive monoclinic cell was selected (with the original B-axis halved and the B- and C- axes transformed) the structure could be solved in P2<sub>1</sub> but with very poor results. Platon [20] suggested that there was still unaccounted for symmetry in the structure and halving the C-axis again gave the still smaller monoclinic cell finally used for the refinement. After taking care of the pseudo-merohedral twinning, the refinement in  $P2_1/c$  proceeded smoothly but gave statistical parameters that were higher than expected. The routine TwinRotMat in the program Platon [20] was used to find the correct twin law for this non-merohedral twinning and to write the HKLF5 file (data merged) used in the refinement. BASF refined to 0.310(1). The fluorine atoms of the BF<sub>4</sub> anion were disordered. Each fluorine atom was split over two positions (A and B), with the B-F bond distances in the anions restrained to be equal and the thermal parameters of each fluorine atom weakly restrained to be similar. One of the fluorine atoms also had restraints placed on it to make its thermal parameters more isotropic. The occupancies of the A and B positions refined to 88.5(7)% and 11.5% respectively. Even after modelling the disorder, there remained a B level and a C level checkcif alert concerning large Hirshfeld differences along some of the B–F bonds. Nothing more was done about these; they arise only because of the large anisotropic motion of the fluorine ligands, even in the disordered model. Compound 2a: The RIGU command was included in the SHELXL refinement to add enhanced rigid bond restraints to the atomic displacement parameters for 1,2- and 1,3- heavy atom pairs. One reflection (110) was partially obscured by the beam stop and so was omitted from the final refinement. The structure was refined as a racemic twin to obtain a value for the Flack parameter with an accurate estimated standard deviation. The value obtained, 0.04(4), suggests that the absolute configuration chosen is the correct one and that this crystal is in fact not a twin. The B–F bond lengths in the disordered anions were restrained to be equal, as were the  $F \cdots F$ distances. The SAME instruction was used in the SHELXL refinement to restrain the two rings to have similar conformations. In addition, specific bonds in the two rings were restrained to be equal. Finally, one carbon atom in each ring (C18) was ill-behaved and restrained to make its motion more isotropic.

### Acknowledgments

Financial support from the Canada Foundation for Innovation (CFI), the Faculties of Science and Graduate Studies and Research of Saint Mary's University, ACEnet (ACEnet Summer Research Fellowship to C.D.R.), and the Strategic Cooperative Education Incentive (summer co-op funding for Z.E.K.) is gratefully acknowledged.

#### Supplementary material

The cif files CCDC-1496204 (1a) and CCDC-1496205 (2a) have been deposited as Supplementary Material. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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