

# On the coordination chemistry of corannulene, the smallest “buckybowl”

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## Abstract

A variety of methods, conventional and non-conventional, are used in attempts to prepare the compounds ( $\eta^6$ -corannulene)M(CO)<sub>3</sub> (M = Cr, Mo, W), all unsuccessful. Conventional methods are also utilized in attempts to prepare the compound [CpFe( $\eta^6$ -corannulene)]PF<sub>6</sub>, but these result in mixtures of cationic CpFe(arene) complexes containing partially hydrogenated corannulene; similar results have been reported for other polyaromatic hydrocarbons. DFT calculations on the compound ( $\eta^6$ -corannulene)Cr(CO)<sub>3</sub> suggest that the ( $\eta^6$ -corannulene)-Cr linkage is only a few kcal/mol weaker than the corresponding bond in ( $\eta^6$ -benzene)Cr(CO)<sub>3</sub>, implying that failures in syntheses arise from kinetic, not thermodynamic problems.

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## 1. Introduction

Because of their unusual electronic structures and high degree of unsaturation, fullerenes such as C<sub>60</sub> (Fig. 1, A) have been much investigated for their abilities to form metal-containing compounds [1–3]. Metal–C<sub>60</sub> compounds generally fall into one of three main categories, endohedral compounds in which the metal atom is encapsulated within the fullerene sphere [1], alkali metal fulleride compounds containing discrete anionic species C<sub>60</sub><sup>n-</sup> (*n* = 1–6) [2a–e], and  $\eta^2$ -transition metal complexes in which the fullerene behaves essentially as an electron deficient alkene ligand [3]. More recent attention has also focused on the possible types of metal-containing

compounds which might be prepared by, e.g., corannulene (Fig. 1, B), which may be thought of as a C<sub>20</sub> fragment cap of C<sub>60</sub>.

Corannulene is a polycyclic aromatic hydrocarbon composed of five six-membered rings fused to each other and to a five-membered central ring [4,5]; the molecule is bowl shaped because of the need of the C<sub>6</sub> rings to accommodate the steric requirements of the central C<sub>5</sub> ring, but bowl inversion is facile [5c–f]. As is indicated in the structure (B), corannulene contains four different types of carbon–carbon bonds which may be designated as hub, flank, spoke and rim bonds. Structural studies indicate that the bond orders are localized essentially as shown [5], with the hub and flank C–C bond lengths being 1.413(3) and 1.440(2) Å, respectively, the spoke and rim bond lengths being 1.391(4) and 1.402(5) Å, respectively [5a]. The three types of carbon atoms in corannulene are numbered in order to facilitate later discussion.

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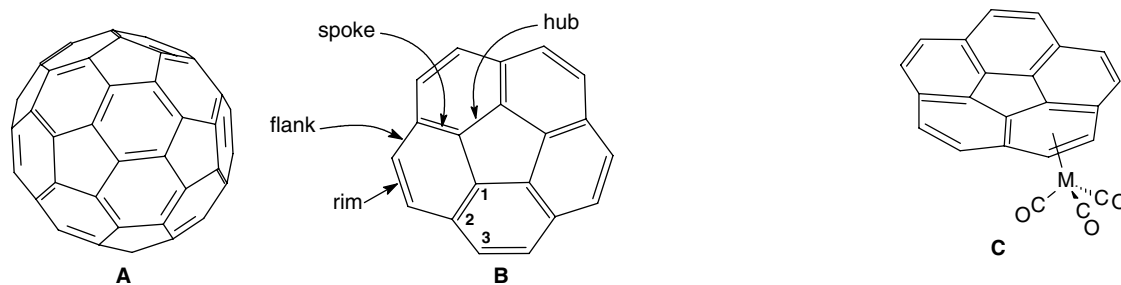


Fig. 1. Structures of  $C_{60}$  (A) and corannulene (B).

The potential for interesting coordination chemistry of corannulene is obvious, as the compound might be expected to bind to a wide variety of metal–ligand moieties in  $\eta^2$ -fashion via the rim C=C bonds, in  $\eta^4$ -fashion to, e.g., an  $Fe(CO)_3$  moiety via a pair of 1,3-spoke C=C bonds, and in  $\eta^6$ -fashion to, e.g., a  $Cr(CO)_3$  moiety via one of the aromatic  $C_6$  rings. Furthermore, of course, coordination to the convex (*exo*) or the concave (*endo*) surface of the bowl seems possible. To date, however, very few examples of metal corannulene complexes are known and even fewer have been characterized crystallographically. The first example of a transition metal complex of corannulene was  $[Cp^*Ru(\eta^6-C_{20}H_{10})](O_3SCF_3)$ , prepared by reaction of  $[Cp^*Ru(NCMe)_3](O_3SCF_3)$  with corannulene in  $CD_2Cl_2$  in 1997 [6a]. Although the  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra of the product showed clearly that the  $C_5$  axis of the corannulene had been broken, the compound was not characterized crystallographically and the  $\eta^6$  structure was inferred largely because of the generally high stability of compounds of the type  $[Cp^*Ru(\eta^6\text{-arene})]$ . More recently, however, an analogous diruthenium compound,  $[(Cp^*Ru)_2(\mu^2-\eta^6, \eta^6-C_{20}H_{10})](PF_6)_2$ , has been prepared and characterized crystallographically, confirming the expected  $\eta^6$  mode of coordination [6b].

The second corannulene complex reported was the very similar  $[Cp^*Ir(\eta^6-C_{20}H_{10})](BF_4)_2$  [6c], but again the compound was too unstable to be fully characterized. A somewhat different series of corannulene compounds is that of Petrukhina et al. [6d], who through metal–vapour deposition reactions obtained the compounds  $\{[Rh_2(O_2CCF_3)_4]_m\}[\eta^2-C_{20}H_{10}]_n$  ( $m:n = 1:1, 3:2$ ); coordination via both *endo* and *exo* faces was demonstrated crystallographically, but the corannulene ligands dissociated when the compounds were dissolved in organic solvents.

Although these results imply a general lack of stability for corannulene–metal complexes, the number of types of metal–ligand moieties investigated is actually very small. We decided, therefore, to attempt to synthesize the series of arene compounds  $(\eta^6\text{-corannulene})M(CO)_3$  ( $M = Cr, Mo, W$ ), of the type C where *exo* coordination is illustrated.

There are many routes to stable  $\eta^6$ -arene compounds of these types [7] and, as we show below, we have tried virtually all without success. In an attempt to possibly assess whether we were in fact dealing with a thermodynamic problem, i.e., very low stability of the target molecules, we have also carried out DFT calculations on the compound  $(\eta^6\text{-corannulene})Cr(CO)_3$  using the B3LYP [8a–c] functional on a self-consistent DFT level of calculation. The calculations strongly suggest that the  $\eta^6$ -corannulene–Cr linkage in  $(\eta^6\text{-corannulene})Cr(CO)_3$  is only a few kcal/mol weaker than the  $\eta^6$ -benzene linkage in  $(\eta^6-C_6H_6)Cr(CO)_3$ , and thus our failures may better be attributed to kinetic problems. We have also extended our synthetic investigations to the attempted syntheses of  $[CpFe(\eta^6\text{-corannulene})](PF_6)$ , a potential member of a well known class of compounds of the type  $[CpFe(\eta^6\text{-arene})](PF_6)$  [9]. In this case we have enjoyed marginal success.

## 2. Experimental

All 1D and 2D NMR spectra were obtained on Bruker AC 200, Avance 400 and Avance 600 NMR spectrometers, chemical shifts being referenced with respect to TMS using the residual proton or carbon resonances of the solvent. IR spectra were acquired on a Perkin Elmer Spectrum One FT-IR spectrometer in cells with NaCl windows at a spectral resolution of  $4\text{ cm}^{-1}$ . ESMS, EIMS and LDMS were obtained on Applied Biosystems/MDS Sciex QSTAR XL, Micromass/VG Quattro Triple Quadrupole and Applied Biosystems Voyager instruments, respectively.

All manipulations were carried out in an Mbraun Labmaster glove box or using standard Schlenk line techniques under argon purified by passage through a column of BASF copper catalyst and a column of  $5\text{ \AA}$  molecular sieves. Solvents were dried by passage through a column of activated alumina and were degassed prior to use. All chemicals, except those noted below, were purchased from Aldrich and used as received. Norbornadiene and dehydroacetic acid were purchased from Lancaster and used as received.

The compounds  $M(CO)_3(MeCN)_3$  ( $M = Cr, Mo, W$ ) were prepared in 80–90% yields by refluxing the

hexacarbonyls in acetonitrile while a constant stream of argon was bubbled directly through the solution to promote the loss of CO [10a,b]. The compounds ( $\eta^6$ -cycloheptatriene) $M(\text{CO})_3$  ( $M = \text{Cr}$  [10c,d],  $\text{W}$  [10e]),  $M(\text{CO})_3(\text{pyridine})_3$  ( $M = \text{Cr}$  [10f],  $\text{Mo}$  [10g]), ( $\eta^6$ -benzene) $\text{Cr}(\text{CO})_3$  [10h,i] were prepared as in the literature.

### 2.1. Synthesis of corannulene

The synthesis of corannulene followed largely the procedures of Scott et al. [4f] albeit with modifications as described below.

#### 2.1.1. 2,4,6-Heptanetrione

In a procedure modified from the literature [4h,i], dehydroacetic acid (100 g, 0.59 mol) and concentrated HCl (400 mL) were placed in a 1 L round bottom flask, fitted with a reflux condenser vented to an oil bubbler to monitor the evolution of  $\text{CO}_2$  gas. The contents of the flask were refluxed until  $\text{CO}_2$  evolution ceased ( $\sim 4$  h). The flask was then allowed to cool to room temperature and further cooled in an ice bath while NaOH pellets (160 g, 4.0 mol) were added and dissolved until the solution was basic to litmus. The contents were transferred to a 2 L flask containing a solution of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  (250 g, 0.84 mol) in 1 L of boiling water. The mixture was cooled to room temperature and the resulting precipitate was filtered. The precipitate was placed in a 3 L flask followed by 1 L of water and 700 mL of diethyl ether. Concentrated HCl (150 mL) was added slowly until all solids dissolved and the aqueous layer was acidic to litmus. The dark orange ether layer was separated, dried over  $\text{MgSO}_4$ , and evaporated to dryness under reduced pressure to yield 27.8 g (33%) 2,4,6-heptanetrione that was stored in the freezer as previous work had found the product to decompose at room temperature [4j].  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.97 (s, 1.51H), 2.07 (s, 2.12H), 2.23 (s, 2.59H), 3.38 (s, 1.30H), 3.69 (s, 0.19H), 5.12 (s, 0.42H), 5.54 (s, 0.57H). Lit.  $\delta$  1.95 (1.51H), 2.05 (2.12H), 2.22 (2.54H), 3.40 (1.37H), 3.68 (0.29H), 5.16 (0.53H), 5.60 (0.65H) [4k].

#### 2.1.2. 7,10-Diacetylfluoranthene

Scott has made significant modifications to his original 3-step synthesis of  $\text{C}_{20}\text{H}_{10}$  [4]. Following the new procedure, acenaphthenequinone (100 g, 0.55 mol), 2,4,6-heptanetrione (78 g, 0.55 mol), methanol (1.6 L) and triethylamine (137 mL) were added to a 6 L flask. The contents were then stirred for 3 h after which 2 L of water were added. Concentrated HCl ( $\sim 125$  mL) was added until the mixture was acidic to litmus and then a further 1 L of water was added. The mixture was then stirred for 20 minutes and the resulting brown precipitate was filtered and allowed to dry in the fume hood for several days. The dry precipitate (135 g) was dissolved in 1.4 L toluene in a 3 L round bottom by

heating to 70 °C. Norbornadiene (250 mL, 2.32 mol) was added down the condenser and the mixture was refluxed for 4 days. The solution was allowed to cool to room temperature and left to crystallize in the freezer overnight. The liquid was decanted off and the crude was recrystallized from toluene to give 108 g (69%) 7,10-diacetylfluoranthene.  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.78 (s, 6H), 7.58 (s, 2H), 7.64 (d,  $J = 7.6$  Hz, 2H), 7.91 (d,  $J = 8.2$  Hz, 2H), 8.33 (d,  $J = 7.6$  Hz, 2H). Lit. 2.77 (6H), 7.59 (2H), 7.64 (2H), 7.93 (2H), 8.34 (2H) [4f].

#### 2.1.3. 7,10-Bis(1-chlorovinyl)fluoranthene

The literature method [4f] for this step resulted in low yields and many impurities due to over chlorination. The preparation was modified as follows, 7,10-diacetylfluoranthene (51 g, 0.178 mol) and  $\text{PCl}_5$  (74 g, 0.356 mol) were added to a 3 L round bottom flask. Methylene chloride (1.5 L) was added and the contents were stirred under argon at room temperature for 6 days, after which the flask was opened to air, cooled in an ice bath and excess  $\text{PCl}_5$  hydrolyzed by the addition of crushed ice. The mixture was washed with water (3  $\times$  1 L) and sat. NaCl (aq) (2  $\times$  1 L). The organic layer was separated, dried over  $\text{MgSO}_4$  and evaporated to dryness under reduced pressure. The crude product was chromatographed on silica gel using a hexanes/dichloromethane mixture (7:3). The entire yellow band was collected from the column as a single fraction while a brown residue was left on the column. The collected fraction was evaporated to dryness leaving yellow crystals. The yellow crystals were sublimed in two fractions at 140 °C overnight to give pure 7,10-bis(1-chlorovinyl)fluoranthene; the yield (reported as a combined average of two complete runs) was 49%.  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.71 (d,  $J = 1$  Hz, 2H), 5.87 (d,  $J = 1.2$  Hz, 2H), 7.30 (s, 2H), 7.64 (dd, 2H), 7.88 (d,  $J = 8.2$  Hz, 2H), 8.30 (d,  $J = 7$  Hz, 2H). Lit. 5.72 (2H), 5.88 (2H), 7.30 (2H), 7.64 (2H), 7.89 (2H), 8.32 (2H).

#### 2.1.4. Corannulene

The apparatus used for the pyrolysis reactions was developed based on that reported by Scott et al. [4f]. In a typical pyrolysis, 7,10-bis(1-chlorovinyl)fluoranthene (1.5 g, 4.6 mmol) was placed in a porcelain sample boat which rested inside a quartz tube (25 mm OD, 85 cm long with O-Ring joints at both ends). The tube rested in an electric tube furnace (30 cm heating zone), and was connected upstream to a cylinder of prepurified argon. Downstream from the furnace, the tube was connected to a liquid nitrogen cooled trap which was in turn connected to a Schlenk line. The system was sealed and evacuated, and the furnace was heated to 1100 °C. A slow leak of argon was initiated and slow sublimation of the 7,10-bis(1-chlorovinyl)fluoranthene in the argon flow was induced by a heating tape wrapped around the upstream portion of the quartz tube. The pyrolysis

was allowed to run until no starting material remained in the sample boat (~4–6 h). The furnace was then turned off and the system was allowed to cool to room temperature. Once at room temperature, the apparatus was opened to air and the tube and nitrogen trap were washed with methylene chloride. The combined washings were filtered to remove graphitic material and evaporated to dryness. The residue was chromatographed using cyclohexane on silica gel and the yellow product was collected as one fraction while a dark brown band was left on the column. Cyclohexane was removed on the rotary evaporator to give pure corannulene. The yield, reported as a combined average of 14 runs of the pyrolysis (20.4 g, 63 mmol of starting material), was 11.4% (1.8 g, 7.2 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80;  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CD}_2\text{Cl}_2$ ) 127.04, 130.96, 135.69. Lit.  $^1\text{H}$ : 7.81 (s),  $^{13}\text{C}\{^1\text{H}\}$ : 127.18, 130.84, 135.81 [4f].

## 2.2. Thermal reactions of $\text{C}_{20}\text{H}_{10}$ and $\text{M}(\text{CO})_6$ ( $\text{M} = \text{Cr}, \text{Mo}$ )

A solution of 0.1 g  $\text{C}_{20}\text{H}_{10}$  (0.4 mmol) and 4 mmol of the appropriate hexacarbonyl was refluxed in 50 mL of hexanes for two weeks (Mo) or four weeks (Cr), after which IR spectra of the solutions exhibited only the carbonyl absorptions of the starting materials.

## 2.3. Attempted reactions of $\text{C}_{20}\text{H}_{10}$ with alternative sources of the $\text{M}(\text{CO})_3$ moieties (Cr, Mo and W)

A mixture of 0.1 g  $\text{C}_{20}\text{H}_{10}$  (0.4 mmol) and 0.1 g  $\text{Mo}(\text{CO})_3(\text{MeCN})_3$  (0.4 mmol) were ground in a mortar to a uniform mixture and transferred to a Schlenk flask. The flask was sealed, put under static vacuum and submerged in an 80 °C oil bath for 4 h. After this time, the material had changed from yellow to dark brown and the mixture was cooled and washed with hexanes to give a black residue, the IR spectrum of which exhibited no  $\nu(\text{CO})$ . A  $^1\text{H}$  NMR spectrum exhibited only the singlet of  $\text{C}_{20}\text{H}_{10}$ . Similarly unproductive were reactions of  $\text{M}(\text{CO})_3(\text{MeCN})_3$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) in THF at 45 °C over several days, of  $\text{Cr}(\text{CO})_3(\text{MeCN})_3$  in refluxing hexanes or diglyme for 24 h, of ( $\eta^6$ -cycloheptatriene) $\text{M}(\text{CO})_3$  ( $\text{M} = \text{Cr}, \text{W}$ ) in hexanes for a month, of  $\text{M}(\text{CO})_3(\text{pyridine})_3$  ( $\text{M} = \text{Cr}, \text{Mo}$ ) in a mixture of ethyl ether and boron trifluoride diethyl etherate for 2 h. In all cases,  $^1\text{H}$  NMR spectra of the products exhibited only the single resonance of free  $\text{C}_{20}\text{H}_{10}$ .

A number of experiments were also preformed utilizing a CEM Discover microwave reactor. Experiments were carried out in 10 mL glass tubes pressure rated to 200 psi and fitted with a magnetic stir bar and a pressure rated septum cap. A variety of experimental parameters were varied, including solvent, temperature, pressure,

power setting and run time, but all experiments involving  $\text{C}_{20}\text{H}_{10}$  and the above reactants failed. In all cases,  $^1\text{H}$  NMR spectra of the products exhibited only the single resonance of free  $\text{C}_{20}\text{H}_{10}$ .

## 2.4. Reaction of $\text{K}_2[\text{C}_{20}\text{H}_{10}]$ with $\text{Cr}(\text{CO})_6$

A mixture of 0.10 g  $\text{C}_{20}\text{H}_{10}$  (0.40 mmol) and 0.08 g potassium metal (2 mmol) in 60 mL THF was sonicated for 2 h, by which time the color had changed from yellow to green and finally the persistent deep red of  $(\text{C}_{20}\text{H}_{10})^{2-}$  [11]. The solution was stirred overnight to ensure complete conversion, filtered to remove excess potassium and added to 0.10 g  $\text{Cr}(\text{CO})_6$  (0.45 mmol). The resulting solution was stirred for 1 h, after which the yellow precipitate was allowed to settle and the solution was cannulated off and evaporated to dryness. The resulting residue was washed with hexanes ( $3 \times 20$  mL) and the washings were also evaporated to dryness. At this point the three separation fractions (yellow precipitate, hexanes soluble residue and hexanes insoluble residue) were examined.

The yellow precipitate exhibited no resonances in the  $^1\text{H}$  NMR spectrum and was therefore characterized by IR spectroscopy and electrospray mass spectrometry (ESMS). Fragments due to the loss of CO groups confirm the complex to be  $\text{K}[\text{H}(\text{Cr}(\text{CO})_5)_2]$ . ESMS,  $m/z$  (amu) Relative intensities are given in parentheses and are referenced individually to the largest peak of each respective isotope pattern;  $[\text{HCr}_2\text{C}_{10}\text{O}_{10}]$ : 385.96 (34), 384.96 (100), 382.97 (10); Calc.: 389 (0.1), 388 (2.1), 387 (11.8), 386 (33.7), 385 (100), 384 (2.2), 383 (10.3), 381 (0.2).  $[\text{HCr}_2\text{C}_9\text{O}_9]$ : 359.97 (2.0), 358.96 (12), 357.96 (37.5), 356.96 (100), 354.97 (12) Calc.: 361 (0.1), 360 (1.8), 359 (11.3), 358 (32.6), 357 (100), 356 (2.2), 355 (10.3), 353 (0.2).  $[\text{HCr}_2\text{C}_8\text{O}_8]$ : 331.96 (2.4), 330.96 (13.4), 329.96 (37.8), 328.95 (100), 327.97 (3.0), 326.96 (37.8) Calc.: 332 (1.6), 331 (10.8), 330 (31.5), 329, (100), 328 (2.1), 327 (10.3), 325 (0.2).  $[\text{HCr}_2\text{C}_7\text{O}_7]$ : 302.96 (10.2), 301.96 (33.3), 300.96 (100), 298.96 (10.2) Calc.: 304 (1.5), 303 (10.1), 302 (30.3), 301, (100), 300 (2.0), 299 (10.3), 297 (0.2). IR  $\nu(\text{CO})$  ( $\text{cm}^{-1}$ , THF) 1942(s), 1884(s) Lit. (sodium salt): 2032(w), 1942(s), 1879(s) [12a,b].

The material that was insoluble in hexanes was determined to be  $\text{K}_2[\text{Cr}_2(\text{CO})_{10}]$ ; IR:  $\nu(\text{CO})$   $\text{cm}^{-1}$  (Nujol) 1919(s), 1893(vs), 1869(2), 1825(m), 1805(m), 1762(w). The pattern was identical to that reported in the literature for  $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ : 1903(s), 1880(vs), 1851(s), 1801(m), 1776(m), 1756(w) [12c]. The  $^1\text{H}$  NMR spectrum of the material did not exhibit any resonances. The IR spectrum of the hexanes soluble material did not exhibit any absorptions in the CO region, while the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra exhibited strong resonances of free corannulene.

### 2.5. Reaction of $K_2[C_{20}H_{10}]$ with $(\eta^6\text{-benzene})Cr(CO)_3$

A solution of  $K_2[C_{20}H_{10}]$  was prepared as above, cooled to  $-78\text{ }^\circ\text{C}$  and transferred to a solution containing a 10-fold molar excess of  $(\eta^6\text{-benzene})\text{tricarboyl chromium}$ . Upon mixing, the deep red color of the dianion turned dark brown, and the mixture was brought to room temperature, stirred for 30 min, treated with  $47\ \mu\text{L}$  of air, stirred for a further 10 min and then taken to dryness under reduced pressure. The resulting residue was a dark brown to black solid. An IR spectrum of the dark residue exhibited no absorptions in the carbonyl region, although a  $^1\text{H}$  NMR spectrum exhibited a strong resonance of free  $C_{20}H_{10}$ .

### 2.6. Attempt to prepare $[CpFe(\eta^6\text{-corannulene})](PF_6)$ in the absence of solvent

A mixture of  $0.65\ \text{g}\ C_{20}H_{10}$  (2.60 mmol),  $0.14\ \text{g}\ \text{Al}$  powder (5.2 mmol),  $3.46\ \text{g}\ \text{AlCl}_3$  (2.60 mmol) and  $4.83\ \text{g}$  ferrocene (2.60 mmol) was heated at  $140\text{ }^\circ\text{C}$  while stirring for 22 h. After this period, the reaction mixture was cooled to  $0\text{ }^\circ\text{C}$  and hydrolyzed with  $\text{NH}_4\text{OH}$ , and the resulting solution was filtered. A solution of  $\text{HPF}_6$  (60% by wt) ( $1.16 \times 10^{-3}$  mol) was then added to the filtrate to precipitate a brown-yellow solid (0.08 g) which was collected via filtration. This solid was dissolved in acetone and precipitated by addition of ethyl ether. Repeated attempts at recrystallization failed to give pure material. This isolated material was passed through alumina using acetone as an eluant to no avail.  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{CO}$ ,  $25\text{ }^\circ\text{C}$ , 400 MHz):  $\delta$  3.46 (s), 3.5–3.7 (br peaks), 3.96 (s), 4.04 (s), 4.14 (s), 4.2–4.5 (br peaks), 6.22 (br), 6.6–6.7 (br), 7.06 (br), 7.46 (d), 7.84 (d), 7.90 (d), 8.1–8.5 (series of br peaks). ESMS: ( $m/z$ ) Pos. Ions, Rel. Int.: 369.2 (6.0), 370.2 (1.5), 371.2 (9.1), 373.1 (100), 374.1 (30.4), 375.1 (86.1), 376.1 (26.2), 377.1 (70.5), 378.1 (22.0), 379.2 (53.4), 380.1 (16.1), 381.1 (74.3), 382.1 (21.8), 383.1 (14.2), 384.1 (4.2), 385.2 (30.2), 386.2 (9.8), 387.2 (7.1), 389.1 (4.6). Calc. for  $C_{25}H_{15}Fe$ : 369 (6.2), 370 (1.6), 371 (100), 372 (29.6), 373 (4.5), 374 (0.2). Calc. for  $C_{25}H_{17}Fe$ : 371 (6.2), 372 (1.6), 373 (100), 374 (29.6), 375 (4.5), 376 (0.2). Calc. for  $C_{25}H_{19}Fe$ : 373 (6.2), 374 (1.6), 375 (100), 376 (29.6), 377 (4.5), 378 (0.2). Calc. for  $C_{25}H_{21}Fe$ : 375 (6.2), 376 (1.6), 377 (100), 378 (29.6), 379 (4.5), 380 (0.2). Calc. for  $C_{25}H_{23}Fe$ : 377 (6.2), 378 (1.6), 379 (100), 380 (29.6), 381 (4.5), 382 (0.2). Calc. for  $C_{25}H_{25}Fe$ : 379 (6.2), 380 (1.6), 381 (100), 382 (29.6), 383 (4.5), 384 (0.2). Calc. for  $C_{25}H_{27}Fe$ : 381 (6.2), 382 (1.6), 383 (100), 384 (29.6), 385 (4.5), 386 (0.2). Calc. for  $C_{25}H_{29}Fe$ : 383 (6.2), 384 (1.6), 385 (100), 386 (29.6), 387 (4.5), 388 (0.2). Calc. for  $C_{25}H_{31}Fe$ : 385 (6.2), 386 (1.6), 387 (100), 388 (29.6), 389 (4.5), 391 (0.2). Calc. for  $C_{25}H_{33}Fe$ : 387 (6.2), 388 (1.6), 389 (100), 390 (29.6), 391 (4.5), 392 (0.2). Calc. for  $C_{25}H_{35}Fe$ : 389

(6.2), 390 (1.6), 391(100), 392 (29.6), 393 (4.5), 394 (0.2). ESMS ( $m/z$ ) Neg. Ions, Rel. Int.: 144.9 (100). Calc. for  $\text{PF}_6$ : 145 (100).

### 2.7. Attempts to prepare $[CpFe(\eta^6\text{-corannulene})](PF_6)$ in decalin

A mixture of  $0.29\ \text{g}\ C_{20}H_{10}$  (1.16 mmol),  $0.03\ \text{g}\ \text{Al}$  powder (1.16 mmol),  $1.55\ \text{g}\ \text{AlCl}_3$  (1.16 mmol),  $2.16\ \text{g}$  ferrocene (1.16 mmol),  $0.02\ \text{mL}$  water (1.16 mmol) and  $35\ \text{mL}$  of decalin was heated at  $140\text{ }^\circ\text{C}$  while stirring for 16 h. After heating, the reaction mixture was cooled to  $0\text{ }^\circ\text{C}$  and hydrolyzed. The aqueous layer was separated before  $\text{NH}_4\text{OH}$  was added, and the resulting solution was filtered. Aqueous  $\text{HPF}_6$  (60% wt.) ( $0.2\ \text{mL}$ ,  $1.16 \times 10^{-3}$  mol) was then added to the filtrate to precipitate a brown-yellow solid (0.06g) which was collected via filtration. This solid was dissolved in acetone and precipitated by addition of  $\text{Et}_2\text{O}$ . Repeated attempts at recrystallization by layering an acetone solution with  $\text{Et}_2\text{O}$  failed to give a pure material. This material was passed through alumina using acetone as an eluant to no avail. During all phases of the reaction and the reaction workup, great care was taken to minimize the exposure of the reaction mixture and products to light.  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{CO}$ ,  $25\text{ }^\circ\text{C}$ , 400 MHz):  $\delta$  3.46 (s), 3.5–3.7 (br peaks), 3.96 (s), 4–4.3 (br peaks), 6.22 (br), 6.60 (br), 7.06 (br), 7.8–7.9 (two br), 8.1–8.5 (br peaks). ESMS ( $m/z$ ) Pos. Ions, Rel. Int.: 371.3 (6.4), 372.3 (2.2), 373.2 (100), 374.3 (30), 375.3 (78.6), 376.2 (22.5), 377.3 (9.5), 378 (2.3), 379.4 (4.9), 380.3 (1.5), 381.3 (8.2), 382.3 (2.6), 383.4 (2.2), 384.3 (0.8), 385.4 (5.4), 386.4 (1.7). ESMS ( $m/z$ ) Neg. Ions, Rel. Int.: 144.9 (100). For calculated mass, see above reaction.

A second attempt using this method gave material with the following NMR and ESMS properties:  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{CO}$ ,  $25\text{ }^\circ\text{C}$ , 400 MHz):  $\delta$  1.45–1.95 (series of singlets), 3.7–3.9 (two br s), 3.95 (br s), 4.2 (br s), 4.8–5.2 (br) 6.2–6.3 (br), 6.8–6.85 (br), 7.05 (br), 7.6–7.8 (two br). Exact mass: ( $C_{25}H_{29}Fe^+$ ) measured: 385.16186. Calc.: 385.1629, error: 2.7 ppm. ( $C_{25}H_{31}Fe^+$ ) measured: 387.17751. Calc.: 387.1770, error: 1.3 ppm.

### 2.8. DFT Calculations

To elucidate the structure of  $(\eta^6\text{-corannulene})Cr(CO)_3$  and obtain an estimate of the Cr–corannulene bond strength, we performed a series of ab initio calculations. These were done with the B3LYP [8a–c] functional on a self-consistent DFT level of calculation utilizing the High Performance Computing Virtual Laboratory (HPCVL) at Queen’s University. We obtained results in three basis sets: the standard “split valence” 6-31G\* basis [8d–i], the same basis set augmented with the Los Alamos Effective Core Potential on Cr [8j–l] and in Dunning’s correlation consistent double-zeta

basis [8m]. All computations were performed using the GAUSSIAN 98 suite of programs [8n].

### 3. Results and discussion

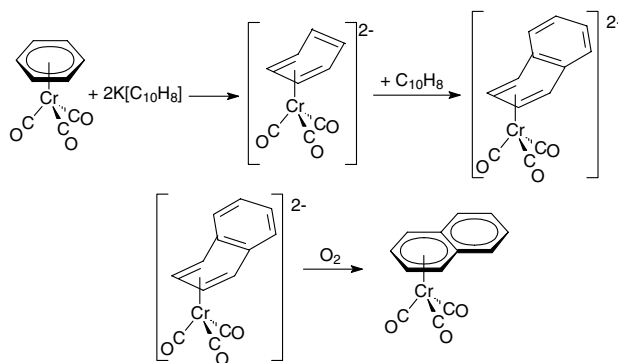
#### 3.1. Attempts to synthesize $\eta^6$ -corannulene complexes of Cr, Mo, W

Considerable time was spent developing and optimizing a procedure for the synthesis of corannulene, described in Section 2. Carbonyl compounds of the Group 6 metals, Cr, Mo and W, are well known to form  $\pi$ -arene complexes of the type  $(\eta^6\text{-arene})\text{M}(\text{CO})_3$ , and a wide range of synthetic routes has been reported, ranging from direct reactions of arenes with the metal hexacarbonyls, through reactions involving labile trisubstituted metal precursors of the type  $\text{M}(\text{CO})_3\text{L}$ , ( $\text{L} = 3\text{CH}_3\text{CN}$ , 3pyridine,  $\eta^6$ -cycloheptatriene,  $\eta^6$ -arene) [7], to multi-step redox exchange reactions [13] which we have attempted to exploit. While there are examples of coordination of the metals to mono and polycyclic planar arenes, no complexes have been reported involving coordination of these metals to curved aromatic molecules although the possibility of coordination of corannulene to Cr and W has been suggested [6c].

Our attempts to coordinate corannulene to the three  $\text{M}(\text{CO})_3$  moieties have involved lengthy (up to several weeks) refluxing of solutions of  $\text{C}_{20}\text{H}_{10}$  with all three hexacarbonyls in various solvents, in addition to the use of a microwave reactor, an approach which was reported for effecting substitution of the hexacarbonyls during the course of our study [14]. We have also utilized as possibly more labile precursors [7], the compounds  $\text{M}(\text{CO})_3(\text{MeCN})_3$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) at various temperatures in THF, hexanes and diglyme as well as in the absence of solvent. We have refluxed hexanes solutions of the compounds  $(\eta^6\text{-cycloheptatriene})\text{-M}(\text{CO})_3$  ( $\text{M} = \text{Cr}, \text{W}$ ) with  $\text{C}_{20}\text{H}_{10}$  for a month, and we have reacted  $\text{M}(\text{CO})_3(\text{pyridine})_3$  ( $\text{M} = \text{Cr}, \text{W}$ ) with  $\text{C}_{20}\text{H}_{10}$  in the presence of boron trifluoride diethyl etherate as a pyridine trap. None of these more or less conventional approaches have produced any material which contained coordinated  $\text{C}_{20}\text{H}_{10}$ .

We have also attempted to utilize a non-conventional, very ingenious sequence of reactions by which Cooper and Leong succeeded in converting  $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$  to the naphthalene analogue,  $(\eta^6\text{-naphthalene})\text{Cr}(\text{CO})_3$  [13]. In this novel, indirect route,  $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$  is initially reduced to  $[(\eta^4\text{-benzene})\text{Cr}(\text{CO})_3]^{2-}$  by potassium naphthalenide as in Scheme 1. The reaction is unusual in that it allows substitution of benzene by a polycyclic arene.

Attempting to exploit this type of unusual approach, we reacted the potassium salt of the corannulene dian-

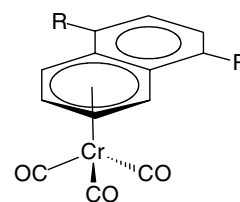


Scheme 1. Conversion of  $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$  to  $(\eta^6)\text{Cr}(\text{CO})_3$  [13].

ion,  $\text{K}_2[\text{C}_{20}\text{H}_{10}]$  [11], with both  $\text{Cr}(\text{CO})_6$  and  $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ . As described in Section 2, reactions did occur but did not yield the desired product. Instead, electron transfer processes occurred with  $\text{Cr}(\text{CO})_6$  to give corannulene and the reduced chromium complexes,  $\text{K}[\text{H}(\text{Cr}(\text{CO})_5)_2]$  and  $\text{K}_2[\text{Cr}_2(\text{CO})_{10}]$  [12], identified by IR spectroscopy and mass spectrometry, while the reaction with  $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$  gave corannulene but no carbonyl-containing products.

The inability of any of these traditional and non-traditional routes to form any of the compounds  $(\eta^6\text{-C}_{20}\text{H}_{10})\text{M}(\text{CO})_3$  ( $\text{M} = \text{Cr}, \text{W}$ ) was something of a surprise. As noted above, all of the routes used have been widely cited in the literature and several have been successfully used to give coordination complexes with polycyclic arenes [15]. We discuss below some of the possible reasons for failure.

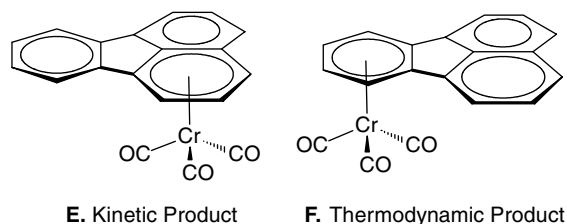
In the case of  $\eta^6$ -arene complexes of planar polyaromatic hydrocarbons (PAHs), we note that the existing library of  $\eta^6$ -arene complexes of the group 6 metals contains many examples that illustrate the preference of the metal for less substituted rings [15b–d]. In studies involving coordinated 1,4-disubstituted naphthalenes to chromium, for example, substituents such as MeO,  $\text{Me}_2\text{N}$ ,  $\text{MeO}_2\text{C}$  and F all result in coordination of a group 6 metal tricarbonyl moiety to the unsubstituted ring as in **D** [15e].



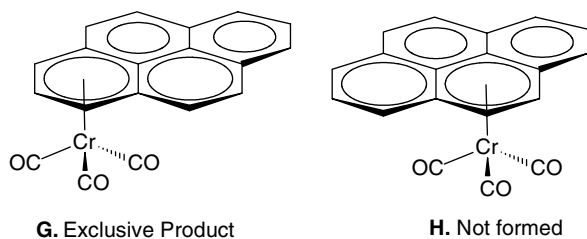
**D**:  $\text{R} = \text{MeO}, \text{Me}_2\text{N}, \text{MeO}_2\text{C}, \text{F}$

In the case of larger fused or condensed ring PAHs, in which two or more atoms are shared between rings, the metals often coordinate preferentially to the least substituted ring [7] although distinctions have been

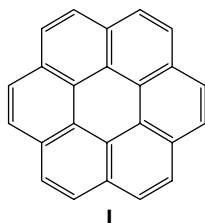
made in cases where thermodynamic and kinetic products have been isolated by different routes. Oprunenko et al. [15b] reported this difference with the isomers of ( $\eta^6$ -fluoranthene) tricarbonyl chromium; kinetic and thermodynamic isomers are shown as **E** and **F**, respectively.



Despite the formation of the kinetic product, isomerisation to the thermodynamic product in which the metal is coordinated to the less substituted ring is evident. Indeed, the preference of the  $\text{Cr}(\text{CO})_3$  unit for less substituted rings is even more pronounced as the number of condensed rings is increased. In the case of pyrene, two different types of aromatic rings exist, those that share three or four carbon atoms with adjacent rings. In this case, the preference for the less substituted ring (**G**) is so great that coordination to the ring with four shared carbon atoms (**H**) has not been observed [15d]. The degree of aromatic stabilization has been suggested as a reason for this preference [15d].



In an effort to gain insight into the problems involved, one might consider coronene (**I**), the closest example of a planar condensed arene to corannulene.



Coronene is the simplest planar PAH in which all of the peripheral rings are equivalent and share four carbon atoms with neighboring rings. Despite the availabil-

ity of six rings for coordination, there have been no reports in which coronene has been coordinated to a group 6 metal. Indeed, the only reported transition metal complexes of  $\text{C}_{24}\text{H}_{12}$  are of iron [16a–c] and ruthenium [16d,e] (see below).

It is interesting to note that no examples exist in the literature in which a group 6 metal has been coordinated to any six-membered ring that is attached to three other rings. This void in the literature and the above examples cannot be used to conclude that coordination of  $\text{C}_{20}\text{H}_{10}$  to Cr, Mo and W cannot occur. However, they do suggest that  $\text{C}_{20}\text{H}_{10}$  is not an isolated example in which coordination does not take place by the same protocols used for simpler planar arenes. Indeed, in view of our theoretical finding that compounds of the type ( $\eta^6$ -corannulene) $\text{Cr}(\text{CO})_3$  should be thermodynamically stable (see below), it would seem that the reason for synthetic failures is kinetic in origin.

### 3.2. Attempts to synthesize $\eta^6$ -corannulene complexes of Fe

The  $[\text{CpFe}]^+$  and  $[\text{Cp}^*\text{Fe}]^+$  ( $\text{Cp}^*$  = pentamethylcyclopentadienyl) cationic moieties are known to coordinate to a variety of aromatic and polyaromatic molecules in  $\eta^6$  fashion [9,16b,17]. Numerous examples of  $[\text{CpFe}(\eta^6\text{-polycyclic aromatic})]^+$  and  $[\text{Cp}^*\text{Fe}(\eta^6\text{-polycyclic aromatic})]^+$  complexes have been reported, including those of coronene, naphthalene, phenanthrene, pyrene, triphenylene and perylene [16b]. We therefore anticipated that use of the  $[\text{CpFe}]^+$  system might provide a route to corannulene complexes.

To this end we have tried two different methods, reported by Lacoste et al., to generate the desired  $[\text{CpFe}(\text{corannulene})]^+$  complex [16b]. In the first a mixture of  $\text{Cp}_2\text{Fe}$ ,  $\text{AlCl}_3$ , Al powder, and corannulene were heated at 140 °C, while in the second method  $\text{Cp}_2\text{Fe}$ ,  $\text{AlCl}_3$ , Al powder,  $\text{H}_2\text{O}$  and corannulene were combined in decalin and heated to 140 °C. The solvent free method is normally used in the melt of the aromatic substrate, but, in view of the high melting temperature of corannulene, we carried out the reaction as a heterogeneous mixture. The experiments resulted in the formation of only very small amounts of products which were characterized by  $^1\text{H}$  NMR spectroscopy and electrospray mass spectrometry (ESMS).

While ESMS on the materials obtained all showed that none of the desired  $[\text{CpFe}(\text{corannulene})]^+$  was present ( $m/z = 371$  Da) (Fig. 2), there were apparent in the spectra a series of peaks which indicated the presence of partially hydrogenated species of the type  $[\text{CpFe}(\text{corannulene} + n\text{H}_2)]^+$  ( $n = 1\text{--}7$  for the materials obtained in the solvent free reactions, 1–9 for the materials obtained in the reactions in decalin), albeit in varying relative amounts from one reaction to the next. In all cases, the isotopic distributions were as expected; in one example

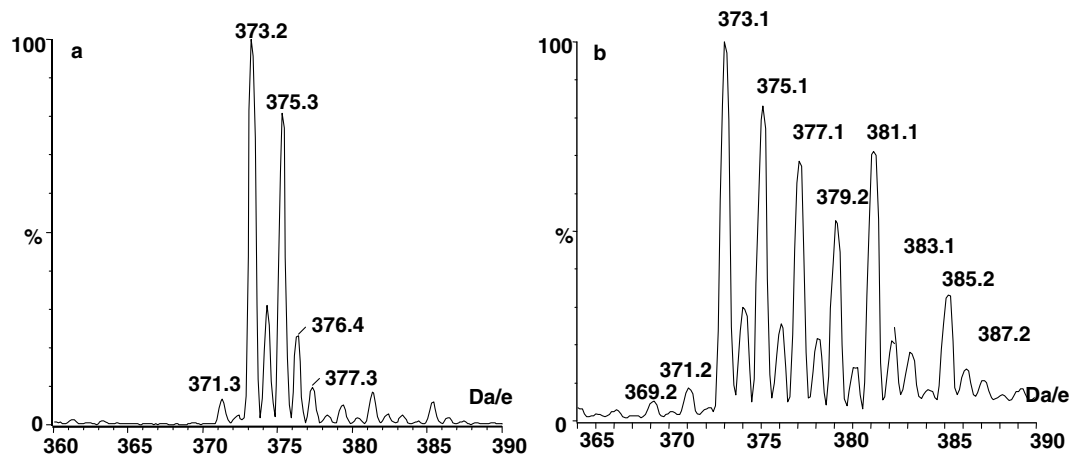


Fig. 2. Partial electrospray mass spectra of mixtures of complexes of the type  $[\text{CpFe}(\text{partially hydrogenated corannulenes})]^+$  (a) from the reaction in decalin, and (b) from the solvent free reaction.

a high resolution mass spectrum was obtained and indicated unequivocally that the species  $[\text{CpFe}(\text{C}_{20}\text{H}_{24})]^+$  and  $[\text{CpFe}(\text{C}_{20}\text{H}_{26})]^+$  had formed, i.e.,  $[\text{CpFe}(\text{corannulene} + 7\text{H}_2)]^+$  and  $[\text{CpFe}(\text{corannulene} + 8\text{H}_2)]^+$ .

The hydrogenation of polycyclic arenes during this type of reaction has precedence in a number of reported examples [16b,17], for instance in reactions involving naphthalene, anthracene, phenanthrene and pyrene. This provides further evidence that the products formed during the course of our reactions with corannulene, are in fact complexes of the type  $[\text{CpFe}(\text{arene})]^+$ . Hydrogenation would lead to a reduction in the ring strain experienced by corannulene, providing a driving force for hydrogenation, and we note that complexes of partially hydrogenated corannulene are known [18].

The  $^1\text{H}$  NMR spectra (Fig. 3) of the materials provided further evidence for the types of complexes suggested by the ESMS data. Thus the spectra exhibited several singlets in the Cp region,  $\delta$  3.9–4.5, consistent with previously published data for cationic complexes of the type  $[\text{CpFe}(\eta^6\text{-polycyclic aromatic})]^+$  [9]. Numerous resonances were also observed in the aromatic region of the spectra, consistent with there being present a mixture of compounds in which the symmetry of the corannulene had been reduced by coordination and par-

tial hydrogenation. Resonances were also observed in the region  $\delta$  3.5–3.7, which is expected for the  $\text{CH}_2$  groups of coordinated partially hydrogenated corannulene. A COSY spectrum exhibited a number of correlations between different peaks in the aromatic region. However because of the number of overlapping peaks and the presence of paramagnetic broadening in all samples, other inferences are difficult to make due to the number of complexes and the several different isomers possible for each hydrogenated complex.

### 3.3. Theoretical results

Calculations were done with the B3LYP [8a–c] functional on a self-consistent DFT level of calculation utilizing three basis sets, the standard “split valence” 6-31G\* basis [8d–i], the same basis set augmented with the Los Alamos Effective Core Potential on Cr [8j–l], and in Dunning’s correlation consistent double-zeta basis [8m]. We obtained two distinct low-energy structures for  $(\eta^6\text{-corannulene})\text{Cr}(\text{CO})_3$ , corresponding to a position of the  $\text{Cr}(\text{CO})_3$  group inside (“endo”) or outside (“exo”) of the corannulene ligand. In both cases, a staggered conformation seems to be slightly favoured, although the barrier to rotation is very low. In all basis sets used, the *exo* isomer depicted as **C** and as in Fig. 4 is more stable than the *endo* isomer, possible because of greater steric hindrance in the latter.

To estimate the relative coordination strengths of  $(\eta^6\text{-corannulene})\text{Cr}(\text{CO})_3$ , we also performed vibrational analyses in the same basis sets and on the same level of calculation, for both structures, as well as for the  $\text{Cr}(\text{CO})_3$  and the corannulene fragments. The results were used to obtain zero-point corrected bond energies. For comparison, the same calculations were performed for the well-known  $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$  for which the experimentally determined Cr–benzene bond dissociation energy is 53 kcal/mol [19]. We imposed  $D_{6h}$

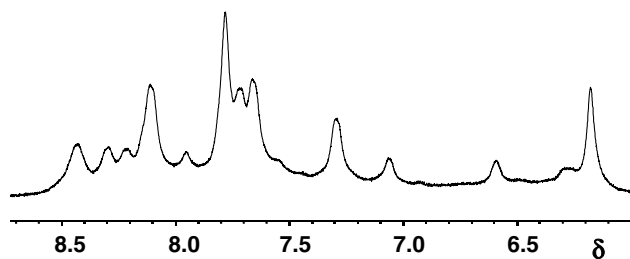


Fig. 3. The aromatic region of the  $^1\text{H}$  NMR spectrum of a mixture of complexes of the type  $[\text{CpFe}(\text{partially hydrogenated corannulenes})]^+$ .



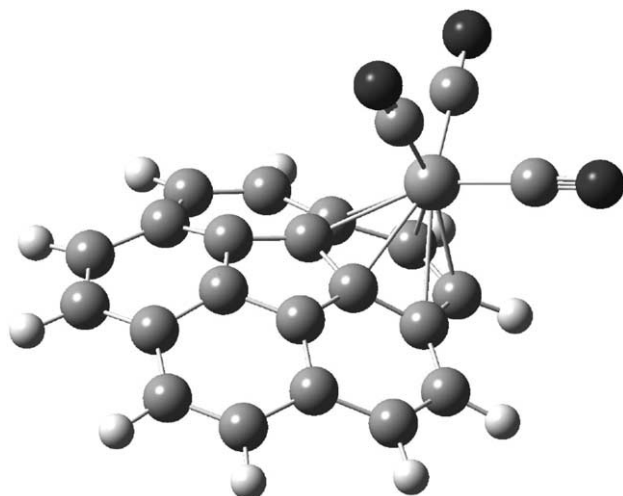


Fig. 4. The optimized structure of  $(\eta^6\text{-corannulene})\text{Cr}(\text{CO})_3$  in its “*exo*” form.

symmetry on benzene,  $C_{5v}$  symmetry on corannulene,  $C_{3v}$  symmetry on the  $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$  and the  $\text{Cr}(\text{CO})_3$  fragment. The *exo* and *endo* isomers of  $(\eta^6\text{-corannulene})\text{Cr}(\text{CO})_3$  have approximate  $C_s$  symmetry, but no restrictions were imposed. The results are summarized in Table 1.

As can be seen, while only two of the basis sets give satisfactory values for the Cr–benzene bond dissociation energy, all basis sets suggest that the chromium–corannulene bond strength of the *exo* isomer is about 5

kcal/mol stronger than that of the *endo* isomer. Moreover, the corresponding bond strength is approximately 7 kcal/mol weaker for the *exo* corannulene isomer than for the corresponding benzene complex. Although the values of the bond strengths differ somewhat for different basis sets, the relative differences are remarkably consistent.

Important calculated bond lengths are given in Table 2, where we compare calculated data for free corannulene with experimental X-ray and electron diffraction data. As can be seen, the calculated and experimental X-ray diffraction data differ only marginally, and the trends in the experimental C–C bond lengths are reflected very closely in the calculations. Also given in Table 2 are the corresponding C–C bond lengths for the arene ring coordinated to the  $\text{Cr}(\text{CO})_3$  fragment. As can be seen, the hub, spoke and flank C–C bonds all lengthen slightly on coordination but the rim C–C bond lengthens considerably. That the latter observation reflects a stronger interaction with the metal is consistent with our finding that the Cr–C(3) distances are notably shorter than the others.

The significant Cr–corannulene bond strength in  $(\eta^6\text{-corannulene})\text{Cr}(\text{CO})_3$ , although less than that of the corresponding benzene–Cr bond strength, suggests that  $(\eta^6\text{-corannulene})\text{Cr}(\text{CO})_3$  should indeed be thermally stable under the experimental conditions described here. Perhaps a kinetic explanation may be found for our inability to prepare  $(\eta^6\text{-corannulene})\text{Cr}(\text{CO})_3$ , since the thermodynamic stability of the compound suggests that

Table 1  
Calculated Cr–arene bond energies (kcal/mol, zero-point corrected)

Compound	6-31G* [8d–i]	6-31G*/LanL2DZ [8d–l]	cc-pVDZ [8m]	Exp.
<i>endo</i> ( $\eta^6\text{-corannulene})\text{Cr}(\text{CO})_3$	51.9	42.3	44.9	
<i>exo</i> ( $\eta^6\text{-corannulene})\text{Cr}(\text{CO})_3$	57.4	47.3	50.5	
$(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$	64.5	54.0	57.7	53 [19]

Table 2  
Bond distances (Å) in corannulene and of the  $\eta^6$  bound ring of  $(\eta^6\text{-corannulene})\text{Cr}(\text{CO})_3$  as determined using the cc-pVDZ [8m] basis set. The C atom numbering is as in Fig. 1 B

C–C Bond in corannulene	This work	X-ray [5a]	Electron diffraction [5b]
Hub	1.420	1.413(2)	1.414(6)
Spoke	1.387	1.391(4)	1.414(20)
Flank	1.450	1.440(2)	1.447(16)
Rim	1.392	1.402(5)	1.380(16)
C–C Bond in <i>exo</i> -( $\eta^6\text{-corannulene})\text{Cr}(\text{CO})_3$			
Hub	1.428		
Spoke	1.394		
Flank	1.453		
Rim	1.431		
Cr–C Bond in <i>exo</i> -( $\eta^6\text{-corannulene})\text{Cr}(\text{CO})_3$			
Cr–C(1)	2.296		
Cr–C(2)	2.413		
Cr–C(3)	2.200		

it should be isolable if prepared. Mechanistic studies of, e.g., arene exchange of compounds of the type ( $\eta^6$ -arene)-Cr(CO)<sub>3</sub> indicate a major role for associate processes [20], and it is possible that this is more difficult for large, polycyclic aromatic hydrocarbons.

#### 4. Summary

In an extensive series of attempts to synthesize the compounds ( $\eta^6$ -corannulene)M(CO)<sub>3</sub> (M = Cr, Mo, W), we have utilized virtually every standard and some non-standard of the published procedures for the synthesis of compounds of the type ( $\eta^6$ -arene)M(CO)<sub>3</sub>. All approaches have failed miserably, none producing even traces of the desired products, and it would seem that the target molecules are for some reason much less stable than are other  $\eta^n$ -corannulene complexes which have been reported. However, DFT calculations suggest that the  $\eta^6$ -corannulene–Cr bond of ( $\eta^6$ -corannulene)Cr(CO)<sub>3</sub> is only marginally weaker than the correspond arene–metal bond in the very stable ( $\eta^6$ -benzene)Cr(CO)<sub>3</sub>, and it seems that the reasons for synthetic failures are kinetic in nature.

#### Acknowledgements

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