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A Metallocene Molecular Gear

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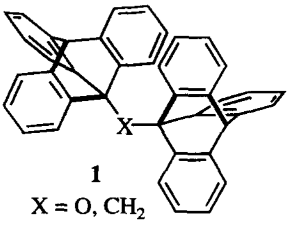
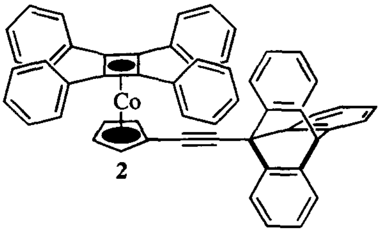
Abstract: In a five step synthesis (ethynylcyclopentadienyl)(tetraphenylcyclobutadiene)cobalt is produced in 19% overall yield from sodium carbomethoxycyclopentadienylide. Subsequent cross-coupling with 9-iodoanthracene (76%) and addition of benzyne (52%) gave (9-triptycylethynylcyclopentadienyl)(tetraphenylcyclobutadiene)cobalt, the first example of a metallocene containing molecular gear. © 1997 Elsevier Science Ltd.

The quest for novel molecular components that function in an analogous fashion to macroscopic mechanical systems has recently led to the synthesis and description of such molecules as a shuttle,[1] a brake[2] and a turnstile.[3] These are providing a basis for the future design of nanoscale systems and materials to perform tasks as varied as catalysis and nanoscale manipulation, information storage, and replication. One of the earliest examples of a molecular component, reported simultaneously by Mislow and Iwamura, utilises oxygen or methylene linked triptycenes to give molecules **1** analogous to a three-toothed bevel gear.[4] Subsequent studies on ring substituted phase isomers of **1** established that the two triptycenes undergo correlated rotation with an energy barrier to this gearing mechanism of only 1-2 kcal mol^{-1}. In contrast, gear slippage requires an activation energy of 30 - 40 kcal mol^{-1} such that disrotatory cog wheeling in these systems is as strictly specified as are rotations in symmetry-controlled reactions.[5]

Simple carbon derived rotors such as triptycene are limited by valency to three cog-teeth. In order to increase the number of cog-teeth available in simple rotors, and to use these for the generation of molecular gears with non-equal gearing ratios, we became interested in the possibility of utilising metallocenes . The low energy barrier to rotation of the π-fragment about the metal may be regarded as analogous to rotation about a low friction ball-bearing. To explore the possibility of using metallocenes in this way we embarked upon a synthesis of **2**, in which an acetylene substituted triptycene is linked to a four-toothed tetraphenyl cyclobutadiene containing metallocene.

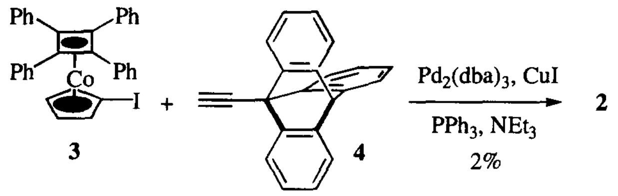


1
X = O, CH$_2$



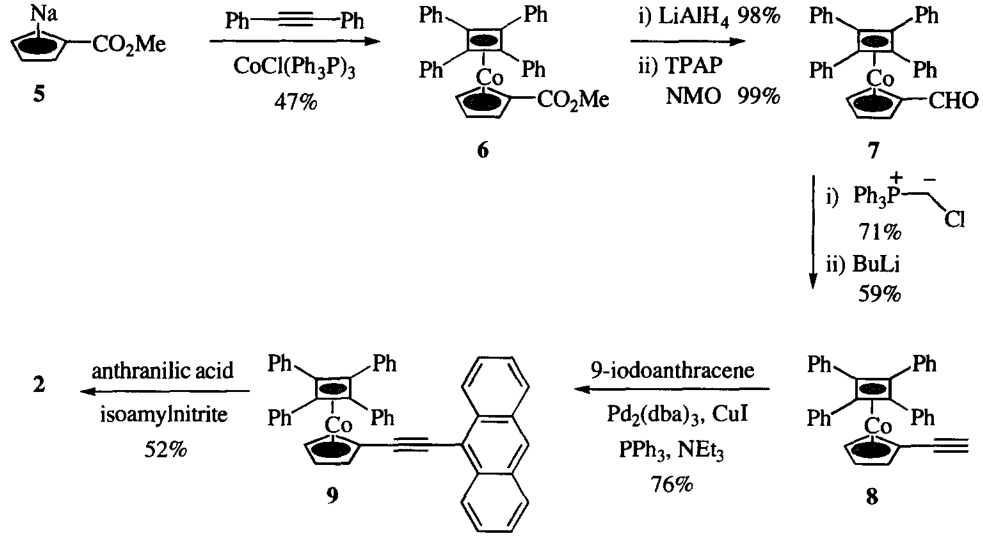
2

The (cyclopentadienyl)(tetraphenylbutadiene)cobalt complex was chosen for the metallocene component as this air and heat stable organometallic is readily synthesised from diphenylacetylene and (cyclopentadienyl)dicarbonylcobalt.[6] After conversion to iodide **3**[6], this was utilised in a Sonogashira coupling with 9-(ethynyl)triptycene **4**[7] in triethylamine heated at reflux (Scheme 1). Only a trace of **2** was isolated from a reaction mixture still containing **3** but no longer the acetylene **4**.



Scheme 1

As **3** is clearly a poor substrate, as an electron rich and bulky cyclopentadienyl iodide, this coupling strategy was reversed with the development of a methodology for the synthesis of the corresponding cyclopentadienyl acetylene complex (Scheme 2). Accordingly, sodium carbomethoxycyclopentadienylide **5**[8] was heated at reflux in toluene/THF with a source of Co(I) and diphenylacetylene to give the new carbomethoxy substituted metallocene **6**.[9] High yielding conversion to aldehyde **7** was followed by a Wittig reaction with the BuLi derived ylide from chloromethyltriphenylphosphonium chloride to give a 1:1 mixture of *E*/*Z* alkenes. Subsequent BuLi promoted elimination of HCl gave the required alkyne **8** in 41% overall yield from **6**. Sonogashira coupling with 9-iodoanthracene[10] now proceeded smoothly to give the disubstituted acetylene **9** in good yield.



Scheme 2

Addition of six equivalents of anthranilic acid to a dioxane solution containing six equivalents of isoamylnitrite and **8** heated at reflux, resulted in a 52 % yield of **2** (62% accounting for recovered starting material) that was identical in all respects with the material previously obtained from the low yielding cross-coupling (Scheme 1).[11] Increasing the number of benzyne equivalents generated *in situ* to nine and then eighteen did not appreciably change either the yield of **2** or the amount of recovered starting material.

The results of a variable temperature NMR investigation into **2** are shown in Figure 1. At 260 K (a) two doublets at 7.36 and 7.47 ppm, and two triplets at 6.99 and 7.04 ppm were observed for the three equivalent aromatic rings of triptycene. As the temperature was lowered through 233 K (b) and 220 K (c) all the peaks in the spectrum slightly change in chemical shift such that at 203 K (d) both doublets have merged with peaks from the four phenyl substituents. However, even at 203 K the two triplets, although slightly broadened, indicate that rotation of the triptycene is still rapid on the NMR timescale. In addition, the simplicity of the peaks from the four phenyl groups reveals that rotation about the metal, and about the phenyl-butadiene bonds, is also rapid at 203 K.

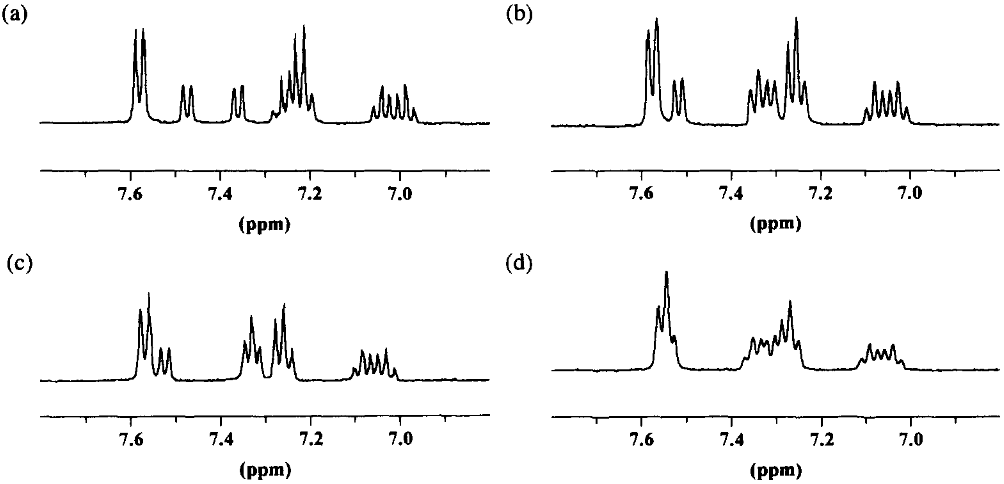


Figure 1. NMR (400 MHz, d_6-acetone) of **2** at: a) 260 K, b) 233 K, c) 220 K and d) 203 K.

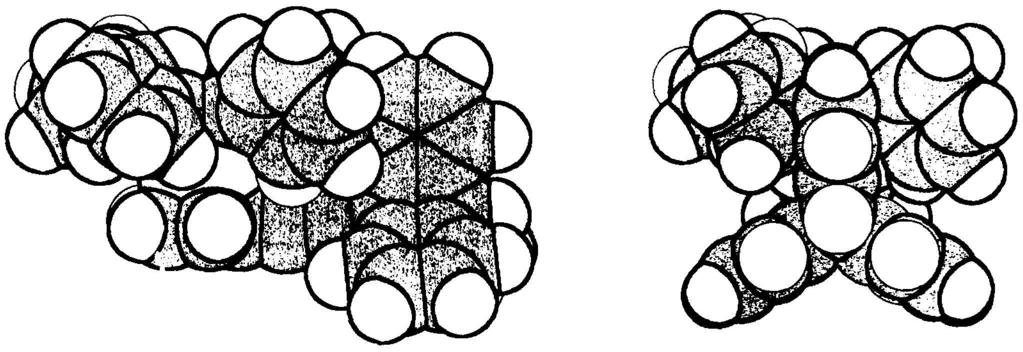


Figure 2. Space-filling representations of **2**.

Although independent rotation of both the tripytcene and the metallocene rotors cannot be ruled out, previous studies on bridgehead-substituted triptycenes have revealed a very high threefold torsional barrier.[12] For **2** this is likely avoided by a low energy correlated gearing mechanism between the two intermeshing cogs of the four and three toothed metallocene gear, as revealed by the space-filling representation of a model of **2** (Figure 2). In our ongoing work we are attempting to make more elaborate gearing arrays to confirm that correlated rotation indeed takes place, and to determine the energy barrier to gear-slippage.

Acknowledgements
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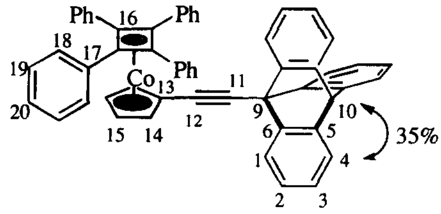
11. Analytical data for **2**: m.p. 218 - 220 °C (Found: C, 87.36; H, 4.92. $C_{55}H_{37}Co$ requires C, 87.29; H, 4.93 %); ν_{max} (nujol) 2224 cm^{-1} (-C≡C-); δ_H (400 MHz, $CDCl_3$) 4.70 (2 H, t, *J* 2.1, 14/15H), 5.12 (2 H, t, *J* 2.1, 14/15H), 5.37 (1 H, s, 10H), 6.92 (3 H, td, *J* 7.4, 1.3, 3H), 6.99 (3 H, td, J 7.4, 1.3, 2H), 7.15 - 7.18 (12 H, m, 19&20H), 7.34 (3 H, dd, *J* 7.2, 1.1, 4H), 7.36 (3 H, dd, *J* 7.3, 1.1, 1H), 7.58 (8 H, dd, *J* 5.8, 1.6, 18H); δ_C {^{1}H} (100 MHz, $CDCl_3$), 53.6 (C10), 55.4 (C9), 76.6 (C16), 79.4 (C11), 82.9 (C12), 85.9, 86.0 (C14/15), 94.7 (C13), 123.2 (C1), 123.6 (C4), 125.6 (C2), 125.8 (C3), 127.0 (C20), 128.6 (C19), 129.3 (C18), 136.0 (C17), 144.8, 144.7 (C5/6); *m/z* (EI) 756 (19%, M^+).



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