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Stopping the Aromatic Ring Current. Synthesis of the First Bis-Metal Complexed Benzannulene. On the Way to a Molecular Conductor with a Photo-Switch.

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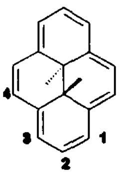
Abstract: The mild ligand exchange reaction between (tricarbonylchromium)naphthalene and the dibenzannulene **4** permits synthesis of the first bis-complexed large ring benzannulene **5**. Progressive reduction of the strong ring current of **1** occurs in going from **1-5**, which in the latter is only about 6% of that in **1**.

Dimethyldihydropyrene, **1**, is a planar, strongly aromatic bridged annulene, with a ring current equivalent to that of benzene.[1] Fusion of another aromatic system to **1**, as in the benzo[a]derivative **2**, causes substantial bond fixation in both the benzene and the [14]annulene rings of **2**, and hence about a 50% reduction in the ring current in each ring.[2] This is very similar to the case of naphthalene which can be considered as benzo[a]benzene. The reduction in ring current is easily followed by observation of the chemical shift of either the internal methyl protons or the external aromatic ring protons, δ -4.25 and -1.62 (internal methyl) and δ 8.67 and 7.62 (external proton H-4) for **1** and **2** respectively. Bond fixation is easily followed by the difference in the ^3J coupling constants for the external ring protons H-1,2 and H-2,3 which is 0 Hz for **1** and 2.33 Hz for **2**.[3] Fusion of a tricarbonylchromium complexed benzene ring on to **1** as in **3**, actually further bond fixes the [14]annulene ring, and reduces the ring current to 37% of that of **1**, a greater extent than benzene itself (50%).[4] Fusion of two benzene rings, as in **4**, reduces the ring current to 18% of that in **1**.[2] *The question then arises "How far can the ring current be reduced, and still retain a stable annulene"?* We thought that synthesis of the bis-complex **5**, would approach this limit.



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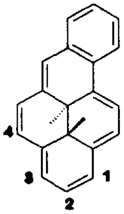

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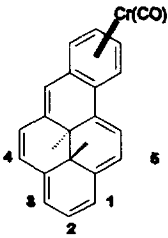

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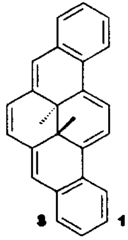

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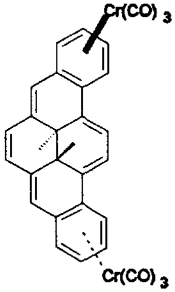

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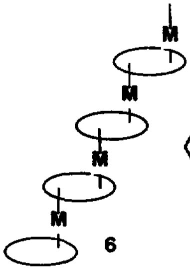
In addition, except for tetraaza[14]annulene,[5] very few metal complexes of large ring annulenes are known, especially π-bonded complexes,[6] and even fewer complexes of benzannulenes.[4,7] This in part is probably because of the synthetic difficulties of obtaining the all carbon annulenes. Our recent aryne based synthesis of benzannulenes,[3,8] has made available compounds like **4** in reasonable quantities such that metal complexation study is now possible. This is attractive because it has been postulated that polymers containing aromatic rings joined by metal atoms such as **6** are potential organic conductors.[9] Inclusion of a dihydropyrene unit as part of the aromatic rings of **6** is especially attractive because dihydropyrene **1** and its derivatives are photo-convertible to the "stepped" cyclophanediene valence isomer **7**, and moreover this conversion is reversible either thermally or photochemically,[10] and thus a *photo-switch* could be built in to such a *conductor*, the switch arising from the conducting "on" state (a flat fully delocalized dihydropyrene) and the non-conducting "off" state (a stepped cyclophane with non-communicating benzene sextets). Attempted bis-complexation of **4** is the first step down this path.



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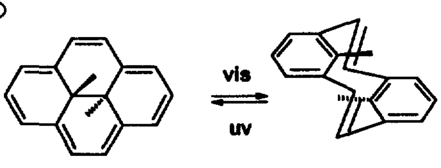

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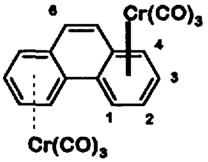

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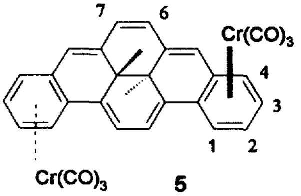
Dihydropyrenes do not survive the rather harsh conditions necessary with use of $Cr(CO)_6$.[4] The ligand exchange reaction using (tricarbonylchromium)naphthalene is better suited, providing the sextet containing ring to be complexed is more delocalized than in naphthalene itself. Such should be the case with **4**, and phenanthrene for example. As a model reaction, phenanthrene with (tricarbonylchromium)naphthalene at 60°C for 15 hours yielded 80% of the bis-complex **8** in somewhat better yield than the literature method.[11] Similar reaction[12] of **4** gave about 50% of bis-complex, 80% of which was the isomer **5**. The remainder was the minor isomers **9** and **10** in about a 1:2 ratio. All isomers gave a CI MS peak at *m/z* = 605 (MH^+). The major isomer **5** obtained as orange-red crystals from cyclohexane, mp 219-221 °C (dec), gave an EI HR MS molecular ion at 604.0093; Calculated for $C_{32}H_{20}Cr_2O_6$ = 604.0070.



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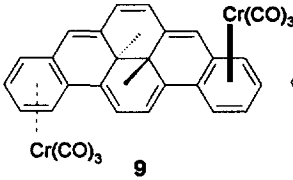

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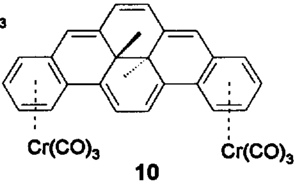

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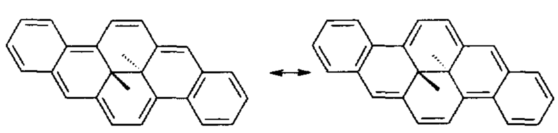
In the case of **3**, the analogous minor isomer was obtained in a 1:3 ratio, and thus the approximate 1:10 ratio observed for **9**:**5** seems reasonable. It is interesting that there is a small (2:1) preference for **10** over **9**. Isomers **5** and **9** gave single internal methyl proton shifts at δ +0.64 and +0.58 respectively, whereas isomer **10** with non-identical methyl groups gave two peaks at δ +0.35 and +0.27. Likewise the ^{13}C NMR for **5** showed only one internal methyl carbon and one internal bridge carbon.[12] Important nmr data for **1-5** are compared in Table 1.

Table 1: Selected NMR data for **1-5** with Ring Current Shielding (ppm) values and relative Ring Currents.

Compound	**1**	**2**	**3**	**4**	**5**
δ (Me)	-4.25	-1.62	-0.97	+0.02	+0.64
RCShielding[a]	5.22	2.59	1.94	0.95	0.33
Ring Current[b]	100%	50%	37%	18%	6%
δ H-ring[c]	8.67	7.62	7.28	7.05	6.49
δ C-Me	14.0	17.0, 17.7	18.4, 20.0	19.2	21.5
δ C-bridge	30.0	35.5, 36.0	36.9, 37.7	39.5	41.0

a: Ring Current Shielding (RCS) = 0.97 - δ(Me) ppm.[2] b: Ring Current (RC) = ring current relative to **1** = {[0.97 - δ (Me)]/5.22}x100%[2] c: **1** (H-4), **2** (H-4), **3** (H-4), **4** (H-5), **5** (H-7)

As can be clearly seen from Table 1, as one progresses from **1** to **5**, the ring current in the macrocyclic ring steadily falls, reaching in the case of **5** only 6%[13] of that of **1**. Note that a corresponding trend is observed for the external ring protons which become progressively less deshielded as the ring current falls, and as well for the internal methyl carbon shifts and the internal bridge carbon shifts which are less shielded on going from **1** to **5** as the ring current reduces. Metal complexation of the benzene rings of **4** has induced the most severe bond fixation of **1** to date, and presumably reflects the need for the complexed rings in **5** to be bond equal. Interestingly though, the ring current is not totally stopped![13] With this successful synthesis of an annulene bis complex, we will now push towards our goal of a molecule like **6**. One promising candidate for study is the related benzannulene **11**, which has the identical energy, equivalent Kekulé structures **11A** and **11B**. With less isolated sextets, connective pathways between metal to metal (in **6**) should be productive.



11A **11B**

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12. *Procedure*: a solution of **4** (40 mg, 0.12 mmol) and (tricarbonylchromium)naphthalene (127 mg, 0.48 mmol) in ether (2 mL) and THF (0.1 mL) in a heavy screw capped vial was stirred magnetically at 60°C for 30 hours. The mixture was then directly pre-absorbed on to silica gel and chromatographed using firstly petroleum ether (bp 30-60°C)(PE) to remove unchanged **4**, and then PE : ethyl acetate (10:1) to elute firstly a trace of mono-complex and then the orange-red bis-complex **5**, 29 mg (41%). Recrystallisation from cyclohexane yielded orange-red crystals, mp 219-221°C (dec). ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.85 (s, H-13,14), 6.55 (s, H-6,7), 6.49 (s, H-5,8), 6.13 (d, J~7Hz, H-1,12), 5.52 (d, J~7Hz, H-4,9), 5.48(t, J~7Hz, H-3,10), 5.39 (t, J~7Hz, H-2,11), 0.64 (s, $-CH_3$)(Assigned by COSY/NOESY); ^{13}C NMR (90.6 MHz) δ 232.9, 141.3, 134.0, 127.6, 122.9, 118.5, 101.5, 96.9, 91.9, 91.7, 90.7, 89.0, 41.0, 21.5; IR (KBr) 1950, 1875 cm^{-1}; UV (CH_2Cl_2) λ_{max} (ϵ_{max}) nm 218 (52,000), 336 (31,100), 438 (20,300).
13. In **3**, $\Delta\delta$(Me) = 0.11 ppm. Thus the $-Cr(CO)_3$ group has only a very small through space anisotropy effect. Assuming the second $-Cr(CO)_3$ group causes an analogous 0.11 ppm deshielding on the less affected methyl group, the ring current in **5** might be 2% higher. We believe the RCS is too large for the RC to be 0%.

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