J. Am. Chem. Soc. **1998,** *120,* 1785−1794

The Synthesis, Aromaticity, and NMR Properties of [14]Annulene Fused Organometallics. Determination of the Effective Bond Localizing Ability (“Relative Aromaticity”) and Diamagnetic Anisotropy of Several Organometallic Moieties

Reginald H. Mitchell,* Yongsheng Chen, Nasr Khalifa,[†] and Pengzu Zhou

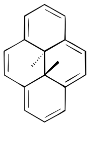
Contribution from the Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, British Columbia, Canada V8W 3V6

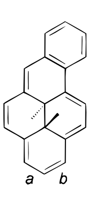
Received August 18, 1997

Abstract: The aromatic ring current probe, the bridged [14]annulene dimethyldihydropyrene, **1**, is used to investigate the bond localization effects of the organometallic species tricarbonylchromiumbenzene, **37**, hexamethylbenzenerutheniumbenzene, **38**, tricarbonylmanganesecyclopentadienyl, **40**, and pentamethylcyclopentadienylrutheniumcyclopentadienyl, **39**, when fused to the annulene. Benzo[*a*]dimethyldihydropyrene **2** was converted to the two isomers of its tricarbonylchromium complex, **9** and **10**, in 60% yield using ligand exchange with naphthalene and to its hexamethylbenzene−ruthenium complexes **11** and **12** with $[RuCl_2(HMB)]_2$ and $AgBF_4$. The cyclopentadienide fused dihydropyrene **5** was synthesized from dimethyldihydropyrene **1** in eight steps, and then on reaction with pentacarbonyl manganese bromide gave the tricarbonylmanganese complex of **5**, as two isomers **28** and **29** in 61% yield, and with $(Cp^*RuCl_2)_n$ gave 70% yield of the dihydropyrene annelated ruthenocene isomers **26** and **27**. Bis(tricarbonylchromium) complexes **32**−**34** were obtained in 50% yield from the dibenzannulene **30**. The ^{1}H NMR spectra for each complex were analyzed in detail with regard to ring current shielding of the internal methyl protons and ring current deshielding of the external protons. The McGlinchey equation was used to remove diamagnetic anisotropy effects, and the resultant chemical shift values were consistent with coupling constant results, which together yielded bond fixation data of the annulene, caused by the organometallic. The relative bond fixing ability of the organometallics was found to be in the order: $Cp{-}Ru{-}Cp^* >$ benzene$-Ru^{2+}-$(HMB) $> Cp{-}Mn(CO)_3 >$ benzene$-Cr(CO)_3 >$ benzene. Alternance parameter evidence is presented that the complexes are **aromatic**, and the authors discuss the relative aromaticity of the complexes to benzene.

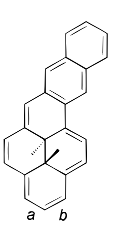
Introduction

We have established[1] that the bridged [14]annulene **1**, *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (DMDHP), is an excellent NMR probe for ring current and bond localization effects. Fusion of an aromatic species such as benzene or naphthalene to **1** as in **2** and **3**, respectively, strongly reduces the ring current that is present in **1** and hence reduces the ring current shielding of the internal methyl protons from δ −4.25 to −1.62 and −0.44, respectively.[1a] This is caused by a strong bond fixation effect that occurs whenever two aromatic species are fused,[2] and affects both fused rings such that adjacent bonds alternate. This can be seen experimentally in the magnitude of adjacent ^3J coupling constants, which become larger for the bond of greater π-bond order and smaller for the more single-like bond than those found in the unfused aromatics.[2f,g] Thus for **2** and **3** the ^3J values for the bonds *b* and *a* in the macrocyclic ring are 8.85 and 6.52, and 9.07 and 6.17, respectively, while for **1** are both 7.54 Hz.[1a] The degree of both the bond alternation effect and the reduction of ring current depend on the bond localization energy of the ring that is fused, i.e., benzene in **2** and naphthalene in **3**, and thus comparison of the NMR data for any fused system, such as **4** with that obtained for **2** and **1**, permits some comment on the relative aromaticity of the fused ring relative to benzene.[1]

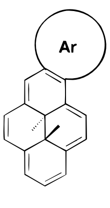

1



2



3



4

[†] Present address: Chemistry, Camosun College, Victoria, BC.

(1) (a) Mitchell, R. H.; Iyer, V. S.; Khalifa, N.; Mahadevan, R.; Venugopalan, S.; Weerawarna, S. A.; Zhou, P. *J. Am. Chem. Soc.* **1995**, *117*, 1514−1532. (b) Mitchell, R. H.; Iyer, V. S. *J. Am. Chem. Soc.* **1996**, *118*, 722−726. (c) Mitchell, R. H.; Iyer, V. S. *J. Am. Chem. Soc.* **1996**, *118*, 2903−2906. (d) Mitchell, R. H.; Khalifa, N. A.; Dingle, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 6696−6697.

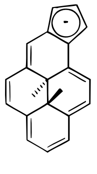
(2) (a) Mitchell, R. H.; Carruthers, R. J.; Mazuch, L.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2544−2551. (b) Mitchell, R. H.; Yan, J. S. H.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2551−2559. (c) Mitchell, R. H.; Williams, R. V.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2560−2571. (d) Mitchell, R. H.; Williams, R. V.; Mahadevan, R.; Lai, Y. H.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2571−2578. (e) Mitchell, R. H. *Isr. J. Chem.* **1980**, *20*, 294−299. (f) Cremer, D.; Günther, H. *Liebigs Ann. Chem.* **1972**, *763*, 87−108. (g) Günther, H.; Shyoukh, A.; Cremer, D.; Frish, *Liebigs Ann. Chem.* **1978**, 150−164. (h) K. H. Balaban, A. T.; Banciu, M.; Ciorba, V. *Annulenes, Benzo-, Hetero-, Homo-Derivatives*; CRC Press: Boca Raton, FL, 1987; Vol. II, Chapter 7.

S0002-7863(97)02913-2 CCC: $15.00

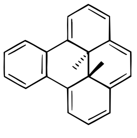
In this paper we fuse several organometallic species to **1**. This is of interest because, while ferrocene is commonly regarded as aromatic, other species such as tricarbonylchromium(0)−benzene are less obvious, in part (see below) because of the approximately 2 ppm upfield shift that is observed for its protons, relative to benzene. This paper thus compares the relative bond fixing ability, which we equate to aromaticity, of some benzene and cyclopentadienide metal complexes.

Syntheses

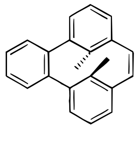
As representative examples, we considered metal complexes of the benz[*a*]annulene, **2**, and the cyclopentadienide fused annulene, **5**, to be suitable targets, since [*e*]-fused annulenes such as **6** added the additional complication of easy valence isomerization to the cyclophane-diene isomer **7**.[2b,3] At the start of this work, no metal complexes of benzannulenes were known. Indeed few metal complexes of any larger annulene were known,[4] probably because of the very limited accessibility and stability of either group of compounds. We first[5] attempted reaction of **2** with both $Cr(CO)_6$ and $Cr(CO)_3(MeCN)_3$ under normal thermal conditions, but obtained only decomposition of **2**. We thus considered the more mild THF catalyzed ligand exchange reaction[6] of (η^6-naphthalene)$Cr(CO)_3$, **8**.



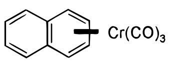
5



6



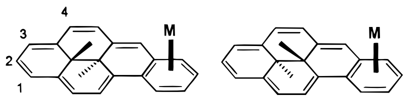
7



8

It was not immediately obvious whether **2** would exchange with the naphthalene in **8**, since the exchange reaction is normally used for benzene derivatives. Since in naphthalene two 6π systems are competing, some loss of resonance energy occurs for the uncomplexed ring in **8**. If **8** were to exchange with **2**, the loss of resonance energy would be in a 14π rather than a 6π system, and thus might be expected to be favorable. We thus thought that the exchange reaction was worth trying.

In the event, reaction of **2** and **8** in ether containing THF as catalyst at 50−60 °C gave 60% of the desired product, as a mixture of the two expected isomers **9** and **10** in a 3:1 ratio. The major isomer, **9**, could be separated by fractional crystallization as deep red crystals, mp 189−190 °C. The overall structures of **9** and **10** were supported by NMR data (see below), mass spectra, and elemental analysis. The relative stereochemistries of **9** and **10** probably could be made from the NMR spectra using anisotropy arguments; however, an X-ray structure determination on **9** unambiguously indicated the stereochemistry shown, where the $Cr(CO)_3$ fragment is attached on the opposite side to the closest attached internal methyl group. The two isomers are then easily distinguished by the chemical shifts of their internal methyl protons (note: these shifts are determined in the same solution), δ −0.871 and −0.977 for **9**, and δ −0.807 and −1.158 for the minor isomer **10**. The hexamethylbenzene ruthenium(II) complexes, **11** and **12**, as $2BF_4$- salts, were also prepared as very dark red crystals from **2** and $[RuCl_2(HMB)]_2$[7] using $AgBF_4$ at room temperature. However, in this case, the pair of isomers (3:2 ratio) could not be separated. The major isomer showed its internal methyl protons at δ −0.517 and −0.864, while those of the minor were at δ −0.558 and −0.891.

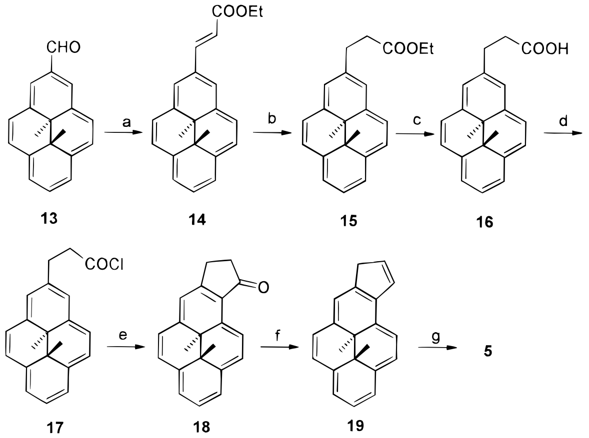


9 M = Cr(CO)$_3$ **10**

11 M = Ru^{2+}HMB **12**

Synthesis of cyclopentadienide derivatives proceeded from **5**, which we reported in preliminary form in 1991.[1d] The route used to **5** is shown in Scheme 1.

Scheme 1[a]



[a]Conditions: (a) $(EtO)_2P(O)CH_2COOEt$/NaH; (b) Pd/H_2; (c) aq NaOH; (d) $(COCl)_2$; (e) $BF_3{\cdot}OEt_2$; (f) LAH then HCl; (g) KH/THF.

Formylation of **1** using Cl_2CHOCH_3 and $TiCl_4$ gave 75% of the 2-formyl derivative **13**, along with 20% of the 1-formyl isomer.[8] Wittig−Horner reaction of **13** gave almost quantitatively the dark red ester **14**, mp 146−147 °C, which could be hydrogenated in 86% yield to the green ester **15**. Hydrolysis then gave the acid **16**, mp 165 °C. Cyclization to the ketone **18** failed with both HF and polyphosphoric acid, and reaction of **16** with thionyl chloride or aluminum chloride caused extensive decomposition. Reaction of the acid **16** with oxalyl chloride did, however, yield the acid chloride **17**, IR at 1802 cm^{-1}, which was directly treated with BF_3-etherate in CH_2Cl_2 at room temperature to give cyclized ketone **18** (green, mp 210−211 °C) in overall 63% yield. Reduction of **18** with $LiAlH_4$ was expected to give the alcohol; however, the sulfuric acid used in workup caused extensive dehydration and decomposition. Use of 20% hydrochloric acid dramatically improved the yield and enabled fused cyclopentadiene **19** to be isolated in 81% yield, as dark green crystals, mp 114−116 °C. These were only stable for about 2 days (<0 °C), so were always chromatographed quickly before use. The internal methyl protons of **19** appeared at δ −4.15 and −4.16, almost unperturbed from those in **1** at δ −4.25. The red anion **5** could be generated from green **19** in THF under argon using either

---

(3) Mitchell, R. H.; Iyer, V. S.; Mahadevan, R.; Venugopalan, S.; Zhou, P. *J. Org. Chem.* **1996**, *61*, 5116−5120.

(4) Fischer, E. O.; Ruhle, H.; Vogel, E.; Grimme, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 518−519. Stockel, K.; Sondheimer, F.; Clarke, T. A.; Guss, M.; Mason, R. *J. Am. Chem. Soc.* **1971**, *93*, 2571−2572. Hilken, G.; Kinkel, T.; Schwamborn, M.; Lex, J.; Schmickler, H.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 784.

(5) For a preliminary report, see: Mitchell, R. H.; Zhou, P.; Venugopalan, S.; Dingle, T. W. *J. Am. Chem. Soc.* **1990**, *112*, 7812−7813.

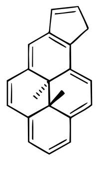
(6) Kundig, E. P.; Perret, C.; Spichiger, S.; Bernardinelli, G. *J. Organomet. Chem.* **1985**, *286*, 183−200.

(7) Bennett, M. A.; Matheson, T. W. *J. Organomet. Chem.* **1979**, *175*, 87−93. Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Smith, A. K.; Tucker, P. A. *Inorg. Chem.* **1980**, *19*, 1014−1021.

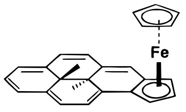
(8) Mitchell, R. H.; Lau, D. Y. K.; Miyazawa, A. *Org. Prep. Proced. Int.* **1996**, *28*, 713−716.

potassium hydride or methyllithium. Protonation of the anion with water returned **19** and its isomer **20** (δ(Me) −4.09) in a 2:3 ratio.

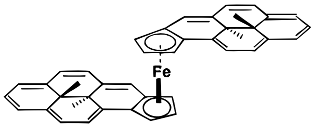
From the anion **5**, the desired targets were the "ferrocene like" molecules **21** and **22**. Bis(π-indenyl)iron, **23**, has been prepared from the indenyl anion and both ferric chloride[9] and ferrous chloride.[10] As well, mixed ferrocenes such as **24** have been prepared[10] by reacting two different cyclopentadienide anions with ferrous chloride in dry THF. Indeed, we were able to obtain both **23** and **24** under these conditions, but failed to obtain either **21** or **22** when anion **5** was used. Use of $FeCl_2{\cdot}2THF$, which dramatically improves the yields of some ferrocenes,[11] did not change the result, nor did use of $Fe(acac)_2$,[12] nor did use of Cp* anion or [Cp*Fe(acac)],[13] reversal of addition order, or change in temperature. Both cyclopentadienide[14] and indenide[15] form air-stable thallium(I) complexes; however, only decomposition was observed from **5**. Gill and Mann[16] have used the cation **25** to deliver the iron−Cp$^+$ unit to a number of electron rich arene substrates under photolytic conditions. We saw no reason a cyclopentadienide anion should not be used in this process, and indeed photolysis of **25** and potassium cyclopentadienide in DMF for 4 h, using an ordinary 150-W flood lamp, yielded 80% of ferrocene, while potassium indenide yielded 69% of the mixed ferrocene **24**. However, both the anion **5** and fluorenyl anion failed in this reaction.



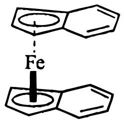
20



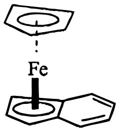
21



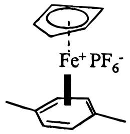
22



23



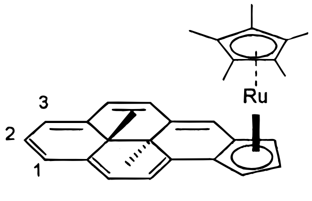
24



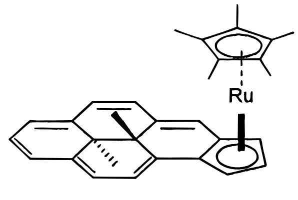
25

Thus, so far we have failed to obtain an iron complexed derivative of **5**. We believe this to be caused in part by too much delocalization of the negative charge around the annulene ring (40% by π-SCF calculation[17]). In support of this, we note that both tetracyano-[18] and penta(carbomethoxy)-[19] cyclopentadienide (which both have strongly electron-withdrawing groups on the cyclopentadienide) do not form a ferrocene on treatment with $FeCl_2$ (rather very unstable Fe(II) salts), nor does in our hands dibenzocyclopentadienide (fluorenide), whereas benzocyclopentadienide (indenide) does. In the latter case, our calculations indicate only about 10% of the negative charge is delocalized around the benzene ring. Despite these discouraging results, we noted that Gassman[20a] had been able to prepare (η^5-fluorenyl)(η^5-Cp*)ruthenium(II), and that Mulay[20b] has suggested that ruthenocene has less electron density in the five-membered rings than does ferrocene, and so we decided that ruthenocenes might be worth pursuing.

Reaction of $(Cp^*RuCl_2)_n$[20,21] with anion **5** at room temperature in THF was successful and gave the ruthenocene in 70% yield as a 3.7:1 mixture of the two isomers **26** and **27**. Neither chromatography, fractional crystallization, nor sublimation would separate these isomers, though they were obtained analytically pure as the mixture, with correct MH$^+$ pattern around 506 in the CI mass spectrum. The major isomer, assigned structure **26** by analogy to **9**, showed internal methyl protons at δ −0.548 and −0.691, while those of the minor isomer were more separated (compare **9** and **10** above) at δ −0.473 and −0.820. The compounds were air-sensitive.

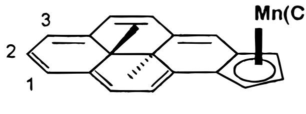


26

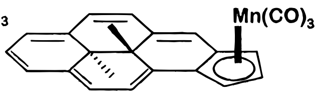


27

Following this success, we anticipated that reaction of anion **5** with dipyridine tricarbonylmanganese(I) bromide,[22] which is prepared from pentacarbonylmanganese(I) bromide,[23] would yield the two tricarbonylmanganese compounds **28** and **29**. This reaction failed. However, reaction of the anion **5** with pentacarbonylmanganese(I) bromide itself gave the two isomers in 61% yield in a 2.5:1 ratio. The major isomer was assigned structure **28**, and showed internal methyl protons at δ −0.728 and −0.784, while **29** was at δ −0.670 and −0.976. Again satisfactory analysis and mass spectral data were obtained, but the two isomers could not be separated. Note that in each case, the major isomer (**9**, **26**, and **28**) was assigned with the closest attached methyl on the opposite side (i.e., as far away as possible) to the metal fragment, and that these isomers showed internal methyl protons with the least different chemical shifts.



28



29

---

[9] Paulson, P. L.; Wilkinson, G. *J. Am. Chem. Soc.* **1954**, *76*, 2024−2026.

[10] King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1964**, *3*, 796−801.

[11] LeVanda, C.; Bechgaard, K.; Cowan, D. O.; Mueller-Westerhoff, U. T.; Eilbracht, P.; Candella, G. A.; Collins, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 3181−3187.

[12] Buckingham, D. A.; Gorges, R. C.; Henry, J. T. *Aust. J. Chem.* **1967**, *20*, 281−296.

[13] Bunel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* **1985**, *4*, 1680−1682.

[14] Meister, H. *Angew. Chem.* **1957**, *69*, 533−534.

[15] Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Smith, A. K.; Tucker, P. A. *Inorg. Chem.* **1980**, *19*, 1014−1021.

[16] Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1980**, *19*, 3007−3010.

[17] PCMODEL v 5.1 (PCWIN) was used from Serena Software, Box 3076, Bloomington, IN 47402-3076.

[18] Webster, O. W. *J. Am. Chem. Soc.* **1966**, *88*, 4055−4060.

[19] Bamfield, P.; Cookson, R. C.; Crabtree, A.; Henstock, J.; Judec, J.; Johnson, A. W.; Whitear, B. *Chem. Ind. (London)* **1964**, 1313−1314.

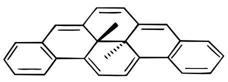
[20] (a) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 6130−6135. (b) Mulay, L. N.; Withstandley, V. *J. Chem. Phys.* **1965**, *43*, 4522−4523.

[21] Oshima, N.; Suzuki, H.; Moro-Oka, Y. *Chem. Lett.* **1984**, 1161−1164; Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274−278.

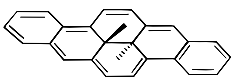
[22] Lynch, T. J.; Helvenston, M. C. *Organometallics* **1989**, *8*, 1959−1963.

[23] Abel, E. W.; Wilkinson, G. *J. Chem. Soc.* **1959**, 1501−1505.

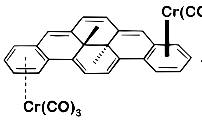
Bis-Complexes. Our recent[1a,24] improved route to the dibenzannulenes **30** and **31** gave us opportunity to attempt bis-complexation.[25a] The *cisoid*-fused system **30** is much more stable than the *transoid*-fused **31**, and has **two** benzenoid rings that could be complexed. Formally **31** has only one benzenoid ring, unless biradicaloid[2c] structures are invoked. Indeed, reaction of **30** with (tricarbonylchromium)naphthalene at 60 °C for 30 h gave 50% of the bis-complex as a mixture of three isomers in a 12:2:1 ratio. These gave clear CI MS peaks for MH^+ at 605. The major isomer would be expected to be **32**, and this could be fractionally crystallized pure, mp 219−220 °C. It and the minor isomer **33** are symmetrical and thus show only one type of methyl proton at δ +0.64 and +0.96, respectively, while the nonsymmetrical isomer **34** shows two peaks at δ +0.86 and +0.42.[25b] A small amount of mono-complexed product **35** is also formed. Disappointingly, the less stable *transoid*-isomer **31** decomposes under these complexing conditions, and no complexed product could be isolated.



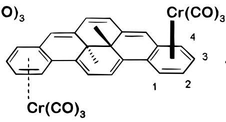
30



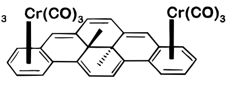
31



32

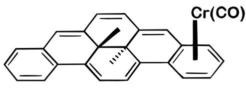


33

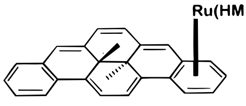


34

Attempted formation of the bis[(hexamethylbenzene)ruthenium(II)] complexes of **30** and **31** failed; only the mono-complex **36** could be obtained as a mixture of two isomers.



35



36

Diamagnetic Anisotropy Effects

We have shown[1a] that the change in chemical shifts that occur between **4** and **2** can be used to estimate the relative aromaticity of the annelating ring in **4** to benzene. Central to this hypothesis is the assumption that the chemical shifts of the internal methyl protons and the most distant external ring protons are too far away from the annelating ring to be affected anisotropically through space. This we have demonstrated for relatively planar systems such as **3**, **6**, **30**, or **31**.[1a,2a−c] It is not quite so obvious whether this holds true for complexed systems such as **9**. Any change in bond-fixation (delocalization) in the macrocyclic ring caused by complexation of the annelating ring would, of course, affect both methyl groups equally. A through-space effect of the metal complexing group might be expected to affect the methyl groups differently since, of course, one methyl group is above the plane of the large ring, while the other is below it. In fact, despite this, as Table 1 shows, the chemical shift differences between the methyl groups are really rather small, especially in comparison to the difference in shift from **2**.

Table 1. Experimental Chemical Shifts in $CDCl_3$ of the Internal Methyl Protons of the Compounds Studied[a]

compd	$\delta(Me)_a$	$\delta(Me)_b$	$\Delta\delta$
1	−4.25		0.000
2	−1.618	−1.626	0.008
9	−0.871	−0.977	0.106
10	−0.807	−1.158	0.351
11	−0.517	−0.864	0.340
12	−0.558	−0.891	0.330
26	−0.548	−0.691	0.143
27	−0.473	−0.820	0.347
28	−0.728	−0.784	0.056
29	−0.670	−0.976	0.306
32	+0.64		0
33	+0.58		0
34	+0.860	+0.422	0.438

[a] Note $(Me)_a$ and $(Me)_b$ are not yet assigned. Their chemical shifts are determined in the same molecule and thus $\Delta\delta$ is given to three decimal places and was consistent to ±0.002.

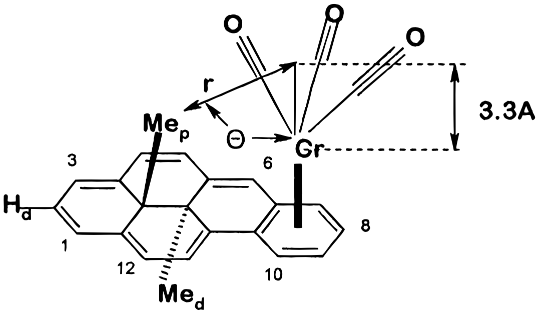


Figure 1. Diagram to show parameters **r** and θ used in eq 1.

It would seem that the through-space anisotropy effect at this distance is rather small. Fortunately the elegant work of McGlinchey[26] enables us to prove this point. McGlinchey has made use of the McConnell equation together with a composite geometric term for the organometallic moiety to determine χ values for several organometallic groups. We can thus use his χ value for the $Cr(CO)_3$ fragment to determine the through-space (de)shielding of this group on any of the protons in our compounds containing the $-Cr(CO)_3$ group. Application to compound **9** is shown in Figure 1.

For $-Cr(CO)_3$, the three carbonyl groups are considered a "super-carbonyl" along the C_3 axis. The center is 3.3 Å from the Cr atom. The distance from this center to the proton under consideration is **r** (Å) and θ (deg) is the angle made by **r** and the C_3 axis as shown in Figure 1. McGlinchey's data then yields eq 2.

In general, σ (ppm, + = shielding),

$$\sigma = -\chi_{SI} \times 10^{36}\,(3\cos^2\theta - 1)/12\pi\mathbf{r}^3 \tag{1}$$

and using McGlinchey's value for χ_{SI} -2124×10^{-36} m^3/molecule

$$\sigma = 56.341(3\cos^2\theta - 1)/\mathbf{r^3} \tag{2}$$

where σ is the shielding (ppm) expected for the proton caused by the anisotropic effect of the $Cr(CO)_3$.

---

(24) Mitchell, R. H.; Chen, Y.; Iyer, V. S.; Lau, D. Y. K.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2907−2911.

(25) (a) For a preliminary report see: Mitchell, R. H.; Chen, Y. *Tetrahedron. Lett.*, **1996**, *37*, 6665−6668. (b) In the preliminary report,[25a] the chemical shifts for the methyl protons of the minor isomers **33** and **34** were erroneously reported.

(26) McGlinchey, M. J.; Burns, R. C.; Hofer, R.; Top, S.; Jaouen, G. *Organometallics* **1986**, *5*, 104−109.

Table 2. Calculated Shielding's (σ, ppm) and Experimental Chemical Shifts (δ) for the Protons of Compounds **9** and **10**

proton	**9**:σ	**9**:δ	**10**:σ	**10**:δ
Me_p	−0.104	−0.871	−0.030	−0.807
Me_d	+0.118	−0.977	+0.090	−1.158
1	−0.011	7.179	+0.001	7.24
2	−0.013	6.882	−0.008	6.925
3	−0.006	7.021	−0.009	7.095
4	+0.005	7.276	+0.001	7.385
5	+0.053	7.276	+0.045	7.287
6	+0.255	7.244	+0.233	7.244
7	+0.456	5.939	+0.456	5.826
8	+0.456	5.613	+0.472	5.645
9	+0.453	5.503	+0.473	5.453
10	+0.443	6.567	+0.451	6.489
11	+0.193	7.594	+0.185	7.563
12	+0.022	7.002	+0.337	7.012

The parameters **r** and θ were obtained from PCMODEL[17] minimized structures, which in our experience[27] gives rather good geometries in both the dihydropyrenes and cyclophanes, agreeing well with X-ray data where available. Whereas the values of **r** and θ for the ring hydrogens are unambiguous, those for the methyl groups, which can rotate, are not. We tried averaging the $(3\cos^2\theta - 1)/\mathbf{r}^3$ term (which we will call the factor, **f**), and then determining σ, averaging θ and **r** first to determine **f** and then σ, and finally considering the methyl protons to be at a point at the center of the circle that they sweep out on rotation. This latter method gave the most consistent results, though it should be stressed that the differences were rather small; for example, for the methyl groups of compound **9**, values for σ for the *proximal* methyl group were found to be −0.077, −0.090 and, −0.104 ppm, respectively, and for the *distal* methyl group +0.119, +0.117, and +0.118 ppm, respectively (the proximal methyl group, Me_p, is on the same side as the $Cr(CO)_3$), and the distal methyl group, Me_d , is on the opposite side).

The values of σ calculated using eq 2 for each proton in compounds **9** and **10** are given in Table 2, together with the experimental chemical shifts. If compounds **9** and **10** had exactly the same geometry, then the calculated value of σ (and the experimental chemical shift) for each *ring* proton in compound **9** would be identical with the corresponding proton in **10**. PCMODEL calculations indicate that the geometries are not exactly the same (see below), and thus slightly different σ values are calculated and chemical shifts observed.

The calculated chemical shifts for the two methyl groups of **9** after removal of the (de)shielding due to the $Cr(CO)_3$ anisotropy are −0.975 (Me_p) and −0.859 (Me_d). This difference is *small* ($\Delta\delta = 0.116$ ppm), suggesting that the skeleton of **9** is not much different from that in **2** where $\Delta\delta(Me) = 0.008$ ppm. The average chemical shift of the two methyl groups of **9** *in the absence of the $Cr(CO)_3$ anisotropy* is thus −0.92 (±0.06) ppm, and this is the value we will use in the aromaticity calculations below. Clearly the $Cr(CO)_3$ group does ***not*** have a large through space (anisotropic) effect on the methyl protons or indeed on any of the more distant protons (see Table 2). Even for the isolated proton *adjacent* to the complexed ring, (H-6), σ is only calculated to be +0.25 ppm! Thus the change in chemical shift on complexation, $\delta(\mathbf{9}) - \delta(\mathbf{2})$ of about 0.7 ppm, is not a through-space anisotropy effect of the $Cr(CO)_3$ group. Nor is it a through-space anisotropy effect of the benzene ring. The Memory equation[28] can be used to calculate the deshielding of the methyl protons in **2** caused by the field of the benzene ring through space to be 0.062 and 0.047 ppm for the closest and furthest methyl group, respectively (note: they actually differ by 0.008 ppm). Even if the entire ring current of the complexed benzene ring in **9** were lost, the *through-space effect* on the methyl protons would not be expected to be larger than in **2**. Thus we believe that the change in chemical shift of the protons on going from **2** to **9**, reflects a real *change in ring current in the macrocyclic ring,* and we will show below that this is caused by a change in the delocalization in the macrocyclic ring.

The data for the minor isomer **10** are not quite so good. As can be seen from Table 2, the observed chemical shift difference between the methyl groups is 0.351 ppm. Using eq 1 above, the calculated difference is 0.120 ppm. This may be because of small geometry differences between **9** and **10**. In fact, in the literature,[29] the α- and β-$Cr(CO)_3$ complexes of methyl podocarpate adopt slightly different geometries. According to our molecular model calculations, the skeleton of this isomer twists slightly away from the plane of the benzene ring (especially around atoms 12, 12a, 1, probably because of a greater nonbonded Me_p−CO interaction in **10** than in **9**. For example, the average deviation of the macrocyclic ring carbons from the plane of the *benzene ring* in **9** is only 4°, with maximum value 12°, while in the case of isomer **10**, the average value is 10° and the maximum value is 42°. This extra deformation of the ring carbons in **10** bends the methyl groups slightly outward from the center of the macrocyclic ring, and thus might be expected to perturb the observed chemical shifts away from their values in **9**. From the point of view of aromaticity calculations that we wish to make below, we thus believe the more planar isomer **9** to be the better choice. Indeed for the isomers **26/27** and **28/29**, similar chemical shift differences are seen between the pairs of methyl groups, and molecular model calculations lead to the same conclusions as for **9/10** above, and thus only data from the major isomers **9**, **11**, **26**, and **28** will be used in the aromaticity calculations below.

McGlinchey[26] reported the value of χ_{SI} for the $Cr(CO)_3$ "supercarbonyl" moiety to be -2124×10^{-36} m^3/molecule. Using his technique, this can be determined experimentally from the difference in chemical shift $\Delta\delta(Me)$ of the *same* methyl group in isomers **9** and **10**, and the difference in the factors Δf, where $f = (3\cos^2\theta - 1)/\mathbf{r}^3$ using

$$\chi_{SI} = 12\pi \text{ x } 10^{-36}\Delta\delta(\mathrm{Me})/\Delta f$$

Thus for **9**, using Me_d of **9** and Me_p of **10**, $\delta(Me_d - Me_p) = -0.170$ ppm and $f_d - f_p = 0.0026342$, giving $\chi = -2432 \times 10^{-36}$ m^3/molecule, in good agreement with McGlinchey's value. This method relies on the fact that the geometry of the molecule does not change between isomers. This is more true for Me_d of **9** and Me_p of **10** than for Me_p of **9** and Me_d of **10**, because of the slight bending of the skeleton as discussed above. The greater twist occurs further from the complexed benzene ring, and hence it is best to use the methyl groups closest to the complexed ring. In a similar fashion, the corresponding methyl groups of the pairs **11/12**, **26/27**, and **28/29** can be used to determine the χ_{SI} values for the $-Ru^{2+}$(HMB), −RuCp*, and $-Mn(CO)_3$ fragments, respectively. These are reported in Table 3.

As explained above, under Table 2, to use the chemical shifts of the internal methyl protons and the most distant protons (H_d,

---

[27] Mitchell, R. H. *Adv. Theor. Interesting Mol.* **1989**, *1*, 135−199.

[28] Memory, J. D. *J. Magn. Reson.* **1977**, *73*, 241−244.

[29] Mailvaganam, B.; Perrier, R. E.; Sayer, B. G.; McCarry, B. E.; Bell, R. A.; McGlinchey, M. J. *J. Organomet. Chem.* **1988**, *354*, 325−340; Cambie, R. C.; Clark, G. R.; Gourdie, A. C.; Rutlidge, P. S.; Woodgate, P. D. *J. Organomet. Chem.* **1985**, *297*, 177−184.

Table 3. Experimental McGlinchey[26] Diamagnetic Anisotropy Values, χ_{SI} (in Units 10^{-36} m^3/Molecule)

molecular fragment	χ_{SI}^{a}
-Cr(CO)$_3$^{b}	−2432
-Mn(CO)$_3$^{c}	−2368
-Ru(Cp*)^d	−478^e
−Ru^{2+}(HMB)^d	−836

^{a} McGlinchey[26] suggests ±10% error. ^{b} McGlinchey[26] value = −2124, and center of anisotropy taken as 3.3 Å from Cr along the C_3 axis. ^{c} Center of anisotropy taken as 3.2 Å from Mn along the C_3 axis. ^{d} Center of anisotropy taken as the metal atom. ^{e} A χ_{cgs} value for the parent RuCp$_2$ has been reported,[20b,30a] which when converted gives a χ_{SI} value of about −325 for Ru(Cp).

Table 4. Anisotropy Free Chemical Shift Values, δ_{calc}, for Use in Relative Aromaticity Calculations

compd	Me$_p$	Me$_d$	Me$_{ave}$	H_d	H_d[eq 4]
9	−0.975	−0.859	−0.92 ± 0.06	6.87	6.87
11	−0.667	−0.780	−0.72 ± 0.06	6.75	6.79
26	−0.557	−0.687	−0.62 ± 0.07	6.57	6.75
28	−0.729	−0.782	−0.76 ± 0.03	6.74	6.81

Figure 1) to determine the relative aromaticities of these fragments, the through-space anisotropies of the metal complexing fragment must first be removed. With the χ_{SI} values in hand, this is now possible using

$$\delta_{calc} = \delta_{exp} + \sigma \tag{3}$$

where σ is the shielding (ppm) calculated using eq 1. Calculated *anisotropy free* values of δ for Me$_p$ and Me$_d$ and H$_d$ are thus shown in Table 4. Also in Table 4 are shown the average value for Me$_d$ and Me$_p$, Me$_{ave}$, together with the value of H_d calculated using[1a]

$$\delta(\mathrm{Me}_{ave}) = 17.515 - 2.685\delta(\mathrm{H}_d) \tag{4}$$

This latter value is important in the sense that we have previously shown[1a] that the chemical shift of the internal methyl protons is linearly related to that of the external proton H$_d$, and thus if the value of H_d calculated from eq 4 differs by much from the experimental value of H_d, an indication that a nonring current effect is operating is obtained. As δ(Me) changes from −4.25 to +1.00, δ(H$_d$) changes from 8.11 to 6.15.

As can be seen, excellent agreement is found for H_d , in support of the fact that the major change is one of a changed ring current, which we will now show is caused by a difference in bond delocalization. For a series of annelated annulenes of type **4**, we have shown that there is a linear relationship between the chemical shift of the internal methyl protons and the ratio of adjacent ^3J coupling constants, eq 5:[1a]

$$\delta(\mathrm{Me}_{ave}) = 7.99(J_b/J_a) - 12.29 \tag{5}$$

where $J_b = {}^3J$(H-1,2) and $J_a = {}^3J$(H-2,3) (see Figure 1). If this relationship holds for the series of compounds in Table 4, we can be reasonably certain that, as in the case of the benzenoid annelated annulenes **4**, it is the change in bond fixation that is causing the change in ring current. Thus Table 5 shows the experimental J_b/J_a values and calculated ones based on eq 5. Clearly the annulene portion of the complexed macrocycles does show the expected amount of bond fixation consistent with the strength of the observed ring current.

We believe that the above analysis clearly indicates that in a metal complexed benzannulene such as **9**, the major effect that the metal has on the system is to change the bond fixation in the macrocyclic ring, reducing the ring current and hence reducing the shielding of the internal methyl groups. There is no *substantial* through-space anisotropy effect. The relative bond fixing ability of the various complexes can thus be compared to that of benzene (from the data of **2**), and this we equate to relative aromaticities.

Table 5. Coupling Constant Ratios for the Compounds Studied

compd	J_b (Hz)	J_a (Hz)	J_b/J_a	δ(Me$_{ave}$)	[J_b/J_a]$_{calc}$ (eq 5)
9	8.97	6.30	1.42	−0.92	1.42
11	∼9.1	∼6.6	∼1.38	−0.72	1.45
26	8.95	6.30	1.42	−0.62	1.46
28	8.72	6.41	1.36	−0.76	1.44

Table 6. RA (RBFA) Compared to Benzene of Several Metal Complexes

complex	compd	δ(Me$_{ave}$)	δ(H$_d$)	RA (eq 6)	RA (eq 7)
benzene−Cr(CO)$_3$, **37**	9	−0.92	6.87	1.27	1.25
benzene−Ru^{2+}(HMB), **38**	11	−0.72	6.73	1.34	1.39
Cp−Ru−Cp*, **39**	26	−0.62	6.57	1.38	1.55
Cp−Mn(CO)$_3$, **40**	28	−0.76	6.74	1.33	1.38

Relative Bond Fixing Ability (RBFA) [Relative “Aromaticity” (RA)]

Having now ruled out anisotropy effects, and having previously established[1a] that ring current changes are correlated to bond delocalization changes in systems such as **4**, we can now estimate the RA (=RBFA) of the complexed species studied. This can be done[1a] using eqs 6 for Me$_{ave}$ and 7 for H$_d$:

$$\mathrm{RA} = [4.25 - \delta(\mathrm{Me}_{ave})]/2.63 \tag{6}$$

The results are shown in Table 6. As can be seen, both

$$\mathrm{RA} = [8.11 - \delta(\mathrm{H}_d)]/0.99 \tag{7}$$

equations yield the same order: Cp-Ru−Cp* > benzene-Ru^{2+}−(HMB) > Cp−Mn(CO)$_3$ > benzene−Cr(CO)$_3$ > benzene.

Thus these all **appear to have a greater bond fixing ability of the annulene ring than does benzene itself, and similarly they also resist bond fixation in their own rings (by the annulene ring) to a greater extent than does benzene** (see below) **and this behavior we equate to mean “effectively” that they have 30−40% greater aromaticity than benzene itself!**

Are the Complexes 37−40 Really Aromatic?

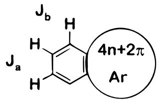
Ferrocene and related species such as **39** are generally considered to be aromatic. However, benzene−chromiumtricarbonyl, **37**, stirs up more controversy. Bursten and Fenske,[30b] on the basis of the ease of Friedel−Crafts acylation reactions claim that **37** is “less aromatic” than both benzene and cyclobutadiene−irontricarbonyl, and that the latter is “more aromatic” than ferrocene or CpMn(CO)$_3$, **40**. Very recently in this journal,[31] Simion and Sorensen claim that **37** is actually *antiaromatic* on the basis of magnetic susceptibility exhaltation calculations. Fortunately, Günther has made extensive studies[2f,g] on the effects of fusing both 4$n\pi$- and (4n+2)π-systems to benzene. When an aromatic system (Ar) is fused to benzene,

---

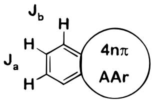
(30) (a) Ritchie, G. L. D.; Cooper, M. K.; Calvert, R. L.; Dennis, G. R.; Phillips, L.; Vrbancich, J. *J. Am. Chem. Soc.* **1983**, *105*, 5215−5219. Mulay, L. N.; Mulay, I. L. *Anal. Chem.* **1966**, *38*, 501−513. (b) Bursten, B. E.; Fenske, R. F. *Inorg. Chem.* **1979**, *18*, 1760−1765.

(31) Simion, D. V.; Sorensen, T. S. *J. Am. Chem. Soc.* **1996**, *118*, 7345−7352.

as in **41**, the ^3J coupling constant $J_b > J_a$. However, when an antiaromatic system (AAr) is fused to benzene, as in **42**, then the reverse is true, $J_b < J_a$.



44



45

Thus for naphthalene, $J_b = 8.28$ Hz and $J_a = 6.85$ Hz, while for biphenylene $J_b = 6.80$ Hz and $J_a = 8.24$ Hz. He has generalized this in terms of an alternance parameter, Q, which is the ratio of the π-SCF bond orders P_b/P_a, which ranges from 0.78 toward 1 (at large n) for $4n\pi$ systems and 1.26 toward 1 (at large n) for $(4n+2)\pi$ systems. The bond orders, P_x are related linearly to the coupling constant J_x by eq 8:

$$P_x(\mathrm{SCF}) = 0.104\,{}^3J_x - 0.120 \qquad (8)$$

These values are not strongly changed by charge in the fused ring; thus the benzocycloheptatrienyl anion, an 8π AAr system, shows a Q value of 0.89, while the aromatic 6π systems, benzocyclopentadienyl anion and benzotropylium cation, show Q values of 1.22 and 1.23, respectively.[2g] Clearly for the compounds studied in this work (see Table 5), in each case for the analogous bonds, J_b is substantially greater than J_a, indicating that unequivocally the fused systems **37**−**40** are **all** behaving in the same way that strongly aromatic systems do.[32] Since we have shown[2d] that eq 6 holds reasonably well for the [*a*]-fused dihydropyrenes, it, together with the data in Table 5, can be used to calculate Q values for **37** (1.52), **39** (1.46), and **40** (1.47). These can be compared with the value for benzene itself (1.39) derived from the coupling constants of the uncomplexed benzannulene **2**, or 1.36 from Günther's theoretical bond orders.[2f] Since a consequence of fusing two aromatic rings is that both rings show bond fixation relative to the parent rings, comparison of two aromatic systems with a common probe as in **4** has as a consequence the fact that the stronger aromatic ring will bond fix the probe ring the most. Clearly from either the coupling constant or the alternance parameter data, the complexes bond fix the parent annulene more than does benzene, in support of our contention that they are "stronger aromatics". A second consequence is that in a series involving the same probe molecule, the most aromatic fused ring will *itself* be the *least* bond fixed.[1] Thus above, if the metal complexed species are indeed *more aromatic or more bond fixing than benzene*, then the benzene ring in **2** should be more localized than the corresponding aromatic ring in **9**, **11**, **26**, or **28**. While the ^3J coupling constants for the benzene ring protons, H-7,8, H-8,9, and H-9,10 in **2** cannot be separated at 360 MHz, the corresponding ones in the [*e*]-fused isomer **6** can and are 8.26 and 6.93 Hz, indicating about the same degree of bond localization as in naphthalene. The benzene ring ^3J coupling constants in the complex **9**, however, are much more equal and are 6.9, 6.5, and 6.4 Hz, similar to those (6.55 and 5.5 Hz) in the complexed ring of tricarbonylchromiumnaphthalene.[33] This indicates to us that the complexed benzene ring in **9** is substantially less localized than the uncomplexed ring in **6** or **2**. Unfortunately, the X-ray structure of **9** would not refine sufficiently to give accurate bond lengths. We hope in the future to overcome this at low temperature. The cyclopentadienyl coupling constants in the complexes **26** and **28** are also approximately equal, indicating that these rings are not much localized at all.

Clearly, in looking at the sum of all the above results, the *metal complexes* ***37*****−*****40*** *cause substantial bond fixation and reduce the ring current when fused to an annulene, more so than does benzene, and themselves resist bond fixation, more so than does benzene*. ***Does this make them more "aromatic" than benzene***? In the absence of some other effect which is causing these results, we would argue "yes".

The relative bond localization energies (RBLE) compared to benzene of the complexes **37**−**40** can be estimated from eq 9:[1a]

$$\mathrm{RA(Me)} = 0.978(\mathrm{RBLE}) + 0.04 \qquad (9)$$

and decrease in the order **39** (1.39) > **38** (1.35) > **40** (1.34) > **37** (1.28) > **benzene** (1.00).

Since the BLE for benzene is 20[34] to 26[35] kcal/mol, our results would suggest that the complexes are harder to bond localize than benzene by some 6−10 kcal/mol. The question then becomes why?

Siegel[36] has suggested that the results for **9** might be explained if the Cr tripod adopts a specific ground-state conformation, which favors one of the resonance forms of the dihydropyrene. This would suggest that in **9**, this specific rotomer is favored by at least 6 kcal/mol. That would seem somewhat high based on rotational barrier experimental results for nonalkyl-substituted arenes and fused arenes (except biphenylene).[37] The (MM2+π)[17] rotational energy barriers in these complexes, are indeed predicted to be small, but, as Siegel remarks,[36] this method gives rather low values. Moreover, it is not obvious how this argument would work for the other ligands. It is reasonably easy to see why the complexed species might resist bond fixation more than benzene itself, however, since to obtain good orbital overlap with the metal orbitals, more or less bond equal arenes are preferred. For the $\mathrm{Cr(CO)_3}$ complexes, benzene is complexed in preference to naphthalene, the end rings in phenanthrene in preference to the center ring.[37a] Is this aromaticity? Recently the driving force behind the so-called aromaticity of benzene has been questioned.[38] Is it σ or π driven? Perhaps it does not matter, because the end result is a "bond-equal" benzene. Since our complexes **37**−**40** cause more bond fixation when fused to dihydropyrene than does benzene, and themselves prefer to remain more "bond-equal" than does even benzene under similar circumstances, we would argue this is aromatic, even though we are not yet sure of the driving force. We hope that these results will stimulate theoreticians into probing this matter further.

---

(32) (a) When an antiaromatic system is less planar and cyclic conjugation is reduced, the effect on the benzene ring is less, and the coupling constants are only slightly perturbed from those in benzene,[32b] unlike the case of biphenylene. However, the coupling constant ratio, J_b/J_a is never >1.2 when an antiaromatic system is fused to benzene. (b) Scott, L. T.; Kirms, M. A.; Günther, H.; Puttkamer, H. *J. Am. Chem. Soc.* **1983**, *105*, 1372−1373. Kirms, M. A. Ph. D. Thesis, University of Nevada, Reno, 1982; p 107.

(33) Deubzer, B.; Fritz, H. P.; Kreiter, C. G.; Ofele, K. *J. Organomet. Chem.* **1967**, *7*, 289−299.

(34) Dewar, M. J. S.; De Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789−795.

(35) Paldus, J.; Li, X. *Isr. J. Chem.* **1991**, *31*, 351−362.

(36) Nambu, M.; Hardcastle, K.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 369−371.

(37) (a) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499−525. (b) Albright, T. A. *Acc. Chem. Res.* **1982**, *15*, 149−155.

(38) Gobbi, A.; Yamaguchi, Y.; Frenking, G.; Schaefer, H. F. *Chem. Phys. Lett.* **1995**, *244*, 27−31; Glendening, E. D.; Faust, R.; Streitweiser, A.; Vollhardt, K. P. C.; Weinhold, F. *J. Am. Chem. Soc.* **1993**, *115*, 10952−10957. Hiberty, P. C.; Ohanessian, G.; Shaik, S. S.; Flament, J. P. *Pure Appl. Chem.* **1993**, *65*, 35−45. Jug, K.; Koster, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 6772−6777. Shaik, S. S.; Hiberty, P. C.; Lefour, J. M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363−374.

Bis-Complexes

In our preliminary report[25] on the bis-complex **32**, we stated that only 6% of the ring current of the [14]annulene ring remains. The current work supports that figure, since from Table 2, for compound **9**, σ's for Me_p and Me_d are almost equal but opposite in sign. Since in **32** Me_d for one $Cr(CO)_3$ group is Me_p for the other $Cr(CO)_3$, each Me group suffers a shielding and a deshielding of equal magnitude, leaving the observed chemical shift almost identical with a calculated anisotropy free shift. Our ring current estimate of 6% thus stands. Clearly fusion of **two** molecules of **37** to dihydropyrene **1** almost, but not completely, kills the annulene ring current. Certainly they do so more than do **two** benzene rings (18% residual current).[25] In the ^1H NMR spectrum of the nonsymmetrical isomer **34**, a 9.5 Hz ^3J coupling for the 6−7 annulene protons can be seen, larger than any of the J_b values in Table 5, supporting the very extensive bond fixation in this molecule.

Conclusions

We have described the synthesis of 13 metal complexed annelated *trans*-dimethyldihydropyrenes (bridged [14]annulenes) and have presented their proton magnetic resonance spectra in detail. Analysis of the latter with respect to the change in ring current in the macrocyclic ring, and in the change in coupling constants, reveals that in each metal complex the [14]annulene is bond localized to a greater extent than in the corresponding uncomplexed annulene. This effect is not local, nor is a through-space anisotropy effect, but is a real change in the delocalization of the whole π-system. The relative bond fixing ability of several organometallic moieties was thus estimated by their effects on the annulene ring and this ability was discussed in terms of the aromaticities of the systems involved. Not all authors would agree with our conclusions concerning aromaticity, but we hope that this work, the first extensive investigation of metal complexed annulenes, will provoke theoreticians to explore this matter further!

Experimental Section

The same general procedures were used as are given in ref 1a.

[7,8,9,10,10a,10b-η^6]-*trans*-12b,12c-Dimethyl-12b,12c-dihydrobenzo[*a*]pyrene chromium(0)tricarbonyl, (9, 10). A mixture of the benzo[*a*]dimethyldihydropyrene **2**[1a] (40 mg, 0.14 mmol), naphthalenetricarbonylchromium[39] (60 mg, 0.22 mmol), and THF (70 μL, 0.86 mmol) in diethyl ether (2 mL) was stirred magnetically in a sealed vial at 50−60 °C for 14 h. The mixture was cooled, preabsorbed on silica gel, and chromatographed on SiGel using dichloromethane−PE (1:4) as eluant. After a small amount of starting material, the complexes **9** and **10** were eluted as a red solid, 40 mg (60%) as a 3:1 ratio (by NMR). Recrystallization from dichloromethane yielded mostly isomer **9**, as deep red crystals, mp 189−190 °C: ^1H NMR (360 MHz) δ 7.59 (d, $J = 6.53$ Hz, 1, H-11), 7.28 (s, 2, H-4,5), 7.24 (s, 1, H-6), 7.18 (d, $J = 8.97$ Hz, 1, H-1), 7.02 (d, $J = 6.30$ Hz, 1, H-3), 7.00 (d, 1, H-12), 6.88 (dd, 1, H-2), 6.57 (d, $J = 6.9$ Hz, 1, H-10), 5.94 (dd, $J = 6.5$, 0.9 Hz, 1, H-7), 5.61 (dt, $J = 6.4$, 1.1 Hz, 1, H-8), 5.50 (ddd, 1, H-9), −0.871 and −0.977 (s, 3 each, $-CH_3$), in benzene-d_6 H-4,5 appear as a doublet, $J = 9.24$ Hz; ^{13}C NMR (62.9 MHz) δ 232.6, 140.7, 140.3, 139.1, 130.5, 128.2, 126.6, 126.0, 125.2, 123.3, 121.1, 120.8, 119.8, 101.5, 98.2, 91.8, 91.7, 90.7, 88.0, 37.7, 36.9, 20.0, 18.4; IR 1950, 1860 cm^{-1}; UV λ_{max} (ϵ_{max}) nm 220 (34 400), 336 (39 600), 435 (20 600); CI MS m/z 419 (MH^+). Anal. Calcd for $C_{25}H_{18}CrO_3$: C, 71.76; H, 4.34. Found: C, 71.60; H, 4.39. An X-ray structure determination was carried out on this isomer, which clearly indicated the carbon skeleton, but would not complete using a least-squares refinement to give the hydrogen atoms ($R = 0.066$). The crystal system was triclinic, space group $P1$, with $a = 14.516$ Å, $b = 9.062$ Å, $c = 7.772$ Å. An ORTEP diagram is provided in the Supporting Information to show the skeleton. We intend to attempt to obtain a low-temperature structure in the future.

The minor isomer, **10**, could not be obtained pure, but its ^1H NMR data was obtained by subtraction: (360 MHz) δ 7.56 (d, $J = 6.69$ Hz, H-11), 7.36 and 7.29 (AB, $J = 9.19$ Hz, H-4,5), 7.24 (s, H-6), 7.24 (d, $J = \sim 9$ Hz, H-1), 7.10 (d, $J = 6.39$ Hz, H-3), 7.01 (d, H-12), 6.93 (dd, H-2), 6.49 (d, $J = 6.9$ Hz, H-10), 5.83 (dd, $J = 6.7$, 1.2 Hz, H-7), 5.65 (ddd, H-8), 5.45 (ddd, H-9), −0.807 and −1.158 (s, $-CH_3$).

Ruthenium Complexes 11 and 12. A solution of benzo[*a*]dimethyldihydropyrene **2**[1a] (74 mg, 0.26 mmol) in anhydrous propylene carbonate (5 mL) was added to a mixture of $[Ru(HMB)Cl_2]_2$[7] (88 mg, 0.13 mmol) and $AgBF_4$ (204 mg, 1.05 mmol) in anhydrous propylene carbonate (5 mL) at 20 °C and was stirred for 12 h under argon. The reaction mixture was then poured into diethyl ether (250 mL) with stirring and the product was collected by filtration. The residue was washed with ether, dissolved in a minimum of acetone, and then filtered. The filtrate was added dropwise to ether with vigorous stirring to give dark red crystals of product, **11** and **12**, 100 mg (53%) as a (3:2) mixture, which could not be separated by fractional recrystallization. ^1H NMR (360 MHz, CD_3CN) [assigned by COSY] δ 8.17 (d, $J = 6.7$ Hz, H-11 (both isomers, δ 8.50 and 8.43 in $(CD_3)_2CO$) (NOESY to H-10), 7.71 and 7.70 (d, $J = 9.1$ Hz, H-5), 7.63 and 7.57 (d, $J = 9.1$ Hz, H-4), 7.49−7.45 (m, H-1, H-10), 7.40−35 (m, H-6, H-10′), 7.32−7.28 (m, H-9), 7.26 and 7.24 (d, $J = 6.7$ Hz, H-12), 7.10 (d, $J = \sim 6.6$ Hz, H-3), 6.96 (d, $J = 6.1$ Hz, H-7), 6.63−6.55 (m, H-2), 6.51 and 6.47 (t, $J = 6.0$ Hz, H-8), 2.31 and 2.21 (s, HMB−CH_3), −0.632, −0.966 and −0.667, −0.985 (s, DHP−CH_3, 3:2 ratio before purification. In $CDCl_3$: δ −0.517, −0.864 and −0.558, −0.891. In $(CD_3)_2CO$: δ −0.484, −0.850 and −0.499, −0.911); UV (acetone) λ_{max} (ϵ_{max}) nm 341 (37 500), 400 (33 500), 615sh (9800); FAB(LSI) MS (m-NBA matrix) 633 (M − BF_4), 546 (M − $2BF_4$), 531 (M − $2BF_4$, $-CH_3$), 516 (M − $2BF_4$, $-2CH_3$) [dihydropyrenes normally show strong peaks corresponding to loss of one and then both internal methyl groups].

Ethyl *trans*-3-(2′-*trans*-10b,10c-Dimethyl-10b,10c-dihydropyrenyl)propenate (14). Triethyl phosphonoacetate (1.32 mL, 6.64 mmol) was added to a suspension of NaH (162 mg, 6.76 mmol) in dry THF (35 mL) at 0 °C under argon. After hydrogen gas evolution had subsided, 2-formyldimethyldihydropyrene **13**[8] (1.90 g, 6.15 mmol) in dry THF (80 mL) was added dropwise. The reaction mixture was allowed to warm to 20 °C, and then was refluxed for 1 h. After cooling, saturated aq NH_4Cl and dichloromethane were then added, and the organic layer was washed, dried, and evaporated to give a maroon solid. This was chromatographed over SiGel using dichloromethane−PE (1:20) as eluant and gave 2.0 g (98%) of **14** as dark red crystals from ether−pentane, mp 146−147 °C: ^1H NMR (250 MHz) δ 8.68 (s, H-1′,3′), 8.59 and 8.50 (AB, $J = 7.9$ Hz, H-4′,5′,9′,10′), 8.46 (d, $J = 7.8$ Hz, H-6′,8′), 8.30 (d, $J = 15.8$ Hz, H-3), 8.03 (t, H-7′), 6.91 (d, H-2), 4.35 (q, $J = 7.1$ Hz, $-OCH_2-CH_3$), 1.40 (t, $-CH_2CH_3$), −3.85 and −3.87 (s, $-CH_3$); ^{13}C NMR (62.9 MHz) δ 167.3, 146.2, 139.0, 136.4, 128.2, 125.8, 124.8, 124.2, 124.0, 123.5, 117.9, 60.4, 31.1, 30.3, 15.1, 14.8, 14.4; IR 1698, 1613, 1270, 1174, 1149 cm^{-1}; UV λ_{max} (ϵ_{max}) nm 348 (79 400), 378 (21 400), 402 (32 400), 522 (20 900), 608 (310), 669 (200); EI MS m/z 330 (M^+). Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.72. Found: C, 83.43; H, 6.78.

Ethyl 3-(2′-*trans*-10b,10c-Dimethyl-10b,10c-dihydropyrenyl)propanoate (15). A solution of the ester **14** (2.03 g, 6.15 mmol) in ethyl acetate (100 mL) was stirred under hydrogen in the presence of Pd/C (10%, 5 mg) at 20 °C for 2.5 h, when 1 equiv of H_2 had been consumed. The mixture was then carefully filtered (argon), washing the catalyst with dichloromethane, and then the filtrate was evaporated. The green gummy residue was chromatographed over SiGel using pentane as eluant, and gave **15** as a dark green gum, 1.75 g (86%), which would not crystallize: ^1H NMR (250 MHz) δ 8.61 and 8.56 (AB, $J = 7.8$ Hz, H-4′,5′,9′,10′), 8.55 (d, $J = 7.7$ Hz, H-6′,8′), 8.45 (s, H-1′,3′), 8.04 (t, H-7′), 4.13 (q, $J = 7.1$ Hz, $-OCH_2CH_3$), 3.66 (t, $J = 7.7$ Hz, H-2), 2.99 (t, H-3), 1.17 (t, $-CH_2CH_3$), −4.159 and −4.164 (s, $-CH_3$); ^{13}C NMR (62.9 MHz) δ 172.6, 136.9, 136.0, 135.6, 123.6, 123.4 (×2), 123.1, 122.3, 60.2, 36.6, 32.9, 29.7, 29.5, 14.1(×2), 13.7; IR 1730 cm^{-1}; UV λ_{max} (ϵ_{max}) nm 338 (95 500), 355 (16 600), 377 (40 800), 455

---

[39] Desobry, V.; Kundig, E. P. *Helv. Chim. Acta* **1981**, *64*, 1288−1297.

(6800), 470 (7100), 529 (85), 594 (89), 625 (110), 642 (170); EI MS m/z 332 (M^+). HRMS Calcd for $C_{23}H_{24}O_2$: 332.178. Found: 332.168.

3-(2′-*trans*-10b,10c-Dimethyl-10b,10c-dihydropyrenyl)propanoic Acid (16). The ester **15** (2.00 g, 6.02 mmol) was refluxed in aq 1 M NaOH (75 mL) for 15 h, cooled to 20 °C, and acidified carefully with concentrated aq HCl; the resulting solid was collected by vacuum filtration. The solid was chromatographed over SiGel using ether as eluant to give 1.65 g (90%) of acid, as short dark green needles from cyclohexane−PE, mp 165−166 °C: ^{1}H NMR (250 MHz) δ 10.98 (bs, −COOH), 8.59 and 8.53 (AB, J = 7.7 Hz, H-4′,5′,9′,10′), 8.55 (d, J = 7.7 Hz, H-6′,8′), 8.44 (s, H-1′,3′), 8.05 (t, H-7′), 3.66 (t, J = 7.9 Hz, H-3), 3.06 (t, H-2), −4.19 and −4.20 (s, $-CH_3$); ^{13}C NMR (62.9 MHz) δ 179.1, 137.1, 136.3, 135.2, 123.9, 123.6, 123.4, 122.6 (×2), 36.4, 32.6, 29.9, 29.7, 14.2, 13.9; IR 3200−2400, 1683, 865, 811 cm^{-1}; UV λ_{max} (ϵ_{max}) nm 338 (53 700), 351 (13 200), 377 (19 500), 455 (3300), 470 (4700), 529 (120), 629 (180), 642 (300); EI MS m/z 304 (M^+). Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.53; H, 6.38.

***trans*-11b,11c-Dimethyl-7,8,11b,11c-tetrahydro-9-oxo-9*H*-cyclopenta[*a*]pyrene (18).** Excess oxalyl chloride (250 mg, 2 mmol) was added to the acid **16** (200 mg, 0.66 mmol) in dichloromethane (15 mL) and the mixture was stirred at 20 °C for 6 h. Removal of solvent and excess oxalyl chloride under vacuum yielded a dark green solid; a sample gave an IR (KBr disk) which indicated conversion to acid chloride **17** by the peak at 1802 cm^{-1} and disappearance of the peak at 1683 cm^{-1}. The residue was dissolved in dry dichloromethane (100 mL) and $BF_3{\cdot}Et_2O$ (0.8 mmol) was added; the mixture was stirred for 9 h. Aqueous potassium carbonate (10%) was then added, and the organic layer was collected, dried, and evaporated. The dark green residue was chromatographed on SiGel using dichloromethane as eluant and gave 120 mg (63%) of ketone **18** as dark green plates from cyclohexane, mp 210−211 °C; ^{1}H NMR (250 MHz) δ 9.66 and 8.51 (AB, J = 7.3 Hz, H-10,11), 8.61 and 8.49 (AB, J = 8.1 Hz, H-5,4), 8.50 (d, J = 7.7 Hz, H-1), 8.47 (d, J = 7.7 Hz, H-3), 8.45 (s, H-6), 7.95 (t, H-2), 3.79−3.68 (m, 2, H-7), 3.09−3.01 (m, 2, H-8), −3.72 and −3.73 (s, $-CH_3$); ^{13}C NMR (62.9 MHz) δ 208.9, 153.6, 142.2, 136.9, 136.8, 130.0, 128.1, 126.9, 126.2 (×2), 126.0, 123.7, 123.3, 120.3, 119.9, 37.3, 32.3, 31.0, 27.5, 14.8, 14.4; IR 1670 cm^{-1}; UV λ_{max} (ϵ_{max}) nm 367 (20 000), 471 (730), 558 (75), 594 (75), 611 (110), 619 (95), 679 (550); EI MS m/z 286 (M^+). Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 87.71; H, 6.43.

***trans*-11b,11c-Dimethyl-11b,11c-dihydro-7*H*-cyclopenta[*a*]pyrene (19).** The ketone **18** (100 mg, 0.35 mmol) and $LiAlH_4$ (20 mg, 0.5 mmol) were stirred in dry THF (20 mL) for 1.5 h at 20 °C and then ice−water was added to destroy excess hydride followed by 20% aq HCl (10 mL) and dichloromethane (30 mL), and the reaction was then stirred for 1 h. The organic layer was washed, dried, and evaporated to yield a green solid which was chromatographed quickly on SiGel using pentane as eluant to yield 77 mg (81%) of alkene **19** as dark green plates from methanol, mp 114−116 °C: ^{1}H NMR (360 MHz) δ 8.86 and 8.67 (AB, J = 7.7 Hz, H-10,11), 8.75 (s, H-6), 8.62 and 8.60 (AB, J = 7.5 Hz, H-5,4), 8.57 (d, J = 7.6 Hz, H-1,3), 8.07 (t, H-2), 8.00 (ddt, J = 5.6, 1.9, 0.8 Hz, H-9), 6.99 (dt, J = 5.7, 2.0 Hz, H-8), 4.07 and 3.98 (AB of t, J = 24.2 Hz, H-7,7′), −4.15 and −4.16 (s, $-CH_3$); ^{13}C NMR (90.6 MHz) δ 139.6, 138.3, 136.6, 136.3, 136.0, 135.2, 130.9, 128.6, 123.1, 122.9 (×2), 122.6 (×2), 122.2, 119.7, 118.9, 40.7, 30.4, 30.3, 14.4, 13.8; UV λ_{max} (ϵ_{max}) nm 356 (37 200), 390 (13 500), 471 (3100), 597 (62), 616 (68), 644 (115), 658 (90); CI MS m/z 271 (MH^+). Anal. Calcd for $C_{21}H_{18}$: C, 93.28; H, 6.72. Found: C, 92.77; H, 7.00.

***trans*-11b,11c-Dimethyl-11b,11c-dihydrocyclopenta[*a*]pyrene, Ion(1−) (5).** Potassium hydride (5 mg) was added to a solution of alkene **19** (27 mg, 0.1 mmol) in dry deaerated THF-d_8 (0.4 mL) in an argon filled glovebox. The intense red solution was filtered into an NMR tube which was previously flushed with argon: ^{1}H NMR (discussed in detail in ref 1d); ^{13}C NMR (62.9 MHz, THF-d_8) δ 137.1, 136.5, 136.0, 131.6, 130.6, 124.6, 124.5, 124.3, 123.8 (×2), 123.4, 123.3, 123.1, 120.6, 119.8, 119.3, 118.1, 31.5, 30.6, 15.5, 14.3; UV (THF-d_8) λ_{max} (ϵ_{max}) nm 357 (95 500), 391 (55 000), 454 (28 200), 477 (26 900), 593 (2500), 645 (3500), 654 (2900). This solution decomposed if left to stand at about 20° for 2 h. If wet THF was added to the anion immediately, then the alkenes **19** and **20** were obtained in a 2:3 ratio. These could not be separated by chromatography, but the ^{1}H NMR spectrum of **20** could be obtained by subtraction: (250 MHz) δ 8.78−8.40 (m, 8H), 7.42 (d, J = 5.6 Hz, H-7), 6.94 (dt, J = 5.6, 2.1 Hz, H-8), 4.26−4.21 (m, H-9,9′), −4.09 (s, 6H, $-CH_3$).

Ferrocene by Photolysis of 25. Potassium hydride (60 mg, 1.5 mmol) was added to cyclopentadiene (100 mg, 1.5 mmol) in dry DMF (6 mL) under argon, and was stirred for 15 min, and then complex **25**[16] (450 mg, 1.2 mmol) was added. The reaction mixture was then irradiated with a 150-W tungsten garden flood lamp for 5 h, and then was extracted with PE (3 × 20 mL). The organic extracts were concentrated and gave 170 mg (80%) of orange crystals of ferrocene, identical with a commercial sample (TLC, mp, ^{1}H NMR).

Indenylferrocene 24. Potassium hydride (45 mg, 1.1 mmol) was added to indene (130 mg, 1.1 mmol) in dry DMF (6 mL) under argon, and the mixture was stirred for 30 min, when complex **25**[16] (370 mg, 1.0 mmol) was added. The reaction mixture was then irradiated with a 150-W tungsten garden flood lamp for 3 h, and then was extracted with PE (4 × 30 mL). The organic extracts were concentrated and gave a red-violet solid which was chromatographed over basic alumina using PE as eluant. Eluted first was ferrocene (10 mg). Eluted second was 163 mg (69%) of indenylferrocene **24**, as red-violet crystals from PE, mp 75 °C, with identical properties as those described.[40]

[6a,7,8,9,9a-μ^5]-*trans*-11b,11c-Dimethyl-11b,11c-dihydrocyclopenta[*a*]pyrene−pentamethylcyclopentadienylruthenium (26, 27). Methyllithium (0.15 mL, 1.4 M in ether) was added to alkene **19** (50 mg, 0.19 mmol) in dry deaerated THF (2 mL) at −78 °C under argon, and then the mixture was stirred at 20 °C for 15 min, when $(Cp^*RuCl_2)_n$[20,21] (58 mg, 0.19 mmol) was added and the reaction stirred for a further 30 min. The reaction was then heated to 40 °C and stirred for a further 15 min. After cooling, the solvent was evaporated and the residue was dissolved in cyclohexane and chromatographed over basic alumina using deaerated cyclohexane as eluant to give 65 mg (70%) of rose-violet solid, a mixture of isomers **26** and **27** in a 3.7:1 ratio, which could not be separated by recrystallization from ethanol or sublimation at 235 °C at 0.1 mmHg. The compounds are air sensitive. Because of the unequal ratio, the NMR peaks of **26** could be assigned: ^{1}H NMR (360 MHz) δ 6.95 and 6.90 (AB, J = 9.09 Hz, H-5,4), 6.94 and 6.67 (AB, J = 6.41 Hz, H-10,11), 6.88 (d, J = 8.95 Hz, H-1), 6.72 (s, H-6), 6.68 (d, J = 6.30 Hz, H-3), 6.57 (dd, H-2), 4.99 (d, J = 2.45 Hz, H-9), 4.70 (d, J = 2.45 Hz, H-7), 4.39 (t, H-8), 1.68 (s, 15H, Cp-CH_3), −0.548 and −0.691 (s, $-CH_3$); ^{13}C NMR (62.9 MHz) δ 139.2, 137.3, 135.8, 135.4, 126.6, 126.0, 123.9, 122.0, 121.4, 121.1, 120.5, 113.7, 85.2 (Cp*), 85.0, 83.9, 74.3, 71.6, 69.3, 39.7, 38.3, 20.1, 18.9, 11.5 (Cp-CH_3). The ^{1}H NMR internal methyl protons of the minor isomer appeared at δ −0.473 and −0.820.

On the mixture of isomers: UV λ_{max} (ϵ_{max}) nm 249 (36 300), 358 (55 000), 502 (sh, 600), 538 (sh, 450), 564 (sh, 300); CI MS m/z 507 (MH^+, correct Ru isotope pattern). Anal. Calcd for $C_{31}H_{32}Ru$: C, 73.63; H, 6.38. Found: C, 73.36; H, 6.08.

[6a,7,8,9,9a-μ^5]-*trans*-11b,11c-Dimethyl-11b,11c-dihydrocyclopenta[*a*]pyrene−tricarbonylmanganese (28, 29). Methyllithium (0.17 mL, 1.4 M in ether) was added to alkene **19** (60 mg, 0.23 mmol) in dry deaerated THF (2 mL) at −78 °C under argon, and then the mixture was stirred at 20 °C for 15 min, when manganese pentacarbonyl bromide[23] (62 mg, 0.23 mmol) was added and the reaction stirred for a further 10 min. The reaction was then heated to 40 °C and stirred for a further 20 min. After cooling, the solvent was evaporated and the residue was dissolved in cyclohexane and chromatographed over basic alumina using deaerated cyclohexane as eluant to give 57 mg (61%) of complex **28**/**29** in a 2.5:1 ratio. Recrystallization from dichloromethane−pentane yielded an analytically pure dark orange-brown sample, but would not separate the isomers. Because of the unequal ratio, the NMR peaks of **28** could be assigned: ^{1}H NMR (250 MHz) δ 7.16 and 6.83 (AB, J = 6.32 Hz, H-10,11), 7.15 (s, H-6), 7.13 and 7.11 (AB, J = 8.76 Hz, H-5,4), 7.05 (d, J = 8.72 Hz, H-1), 6.89 (d, J = 6.31 Hz, H-3), 6.74 (dd, H-2), 5.54 (bs, H-9), 5.09 (bs, H-7), 5.07 (bs, H-8), −0.728 and −0.784 (s, $-CH_3$); ^{13}C NMR (62.9 MHz) δ 226, 140.7, 139.4, 138.4, 135.8, 127.3, 126.6, 126.0, 124.3,

---

[40] King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1964**, *3*, 796−801.

124.1, 120.8, 118.4, 116.5, 85.1, 77.8, 76.2, 74.5, 74.0, 37.9, 37.1, 20.4, 18.9. The ^{1}H NMR internal methyl protons of the minor isomer appeared at δ −0.670 and −0.976. On the mixture of isomers: IR 2028 and 1935 cm^{-1}; UV λ_{max} (ϵ_{max}) nm 346 (30 200), 473 (1400), 646 (180); CI MS *m/z* 409 (MH^{+}). Anal. Calcd for $C_{24}H_{17}MnO_3$: C, 70.58; H, 4.20. Found: C, 70.16; H, 4.24.

Bis(tricarbonylchromium) Complexes of Dibenzannulene 30, (32, 33, 34). A solution of dibenzannulene **30**^{1a} (200 mg, 0.613 mmol) and naphthalenetricarbonylchromium (1.0 g, 3.8 mmol) in ether (15 mL) and THF (1 mL) in a heavy screw capped vial was stirred magnetically at 60 °C for 30 h. After cooling to 20 °C, 15 mg of isomer **32** directly crystallized from the reaction mixture. The filtrate was directly preabsorbed onto SiGel and chromatographed using PE−ethyl acetate (10:1) as eluant. Unchanged **30** and monocomplex **35** were sometimes present in trace amounts and were eluted first; next eluted was a further 170 mg of the mixture of bis-complexes **32**−**33**−**34**. The total yield was 50% and the ^{1}H NMR spectrum indicated a total ratio of isomers 12:1:2. The first isomer eluted was **32**, which upon fractional crystallization from cyclohexane yielded pure isomer **32** as red-orange crystals, mp 219−220 °C (dec): ^{1}H NMR (360 MHz) δ 6.85 (s, H-13,14), 6.55 (s, H-6,7), 6.49 (s, H-5,8), 6.13 (d, $J = \sim 7$ Hz, H-1,12), 5.52 (d, $J = \sim 7$ Hz, H-4,9), 5.48 (t, $J = \sim 7$ Hz, H-3, 10), 5.39 (t, $J = \sim 7$ Hz, H-2,11), 0.64 (s, $-CH_3$); ^{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 1950, 1875 cm^{-1}; UV (CH_2Cl_2) λ_{max} (ϵ_{max}) nm 336 (31 100), 438 (20 300) tail to 630 nm. EI HR MS: Calcd for $C_{32}H_{20}Cr_2O_6$: 604.0070. Found: 604.0093. Anal. Calcd: C, 63.58; H, 3.34. Found: C, 62.91; H, 3.08.

The second isomer eluted was mostly **34**, which could be obtained pure by fractional crystallization from cyclohexane−THF as red-orange crystals, mp 214−216 °C (dec); ^{1}H NMR (360 MHz, THF-d_8) δ 7.03 (s, H-13,14), 6.71 (s, H-8), 6.71 and 6.65 (AB, $J = 9.5$ Hz, H-7,6), 6.67 (s, H-5), 6.45 (d, $J = 6.9$ Hz, H-12), 6.30 (d, $J = 6.9$ Hz, H-1), 5.78 (dd, $J = \sim 7$, 1 Hz, H-9), 5.78 (t, $J = \sim 7$ Hz, H-3), 5.69 (t, $J = \sim 7$ Hz, H-10), 5.63 (dd, $J = 6.7$, 1.1 Hz, H-11), 5.55 (dt, $J = \sim 7$, 1.1 Hz, H-11), 5.49 (dt, $J = \sim 7$, ~ 1 Hz, H-2), 0.90 and 0.45 (s, $-CH_3$) [in $CDCl_3$ these were at δ 0.86 and 0.42]; ^{13}C NMR (90.6 MHz, THF-d_8) δ 234.03, 233.99, 142.1, 141.9, 137.0, 135.0, 129.2, 128.3, 124.5, 123.3, 119.7, 118.4, 103.9, 102.6, 98.7, 98.4, 94.6, 93.7, 92.9, 92.1, 91.5, 91.3, 90.3, 88.7, 41.8, 41.1, 21.7, 20.3; IR 1944 and 1856 cm^{-1}; UV (CH_2Cl_2) λ_{max} (ϵ_{max}) nm 337 (48 100), 434 (23 800) tail to 630 nm. EI MS *m/z* 604 (M^{+}); Anal. Calcd for $C_{32}H_{20}Cr_2O_6$: C, 63.58; H, 3.34. Found: C, 63.72; H, 3.69.

The third isomer, **33**, could not be obtained pure, but was present in the mother liquors above; its internal methyl protons appeared at δ 0.96 ($CDCl_3$) and 0.99 (THF-d_8).

Monoruthenium Complex 36. A solution of dibenzannulene **30**^{1a} (25 mg, 0.075 mmol) in anhydrous propylene carbonate (5 mL) was added to a mixture of $[Ru(HMB)Cl_2]_2$[7] (75 mg, 0.113 mmol) and $AgBF_4$ (110 mg, 0.565 mmol) in anhydrous propylene carbonate (5 mL) and was stirred for 12 h and then was poured in to ether (200 mL) with stirring. The crude product was collected by filtration, dissolved in a minimum of acetone, and filtered again. Ether was slowly diffused into this acetone solution and 25 mg (45%) of dark red crystals of complex **36** was formed. This was a 1:1 mixture of the two isomers, and these could not be separated by fractional crystallization: ^{1}H NMR (360 MHz, $(CD_3)_2CO$, mixture of isomers) δ 8.35 and 8.30 (d, $J = 8.4$ Hz, H-12), 8.02 and 7.96 (d, $J = 6.6$ Hz, H-11), 7.79 (s, H-7), 7.76−6.90 (m), 2.14 and 2.05 (s, HMB$-CH_3$), 0.69, 0.29 and 0.58, 0.20 (s, $-CH_3$); FAB (LSI) MS *m/z* 683 (small, M − BF_4), 596 (M − $2BF_4$), 581 (M − $2BF_4$,CH_3), 566 (M − $2BF_4$,$2CH_3$).

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for financial support of this work.

Supporting Information Available: Tables of **r**, θ, f, σ (see eqs 2 and 3) for compounds **9**, **10**, **11**, **12**, **26**, **27**, **28**, **29** (6 pages). An ORTEP diagram of **9** to indicate the carbon skeleton. See any current masthead page for ordering and Web access instructions.

JA9729138