

Facile Haptotropic Shifts in Organometallic Complexes of 4*H*-Cyclopenta[*def*]phenanthrene via Naphthalene-Type Transition States: Synthetic, X-ray Crystallographic, NMR Spectroscopic, and EHMO Studies

Andreas Decken, James F. Britten, and Michael J. McGlinchey*

Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

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Abstract: The tetracyclic system 4*H*-cyclopenta[*def*]phenanthrene (cppH) forms the complexes (η^6 -cppH)Cr(CO)₃ (**2**) and [(η^5 -cppH)Mn(CO)₃]PF₆ (**13**); in both cases the metal is bonded to a terminal ring. Molecule **2** crystallizes in the orthorhombic space group *Pbca*, with *a* = 13.924(2) Å, *b* = 12.639(2) Å, *c* = 15.666(3) Å, and *Z* = 8. Deprotonation of **2** and **13** at room temperature yields [(η^5 -cpp)Cr(CO)₃]⁻ (**7**) and (η^5 -cpp)Mn(CO)₃ (**15**), respectively, with no detectable zwitterionic intermediate. **15** crystallizes in the monoclinic space group *P2₁/c*, with *a* = 11.274(2) Å, *b* = 8.752(2) Å, *c* = 14.404(3) Å, β = 98.64(3)°, and *Z* = 4. The corresponding 8,9-dihydro-cpp derivatives (η^6 -H₂-cppH)Cr(CO)₃ (**24**) and [(η^6 -H₂-cppH)Mn(CO)₃]PF₆ (**17**) have also been prepared. **24** crystallizes in the orthorhombic space group *Pbca*, with *a* = 12.662(3) Å, *b* = 14.594(3) Å, *c* = 15.761(3), and *Z* = 8. Upon deprotonation, **17** yields an intermediate neutral complex (**18**) which undergoes an η^6 -to- η^5 -haptotropic shift only upon being heated to 60 °C for 1 h. The whole process can be followed readily by NMR. The corresponding neutral intermediate derived by deprotonation of **13** can be trapped at -40 °C. The relative ease of haptotropic shifts in the cpp complexes relative to the analogous H₂-cpp systems can be rationalized in terms of a transition state in which the migrating organometallic fragment is η^3 -bonded to the polycyclic ligand such that a 10 π (naphthalene-like) character is retained.

Introduction

The molecule 4*H*-cyclopenta[*def*]phenanthrene (cppH) (**1**) not only contains the carbon skeletons of indene, acenaphthylene, phenanthrene, and fluorene (see Figure 1), but, as shown in Figure 2, it also represents 25% of the C₆₀ framework. It is an attractive ligand because it offers multiple sites for the attachment of organometallic moieties which can potentially bind in an η^6 -, η^5 -, η^4 -, η^3 -, η^2 -, or η^1 -fashion. To our knowledge, no transition-metal complexes of this ligand have been reported.

Moreover, deprotonation of η^6 -complexes of the cppH ligand provides the opportunity for haptotropic shifts by ML_{*n*} units from (or through) six-membered rings to a five-membered ring. Such inter-ring migrations have been the subject of considerable theoretical analysis, notably by Albright, Hoffmann, and their colleagues.¹ These calculated barriers compare very favorably with the reported experimental data.² In particular, it has been shown that the ability of organometallic fragments to migrate across the surfaces of polycyclic systems can be rationalized in terms of the interactions between the frontier orbitals of the ML_{*n*} moiety and of the π system. For example, the metallotropic shift of a (C₅H₅)Fe unit in the indenyl anion, shown in Figure 3a, is calculated to proceed not via a least-motion pathway from ring center to ring center (route A) but rather via an exocyclic η^3 -transition state (B).¹ In contrast, EHMO calculations on the [(pentalene)Fe(C₅H₅)⁺] system, shown in Figure 3b, suggest that a (C₅H₅)Fe moiety can move across the common bond between the two rings; however, even in this case, the trajectory does not follow the least-motion pathway.¹

Of particular significance here is the fact that the π -electron count in the 4*H*-cyclopenta[*def*]phenanthrene system can be conveniently reduced by 2 merely by hydrogenating the C(8)=C(9) double bond. Thus one can make direct comparisons between

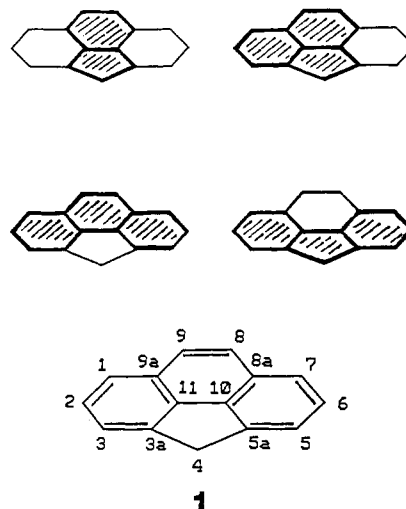


Figure 1. Polycyclic fragments contained in the cppH skeleton, also showing the numbering system.

polycyclic molecules possessing the same skeletal geometry but having different frontier orbital patterns.

Results and Discussion

Synthetic Aspects. The reaction of 4*H*-cyclopenta[*def*]phenanthrene (cppH) (**1**) with chromium hexacarbonyl yields the complex (η^6 -cppH)Cr(CO)₃ (**2**), in which the tripod fragment is attached to a terminal six-membered ring. Formation of this isomer parallels the behavior of other polyaromatic complexes, such as (phenanthrene)Cr(CO)₃ (**3**), (anthracene)Cr(CO)₃ (**4**), or (triphenylene)Cr(CO)₃ (**5**); in all these cases, the metal binds preferentially to an outer ring of the polycyclic

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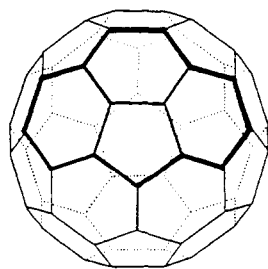


Figure 2. Diagram of the cpp unit as a fragment of C₆₀.

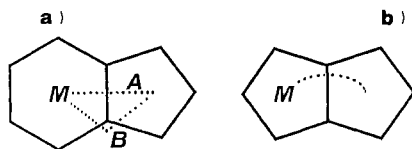
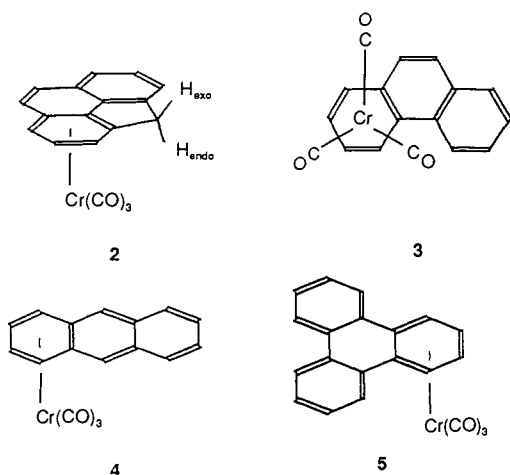


Figure 3. (a) Metallotropic shift pathways in indenyl-metal complexes. (b) Favored pathway for a metallotropic shift in the pentalene system.



system.³ This has been explained either by attributing greater aromatic character to a terminal ring⁴ or, alternatively, by noting that in each case the observed isomer leaves conjugated the maximum number of noncomplexed rings.⁵ Although the assignments of the ¹³C and ¹H NMR resonances of **2** were made by standard one- and two-dimensional techniques, the attribution of the *exo* and *endo* methylene protons at C(4) was not so trivial. This was achieved by taking advantage of the anisotropic solvent-induced shift (ASIS) effect.⁶ As depicted in Figure 4, successive addition of aliquots of benzene to a CD₂Cl₂ solution of **2** led to a greater increase in shielding of one of the aforementioned methylene protons. It is the *exo* hydrogen which is the more exposed to the anisotropic solvent and so the attributions are evident.

As expected from the published data for the analogous fluorene complex,⁷ deprotonation of (η⁶-cppH)Cr(CO)₃ (**2**) yields a complex whose NMR spectra reveal that the Cr(CO)₃ fragment has migrated onto the cyclopentadienyl ring. The NMR spectra are consistent only with a molecule (**7**) possessing a single mirror plane, and the aromatic resonances are typical for noncomplexed

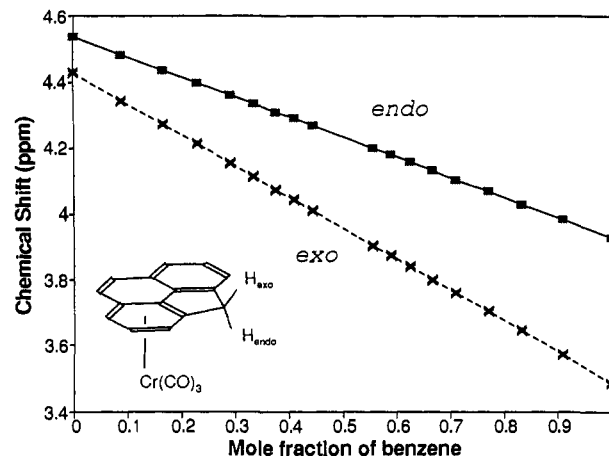
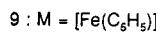
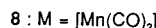
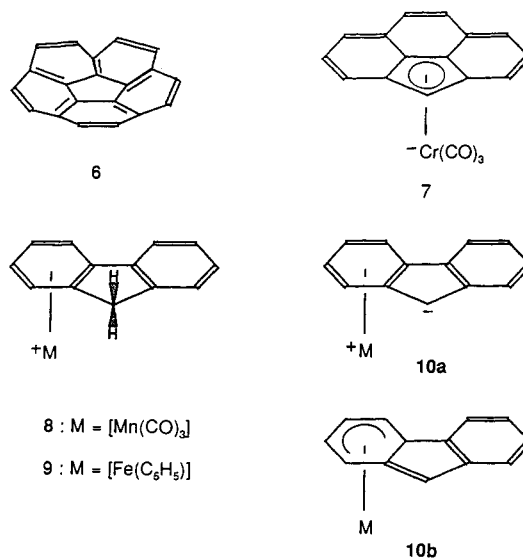


Figure 4. Use of the ASIS effect to distinguish *exo* and *endo* methylenes in (η⁶-cppH)Cr(CO)₃ (**2**).

arene rings. Moreover, the appearance of the C(4) and Cr(CO)₃ resonances at δ 60.4 and 245.8, respectively, provide compelling evidence for an η⁵-complex. Our studies on the anionic species **7** were restricted to spectroscopic investigations in solution; however, we anticipated that use of cationic η⁶-precursors should yield neutral η⁵-complexes which might be more readily amenable to X-ray diffraction techniques.



In his pioneering studies on fluorenyl complexes, Treichel showed that deprotonation of the cationic complexes **8** and **9** bearing such η⁶-bonded fragments as Mn(CO)₃⁺ or (C₅H₅)Fe⁺ yields isolable intermediates in which the metal remains attached to the six-membered ring.⁸ These neutral intermediates have been represented either as zwitterions, as in **10a**, or as molecules possessing a formal C(9)=C(10) double bond, as in **10b**. X-ray diffraction studies on (fluorene)Fe(C₅H₅) and (fluorene)Mn(CO)₃ revealed that the ligand is apparently bonded in a pentahapto fashion.^{9,10} In the manganese case, the reaction continues whereby the Mn(CO)₃ moiety eventually moves into the five-membered ring, **11**. In the (cyclopentadienyl)iron analogue, Treichel was unable to detect (η⁵-fluorenyl)(η⁵-cyclopentadienyl)iron (**12**), but Ustynyuk *et al.* have claimed

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(9) Johnson, J. W.; Treichel, P. M. *J. Chem. Soc., Chem. Commun.* 1976, 688.

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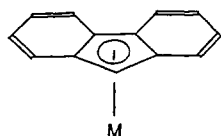
(3) (a) Muir, K. W.; Ferguson, G.; Sim, G. A. *J. Chem. Soc. B* 1968, 467. (b) Hanic, F.; Mills, O. S. *J. Organomet. Chem.* 1968, 11, 151. (c) Rogers, R. D.; Atwood, J. L.; Albright, T. A.; Lee, W. A.; Rausch, M. D. *Organometallics* 1984, 3, 263.

(4) Elschenbroich, Ch.; Salzer, A. *Organometallics—A Concise Introduction*, 2nd ed.; VCH Publishers: Weinheim, Germany, 1989; p 345.

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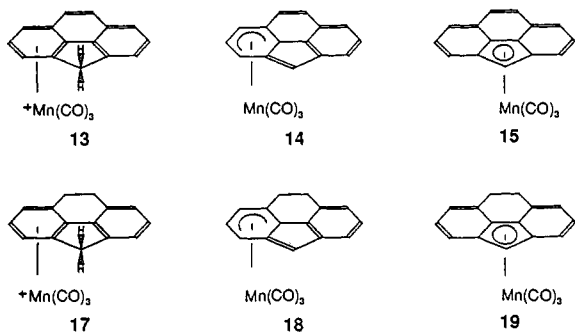
(6) (a) Laszlo, P. *Prog. NMR Spectrosc.* 1967, 3, 231. (b) Ustynyuk, N. A.; Novikova, L. N.; Bel'skii, V. K.; Oprunenko, Yu. F.; Malyugina, S. G.; Trifonova, O. I.; Ustynyuk, Yu. A. *J. Organomet. Chem.* 1985, 294, 31.

(7) Nicholas, K. M.; Kerber, R. C.; Stiefel, E. I. *Inorg. Chem.* 1971, 10, 1519.

11 : M = Mn(CO)₃12 : M = Fe(C₅H₅)

that this ferrocene analogue is produced.¹¹ We are currently investigating the possible formation of (η^5 -cpp)Fe(η^5 -C₅H₅) and have already crystallographically characterized [(η^6 -cppH)-Fe(η^5 -C₅H₅)]⁺PF₆⁻.¹² In contrast to the synthesis of the cation [(η^6 -phenanthrene)Fe(C₅H₅)]⁺, which is always accompanied by much hydrogenation of the C(8)=C(9) double bond,¹³ this is not a particular problem with [(η^6 -cppH)Fe(η^5 -C₅H₅)]⁺PF₆⁻.

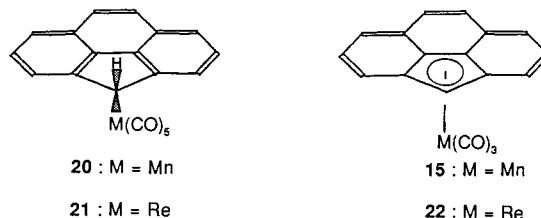
The reaction of cppH with bromo(pentacarbonyl)manganese in the presence of AlCl₃ yields the cationic manganese complex [(η^6 -cppH)Mn(CO)₃]⁺PF₆⁻ (13). Unlike the situation with [(η^6 -cppH)Fe(η^5 -C₅H₅)]⁺PF₆⁻, where hydrogen abstraction is not problematical, 13 is seriously contaminated with [(η^6 -H₂-cppH)Mn(CO)₃]⁺PF₆⁻ (17) unless the solvent is very carefully dried. Interestingly, Nesmeyanov has noted that the use of very dry AlCl₃ in the preparation of [(arene)Fe(C₅H₅)]⁺ complexes leads to extremely poor yields; apparently, traces of water are necessary for the reaction to proceed satisfactorily.¹⁴



Deprotonation of the manganese cation [(η^6 -cppH)Mn(CO)₃]⁺PF₆⁻ (13) at room temperature leads to (η^5 -cpp)Mn(CO)₃ (15) with no detectable intermediacy of 14. However, generation of 14 can be accomplished readily at -40 °C by treatment of a dichloromethane solution of 13 with 1,8-bis(dimethylamino)naphthalene (Proton Sponge, Aldrich). Rearrangement to the η^5 -isomer 15 is evident at temperatures above 15 °C. In contrast, prior reduction of the C(8)=C(9) double bond of cppH to give H₂-cppH (16), followed by complexation with Mn(CO)₃⁺, yields 17. Subsequent deprotonation of 17 results in metal migration, but this process clearly occurs in a stepwise manner. Indeed, 18 is stable at room temperature in acetone solution for at least 24 h or in the solid state for several weeks at -20 °C. However, upon heating a hexane solution of 18 for 1 h, it is slowly transformed into the centrally-bonded isomer 19. This result mirrors the behavior of the (fluorenyl)Mn(CO)₃ system originally studied by Treichel.⁸ The ¹H NMR spectra of 17, 18, and 19 are shown in Figure 5.

The pentahapto complex (η^5 -cpp)Mn(CO)₃ (15) can be independently synthesized in surprisingly good yield via the reaction of the cpp anion C₁₅H₅⁻ with bromo(pentacarbonyl)-

manganese;¹⁵ presumably, the reaction proceeds via the initially formed η^1 -species 20, but this was not isolable. In contrast, the analogous reaction with iodo(pentacarbonyl)rhenium yields the mono- and pentahapto complexes 21 and 22, respectively.¹²



20 : M = Mn

21 : M = Re

15 : M = Mn

22 : M = Re

X-ray Crystallography. The structure of (η^6 -cppH)Cr(CO)₃ (2) was readily deduced from its ¹H and ¹³C NMR spectra, but the establishment of the orientation of the tripodal substituent required an X-ray crystallographic determination. The preferred orientation of the tripod has been calculated in (phenanthrene)-Cr(CO)₃ (3), and X-ray data are in accord with this prediction.^{3c} Our EHMO calculations on (η^6 -cppH)Cr(CO)₃ (2) indicate that it should mirror the behavior of 3. Indeed, as shown in Figure 6, the molecular orbital pattern of cppH itself closely resembles that for phenanthrene; in contrast, the frontier orbitals of C₁₅H₅⁻, i.e., the cpp anion, match those of the fluorenyl anion in that the HOMO has a large p_z coefficient at the C(4) position.

The X-ray crystallographically determined structure of 2 appears as Figure 7 and reveals that the tricarbonylchromium tripod adopts the EHMO-predicted orientation. Numbers related to data collection are in Table I, and atomic coordinates and bond lengths are listed in Tables II and III. It is noteworthy that the tetracyclic ring system in 2 is not planar but instead bends in a gentle arc away from the organometallic fragment. Such a tendency to fold away from the π -bonded ML_n group has been noted previously in such polycyclic molecules as the α - and β -Cr(CO)₃ complexes of methyl *O*-methylpodocarpate¹⁶ and also for the Cr(CO)₂CS and (C₅H₅)Ru derivatives of estradiol or estrone.¹⁷ The free ligand cppH, 1, crystallizes in thin plates unsuitable for an X-ray structural determination, so the extent of deviation from planarity is unknown; of course, it was established many years ago that corannulene (6) is distinctly bowl-shaped.¹⁸ However, in corannulene each edge of the central five-membered ring is also part of a six-membered ring. In contrast, in cppH only three of these pentagonal sides are shared with peripheral six-membered rings.

The molecule (η^5 -cpp)Mn(CO)₃ (15) poses several interesting structural questions. One might wonder whether the metal binds in a genuinely pentahapto fashion, or does it perhaps have a tendency toward trihapto bonding, as has been found for (indenyl)-Rh(C₂H₄)₂ and related systems?¹⁹ Moreover, the recently published structure of bis(fluorenyl)barium tetrakis(ammonia) reveals that the metal is considerably displaced from the ring

(15) The isolated yields of 40% for (η^5 -cpp)Mn(CO)₃ may be compared to those of (η^5 -C₅H₅)Mn(CO)₃ (56%) and (η^5 -C₁₃H₉)Mn(CO)₃ (11%): King, R. B.; Efraty, A. *J. Organomet. Chem.* 1970, 23, 527.

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(13) Lee, C. C.; Demchuk, K. J.; Pannekoek, W. J.; Sutherland, R. G. *J. Organomet. Chem.* 1978, 162, 253.

(14) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N.; Polkovnikova, L. S. *Koord. Khim.* 1975, 1, 1252.

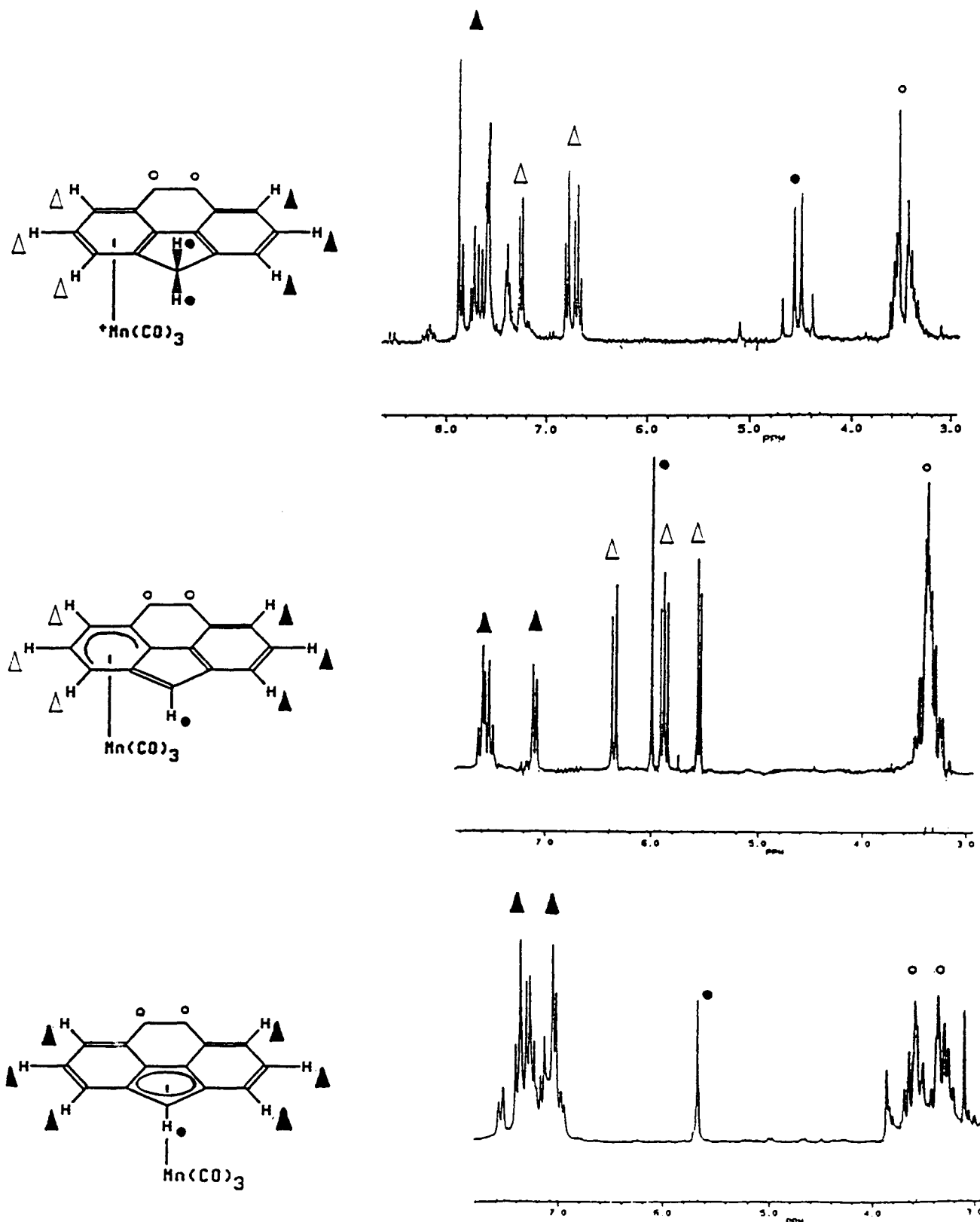


Figure 5. ^1H NMR spectra of the (dihydro-cpp)manganese **17**, **18**, and **19**.

centers.²⁰ Extended Hückel molecular orbital calculations on **15** tell us not only that the metal fragment should be situated at a position displaced ≈ 0.1 Å from the center of the five-membered ring toward C(4) but also that the tripod is preferentially oriented such that a carbonyl ligand is *trans* to the C(4) carbon. This situation arises as a result of the very considerable localization

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of the HOMO of the cpp⁻ anion at C(4) (see Figure 6). Analogously, in (η^5 -fluorenyl)Cr(CO)₂NO (**23**) the chromium is displaced slightly toward the unique ring carbon; furthermore, it is the nitrosyl ligand which is found *trans* to the CH unit of the five-membered ring thus aligning the most strongly donating site with the best π -acceptor ligand.²¹ Although there is a preferred orientation of the Mn(CO)₃ tripod of **15** in the solid state, the barrier to tripod rotation is too low to be measurable

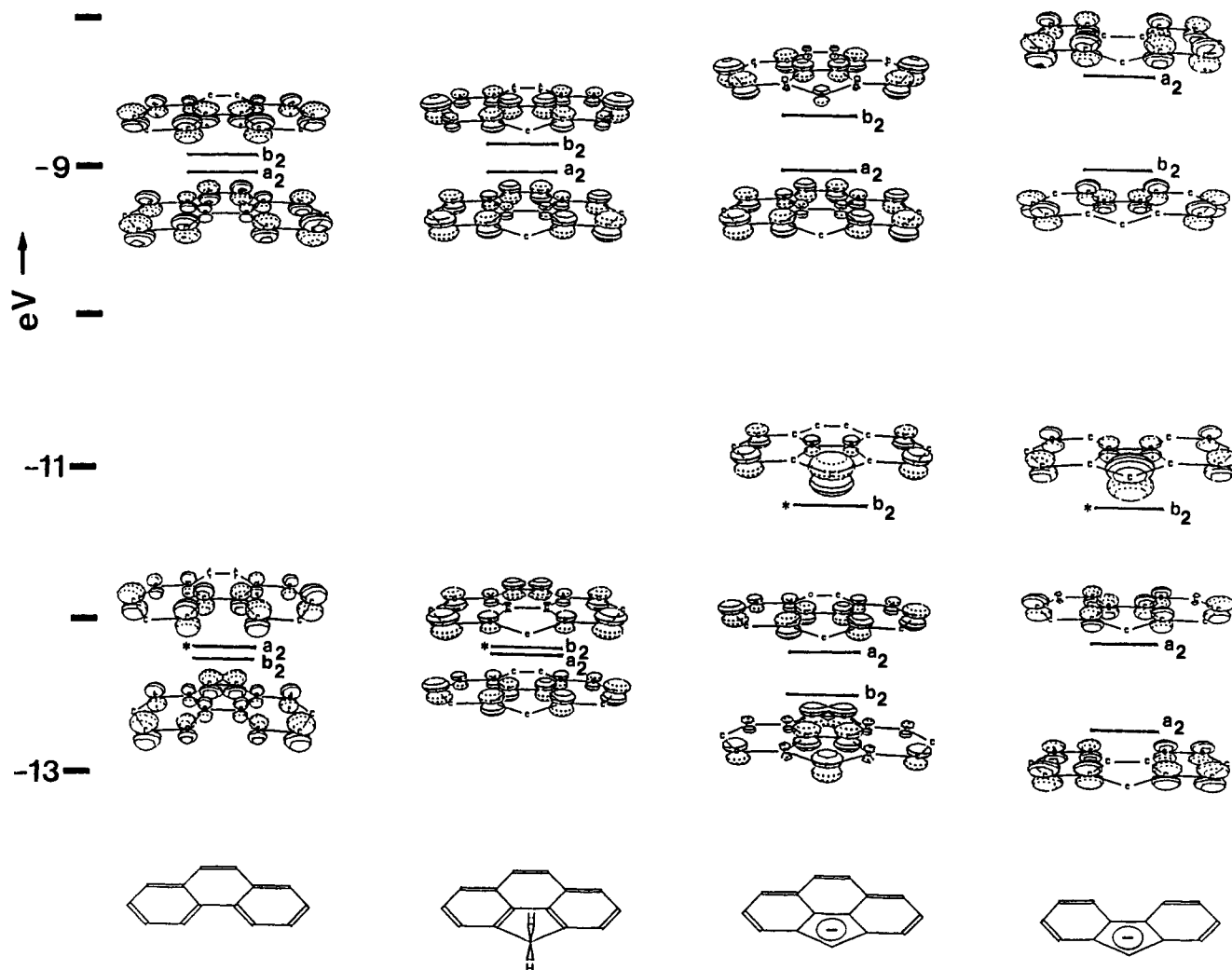


Figure 6. Frontier orbital patterns for phenanthrene, cphH, cph⁻, and for fluorenyl; the HOMO in each case is marked with an asterisk.

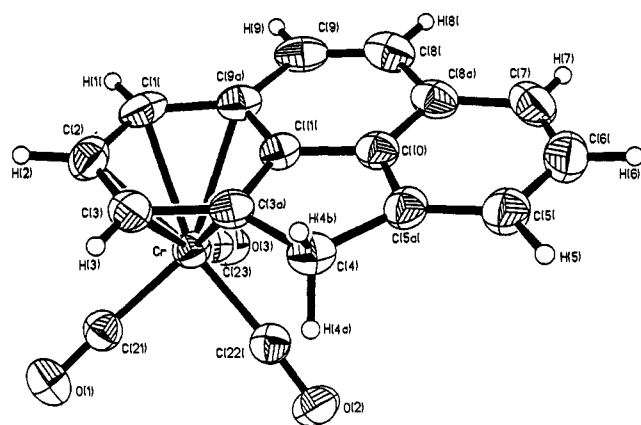


Figure 7. View of (η^6 -cppH)Cr(CO)₃ (**2**) showing the atom numbering. Thermal parameters at 30% probability. For clarity, hydrogen atoms have arbitrary temperature factors.

in solution by NMR spectroscopy. Indeed, the Mn(CO)₃ moiety still exhibits a very sharp ¹³CO singlet at -100 °C on a 500-MHz spectrometer. The factors controlling slowed tripodal rotation have been extensively explored in recent years.²²

Crystals of (η^5 -cpp)Mn(CO)₃ (**15**) were grown from 1,2-dichloroethane/heptane by using solvent diffusion techniques, and the structure was determined by X-ray crystallography. Atomic coordinates and bond lengths are listed in Tables IV and

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V. In accord with the NMR data, the Mn(CO)₃ moiety is indeed bonded to the five-membered ring, as shown in Figure 8. However, the metal is not attached centrally but rather is displaced toward the C(4) position such that the manganese-ring carbon distances are found to be Mn-C(4) 2.121(2) Å, Mn-C(3a/5a) 2.204(2) Å, Mn-C(10/11) 2.206(2) Å. These findings corroborate the EHMO predictions. A further noteworthy structural result is the fact that the three six-membered rings attached to the cyclopentadienyl moiety are slightly folded away from the Mn(CO)₃ tripod.

We have commented already on the molecular geometry of (η^6 -cphH)Cr(CO)₃ (**2**), and it should be compared with the molecular and crystal structure of the analogous 8,9-dihydro complex (η^6 -H₂-cphH)Cr(CO)₃ (**24**), a view of which appears as Figure 9. Atomic coordinates and bond lengths are listed in Tables VI and VII. The most obvious point is that the ligand is no longer a flat molecule with a gentle arc but instead is markedly twisted. The C(8)-C(9) bond is no longer coplanar with the "fluorene-like" tricyclic unit but rather adopts a half-chair conformation such that the benzylic methylene unit bonded to the chromium-complexed ring is *exo* with respect to the metal

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Table I. Crystallographic Data for (η^6 -cppH)Cr(CO)₃ (**2**), (η^6 -H₂-cppH)Cr(CO)₃ (**24**), and (η^5 -cpp)Mn(CO)₃ (**15**)

2		24	15
empirical formula	C ₁₈ H ₁₀ CrO ₃	Crystal Data C ₁₈ H ₁₂ CrO ₃	C ₁₈ H ₉ MnO ₃
color	orange-red	yellow	red
habit	square biprism	parallelepiped	square biprism
crystal size, mm ³	0.65 × 0.5 × 0.45	0.7 × 0.4 × 0.4	0.35 × 0.4 × 0.45
crystal system	orthorhombic	orthorhombic	monoclinic
space group	<i>Pbca</i>	<i>Pbca</i>	<i>P2₁/c</i>
<i>a</i> , Å	13.924(2)	12.662(3)	11.274(2)
<i>b</i> , Å	12.639(2)	14.594(3)	8.752(2)
<i>c</i> , Å	15.666(3)	15.761(3)	14.404(3)
β , deg			98.64(3)
<i>V</i> , Å ³	2757(1)	2913(1)	1405.1(7)
<i>Z</i>	8	8	4
formula weight	326.3	328.3	328.2
<i>d</i> (calc), Mg/m ³	1.572	1.497	1.551
μ , cm ⁻¹	9.40	7.94	5.0
Data Collection			
diffractometer	Siemens P4	Siemens P4	Siemens R3m/V
radiation	Mo K α ($\lambda = 0.710\ 73\ \text{\AA}$)	Mo K α ($\lambda = 0.710\ 73\ \text{\AA}$)	Ag K α ($\lambda = 0.560\ 86\ \text{\AA}$)
<i>T</i> , K	300	300	300
monochromator	graphite	graphite	graphite
2 θ range, deg	3.5–50.0	7.0–45.0	7.0–45.0
scan type	2 θ - θ	ω	ω
std refln	3 std/97 refln	3 std/97 refln	3 std/97 refln
index ranges	0 ≤ <i>h</i> ≤ 15, 0 ≤ <i>k</i> ≤ 14, -17 ≤ <i>l</i> ≤ 0	-1 ≤ <i>h</i> ≤ 15, -1 ≤ <i>k</i> ≤ 17, -1 ≤ <i>l</i> ≤ 18	0 ≤ <i>h</i> ≤ 15, 0 ≤ <i>k</i> ≤ 11, -19 ≤ <i>l</i> ≤ 19
rflns collected	2493	3240	3938
indepdt rflns	2136	2546	3764
obsd rflns	1642 (<i>F</i> ≤ 2.0 σ (<i>F</i>))	2012 (<i>F</i> ≤ 4.0 σ (<i>F</i>))	2609 (<i>F</i> ≤ 4.0 σ (<i>F</i>))
min/max transm	0.4332/0.4690	0.579/0.615	0.724/0.786
abs. corr.	ψ scan	ψ scan	ψ scan
Solution and Refinement			
extinction correction ^a	$\chi = 0.0019(7)$	$\chi = 0.000\ 45(8)$	N/A
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0009 * F^2$	$w^{-1} = \sigma^2(F) + 0.000\ 032 * F^2$	$w^{-1} = \sigma^2(F) + 0.0015 * F^2$
no. parameters refined	201	201	235
<i>R</i> , %	5.36	5.94	3.71
<i>R</i> _w , %	6.39	6.46	4.68
GOF ^d	1.42	4.01	0.92
Δ/σ (max)	0.019	3.638 ^e	0.021
Δ/σ (mean)	0.003	0.224 ^e	0.002
<i>N</i> _o / <i>N</i> _v	8.2	10.0	11.1
$\Delta\rho_{\text{max}}$, e Å ⁻³	0.23	0.50	0.45
$\Delta\rho_{\text{min}}$, e Å ⁻³	-0.25	-0.40	-0.25

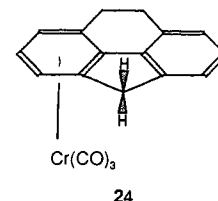
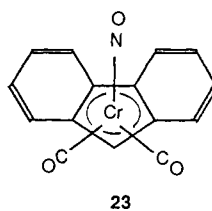
^a $F = F[1 + 0.002\chi^2 F^2 / \sin(2\theta)]^{-1/4}$. ^b $R = \sum(|F_{\text{obs}} - F_{\text{calc}}|) / \sum F_{\text{obs}}$. ^c $R_w = [(\sum(w_i(|F_{\text{obs}} - F_{\text{calc}}|)^2) / \sum(w_i F_{\text{obs}}^2))]^{1/2}$. ^d GOF = $[(\sum(w_i(|F_{\text{obs}} - F_{\text{calc}}|)^2) / (N_o - N_v))]^{1/2}$. ^e Nonresolvable disorder in ligand position causes fluctuating temperature factors.

Table II. Atomic Coordinates (×10⁴) for (η^6 -cppH)Cr(CO)₃ (**2**)

	<i>x</i>	<i>y</i>	<i>z</i>
Cr	2059(1)	-26(1)	1335(1)
C(1)	1837(3)	-323(4)	049(3)
C(2)	1504(3)	-1183(4)	412(3)
C(3)	795(3)	-1093(3)	1082(3)
C(3A)	444(3)	-90(3)	1259(2)
C(4)	-315(3)	345(3)	1870(3)
C(5A)	-377(3)	1508(3)	1622(3)
C(5)	-927(3)	2343(4)	1867(3)
C(6)	-794(4)	3320(4)	1464(3)
C(7)	-154(4)	3498(4)	828(4)
C(8A)	434(3)	2639(4)	536(3)
C(8)	1110(3)	2599(4)	-129(3)
C(9)	1599(3)	1701(4)	-346(3)
C(9A)	1441(3)	708(3)	98(3)
C(10)	289(3)	1696(3)	962(3)
C(11)	761(3)	764(3)	747(2)
C(21)	2743(3)	-1067(3)	1879(3)
C(22)	1932(3)	618(3)	2376(3)
C(23)	3193(3)	695(4)	1165(3)
O(1)	3168(2)	-1712(3)	2236(2)
O(2)	1853(2)	970(3)	3058(2)
O(3)	3911(3)	1144(3)	1076(2)

Table III. Bond Length (Å) for (η^6 -cppH)Cr(CO)₃ (**2**)

Cr-C(1)	2.224(4)	Cr-C(2)	2.197(5)	Cr-C(3)	2.251(4)
Cr-C(3A)	2.252(4)	Cr-C(9A)	2.314(4)	Cr-C(11)	2.261(4)
Cr-C(21)	1.835(4)	Cr-C(22)	1.832(5)	Cr-C(23)	1.843(5)
C(1)-C(2)	1.381(7)	C(1)-C(9A)	1.428(7)	C(2)-C(3)	1.446(6)
C(3)-C(3A)	1.387(6)	C(3A)-C(4)	1.528(6)	C(3A)-C(11)	1.415(5)
C(4)-C(5A)	1.523(6)	C(5A)-C(5)	1.360(7)	C(5A)-C(10)	1.408(6)
C(5)-C(6)	1.400(7)	C(6)-C(7)	1.356(8)	C(7)-C(8A)	1.434(7)
C(8A)-C(8)	1.405(7)	C(8A)-C(10)	1.381(6)	C(8)-C(9)	1.366(7)
C(9)-C(9A)	1.451(7)	C(9A)-C(11)	1.391(5)	C(10)-C(11)	1.391(6)
C(21)-O(1)	1.152(6)	C(22)-O(2)	1.162(6)	C(23)-O(3)	1.158(6)



peared a number of years ago,²³ and the nonplanarity of the tricyclic ligand was detected.

It is also instructive to look at the packing of the molecules in the unit cell. The molecules of **2** are arranged in a head-to-head

fragment. This has the effect of twisting the noncomplexed half of the molecule. We note that a preliminary report on the molecular structure of (9,10-dihydrophenanthrene)Cr(CO)₃ ap-

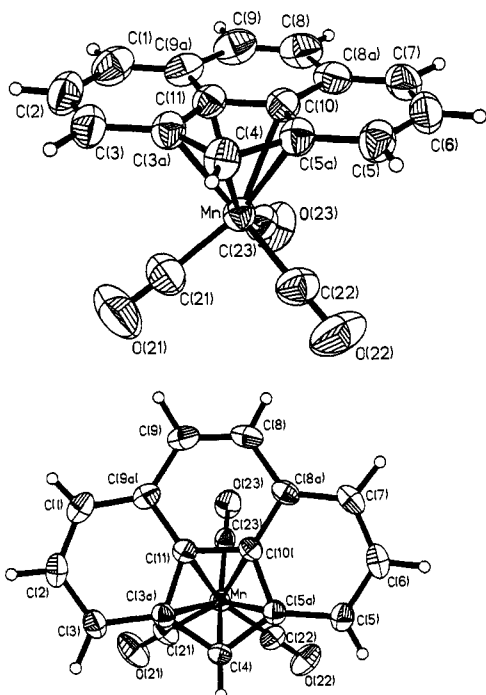
(23) Muir, K. W.; Ferguson, G.; Sim, G. A. *J. Am. Chem. Soc. B* 1968, 476.

Table IV. Atomic Coordinates ($\times 10^4$) for $(\eta^5\text{-cpp})\text{Mn}(\text{CO})_3$ (**15**)

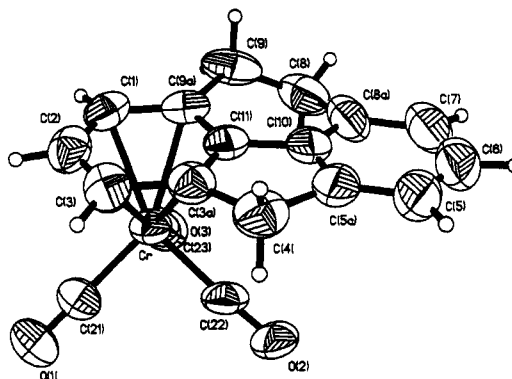
	x	y	z
Mn	-2408(1)	-2175(1)	-391(1)
C(1)	-931(3)	-4467(3)	-2311(2)
C(2)	4(3)	-3458(3)	-1953(2)
C(3)	163(2)	-2860(3)	-1056(2)
C(3A)	-664(2)	-3283(3)	-447(2)
C(4)	-870(2)	-2968(3)	510(2)
C(5A)	-1860(2)	-3914(3)	694(1)
C(5)	-2471(2)	-4260(3)	1465(2)
c(6)	-3383(2)	-5314(4)	1330(2)
C(7)	-3766(3)	-6062(3)	474(2)
C(8)	-3447(3)	-6358(3)	-1259(2)
C(8A)	-3240(2)	-5754(3)	-308(2)
C(9)	-2770(3)	-5970(3)	-1922(2)
C(9A)	-1766(6)	-4920(3)	-1754(2)
C(10)	-2306(2)	-4669(3)	-156(2)
C(11)	-1597(2)	-4284(3)	-843(1)
C(21)	-3637(2)	-2211(3)	-1347(2)
C(22)	-1844(2)	-422(3)	-771(2)
C(23)	-3277(3)	-1176(4)	358(2)
O(1)	-4402(2)	-2249(3)	-1962(1)
O(2)	-1454(2)	693(3)	-1016(2)
O(3)	-3836(2)	-552(3)	838(2)

Table V. Bond Length (\AA) for $(\eta^5\text{-cpp})\text{Mn}(\text{CO})_3$ (**15**)

Mn-C(3A)	2.205(2)	Mn-C(4)	2.121(2)	Mn-C(5A)	2.204(2)
Mn-C(10)	2.210(2)	Mn-C(11)	2.202(2)	Mn-C(21)	1.801(2)
Mn-C(22)	1.778(3)	Mn-C(23)	1.790(3)	C(1)-C(2)	1.412(4)
C(1)-C(9A)	1.385(4)	C(2)-C(3)	1.380(4)	C(3)-C(3A)	1.423(4)
C(3A)-C(4)	1.458(3)	C(3A)-C(11)	1.421(3)	C(4)-C(4A)	1.447(3)
C(5A)-C(5)	1.424(3)	C(5A)-C(10)	1.415(3)	C(5)-C(6)	1.374(4)
C(6)-C(7)	1.405(4)	C(7)-C(8A)	1.376(4)	C(8)-C(8A)	1.454(4)
C(8)-C(9)	1.352(4)	C(8A)-C(10)	1.410(3)	C(9)-C(9A)	1.450(4)
C(9A)-C(11)	1.410(3)	C(10)-C(11)	1.404(3)	C(21)-O(1)	1.140(3)
C(22)-O(2)	1.148(4)	C(23)-O(3)	1.142(4)		

**Figure 8.** Views of $(\eta^5\text{-cpp})\text{Mn}(\text{CO})_3$ (**15**) showing the atom numbering. Thermal parameters at 30% probability. For clarity, hydrogen atoms have arbitrary temperature factors.

manner such that closest neighbors have their tetracyclic ligands aligned parallel to each other at an interplane distance of 3.45 \AA . From a comparison of the crystal packing of $(\eta^6\text{-H}_2\text{-cppH})\text{Cr}(\text{CO})_3$ (**24**) with $(\eta^6\text{-cppH})\text{Cr}(\text{CO})_3$ (**2**), it appears superficially (see Figure 10) that the two are rather similar. However, a view along an orthogonal direction (Figure 11) reveals that in the

**Figure 9.** View of $(\text{H}_2\text{-}\eta^6\text{-cppH})\text{Cr}(\text{CO})_3$ (**24**) showing the atom numbering. Thermal parameters at 30% probability after correction for librational motion. For clarity, hydrogen atoms have arbitrary temperature factors.**Table VI.** Atomic Coordinates ($\times 10^4$) for $(\eta^6\text{-H}_2\text{-cppH})\text{Cr}(\text{CO})_3$ (**24**)

	x	y	z
Cr	552(1)	2034(1)	1291(1)
C(1)	386(7)	2991(4)	2382(3)
C(2)	-569(7)	2628(5)	2184(5)
C(3)	-1038(4)	2696(4)	1375(5)
C(3A)	-472(4)	3157(3)	754(3)
C(4)	-700(6)	3420(4)	-161(4)
C(5A)	335(8)	3898(4)	-430(4)
C(5)	708(12)	4276(5)	-1169(5)
C(6)	1771(17)	4623(9)	-1133(9)
C(7)	2406(12)	4588(8)	-473(9)
C(8A)	2020(6)	4225(4)	278(7)
C(8)	2655(5)	4020(6)	1023(9)
C(9)	2018(6)	3934(4)	1838(5)
C(9A)	985(4)	3437(3)	1758(3)
C(10)	1025(5)	3916(3)	260(4)
C(11)	527(3)	3500(3)	965(3)
C(21)	62(4)	879(3)	1489(4)
C(22)	933(5)	1733(3)	205(4)
C(23)	1837(4)	1608(3)	1631(3)
O(1)	-238(3)	150(3)	1631(3)
O(2)	1165(4)	1589(3)	-488(3)
O(3)	2639(3)	1333(2)	1861(3)

Table VII. Bond Length (\AA) for $(\eta^6\text{-H}_2\text{-cppH})\text{Cr}(\text{CO})_3$ (**24**)

Cr-C(1)	2.225(6)	Cr-C(2)	2.179(8)	Cr-C(3)	2.238(6)
Cr-C(3A)	2.255(5)	Cr-C(9A)	2.244(5)	Cr-C(11)	2.200(4)
Cr-C(21)	1.823(5)	Cr-C(22)	1.831(6)	Cr-C(23)	1.823(5)
C(1)-C(2)	1.355(12)	C(1)-C(9A)	1.402(8)	C(2)-C(3)	1.410(11)
C(3)-C(3A)	1.389(8)	C(3A)-C(4)	1.519(8)	C(3A)-C(11)	1.401(6)
C(4)-C(5A)	1.544(11)	C(5A)-C(5)	1.371(11)	C(5A)-C(10)	1.396(10)
C(5)-C(6)	1.439(25)	C(6)-C(7)	1.316(22)	C(7)-C(8A)	1.385(17)
C(8A)-C(8)	1.454(15)	C(8A)-C(10)	1.339(10)	C(8)-C(9)	1.522(14)
C(9)-C(9A)	1.501(9)	C(9A)-C(11)	1.380(7)	C(10)-C(11)	1.414(7)
C(21)-O(1)	1.152(6)	C(22)-O(2)	1.150(7)	C(23)-O(3)	1.151(6)

dihydro complex **24** there has been a slippage of one molecule relative to its nearest neighbor. The net result of hydrogenating the C(8)=C(9) bond is not only an increase in the interplane distance from 3.45 \AA in **2** to 3.6 \AA in **24** but also in the volume of the unit cell by 5.5% relative to that of **2**. The corresponding interplanar separations in $(\eta^5\text{-cpp})\text{Mn}(\text{CO})_3$ (**15**) and in $[(\eta^6\text{-cppH})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]^+\text{PF}_6^-$ are 3.40 and 3.35 \AA , respectively.

Extended Hückel Molecular Orbital Studies. We turn now to the question of the trajectory taken by the ML_n moieties as they migrate from the six- to the five-membered ring. As noted previously,¹ the orientations of tripodal fragments (such as $\text{Mn}(\text{CO})_3$ or $\text{Cr}(\text{CO})_3$) relative to the hydrocarbon play an important

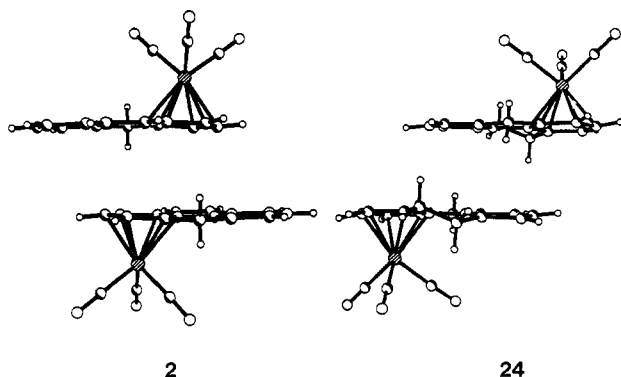


Figure 10. View of two nearest neighbors in the unit cells of $(\eta^6\text{-cppH})\text{Cr}(\text{CO})_3$ (**2**) and of $(\text{H}_2\text{-}\eta^6\text{-cppH})\text{Cr}(\text{CO})_3$ (**24**).

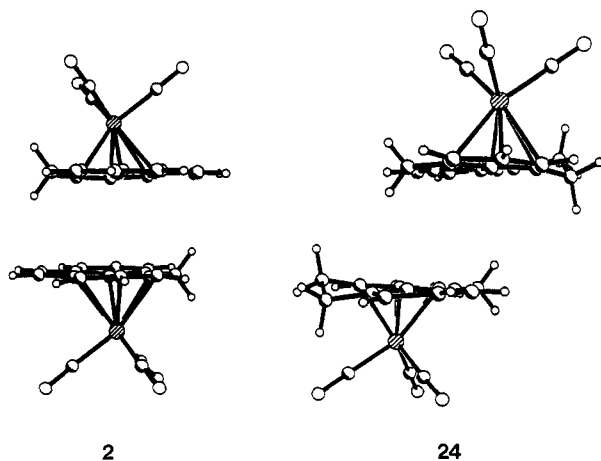


Figure 11. View of the packing of **2** and of **24** orthogonal to that in Figure 10, showing how the molecules of **24** are slipped relative to each other.

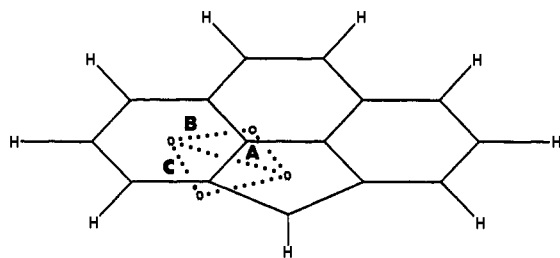


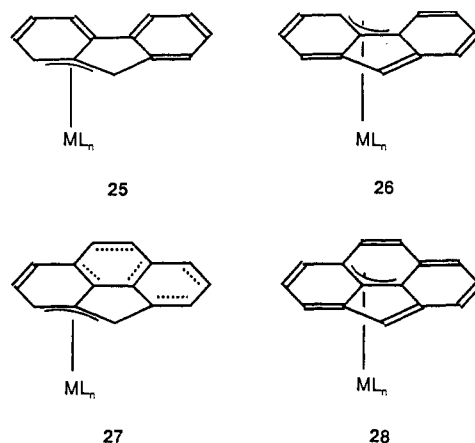
Figure 12. Possible pathways for haptotropic migrations in $(\text{cpp})\text{Fe}(\text{Cp})$.

role in maximizing orbital overlap. This problem is greatly alleviated by allowing an $\text{Fe}(\text{C}_5\text{H}_5)$ unit to move over the surface of the polycyclic ligand; use of a fixed orientation of the cyclopentadienyl ring is justifiable in terms of its very low barrier to rotation. In all cases, EHMO calculations were carried out for $(\text{C}_5\text{H}_5)\text{Fe}$ migrations over fluorenyl or cpp^- surfaces with a constant CpFe -ligand distance of 1.59 Å. The center of the six-membered ring was selected as the origin for all metal migrations, and this structure represents the arbitrary zero relative to which all other calculated energies are reported.

In accord with the calculations of Albright, Hoffmann, and their co-workers on indenyl and fluorenyl complexes,¹ we find that there will be an unacceptably high barrier to the least-motion pathway (route A) of an $\text{Fe}(\text{C}_5\text{H}_5)$ unit directly across the $\text{C}(3a)\text{-C}(11)$ bond in the cpp system. As shown in Figure 12, the transit through the central six-membered ring (route B) provides a lower activation energy pathway, but the favored route (C) proceeds via an exocyclic π -allylic structure. The calculated barriers for these three migration pathways are 50.3, 39.3, and 32.5 kcal mol⁻¹, respectively. These compare with our EHMO-derived values of 56.0, 39.3, and 36.8 kcal mol⁻¹, respectively, for the

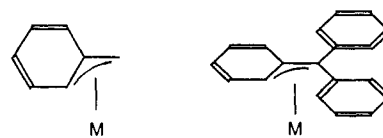
analogous migrations in the fluorenyl case. In both cases, the η^5 -isomer is the favored structure; $(\eta^5\text{-fluorenyl})\text{FeCp}$ is stabilized by 10.5 kcal mol⁻¹ and $(\eta^5\text{-cpp})\text{FeCp}$ by 13.4 kcal mol⁻¹.

The enhanced ease of migration in cpp complexes relative to the $\text{H}_2\text{-cpp}$ or fluorenyl systems can be explained either on the basis of these molecular orbital calculations or, more straightforwardly, by using the simple bonding pictures **25–28**. It is only



in the cpp complexes, if the migration proceeds via the exocyclic π -allylic transition state **27**, that one can maintain the 10π (naphthalene-like) aromatic character of two rings throughout the course of the reaction. This proposal gains support from the observation that the migration of an $\text{Mn}(\text{CO})_3$ group upon deprotonation of the cppH complex **13** is very facile, whereas the corresponding reactions using the dihydro- cppH complex **17** are rather slow; moreover, the intermediate $(\text{H}_2\text{-cpp})\text{Mn}(\text{CO})_3$ (**18**) can be isolated. Since we can detect the intermediates **14** and **18**, detailed kinetic studies are currently in progress with the goal of obtaining activation energies for these haptotropic shifts. These data will allow us to establish unambiguously whether the transformations **14** → **15** (fast) and **18** → **19** (slow) are genuinely kinetically controlled.

Concluding Remarks. It would be of considerable interest to synthesize and characterize a genuinely trihapto- cpp complex to see whether the organometallic fragment can be trapped at the exocyclic binding site, as in **27**, and experiments aimed at accomplishing this goal are currently being undertaken. We note that several η^3 -benzylic systems in which the metal binds in an exocyclic fashion have been reported.^{24,25} These examples include the cases where the ML_n units were either $(\text{C}_5\text{H}_5)\text{M}(\text{CO})_2$ ($\text{M} = \text{Mo}, \text{W}$) (**29**, **30**) or $(\text{acac})\text{M}$ ($\text{M} = \text{Pd}, \text{Pt}$) (**31**, **32**). The syntheses and rearrangement behavior of cpp complexes containing these ML_n fragments will be the subject of a future report.



29 : $\text{M} = \text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)$

31 : $\text{M} = \text{Pd}(\text{acac})$

30 : $\text{M} = \text{W}(\text{CO})_2(\text{C}_5\text{H}_5)$

32 : $\text{M} = \text{Pt}(\text{acac})$

Finally, as we recall that the cpp ligand represents one quarter of the C_{60} skeleton, it is interesting to speculate whether it may be possible to bind an ML_n tripod to buckminsterfullerene in an

(24) (a) King, R. B.; Fronzaglia, A. *J. Am. Chem. Soc.* **1966**, *88*, 709. (b) Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 1339.

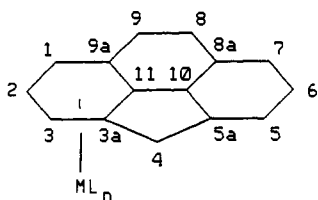
(25) (a) Sonoda, A.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1975**, 108. (b) Roberts, J. S.; Klabunde, K. J. *J. Am. Chem. Soc.* **1977**, *99*, 2509. (c) Craswell, L. E.; Litster, S. A.; Redhouse, A. D.; Spencer, J. L. *J. Organomet. Chem.* **1990**, *394*, C35 and references therein.

η^5 - or η^6 -manner. Thus far, the crystallographically characterized complexes of C_{60} in which metals are bonded to the outside of the cage are ones in which the fullerene functions as a polyalkene.²⁶ In fact, the frontier orbitals of C_{60} are 5-fold degenerate sets which are disposed in an essentially equatorial manner over the surface.²⁷ The orbitals which are more localized on individual six- or five-membered rings and which are potential donors to ML_3 fragments are energetically rather inaccessible. Nevertheless, when molecules of the type (fullerene) ML_3 become available, they may exhibit spectacular fluxional behavior.

Experimental Section

All preparations were carried out under an atmosphere of dry nitrogen, and solvents were dried according to standard procedures.²⁸ NMR spectra were recorded on Bruker AM-500 or AC-200 spectrometers by using a 5-mm dual frequency 1H - ^{13}C probe and are reported relative to tetramethylsilane. Typical proton spectra were obtained at 500.135 MHz in 8 scans in 32K data points over a 5-kHz spectral width or at 200.133 MHz in 8 scans in 16K data points over a 2-kHz spectral width. Carbon spectra were obtained at 125.76 MHz in 16K data points over a 30-kHz spectral width or at 50.32 MHz in 16K data points over a 15-kHz spectral width. Proton-carbon shift-correlated spectra were recorded by using the 5-mm dual frequency 1H - ^{13}C inverse probe. Fast atom bombardment (FAB) mass spectra were performed on a VG analytical micromass ZAB-ZE spectrometer with an accelerating power of 8 kV and a resolving power of 10 000 and a VG11/250 data system. 3-Nitrobenzyl alcohol was used as the sample matrix and helium as the bombarding gas. Microanalytical data are from Guelph Chemical Laboratories, Guelph, Ontario.

The numbering scheme for cppH and metal complexes is shown below:



4H-Cyclopenta[def]phenanthrene (cppH, 1) was obtained from Aldrich Chemical Company and was used without further purification. 1H NMR (200 MHz, acetone- d_6): δ 7.87 (s, 2H, H-8,9), 7.85 (d, J = 7.9 Hz of d, J = 0.5 Hz, 2H, H-1,7), 7.72 (d, J = 7.1 Hz of d, J = 0.5 Hz, 2H, H-3,5), 7.65 (d, J = 7.9 Hz of d, J = 7.1 Hz, 2H, H-2,6), 4.35 (s, 2H, H-4). The H-3,5 attributions were made on the basis of their NOE interactions with the H-4 protons at 4.35 ppm. ^{13}C NMR (50 MHz, acetone- d_6): δ 142.7 (C-8a,9a), 139.0 (C-3a,5a), 128.9 (C-10,11), 128.0 (C-2,6), 125.9 (C-8,9), 121.9 (C-3,5), 123.4 (C-1,7), 37.8 (C-4). The C-3a,5a and C-8a,9a carbons were assigned on the basis of a 1H - ^{13}C coupled experiment with the delays adjusted for long-range couplings.

(η^6 -4H-Cyclopenta[def]phenanthrene)Cr(CO) $_3$ (2). CppH (1 g, 5.25 mmol) and Cr(CO) $_6$ (1.15 g, 5.25 mmol) were heated under reflux in 1,2-dimethoxyethane (70 mL) for 30 h. After unreacted Cr(CO) $_6$ was separated by filtration, the solvent was removed on a rotary evaporator. Unreacted cppH was recovered by flash chromatography on silica using hexane as eluent; upon changing the solvent to 1:1 hexane/CH $_2$ Cl $_2$, **2** was eluted and yielded an orange-red solid (340 mg, 1.04 mmol, 20%), mp 193 °C dec. 1H NMR (500 MHz, 9:1 acetone- d_6 /benzene- d_6): δ 7.79 (d, J = 9.1 Hz, 1H, H-8), 7.76 (d, J = 7.2 Hz, 1H, H-7), 7.73 (d, J = 7.2 Hz, 1H, H-5), 7.67 (t, J = 7.2 Hz, 1H, H-6), 7.62 (d, J = 9.1 Hz, 1H, H-9), 6.22 (d, J = 6.5 Hz, 1H, H-1), 6.14 (d, J = 6.0 Hz, 1H, H-3), 5.64 (t, J = 6.3 Hz, 1H, H-2), 4.52 (s, 2H, H-4) (Using benzene- d_6 , the AB-system can be resolved: δ 3.98 (d, J = 20.0 Hz, 1H, H-4 $_{endo}$), 3.56 (d, J = 20.0 Hz, 1H, H-4 $_{exo}$)). ^{13}C NMR (50 MHz, 9:1 acetone- d_6 /benzene- d_6): δ 234.5 (Cr-CO); 130.4 (C-6), 129.8 (C-9),

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125.6 (C-8), 124.6 (C-7), 124.4 (C-5), 93.8 (C-2), 91.1 (C-3), 88.9 (C-1) (aromatic Cs); 141.9, 129.1, 128.2, 123.3, 114.0, 102.1 (ring junction Cs); 36.5 (C-4). Mass spectrum (FAB +) m/z (relative intensity): 326 (86) (M) $^+$, 270 (100) (M - 2CO) $^+$, 242 (57) (M - 3CO) $^+$, 190 (58) (C $_{15}$ H $_{10}$) $^+$. Anal. Calcd for C $_{18}$ H $_{10}$ CrO $_3$: C, 66.12; H, 3.30. Found: C, 65.87; H, 3.21.

Deprotonation of (η^6 -4H-Cyclopenta[def]phenanthrene)Cr(CO) $_3$ (2). In an NMR tube, an excess of solid NaH was treated with a solution of (η^6 -cppH)Cr(CO) $_3$ in THF- d_8 at room temperature. The mixture was cooled to -30 °C immediately after completion of the reaction. 1H NMR (500 MHz, THF- d_8 , -30 °C): δ 7.68 (m, 2H), 7.53 (d, J = 6.7 Hz, 2H), 7.26 (m, 2H), 7.15 (m, 2H), 5.40 (s, 1H). ^{13}C NMR (125 MHz, THF- d_8 , -30 °C): δ 245.8 (Cr-CO); 126.1, 125.1, 122.5, 113.0 (aromatic Cs); 134.1, 109.7, 101.4 (ring junction Cs); 60.4 (C-4).

[(η^6 -4H-Cyclopenta[def]phenanthrene)Mn(CO) $_3$] $^+$ PF $_6$ $^-$ (13). BrMn(CO) $_5$ (280 mg, 1 mmol), cppH (190 mg, 1 mmol), and AlCl $_3$ (250 mg, 1.9 mmol) were heated under reflux in *n*-hexane (50 mL, dried over NaH for 3 days, and freshly distilled prior to use) for 5 h. Upon the solution cooling, water (7.5 mL) and toluene (7.5 mL) were added, and the precipitate was removed on a sintered funnel. The aqueous layer was added dropwise to NH $_4$ PF $_6$ (1.6 g, 9.8 mmol) in 5 mL of water. The organic layer was extracted with water (25 mL), and the combined aqueous layers were added to the NH $_4$ PF $_6$ solution. The precipitate was filtered on a sintered funnel, washed with water, and dried in vacuo to yield the product **13** as a yellow powder (290 mg, 0.61 mmol, 61%), mp 137 °C. 1H NMR (200 MHz, acetone- d_6): δ 8.48 (d, J = 9.1 Hz, 1H), 8.2-8.0 (m, 3H), 7.71 (d, J = 6.9 Hz, 1H), 7.51 (d, J = 6.9 Hz, 1H), 7.26 (d, J = 6.2 Hz, 1H), 6.86 (t, J = 6.5 Hz, 1H), 5.09 (d, J = 22.9 Hz, 1H), 4.96 (d, J = 22.9 Hz, 1H). ^{13}C NMR (50 MHz acetone- d_6): δ 137.0, 134.0, 126.7, 126.3, 97.0, 95.7, 95.2 (aromatic Cs); 143.0, 139.2, 124.9, 127.1, 119.1, 118.0 (ring junction Cs); 39.2 (C-4). Mass spectrum (FAB +) m/z (relative intensity): 329 (100) ((C $_{15}$ H $_{10}$)Mn(CO) $_3$) $^+$, 245 (9) ((C $_{15}$ H $_{10}$)Mn) $^+$, 190 (9.5) (C $_{15}$ H $_{10}$) $^+$.

(η^5 -4H-Cyclopenta[def]phenanthrenyl)Mn(CO) $_3$ (15). (a) **By Deprotonation of 13.** (η^6 -cppH)Mn(CO) $_3$ PF $_6$ (0.35 g, 0.75 mmol) and 1,8-bis(dimethylamino)naphthalene (0.16 g, 0.75 mmol) were dissolved in 15 mL of CH $_2$ Cl $_2$. The color of the reaction mixture changed from yellow to red immediately; stirring was continued for 3 h. The solvent volume was reduced to 5 mL, 15 mL of *n*-hexane was added, and the precipitate was filtered using Schlenk techniques. The solvent was removed under high vacuum, and the crude product was purified via flash chromatography on silica using ether/hexanes 1:9 to yield a red solid, mp 77 °C. 1H NMR (200 MHz, acetone- d_6): δ 7.87 (s, 2H, H-8,9), 7.77 (d, J = 8.0 Hz of d, J = 1.2 Hz, 2H, H-3,5), 7.68 (d, J = 7.9 Hz of d, J = 8.0 Hz, 2H, H-2,6), 7.61 (d, J = 7.9 Hz of d, J = 1.2 Hz, 2H, H-1,7), 5.88 (s, 1H, H-4). H-1,7 attributions were made on the basis of their NOE interactions with H-8,9 at 7.87 ppm. ^{13}C NMR (125 MHz, acetone- d_6): δ 130.8 (C-2,6), 129.0 (C-8,9), 124.2 (C-3,5), 120.0 (C-1,7) (aromatic Cs); 133.9, 104.9, 98.2 (ring junction Cs); 58.2 (C-4). Mass spectrum (FAB +) m/z (relative intensity): 328 (27) (M) $^+$, 300 (21) (M - CO) $^+$, 272 (58) (M - 2CO) $^+$, 244 (26) (M - 3CO) $^+$, 189 (100) (C $_{15}$ H $_9$) $^+$. Anal. Calcd for C $_{18}$ H $_9$ MnO $_3$: C, 65.75; H, 2.95. Found: C, 65.26; H, 2.67.

(b) **From BrMn(CO) $_5$.** CppH (190 mg, 1 mmol) and NaH (24 mg, 1 mmol) were heated to reflux in 5 mL of THF for 10 h. The dark red mixture was filtered into a solution of BrMn(CO) $_5$ (274 mg, 1 mmol) in 10 mL of THF, and the reaction mixture was heated under reflux for 12 h. The precipitate was filtered off, and the solvent was removed under reduced pressure. The crude product was purified via flash chromatography on silica using hexanes/ether 9:1 and yielded a red solid (132 mg, 0.40 mmol, 40%). Spectral data were identical to those reported above.

(η^6 -cpp)Mn(CO) $_3$ (14). In an NMR tube, an excess of solid 1,8-bis(dimethylamino)naphthalene was treated with a solution of (η^6 -cppH)Mn(CO) $_3$ PF $_6$ in CD $_2$ Cl $_2$ at -40 °C. The solution turned red immediately. 1H NMR (500 MHz, CD $_2$ Cl $_2$, -25 °C): δ 8.21 (d, 9.0 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.91 (t, J = 7.5 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.80 (d, J = 7.5 Hz), 6.22 (s, H-4), 6.06 (d, J = 7.1 Hz, 1H), 5.78 (d, J = 5.7 Hz, 1H), 5.64 (d, J = 7.1 Hz of d, J = 5.7 Hz, 1H). ^{13}C NMR (125 MHz, CD $_2$ Cl $_2$, -40 °C): δ 222.1, 134.2, 128.7, 122.6, 120.5, 118.2, 95.4, 90.8, 77.1, 66.6.

(η^6 -4H-Cyclopenta[def]phenanthrene)Fe(C $_5$ H $_5$)PF $_6$ (9). By analogy to the general procedure of Helling and Hendrickson,³⁰ cppH (0.95 g,

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5 mmol), Cp₂Fe (0.94 g, 5 mmol), aluminum powder (0.135 g, 5 mmol), and AlCl₃ (1.335 g, 10 mmol) were heated in 10 mL of decalin at 140 °C for 4 h. The mixture was cooled to 0 °C, 25 mL of water was added, and the inorganic solids were removed on a sintered funnel. The aqueous layer was isolated and extracted with ether (2 × 25 mL) and then treated with NH₄PF₆ (2 g, 12.5 mmol) in 5 mL of water. The precipitate was collected on a sintered funnel and dried under high vacuum to yield a brown solid (0.52 g, 1.44 mmol, 23% based on cppH), decomposing at 143 °C. ¹H NMR (200 MHz, CD₂Cl₂): δ 8.09 (d, *J* = 9.2 Hz, 1H), 7.92 (m, 2H), 7.88 (d, *J* = 6.2 Hz, 1H), 7.79 (d, *J* = 9.2 Hz, 1H), 6.93 (d, *J* = 5.7 Hz, 1H), 6.81 (d, *J* = 5.7 Hz, 1H), 6.19 (t, *J* = 5.7 Hz, 1H), 5.12 (d, *J* = 21.9 Hz, 1H), 4.69 (d, *J* = 21.9 Hz, 1H), 4.29 (s, 5H). ¹³C NMR (50 MHz, acetone-*d*₆): δ 133.5, 131.8, 125.7, 93.3, 85.1, 84.1, 82.6, 77.8 (aromatic Cs); 142.8, 137.8, 129.8, 126.1, 105.9, 100.4 (ring junction Cs); 39.4 (C-4). Mass spectrum (FAB+) *m/z* (relative intensity): 311 (100) ((C₁₅H₁₀)FeCp)⁺, 189 (14) (C₁₅H₉)⁺. Anal. Calcd for C₂₀H₁₅F₆FeP: C, 52.66; H, 3.32. Found: C, 52.77; H, 3.16. Traces of a second product were identified as (*trans*-η⁶,η⁶-4*H*-Cyclopenta[*def*]phenanthrene)(Fe(C₅H₅)₂(PF₆)₂). ¹H NMR (200 MHz, acetone-*d*₆): δ 7.49 (d, 6.0 Hz, 2H), 6.89 (d, 6.0 Hz, 2H), 6.30 (t, 6.0 Hz, 2H), 5.62 (s, 2H), 4.84 (s, 10H).

8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthrene (H₂-cppH) (16). Ethyl acetate (50 mL) and 30 mg of Pd/C 5% were stirred at room temperature. H₂ gas was admitted, and the apparatus was flushed with H₂ three times. After 1 h was allowed for saturation of the catalyst, cppH (190 mg, 1 mmol) was added, and the reaction mixture was stirred for 3 days. The catalyst was filtered off using Celite, and the solvent was evaporated under reduced pressure to yield a white powder (190 mg, 0.99 mmol, 99%). ¹H NMR (200 MHz, acetone-*d*₆): δ 7.31 (d, *J* = 7.2 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 2H), 7.07 (d, *J* = 7.2 Hz, 2H), 3.82 (s, 2H), 3.07 (s, 4H). ¹³C NMR (50 MHz, acetone-*d*₆): δ 128.1, 125.4, 123.5 (aromatic Cs); 141.2, 139.9, 131.1 (ring junction Cs); 37.7 (C-4), 26.7 (C-8,9).

[η⁶-8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthrene]Mn(CO)₃PF₆ (17). By analogy to **13**, reaction of H₂-cppH (190 mg, 1 mmol), BrMn(CO)₅ (275 mg, 1 mmol), and AlCl₃ (250 mg, 1.9 mmol) yielded a pale yellow powder (404 mg, 0.85 mmol, 85%), mp 168 °C dec. ¹H NMR (200 MHz, acetone-*d*₆): δ 7.59 (m, 2H), 7.40 (t, 1H), 7.20 (d, *J* = 6.4 Hz, 1H), 6.75 (d, *J* = 6.4 Hz, 1H), 6.66 (t, 6.4 Hz, 1H), 4.62 (d, *J* = 22.9 Hz, 1H), 4.43 (d, *J* = 22.9 Hz, 1H), 3.43 (m, 2H), 3.34 (m, 2H). ¹³C NMR (50 MHz, acetone-*d*₆): δ 217.1 (Cr-CO); 134.2, 127.1, 124.9, 100.4, 98.7, 98.0 (aromatic Cs); 143.1, 120.6, 115.6, 113.2, 97.1 (ring junction Cs); 38.7 (C-4); 25.3, 25.0 (C-8,9). Mass spectrum (FAB+) *m/z* (relative intensity): 331 (100) ((C₁₅H₁₂)Mn(CO)₃)⁺, 247 (14) ((C₁₅H₁₂)Mn + H)⁺, 191 (8) C₁₅H₁₁⁺. Anal. Calcd for C₁₈H₁₂F₆MnO₃P: C, 45.40; H, 2.54. Found: C, 45.65; H, 2.69.

[η⁶-8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthrene]Mn(CO)₃ (18). By analogy to the preparation of **15**, reaction of (H₂-cppH)Mn(CO)₃PF₆ (200 mg, 0.42 mmol) and 1,8-bis(dimethylamino)naphthalene (90 mg, 0.42 mmol) afforded a dark red solid (71 mg, 0.21 mmol, 50%). ¹H NMR (200 MHz, acetone-*d*₆): δ 7.64 (d, *J* = 8.2 Hz of d, *J* = 7.1 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.10 (d, *J* = 7.0 Hz, 1H), 6.35 (t, *J* = 7.8 Hz, 1H), 5.99 (s, 1H), 5.88 (d, *J* = 5.8 Hz of d, *J* = 7.8 Hz, 1H), 5.55 (d, *J* = 5.8 Hz, 1H), 3.39 (m, 4H). ¹³C NMR (50 MHz, acetone-*d*₆): δ 222.7 (Cr-CO); 129.2, 119.3, 117.8, 96.0, 93.3, 84.0 (aromatic Cs); 144.8, 131.9, 130.2, 127.6, 116.3, 89.5 (ring junction Cs); 71.1 (C-4); 27.7, 26.3 (CH₂ Cs). Mass spectrum (FAB+) *m/z* (relative intensity): 660 (8) (2M)⁺, 576 (10) (2M-3CO)⁺, 331 (100) (M+H)⁺, 274 (38) (M-2CO)⁺, 247 (42) (M-3CO)⁺, 191 (80) (C₁₅H₁₁)⁺.

[η⁵-8,9-Dihydro-4*H*-Cyclopenta[*def*]phenanthrenyl]Mn(CO)₃ (19). Isomerization of **18** to **19** did not occur in solution (acetone) at ambient temperature within 72 h. (η⁶-H₂-cppH)Mn(CO)₃ was heated to reflux in *n*-hexane for 1 h. The solvent was removed under reduced pressure, and the orange solid was dried under high vacuum, mp 79 °C. ¹H NMR (200 MHz, acetone-*d*₆): δ 7.38 (d, *J* = 8.6 Hz, 2H, H-3,5), 7.27 (d, *J* = 8.6 Hz of d, *J* = 6.7 Hz, 2H, H-2,6), 7.03 (d, *J* = 6.7 Hz, 2H, H-1,7), 5.66 (s, 1H, H-4), 3.6-3.4 (m, 2H), 3.4-3.2 (m, 2H). ¹³C NMR (50 MHz, acetone-*d*₆): δ 130.8 (C-2,6), 122.6 (C-3,5), 121.3 (C-1,7) (aromatic Cs); 137.1, 105.3, 97.2 (ring junction Cs); 58.3 (C-4), 26.7 (C-8,9). Mass

spectrum (FAB+) *m/z* (relative intensity): 660 (2) (2M)⁺, 576 (15) (2M-3CO)⁺, 331 (80) (M)⁺, 274 (34) (M-2CO)⁺, 247 (75) (M+H-3CO)⁺, 191 (100) (C₁₅H₁₁)⁺.

[η⁶-8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthrene]Cr(CO)₃ (24). By analogy to the preparation of **2**, H₂-cppH (310 mg, 1.6 mmol) and Cr(CO)₆ (540 mg, 2.45 mmol) were heated under reflux in 7 mL of ⁿBu₂O and 3 mL of THF for 3.5 days. Unreacted Cr(CO)₆ was filtered using Schlenk techniques, and the solvent was evaporated. The pure product was obtained via flash chromatography using CH₂Cl₂:hexanes, 2:1 to yield a yellow solid (246 mg, 0.75 mmol, 47%), mp 148 °C. ¹H NMR (200 MHz, acetone-*d*₆): δ 7.31 (d, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 7.1 Hz, 1H), 5.99 (d, *J* = 6.1 Hz, 1H), 5.57 (t, *J* = 6.2 Hz, 1H), 5.49 (d, *J* = 6.2 Hz, 1H), 4.13 (d, *J* = 21.4 Hz, 1H), 3.92 (d, *J* = 21.4 Hz, 1H), 3.1-3.0 (m, 4H). ¹³C NMR (50 MHz, acetone-*d*₆): δ 235.3 (Cr-CO); 130.1, 126.0, 123.7, 94.3, 90.7 (2C) (aromatic Cs); 140.5, 136.7, 131.4, 114.6, 108.4, 107.2 (ring junction Cs); 38.0 (C-4); 25.7, 25.6 (C-8,9). Mass spectrum (DEI+) *m/z* (relative intensity): 328 (25) (M)⁺, 272 (27) (M-2CO)⁺, 244 (100) (M-3CO)⁺, 189 (8) (C₁₅H₉)⁺.

X-ray Crystal Structure Determinations for 2, 24, and 15. Crystal data and refinement parameters are collected in Table I, and atomic coordinates and bond lengths are listed in Tables II-VI. All crystals were grown by vapor diffusion techniques²⁹ using 1,2-dichloroethane and *n*-heptane at -22 °C. The crystals were mounted on fine glass fibres with epoxy cement. The unit cells were determined by automatic indexing of 25 centered reflections. Intensity data for **2** and **24** were collected on a Siemens P4 diffractometer fitted with a rotating anode using graphite-monochromated Mo Kα X-radiation (λ = 0.710 73 Å) at room temperature. Data collection for **15** was performed on a Siemens R3m/V diffractometer using graphite-monochromated Ag Kα (λ = 0.560 86 Å). Three check reflections were measured every 97 reflections. The heavy atom positions were obtained using Patterson methods, and phase extension and Fourier difference techniques revealed the remaining non-hydrogen atoms. Hydrogen atoms for **2** and **24** were included in calculated positions (*d*(C-H) = 0.96 Å) and refined using a riding model and common isotropic temperature factors. Hydrogen atom positions for **15** were determined by difference Fourier analysis and refined isotropically using individual *U*s. Thermal motion of the ligand in **24** was corrected employing librational rigid-body motion analysis.³² Scattering factors were supplied by the software.

Data reduction, structure solution, refinement, graphics, and table generation programs are contained in the SHELXTL program library.³¹

Molecular Orbital Calculations were performed via the extended Hückel method using weighted H_{*j*} values;³³ orbital drawings were obtained by use of the program CACAO.³⁴ The geometry of the polycyclic ligand was an idealized, planar version taken from the X-ray crystal structure of (η⁵-cpp)Mn(CO)₃. The following distances were used: Fe-Cp = 1.66 Å and Fe-cpp = 1.59 Å. Orbital parameters were taken from ref 1.

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Supplementary Material Available: Tables listing bond angles and displacement coefficients for **2**, **24**, and **15** (8 pages); observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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