Journal of Organometallic Chemistry 637–639 (2001) 372–381

www.elsevier.com/locate/jorganchem

Ferrocenes derived from cyclopenta[*l*]phenanthrene: dibenzindene–metal complexes that resist haptotropic shifts

Suzie S. Rigby [a], Andreas Decken [b], Alex D. Bain [a], Michael J. McGlinchey [a,*]

[a] *Department of Chemistry, McMaster University Hamilton, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4M1*
[b] *Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3*

Received 12 January 2001; received in revised form 14 March 2001; accepted 19 March 2001

Abstract

The complexes (η^5-cyclopenta[*l*]phenanthrenyl)ML_n, where $ML_n = Fe(C_5H_5)$, $Fe(C_{17}H_{11})$, $Mn(CO)_3$ or $Rh(C_2H_4)_2$ show no propensity to undergo η^5 to η^6 haptotropic shifts upon protonation, nor to undergo ready replacement of a carbonyl or ethylene ligand by a phosphine. Thus, these systems mimic the behavior of cyclopentadienyl rather than indenyl rings. Molecular orbital calculations on $(C_{17}H_{11})Fe(C_5H_5)$ indicate that migration of an organometallic fragment from a peripheral arene into the five-membered ring is thermodynamically favorable, but that a least-motion pathway passing through the central six-membered ring is strongly disfavored. Attempted synthesis of (η^6-cyclopenta[*l*]phenanthrene)$Cr(CO)_3$ gave instead the corresponding dihydro complex, $(C_{17}H_{13})Cr(CO)_3$, and the Diels–Alder dimer of cyclopenta[*l*]phenanthrene with its own isoindene. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Benzoferrocenes; Cyclopenta[*l*]phenanthrene; Haptotropic shifts; EHMO calculations

---

1. Introduction

While the establishment of the structure and reactivity of ferrocene and its derivatives led to the development of many new areas of chemistry, one should also emphasise its significance in the field of molecular dynamics. In 1956, Piper and Wilkinson noted that carbonylation of ferrocene yielded $(C_5H_5)_2Fe(CO)_2$ (**1**), a molecule that exhibited unusual NMR behavior [1]. Subsequently, in a now classic study [2], Cotton, Davison and their co-workers described the first organometallic fluxional process to be fully elucidated. They not only showed that **1** possesses σ- and π-bonded cyclopentadienyl rings, but also that the fluxional process involved the circumambulation of the (η^5-cyclopentadienyl)iron dicarbonyl moiety round the σ-bonded C_5H_5 ring (see Scheme 1), with an activation energy barrier of 10.7 kcal mol^{-1}.

In Woodward–Hoffmann terms, we now recognize this process as a symmetry-allowed [1,5]-suprafacial sigmatropic shift. A crucial piece of evidence in favor of the migration of the iron between adjacent sites (rather than executing 1,3 shifts) was the failure to detect fluxionality in the indenyl system, **2**, since this would involve loss of aromaticity in the presumed isoindene intermediate **3** [3]. In fact, this latter result is somewhat ambiguous since attempts to observe coalescence of the ^{1}H-NMR resonances for H(1) and H(3) by raising the temperature were thwarted by the thermal instability of **2** which readily loses both carbonyls to form benzoferrocene **4**. More recently, the fluxional character of **2** has been unequivocally demonstrated via 2D-EXSY spectroscopy by which one can monitor the rate of the rearrangement while still maintaining the chemical integrity of the molecule [4]. As anticipated, the migration barrier of ≈20 kcal mol^{-1} is markedly higher than that found for the cyclopentadienyl system **1**. As further evidence of the intermediacy of isoindene, **3**, it has been intercepted by TCNE, and the resulting Diels–Alder adduct, **5**, characterized by X-ray crystallography [4].

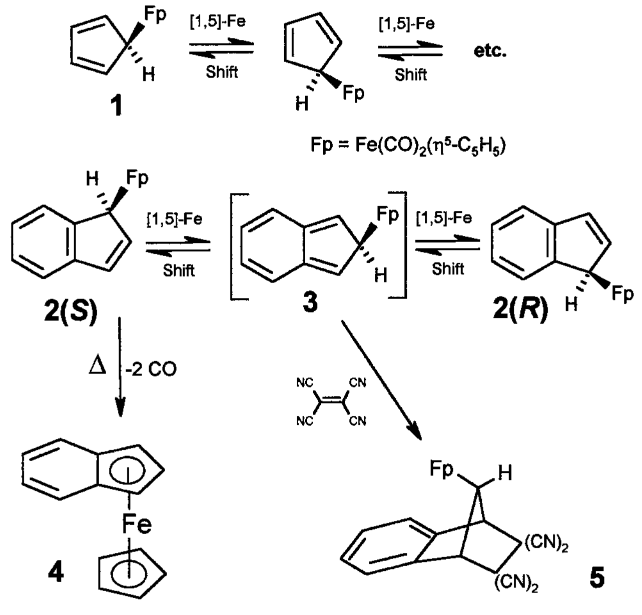
A second type of molecular rearrangement found in benzoferrocene and related complexes is the haptotropic shift of a π-bonded metal atom from a six-

---

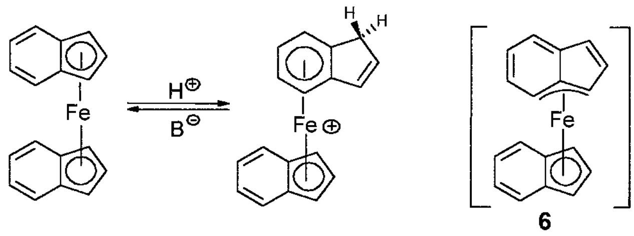
* Corresponding author. Tel.: +1-905-525-9140x27318; fax: +1-905-522-2509.

E-mail address: mcglinc@mcmaster.ca (M.J. McGlinchey).

PII: S0022-328X(01)00937-8



Scheme 1.



Scheme 2.

membered to a five-membered ring [5], as in Scheme 2. In fact, such η^6 to η^5 migrations are now known in numerous indenyl, fluorenyl and other polycyclic aromatic complexes [6]. Moreover, a molecular orbital analysis of possible rearrangement mechanisms showed that the least-motion route directly across the common bond between the rings is strongly disfavored; instead, a trajectory passing through an η^3 structure, **6**, is the preferred pathway [7].

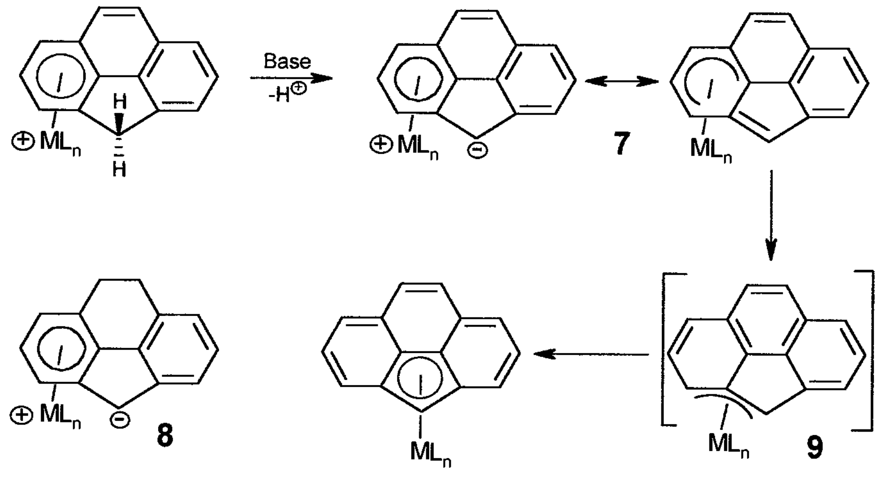
We have previously reported that in (cyclopenta[*def*]phenanthrenyl)ML$_n$ complexes, **7**, η^6 to η^5 haptotropic shifts are very facile, whereas in the corresponding (4,5-dihydrocyclopenta[*def*]phenanthrenyl)ML$_n$ systems, **8**, the barriers are very much greater. These results were rationalized in terms of the enhanced (10π-naphthalene type) aromatic character of the transition state, **9**, in the former cases, but which are lacking in the dihydrogenated molecules **8** [8,9] (Scheme 3).

We here present synthetic, spectroscopic and calculational data that extend these concepts to ferrocenyl and other complexes derived from 1*H*-cyclopenta[*l*]phenanthrene (**10**).

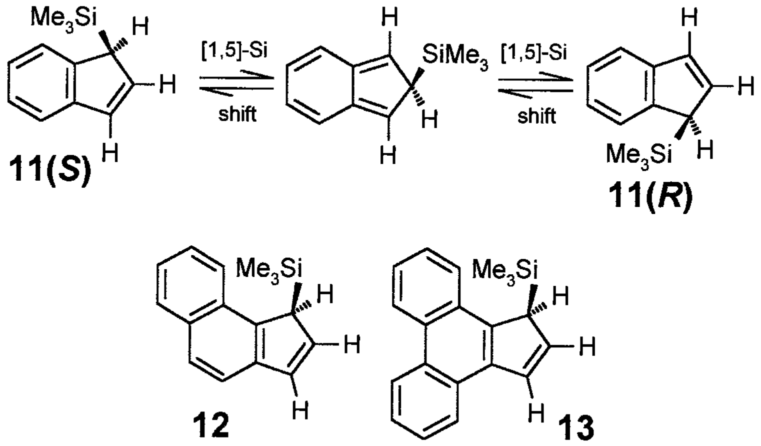
2. Results and discussion

The availability of 1*H*-cyclopenta[*l*]phenanthrene [10] prompted us to prepare a series of transition metal complexes of this ligand with a view to comparing its organometallic chemistry with that of indene — in particular, the possibility of observing haptotropic shifts over this polycyclic surface. Moreover, we wished to investigate the ability of the phenanthrene framework, with its potential to provide an aromatic (14π-electron) unit to facilitate ligand substitutions, by analogy to the well-known 'indenyl effect' [11].

In this vein, we had previously demonstrated that the ability of a trimethylsilyl group to migrate over the surface of an indenyl framework can been correlated with the stability of the intermediate isoindene [12]. The strategic incorporation of additional aromatic rings into the trimethylsilylindene framework results in a marked reduction in the barrier to [1,5]-suprafacial



Scheme 3.



Scheme 4.

sigmatropic shifts, as illustrated in Scheme 4. Thus, the experimentally observed $\Delta G^{\#}$ values for silatropic shifts in trimethylsilylindene, **11**, trimethylsilylbenzindene, **12**, and 1-trimethylsilylcyclopenta[*l*]phenanthrene, **13**, are 25, 22 and 18 kcal mol^{-1}, respectively [12].

2.1. *η⁵-Indenyl and η⁵-cyclopenta[l]phenanthrenyl complexes of Fe, Mn and Rh*

The complexes (η^5-indenyl)ML$_n$, where ML$_n$ = Fe(C_5H_5) (**14**) [13], Fe(C_9H_7) (**15**) [14], Mn$(CO)_3$ (**16**) [15], and Rh$(C_2H_4)_2$ (**17**) [16], have been described previously, and their reactivity towards acids and/or phosphines has been reported. The chemistry of the molecules **14**–**17** differs markedly from that of the corresponding cyclopentadienyl complexes. Thus, protonation of $(C_5H_5)Rh(C_2H_4)_2$, involves a complex series of reactions culminating in the formation of 1-butene via coupling of the two ethylene ligands on rhodium [17]. In contrast, treatment of (η^5-indenyl)Rh$(C_2H_4)_2$ (**17**), with trifluoroacetic acid yields [(η^6-indene)Rh-$(C_2H_4)_2$]$^+$ [18]. This reaction apparently involves initial protonation at rhodium since use of CF_3CO_2D also deuterates the alkenes, presumably via a Rh-ethyl intermediate [18]. Analogously, as illustrated in Scheme 2, the benzoferrocene **15** undergoes an η^5 to η^6 haptotropic shift upon protonation [5]. Moreover, both **16** and **17** react readily with phosphines with loss of CO or C_2H_4 ligands, respectively [19,20], while (C_5H_5)Mn-$(CO)_3$ is substitution inert [21].

1*H*-Cyclopenta[*l*]phenanthrene (**10**), is readily deprotonated, and the ^{1}H- and ^{13}C-NMR spectra of the resulting anion, **18**, are in accord with the overall aromatic character of this 18π-electron species [10]. As summarized in Scheme 5, treatment of the anion **18** with $FeCl_2$, BrMn$(CO)_5$ or [Rh$(C_2H_4)_2$Cl]$_2$ yields the η^5-complexes **19**–**21**. The anion also reacts with $(C_5H_5)Fe(CO)_2I$ to give, after decarbonylation, the unsymmetrical ferrocene derivative **22**. As anticipated from Rausch's synthesis of (η^5-indenyl)$TiCl_3$ [22], reaction of the anion **18** with chlorotrimethylsilane, and then titanium tetrachloride, gives the $TiCl_3$ complex **23**, as recently noted by Brintzinger [23,24].

The molecules **19**–**22** were characterized by mass spectrometry and NMR spectroscopy. The mass spectra generally followed established fragmentation patterns but, surprisingly, the rhodium complex **21** exhibited a relatively strong peak assignable to [$(C_{17}H_{11})_2$Rh]$^+$, analogous to the 18-electron rhodicinium cation [$(C_5H_5)_2$Rh]$^+$. In each case, the ^{1}H-NMR spectrum exhibited the expected doublet (2H) and triplet (1H) patterns for the complexed five-membered ring. The aromatic protons and carbons were assigned by means of 2D ^{1}H–^{1}H COSY, ^{1}H–^{13}C shift-correlated, and ^{1}H–^{1}H NOESY spectra, and are fully listed in Section 3.

Interestingly, during the synthesis of (η^5-cyclopenta[*l*]phenanthrenyl)Mn$(CO)_3$ (**20**), traces of the monohapto dihydro complex **24** were also obtained. As we shall see later, the cyclopenta[*l*]phenanthrene system is apparently very sensitive to the presence of minute quantities of water.

In an attempt to promote η^5 to η^6 haptotropic shifts of the type previously noted for the indenyl complexes **14**–**17**, the cyclopenta[*l*]phenanthrenyl systems **19**–**22** were protonated with HBF_4. The NMR spectra of the iron and manganese complexes **19**, **20**, and **22** were essentially unchanged on protonation; in contrast, acidification of the rhodium complex **21** produced signals assignable to Rh-ethyl and Rh-π-methallyl units, and also 1- and 2-butene. However, a detailed discussion of the protonation of **21** is deferred to a future, more mechanistic manuscript.

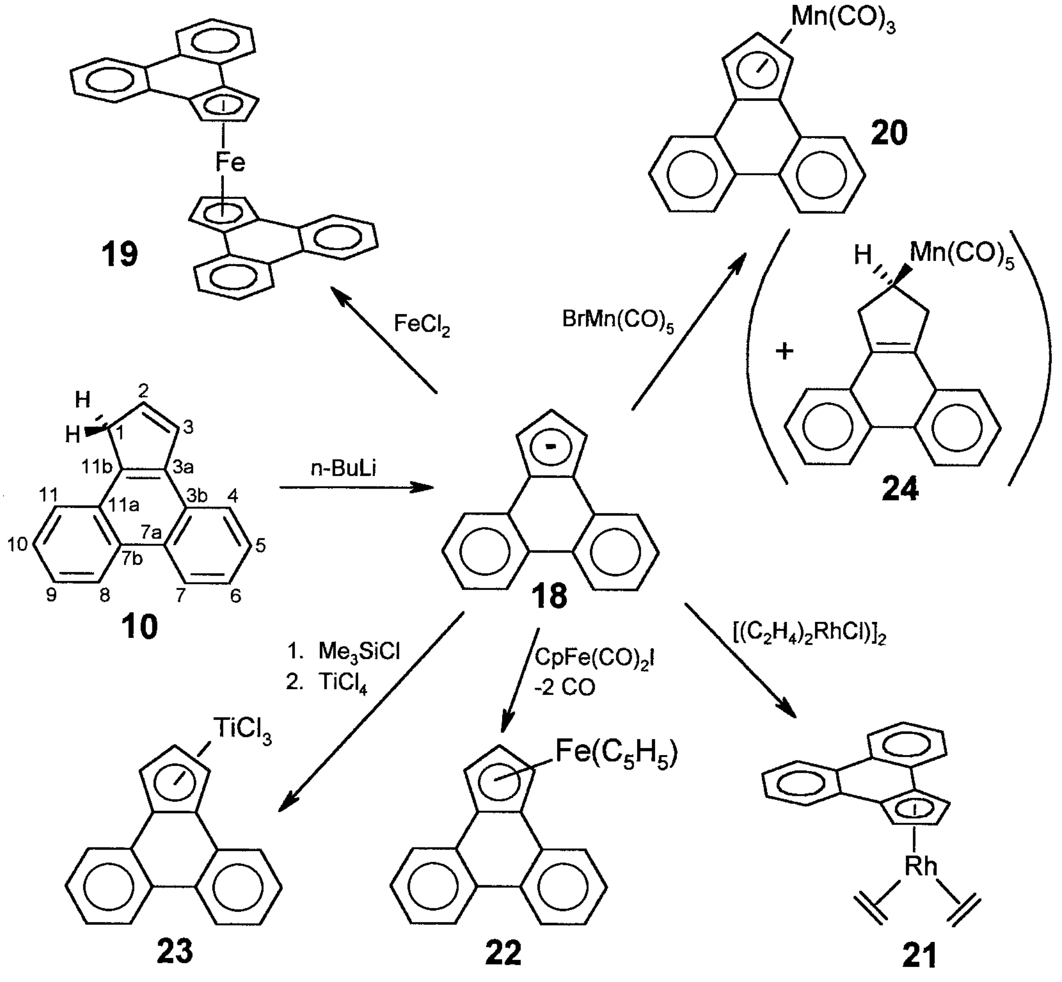
These results, together with the observation that phosphines do not readily displace a carbonyl in the manganese system **20**, nor the ethylene ligands from the Rh complex **21**, all indicate that complexes **19**–**22** possess the characteristics of cyclopentadienyl rather than of indenyl ligands. Interestingly, the barrier to ethylene rotation in **21** was measured as 13.5 ± 0.5 kcal mol^{-1}, between the values of 10.5 and 15 kcal mol^{-1}, reported for (η^5-indenyl)Rh(C_2H_4)$_2$ and (η^5-cyclopentadienyl)Rh(C_2H_4)$_2$, respectively [16,25].

In essence, the molecules **19**–**22** behave as though they are comprised of three independent 6π-aromatic systems and not as dibenzo–indenyl complexes. One can rationalize this behavior in terms of the reluctance of these η^5-bonded systems to sacrifice the aromaticity of three rings by placing an organometallic fragment on the central ring. This view is reinforced by molecular orbital calculations at the extended Hückel level which reveal that the favored site for complexation of an Fe(C_5H_5) moiety is at the five-membered ring, as in **22**.

Fig. 1 depicts the energy hypersurface calculated by allowing an Fe(C_5H_5) fragment to migrate over the cyclopenta[*l*]phenanthrenyl tetracyclic skeleton at a constant distance of 1.59 Å. Local η^6-type minima are found in the peripheral arene rings, but the global minimum is located in the cyclopentadienyl ring; the η^5 geometry is ≈ 23 kcal mol^{-1} more stable than the peripheral η^6-arene ring isomer, which in turn is favored by 18 kcal mol^{-1} over the centrally bonded Fe(C_5H_5) system. These differences are comparable to those previously found for the (indenyl)Fe(C_5H_5) system for which calculations reveal the η^5-bonded structure to be preferred over the η^6-isomer by 23 kcal mol^{-1} [7].

Moreover, as was previously reported for the indenyl case [7], and also for the cyclopenta[*def*]phenanthrenyl skeleton [9], π-bonded Fe(C_5H_5) or Mn(CO)$_3$ fragments cannot undertake an η^6 to η^5 haptotropic shift via the shortest path between ring centers. In **22**, not only is there a very large barrier (60–70 kcal mol^{-1}) towards traversing the common bond between any pair of rings, but also placement of the organometallic fragment in the central ring is greatly disfavored. This behavior parallels that of triphenylene [26], and the tri-anions of truxene [27] or trindene [28] in which metals coordinate exclusively to peripheral rings [29].

The lowest energy route from a six-membered peripheral ring to the favored η^5 site is depicted in Fig. 2 and follows the pattern of circuitous pathways estab-



Scheme 5.

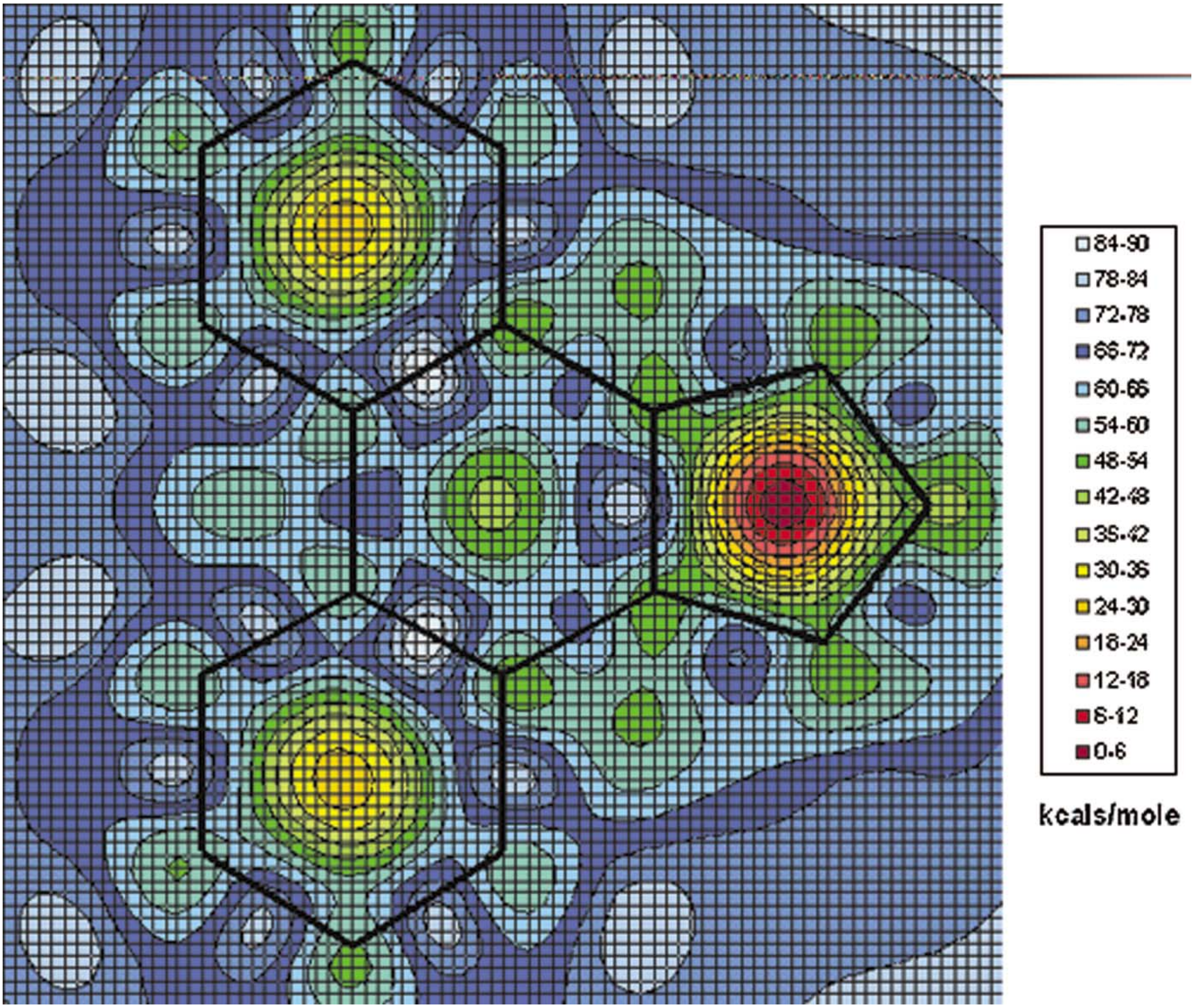


Fig. 1. The EHMO-derived hypersurface for the migration of $(C_5H_5)Fe$ across the $C_{17}H_{11}$ framework. Energy contours are incremented in units of 6 kcal mol^{-1} with red indicating the energy minimum, and blue representing the maxima; the mesh is incremented in units of 0.1 Å.

lished for the aforementioned polycyclic systems. At the EHMO level of approximation, the barrier towards exchange between peripheral η^6 positions is evaluated to be 38 kcal mol^{-1}, whereas the η^6 to η^5 migration requires 39 kcal mol^{-1}.

As noted above, the separation, *r*, of the CpFe unit from the ligand plane was maintained at 1.59 Å, and optimization of this distance at the η^6 and η^5 minima yields values of 1.59 and 1.58 Å, respectively, which maintains the 23 kcal mol^{-1} in favor of the five-membered ring binding site. The distance *r* was also optimized for the transition states associated with the lowest energy $\eta^6 \rightarrow \eta^6$ and $\eta^6 \rightarrow \eta^5$ trajectories; the optimal *r* values were found to be 1.78 and 1.76 Å, corresponding to somewhat reduced barriers of 34 and 30 kcal mol^{-1}, respectively. Since vibronic analyses were not performed, we emphasize that the 'transition states' discussed here are merely the highest points along the favored EHMO-calculated trajectories, and we make no claims beyond that. Nevertheless, it is now evident, both experimentally and theoretically, that metal complexes of the cyclopenta[*l*]phenanthrenyl system are much more resistant toward $\eta^5 \rightarrow \eta^6$ haptotropic shifts than are their indenyl analogues.

2.2. Attempted syntheses of η^6-ML_n complexes of **10**

In view of the marked stability of the η^5 complexes **19**–**22**, we attempted to prepare the η^6-$Cr(CO)_3$ complex, **25**, with a view to deprotonating this system and observing whether the $Cr(CO)_3$ moiety could migrate to the η^5 site. However, upon heating 1*H*-cyclopenta[*l*]phenanthrene (**10**), under reflux with chromium hexacarbonyl in Bu_2O and THF, we were unable to detect **25** and the only isolable organometallic product was the partially saturated tetracyclic system **26**, that was characterized by NMR, mass spectrometry and X-ray crystallography. The structure of **26** appears as Fig. 3 and confirms the assignment as a dihydrocyclopenta[*l*]phenanthrene complex in which the tricarbonylchromium tripod is oriented in the *exo* conformation. The tetracyclic system in **26** is not planar but slightly arced away from the organometallic moiety; the interplanar angle between the two external six-membered rings is 9°. This compares well with the structure of the 2-methyl analogue of **23** in which the ligand is again slightly curved away from the $TiCl_3$ unit [23] (Table 1).

One can also compare the structure of **26** with that of (phenanthrene)$Cr(CO)_3$ (**27**), for which the X-ray data [30] and molecular orbital calculations [31] are in accord; likewise (cyclopenta[*def*]phenanthrene)$Cr(CO)_3$ (**28**) [8], and (triphenylene)$Cr(CO)_3$ (**29**) [31], adopt *exo* conformations (Scheme 6). These data contrast with the crystal structure of (biphenylene)$Cr(CO)_3$ (**30**), wherein the tripodal moiety adopts the *endo* orientation [31]. In all cases where the tripod adopts the *exo* conformation, the chromium is displaced slightly away from the ring junction carbons (labeled a and b in Scheme 6), as summarized in Table 2.

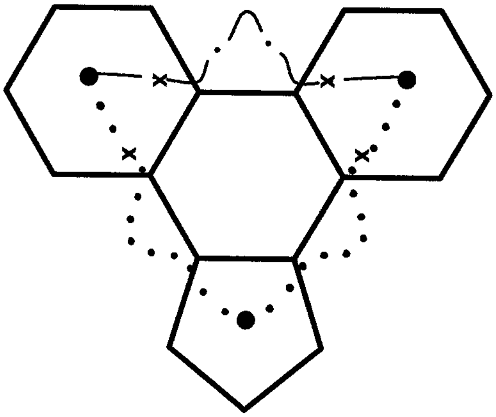


Fig. 2. The lowest energy trajectories for η^6 to η^5, and for η^6 to η^6 haptotropic shifts; the highest point on each route is marked with an X.

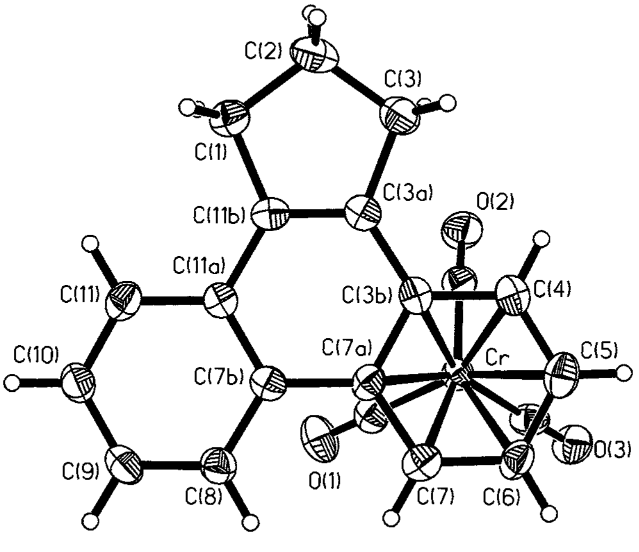
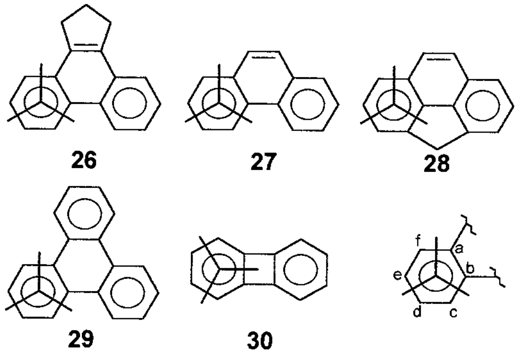


Fig. 3. X-ray crystal structure of (η^6-$C_{17}H_{14}$)$Cr(CO)_3$ (**26**), showing the atom numbering system. Thermal ellipsoids are drawn at the 30% level.

Table 1
Summary of crystal data and structure refinement for (2,3-dihydro-1*H*-cyclopenta[*l*]phenanthrene)$Cr(CO)_3$ (**26**)

Empirical formula	$C_{20}H_{14}CrO_3$
M_r	354.31
T (K)	293(2)
λ (Å)	0.71073
Description	Orange needle
Crystal size (mm)	0.13 × 0.13 × 0.62
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	10.264(6)
b (Å)	9.326(3)
c (Å)	16.077(6)
β (°)	93.03(4)
V (Å^3)	1536.8(12)
Z	4
ρ_{calc} (g cm^{-3})	1.531
Absorption coefficient (mm^{-1})	7.59
F(000)	728
Theta range for collection (°)	2.30–24.99
Limiting indices	$-1<h<12$, $-1<k<11$, $-19<l<19$
Reflections collected	3469
Independent reflections	2626
R_{int}	0.0586
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	2626/0/219
Goodness-of-fit on F^2	1.094
Final R indices [$I>2\sigma(I)$] [a]	$R_1 = 0.0630$, $wR_2 = 0.1698$
R indices (all data) [a]	$R_1 = 0.1334$, $wR_2 = 0.2023$
Largest diff. peak and hole (e Å^{-3})	0.652 −0.584

[a] $R_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$.



Scheme 6.

Table 2
Chromium–carbon bond lengths (Å) in selected (polycyclic arene) $Cr(CO)_3$ complexes

Complex	Cr–C(a)	Cr–C(b)	Cr–C(c)	Cr–C(d)	Cr–C(e)	Cr–C(f)
26	2.295(6)	2.296(6)	2.212(7)	2.213(6)	2.198(7)	2.203(7)
27	2.278(5)	2.289(4)	2.208(5)	2.213(5)	2.214(5)	2.207(5)
28	2.261(4)	2.314(4)	2.224(4)	2.252(4)	2.251(4)	2.197(5)
29	2.258(3)	2.258(3)	2.198(3)	2.209(3)	2.209(3)	2.198(3)

Suspecting that **26** arose because of traces of adventitious water [32], we repeated the synthesis with very carefully dried solvents; however, the reaction did not yield **26**, but instead gave **31**, the Diels–Alder adduct of **10** with its isomeric isoindene, **32**, as illustrated in Scheme 7. The details of this latter reaction, and the X-ray crystal structure of **31** have been described elsewhere [33]. Despite numerous attempts to incorporate other η^6-bonded organometallic fragments, including $[(C_5H_5)Fe]^+$, $RuCl_2$ and $[Mn(CO)_3]^+$, we have not yet been able to obtain useful quantities of characterizable products; this aspect of the project is continuing.

To conclude, complexes of the type (η^5-cyclopenta[*l*]phenanthrenyl)ML_n show no propensity to undergo η^5 to η^6 haptotropic shifts upon protonation. Molecular orbital calculations indicate that migration of an organometallic fragment from a peripheral arene into the five-membered ring is thermodynamically favorable, but that a least-motion pathway passing through the central six-membered ring is strongly disfavored. Thus, these systems mimic the behavior of cyclopentadienyl rather than indenyl rings. Furthermore, as noted by Brintzinger [23], the tetracyclic ligand can also provide considerable steric protection to metal centers, and so enhance the stereospecificity of potential catalytic sites.

3. Experimental

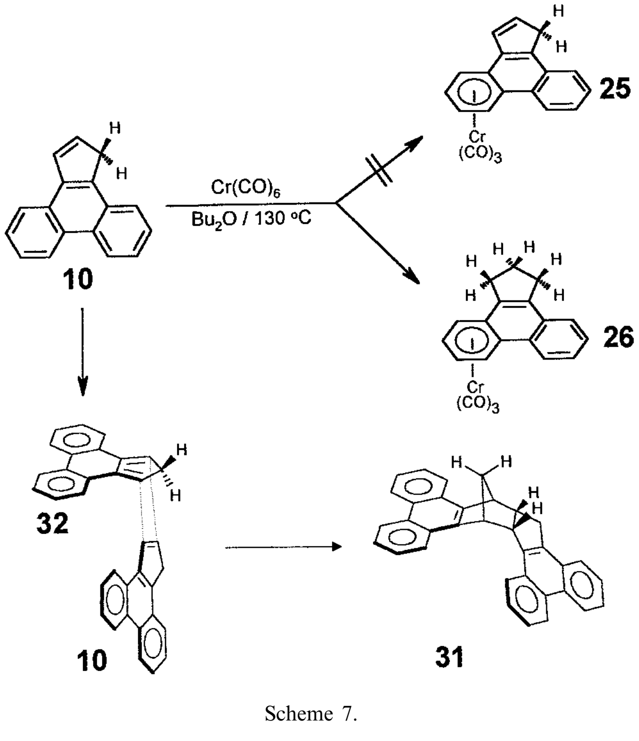
3.1. Syntheses

3.1.1. General methods

All reactions were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. All solvents were dried according to standard procedures before use [34]. Silica gel (particle size: 20–45 μm) was employed for flash column chromatography. ^1H and ^{13}C solution NMR spectra were acquired on Bruker DRX 500 or AC 300 spectrometers and were referenced to the residual proton or ^{13}C solvent signal, respectively. Direct electron impact (DEI) mass spectra were obtained by using a Finnigan 4500 spectrometer; high resolution mass spectra (HRMS) were measured on a VG Analytical ZAB-SE spectrometer with an accelerating potential of 8 kV and a resolving power of 10000. Infrared spectra were recorded on a Bio-Rad FTS-40 spectrometer. Melting points (uncorrected) were determined on a Thomas–Hoover melting point apparatus. Elemental analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario.

3.1.2. Bis(η^5-cyclopenta[l]phenanthrenyl)iron (19)

Following the, procedure for the analogous (indenyl)$_2$Fe [5], *n*-BuLi (1.16 ml of a 1.6 M hexane solution, 1.856 mmol) was added dropwise to a solution of cyclopenta[*l*]phenanthrene (0.400 g, 1.852 mmol) in dry THF (20 ml) at − 78 °C, and the dark red solution was stirred for 1 h. at this temperature. In a separate flask, $FeCl_3$ (0.100 g, 0.617 mmol) and Fe powder (0.018 g, 0.305 mmol) were stirred in dry THF (10 ml) for 1 h at room temperature (r.t.). This mixture was syringed drop by drop into the cold (− 78 °C) flask containing the anion, the mixture was stirred overnight and the solvent was removed under vacuum. The orange residue was extracted first with ether to remove any unreacted ligand, and then with hot benzene. Removal of the solvent under reduced pressure gave **19** as



Scheme 7.

an orange solid (0.150 g, 0.309 mmol; 33%) that was subsequently recrystallized from benzene to give orange microcrystals, m.p. 246–247 °C. ^{1}H-NMR (C_6D_6, 500 MHz): $\delta = 7.68$ (d, ^{3}J(H–H) = 8.1 Hz, 4H, $H_{7,8}$), 7.17 (t, ^{3}J(H–H) = 7.6 Hz of d, ^{4}J(H–H) = 1.1 Hz, 4H, $H_{6,9}$), 7.12 (d, ^{3}J(H–H) = 7.8 Hz of d, ^{4}J(H–H) = 1.2 Hz, 4H, $H_{4,11}$), 6.96 (t, ^{3}J(H–H) = 7.4 Hz of d, ^{4}J(H–H) = 1.0 Hz, 4H, $H_{5,10}$), 4.66 (d, ^{3}J(H–H) = 2.5 Hz, 4H, $H_{1,3}$), 4.14 (t, ^{3}J(H–H) = 2.5 Hz, 2H, H_2). ^{13}C-NMR (C_6D_6, 125 MHz): $\delta = 130.8$ ($C_{3b,11a}$), 129.9 ($C_{7a,7b}$), 126.9, 124.9 ($C_{5,6,9,10}$), 123.7 ($C_{4,11}$), 123.5 ($C_{7,8}$), 82.9 ($C_{3a,11b}$), 69.9 (C_2), 63.5 ($C_{1,3}$). MS (DEI, *m*/*z* (%)): 486 (100) ($[M]^+$), 271 (5) ($[M - C_{17}H_{11}]^+$), 243 (15) ($[M]^{2+}$), 215 (40) ($[C_{17}H_{11}]^+$). HRMS Calc. for $^{12}C_{34}H_{22}Fe$ ($[M]^+$), 486.1071 amu; observed 486.1079 amu. Anal. Found: C, 84.02; H, 4.51. Calc. for $C_{34}H_{22}Fe$: C, 83.96; H, 4.56%.

3.1.3. (η^5-Cyclopenta[l]phenanthrenyl)Mn(CO)$_3$ (***20***)

To a solution of cyclopenta[*l*]phenanthrene (0.200 g, 0.926 mmol) in dry THF (20 ml) was added dropwise *n*-BuLi (0.7 ml of a 1.6 M hexane solution, 1.12 mmol) at −78 °C. The dark red solution was stirred at this temperature for 1 h after which time $BrMn(CO)_5$ (0.254 g, 0.924 mmol) in dry THF (20 ml) was added dropwise. The reaction vessel was allowed to warm to r.t., and was heated under reflux overnight. Removal of the solvent left a dark red oil which was purified by flash chromatography on silica with hexane–ether 9:1 as eluent to give 20 as red microcrystals (0.069 g, 0.195 mmol; 21%), m.p. 192–193°C. ^{1}H-NMR (CD_2Cl_2, 500 MHz): $\delta = 8.49$ (m, 2H, $H_{7,8}$), 7.97 (m, 2H, $H_{4,11}$), 7.62 (m, 4H, $H_{5,10}$, $H_{6,9}$), 5.60 (d, ^{3}J(H–H) = 2.8 Hz, 2H, $H_{1,3}$), 5.17 (t, ^{3}J(H–H) = 2.8 Hz, 1H, H_2). ^{13}C-NMR (CD_2Cl_2, 125 MHz): $\delta = 221.0$ (Mn–CO's), 130.5 ($C_{3b,11a}$, $C_{7a,7b}$), 128.4, 128.3 ($C_{5,6,9,10}$), 124.6 ($C_{4,11}$), 124.5 ($C_{7,8}$), 99.0 ($C_{3a,11b}$), 86.3 (C_2), 73.3 ($C_{1,3}$). IR (CCl_4, cm^{-1}): 2022 (vs), 1943 (vs). MS (DEI, *m*/*z* (%)): 298 (30) ($[M - 2CO]^+$), 270 (100) ($[M - 3CO]^+$), 215 ($[M - Mn(CO)_3]^+$), 55 (40) ($[Mn]^+$). HRMS Calc. for $^{12}C_{17}H_{11}Mn$ ($[M - 3(CO)]^+$), 270.0241 amu; observed 270.0248 amu. Anal. Found: C, 67.72; H, 2.98. Calc. for $C_{20}H_{11}MnO_3$: C, 67.81; H, 3.13%.

3.1.4. (2-(η^1-Pentacarbonylmanganese))-2,3-dihydrocyclopenta[l]phenanthrene (***24***)

During one synthesis of (η^5-cyclopenta[*l*]phenanthrenyl)$Mn(CO)_3$ (**20**), the system had perhaps not been as thoroughly dried as normal and traces of a second product were obtained after chromatographic separation. This was identified spectroscopically as **24**. ^{1}H-NMR (CD_2Cl_2, 500 MHz): $\delta = 8.7$ (m, 2H, $H_{7,8}$), 7.8 (m, 2H, $H_{4,11}$), 7.5 (m, 4H, $H_{5,6,9,10}$), 3.50 (d, ^{2}J(H–H) = 15 Hz of d, ^{3}J(H–H) = 8.6 Hz, 2H, $H_{1a,3a}$)*, 2.93 (d, ^{2}J(H–H) = 15 Hz of d, ^{3}J(H–H) = 6.8 Hz, 2H, $H_{1a',3a'}$)*, 2.70 (pseudo-quintet, ^{3}J(H–H) = 7 Hz, 1H, H_2); (assignments marked * may be interchanged). MS (DEI, *m*/*z* (%)): 384 (30) ($[M - CO]^+$), 356 (25) ($[M - 2CO]^+$), 328 (15) ($[M - 3CO]^+$), 300 (18) ($[M - 4CO]^+$), 272 (60) ($[M - 5CO]^+$), 217 (100) ($[M - Mn(CO)_5]^+$), 55 (50) ($[Mn]^+$).

3.1.5. (η^5-Cyclopenta[l]phenanthrenyl)bis(ethylene)-rhodium(I) (***21***)

As for the manganese complex **20**, the lithium salt **18** (2.47 mmol) in dry THF (20 ml) was syringed into a suspension of $[Rh(C_2H_4)_2Cl]_2$ (0.464 g, 1.193 mmol) in dry THF (20 ml) at −78 °C. The mixture was stirred for 1 h, allowed to warm to r.t. and the solvent removed under vacuum. The dark red residue was extracted repeatedly (8 × 50 ml) with hexanes, and then removal of the solvent under reduced pressure gave **21** as a yellow solid (0.485 g, 1.30 mmol; 54%), m.p. 96 °C. ^{1}H-NMR (CD_2Cl_2, 500 MHz): $\delta = 8.6$ (m, 2H, $H_{7,8}$), 7.82 (m, 2H, $H_{4,11}$), 7.57 (m, 4H, $H_{5,6,9,10}$), 6.16 (t, ^{3}J(H–H) = 2.8 Hz of d, ^{2}J(Rh-H) = 1.5 Hz, 2H, H_2), 5.68 (d, ^{3}J(H–H) = 2.8 Hz, 2H, $H_{1,3}$), 1.84 (s, broad, 8H, C_2H_4's). ^{13}C-NMR (CD_2Cl_2, 125 MHz): $\delta = 129.0$ ($C_{3b,11a}$), 127.7 ($C_{5,10}$), 127.6 ($C_{7a,7b}$), 126.0 ($C_{6,9}$), 124.2 ($C_{7,8}$), 123.7 ($C_{4,11}$), 102.8 ($C_{3a,11b}$), 89.2 (d, ^{1}J(Rh-C) = 4.5 Hz, (C_2), 80.2 (d, ^{1}J(Rh-C) = 3.0 Hz), $C_{1,3}$), 44.5, 44.2 (C_2H_4's). MS (DEI, *m*/*z* (%)): 533 (18) ($[(C_{17}H_{11})_2Rh]^+$), 374 (5) ($[M]^+$), 346 (20) ($[M - C_2H_4]^+$), 318 (100) ($[M - 2(C_2H_4)]^+$), 216 (30) ($[C_{17}H_{12}]^+$). HRMS Calc. for $^{12}C_{17}H_{11}Rh$ ($[M - 2(C_2H_4)]^+$), 317.9916 amu; observed 317.9913 amu. Anal. Found: C, 67.45; H, 5.30. Calc. for $C_{21}H_{19}Rh$: C, 67.39; H, 5.12%.

3.1.6. Protonation of ***21***

In an NMR tube, a CD_2Cl_2 solution of **21** was treated with one drop of CF_3COOH at −90 °C and the solution immediately changed color from yellow to red. As the sample was gradually allowed to warm to 10 °C in the NMR probe, ^{1}H, ^{13}C and 2-D COSY spectra were recorded at 10 °C intervals. Signals assignable to Rh-ethyl, Rh-π-methallyl and 1- and 2-butenes were observed.

3.1.7. (η^5-Cyclopentadienyl)(η^5-cyclopenta[l]phenanthrenyl)iron (***22***)

As for **20**, anion **18** (1.39 mmol) was treated with (η^5-C_5H_5)$Fe(CO)_2I$ (0.422 g, 1.39 mmol) at −78 °C. The mixture was allowed to warm to r.t., stirred overnight, and the solvent was removed under vacuum. Flash chromatography on silica using hexanes–CH_2Cl_2 followed by use of a Chromatotron using hexanes as eluent gave recovered ligand (0.259 g, 1.12 mmol) and **22** an orange solid (0.025 g, 0.074 mmol; 28%), m.p. 201–202°C. ^{1}H-NMR (THF-d_8, 500 MHz): $\delta = 8.42$ (m, 2H, $H_{7,8}$), 7.97 (m, 2H, $H_{4,11}$), 7.44 (m, 4H, $H_{5,6,9,10}$), 5.28 (d, ^{3}J(H–H) = 6.3 Hz, 2H, $H_{1,3}$), 4.39 (t,

^3J(H–H) = 6.3 Hz, 1H, H_2), 3.59 (s, 5H, Cp). ^{13}C-NMR (THF-d_8, 125 MHz): $\delta = 135.5$ ($C_{3b,11a}$), 131.0 ($C_{7a,7b}$), 128.1, 126.4 ($C_{5,10}$, $C_{6,9}$), 124.7 ($C_{4,11}$), 124.4 ($C_{7,8}$), 82.2 ($C_{3a,11b}$), 70.6 (C_5H_5), 69.9 (C_2), 63.3 ($C_{1,3}$). MS (DEI, *m*/*z* (%)): 336 (100) ($[M]^+$), 215 (15) ($[C_{17}H_{11}]^+$), 121 (5) ($[C_5H_5Fe]^+$). HRMS Calc. for $^{12}C_{22}H_{16}Fe$ ($[M]^+$), 336.060 amu; observed 336.061 amu. Anal. Found: C, 78.78; H, 4.92. Calc. for $C_{22}H_{16}Fe$: C, 78.59; H, 4.80%.

3.1.8. Attempted synthesis of (η^6-1*H*-cyclopenta[*l*]phenanthrene)Cr(CO)$_3$ (**25**)

Cyclopenta[*l*]phenanthrene (0.600 g, 2.778 mmol) and $Cr(CO)_6$ (0.611 g, 2.778 mmol) in di-*n*-butyl ether (60 ml) were heated under reflux for 3 days. The green solid remaining after removal of solvent was flash chromatographed on silica using hexane–ether 1:1 to give 2,3-dihydro-1*H*-cyclopenta[*l*]phenanthrene (**33**), as a colorless solid (0.238 g, 1.09 mmol; 39%), m.p. 152–153 °C, and yellow crystals of (η^6-2,3-dihydro-1*H*-cyclopenta[*l*]phenanthrene)Cr(CO)$_3$ (**26**), (0.050 g, 0.14 mmol; 8%), m.p. 186–187 °C. Data for **33**: ^{1}H-NMR (CD_2Cl_2, 500 MHz): $\delta = 8.72$ (m, 2H, $H_{7,8}$), 7.89 (m, 2H, $H_{4,11}$), 7.63 (m, 4H, $H_{5,10}$, $H_{6,9}$), 3.37 (t, ^3J(H–H) = 7.5 Hz, 4H, $H_{1,3}$), 2.37 (quintet, ^3J(H–H) = 7.5 Hz, 2H, H_2). ^{13}C-NMR (CD_2Cl_2, 125 MHz): $\delta = 138.0$ ($C_{3a,11b}$), 130.5, 130.4 ($C_{3b,11a}$, $C_{7a,7b}$), 126.9 ($C_{6,9}$), 125.9 ($C_{5,10}$), 125.3 ($C_{4,11}$), 123.4 ($C_{7,8}$), 32.6 ($C_{1,3}$), 23.8 (C_2). HRMS Calc. for $^{12}C_{17}H_{14}$ ($[M]^+$), 218.1096 amu; observed 218.1091 amu. Data for **26**: ^{1}H-NMR (CD_2Cl_2, 500 MHz): $\delta = 8.41$ (m, 1H, H_8), 7.84 (m, 1H, H_{11}), 7.71–7.69 (m, 2H, H_9, H_{10}), 6.80 (d, ^3J(H–H) = 6.9 Hz, 1H, H_7), 6.08 (d, ^3J(H–H) = 6.7 Hz, 1H, H_4), 5.67 (t, ^3J(H–H) = 6.7 Hz, 1H, H_5), 5.60 (t, ^3J(H–H) = 6.7 Hz, 1H, H_6), 3.39–3.18 (m, 4H, $H_{1,1'}$, $H_{3,3'}$), 2.42–2.30 (m, 2H, $H_{2,2'}$). IR (cm^{-1}, CCl_4): 2022 (s), 1943 (s). MS (DEI, *m*/*z* (%)): 354 (15) ($[M]^+$), 298 (10) ($[M-2CO]^+$), 270 (80) ($[M-3CO]^+$), 215 (15) ($[C_{17}H_{11}]^+$), 52 (100) ($[Cr]^+$). HRMS Calc. for $^{12}C_{17}H_{14}Cr$ ($[M-3CO]^+$), 270.0501 amu; observed 270.0506 amu. Anal. Found: C, 67.91; H, 3.96. Calc. for $C_{20}H_{14}CrO_3$: C, 67.80; H, 3.98%.

When the reaction of cyclopenta[*l*]phenthrenane, **10**, and $Cr(CO)_6$ was repeated with use of meticulously dried solvents, no organometallic products were isolated, but instead the Diels–Alder dimer, **31**, derived from **10** and its corresponding iso-indene **32** was obtained; **31** has been fully characterized both spectroscopically and by X-ray crystallography [33].

3.2. Crystal structure determination

X-ray quality crystals of **26**, grown from CH_2Cl_2–hexane, were mounted on a glass fiber. Data were collected on a Enraf–Nonius CAD4 diffractometer equipped with graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Three standard reflections that were measured after every 30 min. of X-ray exposure time showed neither instrument instability nor crystal decay. The structure was solved by using the Patterson Methods procedure in the SHELX-PLUS program library [35]. Carbon and oxygen atoms were found in a Fourier difference map, and the hydrogen atoms were included in calculated positions and refined anisotropically. Aromatic hydrogens and methylene hydrogen atoms have a common thermal parameter *U*. Crystallographic data are collected in Table 1.

3.3. Molecular orbital calculations

Calculations were performed within the extended Hückel formalism using weighted $H_{i,j}$ values [36]. Computations were carried out by use of the program CACAO [37]. The molecular geometry of the $C_{17}H_{11}$ framework was an idealized planar version taken from the X-ray structure of **26**. To generate the energy hypersurface, the $Fe(C_5H_5)$ coordinates were incremented in units of 0.1 Å, as previously described in our earlier trajectory calculations [8,9].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 159170. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial support from Natural Sciences and Engineering Research Council of Canada, and from the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Mass spectra were acquired courtesy of Dr Richard Smith of the McMaster Regional Mass Spectrometry Center.

References

[1] T.S. Piper, G. Wilkinson, J. Inorg. Nucl. Chem. 3 (1956) 104.
[2] M.J. Bennett, F.A. Cotton, A. Davison, J.W. Faller, S.J. Lippard, S.M. Morehouse, J. Am. Chem. Soc. 88 (1966) 4371.
[3] F.A. Cotton, A. Musco, G. Yagupsky, J. Am. Chem. Soc. 89 (1967) 6136.
[4] M. Stradiotto, D.W. Hughes, A.D. Bain, M.A. Brook, M.J. McGlinchey, Organometallics 16 (1997) 5563.
[5] P.M. Treichel, J.W. Johnson, J. Organomet. Chem. 88 (1975) 207.

[6] (a) A.N. Nesmeyanov, N.A. Ustynyuk, L.G. Makarova, S. Andre, Yu.A. Ustynyuk, L.N. Novikova, Yu.N. Luzikov, J. Organomet. Chem. 154 (1978) 45;
(b) C. White, J. Thompson, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1977) 1654;
(c) K.M. Nicholas, R.C. Kerber, E.I. Steifel, Inorg. Chem. 10 (1971) 1519;
(d) P.M. Treichel, J.W. Johnson, Inorg. Chem. 16 (1977) 749;
(e) P.M. Treichel, J.W. Johnson, J. Am. Chem. Soc. 99 (1977) 1427;
(f) P.M. Treichel, K.P. Fivizzani, K.J. Haller, Organometallics 1 (1982) 931.

[7] T.A. Albright, P. Hofmann, R. Hoffmann, C.P. Lillya, P.A. Dobosh, J. Am. Chem. Soc. 105 (1983) 3396.

[8] A. Decken, J.F. Britten, M.J. McGlinchey, J. Am. Chem. Soc. 115 (1993) 7275.

[9] A. Decken, S.S. Rigby, L. Girard, A.D. Bain, M.J. McGlinchey, Organometallics 16 (1997) 1308.

[10] B. Eliasson, M.H. Nouri-Sorkhabi, L. Trogen, I. Sethson, U. Edlund, A. Sygula, M. Rabinowitz, J. Org. Chem. 54 (1989) 171.

[11] (a) R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, 2nd ed., Wiley, New York, 1993 (pp. 91–92, and references therein);
(b) J.M. O'Connor, C.P. Casey, Chem. Rev. 87 (1987) 307.

[12] (a) S.S. Rigby, H.K. Gupta, N.H. Werstiuk, A.D. Bain, M.J. McGlinchey, Polyhedron 14 (1995) 2787;
(b) S.S. Rigby, H.K. Gupta, N.H. Werstiuk, A.D. Bain, M.J. McGlinchey, Inorg. Chim. Acta 251 (1996) 355;
(c) M. Stradiotto, M.A. Brook, M.J. McGlinchey, New J. Chem. 23 (1999) 317;
(d) M. Stradiotto, P. Hazendonk, A.D. Bain, M.A. Brook, M.J. McGlinchey, Organometallics 19 (2000) 590;
(e) M. Stradiotto, M.A. Brook, M.J. McGlinchey, J. Chem. Soc. Perkin Trans. 2 (2000) 611.

[13] (a) R.B. King, M.B. Bisnette, Inorg. Chem. 3 (1964) 796;
(b) J.A. Belmont, M.S. Wrighton, Organometallics 5 (1986) 1421.

[14] (a) E.O. Fischer, D.Z. Seus, Naturforsch. B 8 (1953) 694;
(b) J. Trotter, Acta Crystallogr. 11 (1958) 355;
(c) H.P. Fritz, C.G. Kreiter, J. Organomet. Chem. 4 (1965) 198;
(d) S.A. Westcott, A.K. Kakkar, G. Stringer, N.J. Taylor, T.B. Marder, J. Organomet. Chem. 394 (1990) 777.

[15] R.B. King, A. Efraty, J. Organomet. Chem. 23 (1970) 527.

[16] (a) P. Caddy, M. Green, E. O'Brien, L.E. Smart, P. Woodward, Angew. Chem. Int. Ed. Engl. 16 (1977) 648;
(b) P. Caddy, M. Green, E. O'Brien, L.E. Smart, P. Woodward, J. Chem. Soc. Dalton. Trans. (1980) 962;
(c) M. Mlekuz, P. Bougeard, B.G. Sayer, M.J. McGlinchey, C.A. Rodger, M.R. Churchill, J.W. Ziller, S.-K. Kang, T.A. Albright, Organometallics 5 (1986) 1656.

[17] R. Cramer, J. Am. Chem. Soc. 87 (1965) 4717.

[18] D.T. Clark, M. Mlekuz, B.G. Sayer, B.E. McCarry, M.J. McGlinchey, Organometallics 6 (1987) 2201.

[19] L.-N. Ji, M.E. Rerek, F. Basolo, Organometallics 3 (1984) 740.

[20] T.B. Marder, J.C. Calabrese, D.C. Roe, T.H. Tulip, Organometallics 6 (1987) 2012.

[21] R.J. Angelici, W. Loewen, Inorg. Chem. 6 (1967) 682.

[22] T.E. Ready, R.O. Day, J.C.W. Chien, M.D. Rausch, Macromolecules 26 (1993) 5822.

[23] (a) N. Schneider, M.E. Huttenloch, U. Stehling, R. Kirsten, F. Schaper, H.H. Brintzinger, Organometallics 16 (1997) 3413;
(b) N. Schneider, M.-H. Prosenc, H.H. Brintzinger, J. Organomet. Chem. 545–546 (1997) 291.

[24] The syntheses of Fe and Ti derivatives of 7-phenylcyclopenta[*l*]phenanthrene have been reported; however, no reactions of these complexes appear to have been described: K. Albrecht, O. Reiser, M. Weber, A. de Meijere, Synlett. (1992) 521.

[25] (a) R. Cramer, J. Am. Chem. Soc. 86 (1964) 217;
(b) R. Cramer, J.B. Kline, J.D. Roberts, J. Am. Chem. Soc. 91 (1969) 2519.

[26] M. Sato, Y. Ishida, Y. Nakamura, M. Kajiwara, Nippon Kagaku Zasshi 91 (1970) 1188.

[27] T.L. Tisch, T.J. Lynch, R. Dominguez, J. Organomet. Chem. 377 (1989) 265.

[28] (a) T.J. Katz, W. Slusarek, J. Am. Chem. Soc. 102 (1980) 1058;
(b) M.C. Helvenston, T.J. Lynch, J. Organomet. Chem. 359 (1989) C50;
(c) T.J. Lynch, M.C. Helvenston, A.L. Rheingold, D.L. Staley, Organometallics 8 (1989) 1959;
(d) H. Bang, T.J. Lynch, F. Basolo, Organometallics 11 (1992) 40;
(e) R. Winter, D.T. Pierce, W.E. Geiger, T.J. Lynch, J. Chem. Soc. Chem. Commun. (1994) 1949.

[29] (a) In contrast, complexation to the central ring of trindane is well precedented: H.K. Gupta, P.E. Lock, M.J. McGlinchey, Organometallics 16 (1997) 3628;
(b) H.K. Gupta, P.E. Lock, D.W. Hughes, M.J. McGlinchey, Organometallics 16 (1997) 4355.

[30] J.M. Guss, R. Mason, J. Chem. Soc. Dalton. Trans. (1973) 1834.

[31] R.D. Rogers, J.L. Atwood, T.A. Albright, W.A. Lee, M.D. Rausch, Organometallics 3 (1984) 263.

[32] It has long been known that traces of water can yield partially hydrogenated (arene)$Cr(CO)_3$ complexes: D.A. Brown, J.P. Hargaden, C.M. McMullin, N. Gogan, H. Sloan, J. Chem. Soc. (1963) 4914.

[33] S.S. Rigby, M. Stradiotto, S. Brydges, D.L. Pole, S. Top, A.D. Bain, M.J. McGlinchey, J. Org. Chem. 63 (1998) 3735.

[34] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, New York, 1980.

[35] G.M. Sheldrick, SHELXTL PC, Release 4.1, Siemens Crystallographic Research Systems, Madison, WI 53719, 1990.

[36] (a) R. Hoffmann, J. Chem. Phys. 39 (1963) 1397;
(b) R. Hoffmann, W.N. Lipscomb, J. Chem. Phys. 36 (1962) 2179 (see also. p. 3489);
(c) J.-H. Ammeter, H.-B. Bürgi, J.C. Thibeault, R. Hoffmann, J. Am. Chem. Soc. 100 (1978) 3686.

[37] (a) CACAO, Version 5.0, 1998;
(b) C. Mealli, D. Proserpio, J. Chem. Educ. 67 (1990) 399.