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Synthesis of 9-anthrylmethyl-functionalised cyclopentadienyl derivatives of rhodium(I) and iridium(I) and study of their luminescence properties

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Dedicated to Professor F. Calderazzo on his 70th birthday.

Abstract

The compound 9-anthrylmethylcyclopentadiene **1** was prepared by reacting 9-bromomethylanthracene with cyclopentadienylsodium and transformed into its thallium(I) derivative on reaction with thallium ethoxide **3**. The 9-anthrylmethylcyclopentadienyl ($AnCH_2C_5H_4$) derivatives of rhodium(I) and iridium(I) of formula $[M(\eta^5\text{-}AnCH_2C_5H_4)L_2]$ (M = Rh or Ir; L = C_2H_4, CO, PPh_3, C_8H_{14}; $L_2 = C_7H_8$, 1,5-C_8H_{12}) **4**–**6** and **9**–**11** were obtained in good yields by reacting the corresponding rhodium(I) and iridium(I) chlorides with **3**. Both $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(\eta^2\text{-}C_2H_4)_2]$ (**4**) and $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(CO)_2]$ (**5**) react with triphenylphosphine, at 130°C to give $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(\eta^2\text{-}C_2H_4)(PPh_3)]$ (**7**) and $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(CO)(PPh_3)]$ (**8**). All complexes were characterised by elemental analysis, mass spectrometry, ^{1}H-NMR and FTIR. The structures of two of them, i.e. $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(\eta^2\text{-}C_2H_4)_2]$ (**4**) and $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(CO)_2]$ (**5**), were elucidated by single crystal X-ray diffraction. Compound **4** crystallises in the triclinic space group $P\bar{1}$ with $a = 11.112(1)$, $b = 12.065(1)$, $c = 15.982(2)$ Å; $\alpha = 99.83(1)$, $\beta = 107.86(1)$, $\gamma = 107.22(1)°$. $V = 1865.6(3)$ Å^3. $Z = 4$, $D_{calc} = 1.475$ g cm^{-1}, $R_1 = 0.0414$ $[I > 2\sigma(I)]$, $wR_2 = 0.0953$. Compound **5** crystallises in the triclinic space group $P\bar{1}$ with $a = 12.232(1)$, $b = 13.463(1)$, $c = 13.488(1)$ Å; $\alpha = 61.25(1)$, $\beta = 68.51(1)$, $\gamma = 67.45(1)°$. $V = 1752.5(2)$ Å^3. $Z = 4$, $D_{calc} = 1.570$ g cm^{-1}, $R_1 = 0.0313$ $[I > 2\sigma(I)]$, $wR_2 = 0.0795$. The UV–vis spectra (280–700 nm) of **1** and of complexes **4**–**11** were recorded. The spectra of **4**–**11** are indicative of important interactions between the anthrylic chromophore and the cyclopentadienyl–metal moiety. When excited at 365 nm, **1** results to be an efficient light-emitting molecule, while its derivatives **4**–**11** are poorly luminescent compounds. Indeed, all complexes exhibit similar fluorescence spectra which are typical of the anthrylic fluorophore but have extremely low intensity (the one observed for 9-methylanthracene was below 5% and taken as the reference compound). The mechanism of fluorescence quenching in the complexes **4**–**11** is discussed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium complexes; Iridium complexes; Electron transfer; Energy transfer; Fluorescence

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1. Introduction

Increasing attention is devoted to the synthesis of transition metal compounds which have interesting electronic, magnetic or photochemical properties so to design new transition metal-containing building blocks which may be used to form assemblies having multiple electron transfer properties or cooperative magnetic behaviour. Such compounds are designed to undergo intramolecular electron transfer so that their chemical and physical behaviour can be controlled through their redox properties. The interest of this research is fundamental: to gain a deeper understanding of electron

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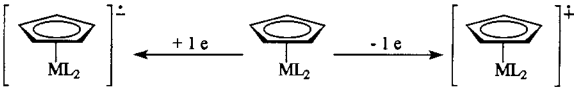
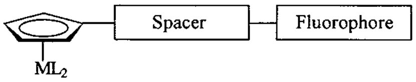
transfer behaviour in metal-containing compounds, and it is also highly relevant to applications in the general field of molecular electronics (optoelectronics, molecular wires, switches, and molecular magnets) [1].

The transition-metal–cyclopentadienyl system can undergo one-electron-reduction or one-electron oxidation, easily, thus giving rise to relatively stable radical species [2]:

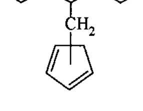


The unpaired electron spin delocalisation varies markedly within these radicals and may be ligand- or metal-centred or may interest the whole complex, depending upon various structural parameters [3]. Thus, owing to its electron donor-acceptor properties, the cyclopentadienyl–metal moiety appears interesting for projecting new two-component supramolecular devices in which it is connected to a luminescent fragment behaving as an 'antenna'. It is expected that the cyclopentadienyl–metal system can behave as a control unit capable of modifying the physical properties characteristic of the antenna (light emitting properties, charge transfer, redox properties, etc.). Therefore, the idea of synthesising new transition-metal cyclopentadienyl derivatives in which the C_5 ring is linked to a fluorophore through a spacer appeared attractive:



Compounds of this type should allow one to test how the active sites, i.e. the cyclopentadienyl–metal system and the fluorophore, communicate under those conditions (chemical, photochemical, and electrochemical) which can induce the intramolecular transmission of electronic effects.

Although a variety of ligands carrying a fluorophore as well as their metal derivatives have been reported in the literature [4], to our knowledge no cyclopentadiene derivative carrying an efficient light-emitting fragment has been so far reported in the literature. We were then attracted by the idea to synthesise an anthryl-substituted cyclopentadiene derivative in which the anthryl group and the cyclopentadiene ring are separated by a methylene group and we have now succeeded in the synthesis of 9-anthrylmethylcyclopentadiene **1**.



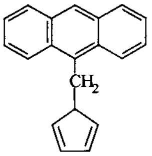
1

We have then started a research aimed to synthesise various transition metal derivatives carrying the 9-anthrylmethylcyclopentadienyl ligand and to study their photophysical properties. Part of this work is reported in this paper which deals with several derivatives of rhodium(I) and iridium(I).

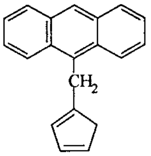
2. Results and discussion

2.1. Preparation of 9-anthrylmethyl-functionalised cyclopentadienyl derivatives of rhodium(I) and iridium(I)

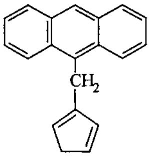
The synthesis of 9-anthrylmethylcyclopentadiene **1** was performed according to the reactions outlined in Scheme 1: commercial 9-hydroxymethylanthracene was converted into the corresponding bromide **2** on reaction with Br_2 in the presence of PPh_3 [5], and the subsequent reaction of **2** with cyclopentadienylsodium [6] furnished **1** in satisfactory yields (75%).Three isomeric structures are possible for **1**, namely **1a**–**1c**:



1a

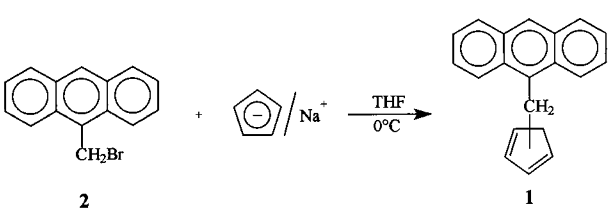


1b



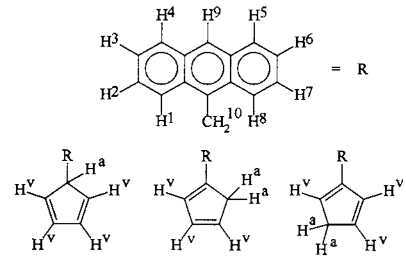
1c

Indeed, GC–MS analysis of **1**, after its isolation from the reaction mixture by column chromatography on silica gel (see Section 4), revealed the presence of three peaks, each having $m/z = 256$. Accordingly, its ^{1}H-NMR spectrum is quite complex. Indeed, apart from the aromatic protons, which give rise to the expected pattern for a 9-anthryl group, the vinylic and allylic protons of the cyclopentadiene ring give rise to two sets of broad signals, respectively, owing to the presence of isomers (Table 1). Six signals of the same intensity are observed for the vinylic protons between δ 6.54 and 5.60 ppm, while the three signals, at δ 3.17, 3.11, and 3.01 ppm, are due to the allylic protons. Since the low-field signal (3.17 ppm) can be associated with the tertiary allylic proton of the isomer **1a** and the other two with the secondary allylic protons of isomers **1b** and **1c** (Table 1), the integrated area of the three signals allows one to conclude that **1a**–**1c** are present in a 1:1:1 ratio. Finally, the broad split signal, centred at δ 4.70 ppm, is attributed to the methylene group which con-



Scheme 1.

Table 1
^{1}H-NMR data for 9-anthrylmethylcyclopentadiene **1** *



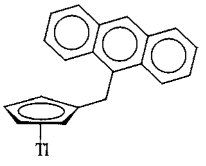
1a **1b** **1c**

Protons	δ (ppm), J (Hz)
H^1, H^8	8.24, 2H, d, J 9
H^4, H^5	8.00, 2H, d, J 9
H^9	8.39, 1H, s
H^2, H^3, H^6, H^7	7.47, 4H, m
H^{10}	4.70, 2H, broad split signal
H^v	6.54, bs; 6.40, bs; 6.32, bs; 6.21, bs; 5.97, bs; 5.60, bs
H^a	3.17, 1H, bs; 3.11, 2H, bs; 3.01, 2H, bs

* Spectra recorded in $CDCl_3$; s, singlet; m, multiplet; d, doublet; bs, broad signal.

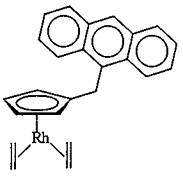
nects the anthrylic moiety with the C_5 ring: these protons should give rise to a doublet in the case of isomer **1a**, and to two singlets in the case of **1b** and **1c** (Table 1).

A suspension of **1** in absolute ethanol reacted with thallium ethoxide, at room temperature (r.t.), to form 9-anthrylmethylcyclopentadienylthallium(I) **3**, which is a yellow–ochre solid that can be stored under dinitrogen at r.t. for long periods of time without apparent decomposition.

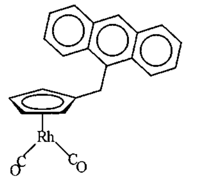


3

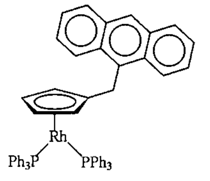
The reaction of **3** with $[Rh_2Cl_2L_4]$ ($L = C_2H_4$ or CO) produced $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(\eta^2\text{-}C_2H_4)_2]$ (**4**) and $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(CO)_2]$ (**5**) ($AnCH_2$ = 9-anthrylmethyl) in good yields. Analogously, $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(PPh_3)_2]$ (**6**) was prepared by reacting $[RhCl(PPh_3)_3]$ with **3**.



4

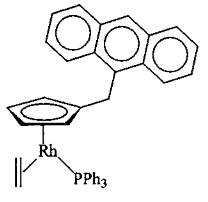


5



6

Both **4** and **5** undergo ligand exchange reaction on reaction with triphenylphosphine in p-xylene, at 130°C, thus giving rise to $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(\eta^2\text{-}C_2H_4)(PPh_3)]$ (**7**) and $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(CO)(PPh_3)]$ (**8**), respectively.



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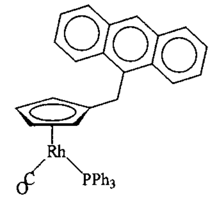
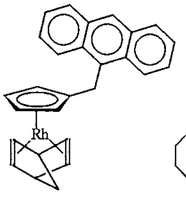
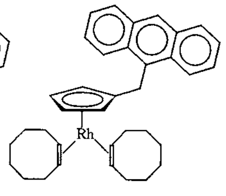


8

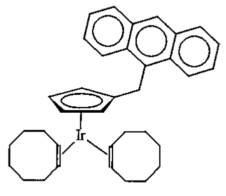
Finally, by reacting **3** with the following rhodium(I) and iridium(I) derivatives: $[Rh_2Cl_2(\eta^4\text{-}C_7H_8)_2]$, $[Rh_2Cl_2(\eta^2\text{-}C_8H_{14})_4]$, $[Ir_2Cl_2(\eta^2\text{-}C_8H_{14})_4]$, $[Rh_2Cl_2(\eta^4\text{-}C_8H_{12})_2]$ and $[Ir_2Cl_2(\eta^4\text{-}C_8H_{12})_2]$, the corresponding 9-anthrylmethylcyclopentadienyl derivatives **9**, **10a**, **10b**, **11a**, and **11b** were obtained in good yields.



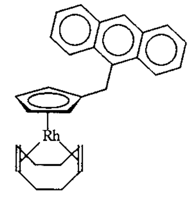
9



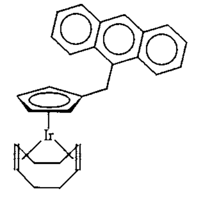
10a



10b



11a

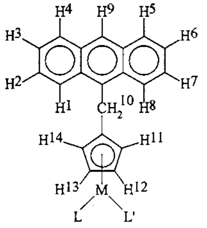


11b

Complexes **4**–**11** are quite thermally stable at the solid state and can be stored under dinitrogen at −20°C for long periods of time without apparent decomposition. They were characterised by elemental analysis, mass spectrometry (EI MS), ^{1}H-NMR, and, where appropriate, also by FTIR. For two of them, i.e. **4** and **5**, the molecular and crystal structure was elucidated by single-crystal X-ray diffraction (see Section 2.2). In all cases, well resolved ^{1}H-NMR were obtained in C_6D_6 (Table 2) which were consistent with the proposed structures and in agreement with the spectral pattern observed for many rhodium(I) complexes of mono-substituted $\eta^5\text{-}C_5H_4X$ rings [7].

The resonances of the cyclopentadienyl ring as well as those of the olefinic protons of the complexes reported in this paper are generally observed at a slightly higher field when compared with the corresponding $\eta^5\text{-}C_5H_5$ derivatives. Furthermore, by examining the resonances of the cyclopentadienylic and olefinic protons exhibited by the complexes **10** and **11**, a high-field

Table 2
^{1}H-NMR data for complexes **4**–**11** [a]



Complex	δ (ppm), J (Hz)
[Rh(η^5-AnCH$_2$C$_5$H$_4$)(η^2-C$_2$H$_4$)$_2$] (**4**)	8.34 (2H, d, J_{HH} 9, H^1 and H^8), 8.13 (1H, s, H^9), 7.80 (2H, d, J_{HH} 9, H^4 and H^5), 7.37–7.18 (4H, m, H^2, H^3, H^6, and H^7), 4.66 (2H, d, J_{HH} 6, H^{12} and H^{13}), 4.56 (2H, d, J_{HH} 6, H^{11} and H^{14}), 4.48 (2H, s, H^{10}), 2.65 (4H, bs, C$_2$H$_4$), 1.10 (4H, bs, C$_2$H$_4$)
[Rh(η^5-AnCH$_2$C$_5$H$_4$)(CO)$_2$] (**5**)	8.12 (2H, d, J_{HH} 9, H^1 and H^8), 8.14 (1H, s, H^9), 7.81 (2H, d, J_{HH} 9, H^4 and H^5), 7.38–7.21 (4H, m, H^2, H^3, H^6, and H^7), 4.86 (2H, d, J_{HH} 6, H^{12} and H^{13}), 4.68 (2H, d, J_{HH} 6, H^{11} and H^{14}), 4.30 (2H, s, H^{10})
[Rh(η^5-AnCH$_2$C$_5$H$_4$)(PPh$_3$)$_2$] (**6**)	8.50 (2H, d, J_{HH} 9, H^1 and H^8), 8.15 (1H, s, H^9), 7.86–7.75 (12H, m, PPh$_3$), 7.09–6.92 (18H, m, PPh$_3$), 7.89 (2H, d, J_{HH} 9, H^4 and H^5), 7.41–7.29 (4H, m, H^2, H^3, H^6, and H^7), 4.94 (2H, d, J_{HH} 6, H^{12} and H^{13}), 4.71 (2H, d, J_{HH} 6, H^{11} and H^{14}), 4.47 (2H, s, H^{10}), 2.65 (4H, bs, C$_2$H$_4$), 1.10 (4H, bs, C$_2$H$_4$)
[Rh(η^5-AnCH$_2$C$_5$H$_4$)(η^2-C$_2$H$_4$)(PPh$_3$)] (**7**)	8.54 (2H, d, J_{HH} 9, H^1 and H^8), 8.27 (1H, s, H^9), 7.92 (2H, d, J_{HH} 9, H^4 and H^5), 7.68–7.58 (6H, m, PPh$_3$), 7.08–7.02 (9H, m, PPh$_3$), 7.42–7.30 (4H, m, H^2, H^3, H^6, and H^7), 5.03 (2H, d, J_{HH} 6, H^{12} and H^{13}), 4.76 (2H, d, J_{HH} 6, H^{11} and H^{14}), 4.56 (2H, s, H^{10}), 2.83 (2H, bs, C$_2$H$_4$), 1.76 (2H, bs, C$_2$H$_4$)
[Rh(η^5-AnCH$_2$C$_5$H$_4$)(CO)(PPh$_3$)] (**8**)	8.49 (2H, d, J_{HH} 9, H^1 and H^8), 8.21 (1H, s, H^9), 7.90 (2H, d, J_{HH} 9, H^4 and H^5), 7.68–7.52 (6H, m, PPh$_3$), 7.04–6.98 (9H, m, PPh$_3$), 7.41–7.29 (4H, m, H^2, H^3, H^6, and H^7), 5.05 (2H, d, J_{HH} 6, H^{12} and H^{13}), 4.81 (2H, d, J_{HH} 6, H^{11} and H^{14}), 4.65 (2H, s, H^{10})
[Rh(η^5-AnCH$_2$C$_5$H$_4$)(η^4-C$_7$H$_8$)] (**9**)	8.40 (2H, d, J_{HH} 9, H^1 and H^8), 8.16 (1H, s, H^9), 7.84 (2H, d, J_{HH} 9, H^4 and H^5), 7.38–7.21 (4H, m, H^2, H^3, H^6, and H^7), 4.88–4.90 (4H, m, H^{11}–H^{14}), 4.50 (2H, s, H^{10}), 3.02 (2H, m, C$_7$H$_8$), 2.86 (4H, m, C$_7$H$_8$), 0.96 (2H, m, C$_7$H$_8$)
[Rh(η^5-AnCH$_2$C$_5$H$_4$)(η^2-C$_8$H$_{14}$)$_2$] (**10a**)	8.58 (2H, d, J_{HH} 9, H^1 and H^8), 8.19 (1H, s, H^9), 7.88 (2H, d, J_{HH} 9, H^4 and H^5), 7.43–7.25 (4H, m, H^2, H^3, H^6, and H^7), 4.74 (4H, m, H^{11}–H^{14}), 4.21 (2H, s, H^{10}), 2.29–2.06 (4H, m, C$_8$H$_{14}$), 1.88–1.20 (24H, m, C$_8$H$_{14}$)
[Ir(η^5-AnCH$_2$C$_5$H$_4$)(η^2-C$_8$H$_{14}$)$_2$] (**10b**)	8.48 (2H, d, J_{HH} 9, H^1 and H^8), 8.18 (1H, s, H^9), 7.83 (2H, d, J_{HH} 9, H^4 and H^5), 7.40–7.22 (4H, m, H^2, H^3, H^6, and H^7), 4.67 (4H, m, H^{11}–H^{14}), 4.32 (2H, s, H^{10}), 2.18–2.00 (4H, m, C$_8$H$_{14}$), 1.78–1.12 (24H, m, C$_8$H$_{14}$)
[Rh(η^5-AnCH$_2$C$_5$H$_4$)(η^4-C$_8$H$_{12}$)] (**11a**)	8.42 (2H, d, J_{HH} 9, H^1 and H^8), 8.19 (1H, s, H^9), 7.86 (2H, d, J_{HH} 9, H^4 and H^5), 7.40–7.24 (4H, m, H^2, H^3, H^6, and H^7), 4.82 (2H, d, J_{HH} 6, H^{11} and H^{14}), 4.71 (2H, d, J_{HH} 6, H^{11} and H^{14}), 4.43 (2H, s, H^{10}), 3.89–3.80 (4H, m, C$_8$H$_{12}$), 2.31–1.90 (8H, m, C$_8$H$_{12}$)
[Ir(η^5-AnCH$_2$C$_5$H$_4$)(η^4-C$_8$H$_{12}$)] (**11b**)	8.31 (2H, d, J_{HH} 9, H^1 and H^8), 8.12 (1H, s, H^9), 7.80 (2H, d, J_{HH} 9, H^4 and H^5), 7.38–7.20 (4H, m, H^2, H^3, H^6, and H^7), 4.74 (2H, d, J_{HH} 6, H^{11} and H^{14}), 4.60 (2H, d, J_{HH} 6, H^{11} and H^{14}), 4.40 (2H, s, H^{10}), 3.78–3.69 (4H, m, C$_8$H$_{12}$), 2.28–1.88 (8H, m, C$_8$H$_{12}$)

[a] Spectra recorded in C$_6$D$_6$; s, singlet; m, multiplet; d, doublet; bs, broad signal.

Table 3
Comparison of the C–O IR stretching frequencies of complexes **5** and **8** with those of the corresponding cyclopentadienyl derivatives

Complex	ν C–O (cm^{-1})
[Rh(η^5-AnCH$_2$C$_5$H$_4$)(CO)$_2$] (**5**)	2042; 1979
[Rh(η^5-C$_5$H$_5$)(CO)$_2$]	2051; 1987
[Rh(η^5-AnCH$_2$C$_5$H$_4$)(PPh$_3$)(CO)] (**8**)	1951
[Rh(η^5-C$_5$H$_5$)(PPh$_3$)(CO)]	1942

shift is observed, as expected [8], on passing from rhodium to iridium derivatives.

Finally, it is interesting to note that the C–O IR stretching frequencies of complexes **5** and **8** result to be slightly lower than those exhibited by [Rh(η^5-C$_5$H$_5$)(CO)$_2$] [9] and [Rh(η^5-C$_5$H$_5$)(PPh$_3$)(CO)] [10] (Table 3), thus showing a moderately higher electron-donating power for the η^5-9-anthrylmethylcyclopentadienyl ligand.

2.2. X-ray crystallographic studies

The asymmetric unit in the crystal structure of (η^5-9-anthrylmethylcyclopentadienyl)bis(η^2-ethylene) rhodium(I) (**4**) consists of two independent molecules arranged as shown in Fig. 1. The main bond distances and angles are listed in Table 4.

The coordination geometry of the metal may be described as trigonal planar referring to the centroids of cp and ethylene ligands (thereafter, we will use the symbols Cp and Eth to indicate these centroids). The larger steric demand by the cyclopentadienyl ligand, if compared with ethylene, makes the angles among the ligands to be very different. In fact, while the Eth(1)–Rh–Eth(2) angle is 94.9°, the mean value of Cp–Rh–Eth angle is 132.6°. Such an effect has been already observed in analogous derivatives of formula [Rh(η^5-RC$_5$H$_4$)(η^2-C$_2$H$_4$)$_2$], where R is an aryl or an alkyl group [11]. In both the independent molecules one of the ethylene ligands, C(3)–C(4), is on the same side of the C(9) atom of the cyclopentadienyl ring, i.e. the carbon atom carrying the bulky 9-anthrylmethyl group. Interestingly, the eclipsed position does not weaken the Rh–Eth(2) bond, this showing a mean length (1.994 Å) which is not much longer than the Rh–Eth(1) one (1.978 Å). A and B show different rotation angles of the 9-anthrylmethyl-substituted cyclopentadienyl groups with respect to the coordination planes as defined above. In fact, while the atom C(3A) is almost eclipsed by the atom C(9A) (dihedral angle, C(3A)–Rh(1)–CpA–C(9A) = − 3.5°) in molecule A, the corresponding atoms are staggered (dihedral angle C(3B)–Rh(2)–CpB–C(9B) = 34.3°) in molecule B. Moreover, the torsion angles C(8)–C(9)–C(10)–C(11), which define the orientation of the 9-antryl group with respect to the rest of the molecule, result to be very different in the two molecules A and B, i.e. 95.7 and 65.7°, respectively.

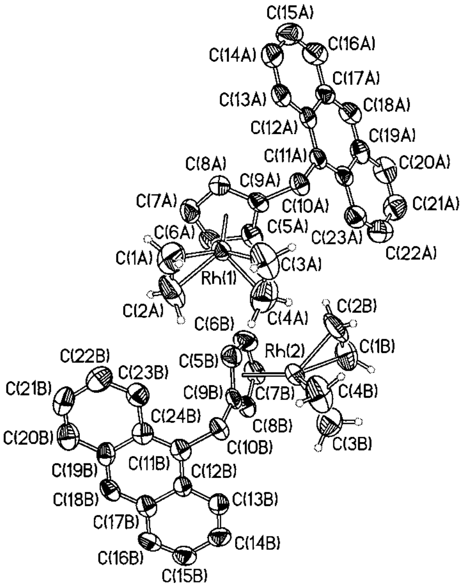


Fig. 1. Drawing of the molecular structure of complex **4**. Thermal ellipsoids are at the 50% probability.

Table 4
Selected bond lengths (Å) and angles (°) for complex **4**

Rh(1)–C(1A)	2.088(9)	Rh(2)–C(1B)	2.100(9)
Rh(1)–C(2A)	2.100(9)	Rh(2)–C(2B)	2.088(9)
Rh(1)–C(3A)	2.112(9)	Rh(2)–C(3B)	2.128(11)
Rh(1)–C(4A)	2.106(10)	Rh(2)–C(4B)	2.109(9)
Rh(1)–Eth1A	1.978(10)	Rh(2)–Eth1B	1.978(11)
Rh(1)–Eth2A	1.994(11)	Rh(2)–Eth2B	1.997(10)
Rh(1)–CpA	1.897(6)	Rh(2)–CpB	1.891(9)
C(1A)–C(2A)	1.377(15)	C(1B)–C(2B)	1.375(15)
C(3A)–C(4A)	1.372(16)	C(3B)–C(4B)	1.414(17)
C(5A)–C(6A)	1.400(11)	C(5B)–C(6B)	1.413(11)
C(5A)–C(9A)	1.408(10)	C(5B)–C(9B)	1.420(10)
C(6A)–C(7A)	1.400(12)	C(6B)–C(7B)	1.418(11)
C(7A)–C(8A)	1.425(11)	C(7B)–C(8B)	1.393(10)
C(8A)–C(9A)	1.400(10)	C(8B)–C(9B)	1.417(10)
C(9A)–C(10A)	1.516(10)	C(9B)–C(10B)	1.512(10)
C(10A)–C(11A)	1.529(9)	C(10B)–C(11B)	1.514(10)
Eth1A–Rh(1)–Eth2A	94.9(5)	Eth1B–Rh(2)–Eth2B	94.9(5)
Eth1A–Rh(1)–CpA	132.4(4)	Eth1B–Rh(2)–CpB	132.5(4)
Eth2A–Rh(1)–CpA	132.8(4)	Eth2B–Rh(2)–CpB	132.6(4)
C(6A)–C(5A)–C(9A)	109.2(7)	C(6B)–C(5B)–C(9B)	107.5(7)
C(5A)–C(6A)–C(7A)	107.4(7)	C(5B)–C(6B)–C(7B)	108.7(7)
C(6A)–C(7A)–C(8A)	108.2(7)	C(6B)–C(7B)–C(8B)	107.2(7)
C(7A)–C(8A)–C(9A)	107.8(7)	C(7B)–C(8B)–C(9B)	109.5(7)
C(5A)–C(9A)–C(8A)	107.3(6)	C(5B)–C(9B)–C(8B)	107.1(6)
C(8A)–C(9A)–C(10A)	126.2(7)	C(8B)–C(9B)–C(10B)	127.1(7)
C(5A)–C(9A)–C(10A)	126.3(7)	C(5B)–C(9B)–C(10B)	125.4(7)
C(9A)–C(10A)–C(11A)	112.6(5)	C(9B)–C(10B)–C(11B)	113.0(6)

A very similar situation is found in (η^5-9-anthrylmethylcyclopentadienyl)dicarbonylrhodium(I) (**5**), whose molecular structure is shown in Fig. 2. Bond distances and angles are listed in Table 5. Also in this case, the asymmetric unit consists of two independent molecules showing rather different conformations. In both the molecules the centroids of the cyclopentadienyl ring and the two coordinated carbonyls define an irregular triangle around the rhodium atom. As already pointed out in discussing the structure of **4**, the presence of the bulky 9-anthrylmethyl group on Cp ring does not weaken the nearest Rh–CO bond that shows the same length as the other one, in both molecules A and B. These structural features have also been observed in closely related rhodium(I) complexes of formula [Rh(η^5-RC_5H_4)$(CO)_2$], where R is an aryl or an alkyl group [7a,12].

Finally, in the case of **5**, the molecules A and B differ in their conformation much more than the two independent molecules do in **4**. In fact, while the torsion angle C(1A)–Rh(1)–CpA–C(7A) is 17.6°, the corresponding C(1B)–Rh(2)–CpB–C(7B) is 56.4°. Moreover, the torsion angles C(6)–C(7)–C(8)–C(9), defining the orientation of the anthryl group, are 134.3 and −155.2°, respectively for the molecules A and B.

Table 5
Selected bond lengths (Å) and angles (°) for complex **5**

Rh(1)–C(1A)	1.845(5)	Rh(2)–C(1B)	1.847(5)
Rh(1)–C(2A)	1.842(5)	Rh(2)–C(2B)	1.835(5)
Rh(1)–CpA	1.911(5)	Rh(2)–CpB	1.916(5)
C(1A)–O(1A)	1.135(5)	C(1B)–O(1B)	1.127(6)
C(2A)–O(2A)	1.142(6)	C(2B)–O(2B)	1.147(6)
C(3A)–C(4A)	1.404(5)	C(3B)–C(4B)	1.424(6)
C(3A)–C(7A)	1.406(5)	C(3B)–C(7B)	1.405(5)
C(4A)–C(5A)	1.418(6)	C(4B)–C(5B)	1.405(6)
C(5A)–C(6A)	1.391(5)	C(5B)–C(6B)	1.408(5)
C(6A)–C(7A)	1.444(5)	C(6B)–C(7B)	1.436(5)
C(7A)–C(8A)	1.524(5)	C(7B)–C(8B)	1.504(5)
C(8A)–C(9A)	1.517(5)	C(8B)–C(9B)	1.516(5)
C(1A)–Rh(1)–C(2A)	91.4(2)	C(2B)–Rh(2)–C(1B)	89.5(2)
C(1A)–Rh(1)–CpA	135.3(2)	C(1B)–Rh(2)–CpB	134.9(2)
C(2A)–Rh(1)–CpA	133.3(2)	C(2B)–Rh(2)–CpB	135.6(3)
C(4A)–C(3A)–C(7A)	107.6(4)	C(4B)–C(3B)–C(7B)	108.3(3)
C(3A)–C(4A)–C(5A)	108.9(3)	C(3B)–C(4B)–C(5B)	109.1(3)
C(4A)–C(5A)–C(6A)	107.9(4)	C(4B)–C(5B)–C(6B)	106.4(3)
C(5A)–C(6A)–C(7A)	107.8(3)	C(5B)–C(6B)–C(7B)	109.7(3)
C(3A)–C(7A)–C(6A)	107.6(3)	C(3B)–C(7B)–C(6B)	106.3(3)
C(3A)–C(7A)–C(8A)	126.2(3)	C(3B)–C(7B)–C(8B)	126.1(3)
C(6A)–C(7A)–C(8A)	125.8(3)	C(6B)–C(7B)–C(8B)	127.4(3)
C(7A)–C(8A)–C(9A)	112.6(3)	C(7B)–C(8B)–C(9B)	115.1(3)

2.3. Spectroscopic studies

The UV–vis spectra (280–700 nm) of complexes **4**–**11**, along with those of 9-methylanthracene (**9-MeAn**) and 9-anthrylmethylcyclopentadiene **3**, are shown in Figs. 3 and 4 and the corresponding parameters are given in Table 6. Moreover, the UV–vis spectra of three reference complexes, i.e. [Rh(η^5-C_5H_5)(η^2-C_2H_4)$_2$], [(η^5-C_5H_5)Rh$(CO)_2$], and [(η^5-C_5H_5)Rh$(PPh_3)_2$], are shown in Fig. 5, which illustrates clearly that only the [(η^5-C_5H_5)Rh$(PPh_3)_2$] still absorbs in the visible while the other two have relatively small absorption coefficients in the near UV.

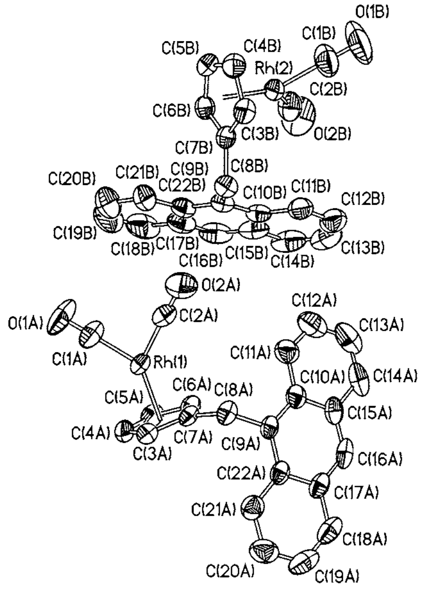


Fig. 2. Drawing of the molecular structure of complex **5**. Thermal ellipsoids are at the 50% probability.

The comparison of the spectrum of 9-methylanthracene (**9-MeAn**) with those of 9-anthrylmethylcyclopentadiene **3** and complexes **4**–**11** points out clearly that the substitution of a methylic hydrogen atom of 9-methylanthracene with the cyclopentadiene ring or with a cyclopentadienyl–metal moiety causes rather little effect on the main parameters of the spectra. In fact, molar absorption coefficients, positions of the maxima, and vibrational structures (Table 6) are all typical of 9-methylanthracene, apart from relatively small displacement of the maxima. Furthermore, the molar absorption coefficients of the metal derivatives are generally lower than those of **9-MeAn** and 9-anthrylmethylcyclopentadiene **3**. Analogously, the spectral resolution, as measured by the ratio between the molar absorption coefficients of the maximum at ca. 390 nm and of the following minimum ($\varepsilon_1/\varepsilon_{min}$), decreases on going from 9-methylanthracene to the metal derivatives **4**–**11** (Table 6). As expected, also the ratio ($\varepsilon_{1max}/\varepsilon_{2max}$) between the molar coefficients of the maxima at ca. 390 and ca. 370 nm, which depends on the changes in geometry between the ground and the excited state, results were influenced by the structural changes. These data, which are summarised below, suggest that significant interactions occur between the anthrylic sub-unit and the cyclopentadienyl–metal moiety:

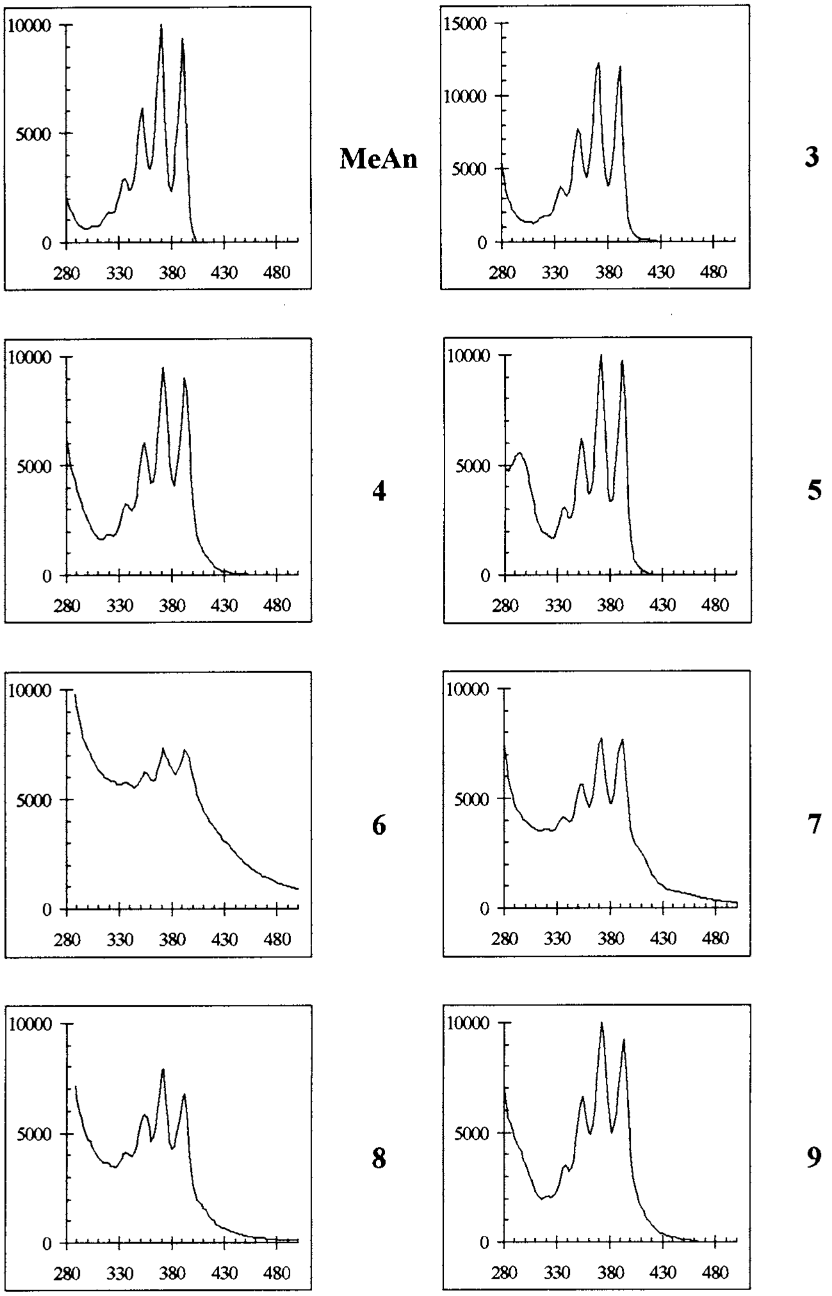


Fig. 3. Absorption spectra (ε vs. λ, nm) of 9-methylanthracene (**MeAn**), 9-anthrylmethylcyclopentadiene **3**, and of complexes [Rh(η^5-AnCH$_2$C$_5$H$_4$)(η^2-C$_2$H$_4$)$_2$] (**4**), [Rh(η^5-AnCH$_2$C$_5$H$_4$)(CO)$_2$] (**5**), [Rh(η^5-AnCH$_2$C$_5$H$_4$)(PPh$_3$)$_2$] (**6**), [Rh(η^5-AnCH$_2$C$_5$H$_4$)(PPh$_3$)(η^2-C$_2$H$_4$)] (**7**), Rh(η^5-AnCH$_2$C$_5$H$_4$)(PPh$_3$)(CO)] (**8**) and [Rh(η^5-AnCH$_2$C$_5$H$_4$)(η^4-C$_7$H$_8$)] (**9**), in 5×10^{-5}–10^{-4} M benzene solution.

$$\varepsilon_{1\max}/\varepsilon_{\min}\text{: } \mathbf{6} < \mathbf{7} = \mathbf{8} < \mathbf{11a} < \mathbf{9} < \mathbf{4} < \mathbf{10a} < \mathbf{5} < \mathbf{3} < \textbf{9-MeAn}$$

$$\varepsilon_{1\max}/\varepsilon_{2\max}\text{: } \mathbf{8} < \mathbf{9} < \textbf{9-MeAn} < \mathbf{11a} < \mathbf{10a} < \mathbf{4} < \mathbf{5} < \mathbf{3} < \mathbf{6} < \mathbf{7}$$

A close look at the spectra of cyclopentadienylic derivatives of rhodium(I) (Fig. 5) shows that only the triphenylphosphine-modified complex, i.e. [Rh(η^5-C$_5$H$_5$)(PPh$_3$)$_2$], exhibits a long but non-structured absorption tail above 450 nm. This also happens in the case of [Rh(η^5-AnCH$_2$C$_5$H$_4$)(PPh$_3$)$_2$] (**6**), [Rh(η^5-AnCH$_2$C$_5$H$_4$)(PPh$_3$)(η^2-C$_2$H$_4$)] (**7**), and [Rh(η^5-AnCH$_2$-C$_5$H$_4$)(PPh$_3$)(CO)] (**8**) (Fig. 3). Nevertheless, the absorption spectra of all complexes **4**–**11** extend above 400 nm (Figs. 3 and 4). The presence of such tails is another indication that important interactions effectively occur between the anthrylic chromophore and the metal-containing moiety. Between 410 and 450 nm, the molar absorption coefficients increase as indicated below:

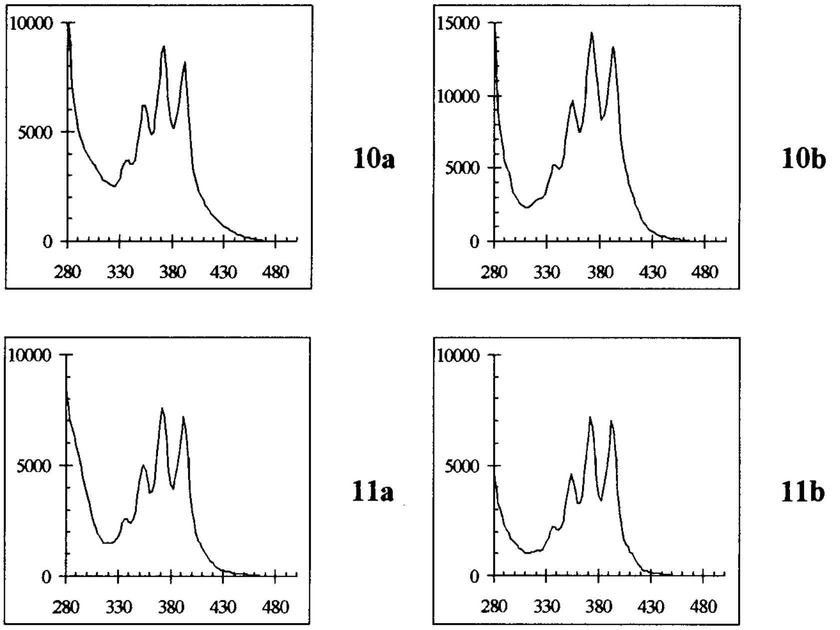


Fig. 4. Absorption spectra (ε vs. λ, nm) of $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(\eta^2\text{-}C_8H_{14})_2]$ (**10a**), $[Ir(\eta^5\text{-}AnCH_2C_5H_4)(\eta^2\text{-}C_8H_{14})_2]$ (**10b**), $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(\eta^4\text{-}1,5\text{-}C_8H_{12})]$ (**11a**) and $[Ir(\eta^5\text{-}AnCH_2C_5H_4)(\eta^4\text{-}1,5\text{-}C_8H_{12})]$ (**11b**), in 5×10^{-5}–10^{-4} M benzene solution.

$\lambda = 410$ nm: **5** < **11a** < **8** < **10a** < **9** < **4** < **7** < **6**

$\lambda = 420$ nm: **5** < **11a** < **9** < **10a** < **4** < **8** < **7** < **6**

$\lambda = 430$ nm: **5** < **4** < **11a** < **9** < **10a** < **8** < **7** < **6**

$\lambda = 450$ nm: **5** < **4** < **11a** < **9** < **10a** < **8** < **7** < **6**

Since these data suggest the presence of a CT absorption band, a more detailed analysis of the absorption spectra is necessary. In Figs. 6–8, the spectra complexes $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(\eta^2\text{-}C_2H_4)_2]$ (**4**), $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(CO)_2]$ (**5**), and $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(PPh_3)_2]$ (**6**), respectively, are compared with those of 9-methylanthracene, which was necessarily adjusted, the corresponding non anthrylmethyl-substituted cyclopentadienyl complex, and with the sum of the latter spectra. In the cases of the complexes **4** and **5** (Figs. 6 and 7) the molar absorption coefficients in the tail appear to be related to the difference in the energies of the anthrylic and the cyclopentadienyl–metal moieties, such a difference being higher in **5** than in **4**.

Indeed, both the corresponding non anthrylmethyl-substituted complexes, i.e. $[Rh(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_2H_4)_2]$ and $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$, show a negligible absorption above 370 nm. Furthermore, the $\varepsilon_{1\max}/\varepsilon_{\min}$ ratios suggest that a stronger interaction between the subunits occurs in **4** rather than **5**. The tails are rather short because, at 450 nm, the molar extinction coefficients are quite negligible, for both complexes. The $\varepsilon_{1\max}/\varepsilon_{2\max}$ ratios (Table 6) have rather similar values in all cases. However, these data, when compared with the $\varepsilon_{1\max}/\varepsilon_{2\max}$ ratio found for 9-methylanthracene, indicate a clear change in the Franck–Condon factor, which again can be accounted for only by invoking an interaction between the anthrylic and cyclopentadienyl–metal moieties. Similarly, in complexes **6**, **7**, and **8**, which contain at least one triphenylphosphine in the coordination sphere of the rhodium(I) centre, the interactions appear to increase in the order: **6** < **7** < **8**. A further indication of a rather strong interaction is given by the fact that to the quite long and intense tail of the model compound, i.e. $[Rh(\eta^5\text{-}C_5H_5)(PPh_3)_2]$, corresponds a reduction of the molar absorption coefficient in the 330–390 nm region and a large reduction of the spectral resolution as measured by $\varepsilon_{1\max}/\varepsilon_{\min}$ ratio. The interaction strength as suggested by these data can be summarised as follows:

5 < **4** < **8** < **7** < **6**

Again, these absorption data support the existence of CT states.

Table 7 reports the fluorescence emission spectra data for complexes **4**–**11**, 9-anthrylmethylcyclopentadiene **3**, and 9-methylanthracene which is taken as a reference compound. A rapid examination of the tabulated figures shows first that 9-anthrylmethylcyclopentadiene **3** results were an efficient light-emitting molecule, when excited at 365 nm, while its derivatives, i.e. the complexes **4**–**11**, are poorly luminescent compounds. Indeed, all complexes exhibit similar fluorescence spectra which are typical of the anthrylic fluorophore but have extremely low intensity: a few percent or less the one observed for 9-methylanthracene (Table 7). In some cases, the fluorescence intensity results were rather high (about 10 to 15%), if the samples were purified by the routine procedure de-

Table 6
UV–vis absorption spectra parameters for 9-methylanthracene (**MeAn**), 9-anthrylmethylcyclopentadiene (AnMeCPD) **1**, and for complexes **4**–**11** [a]

Compound	λ_{1max}	ε_{1max}	λ_{2max}	ε_{2max}	λ_{min}	ε_{min}	$\varepsilon_{1max}/\varepsilon_{min}$	$\varepsilon_{1max}/\varepsilon_{2max}$
MeAn	390	9313	370	10 000	380	2351	3.96	0.93
AnMeCPD **1**	392	11 960	372	12 200	380	3800	3.14	0.98
4	393	9000	372	9500	382	4100	2.19	0.95
5	392	9720	372	10 000	380	3320	2.93	0.97
6	392	7300	372	7350	384	6150	1.19	0.99
7	392	7650	372	7700	380	4800	1.60	0.99
8	392	6800	372	7900	380	4300	1.58	0.86
9	393	9200	372	10 000	382	5000	1.84	0.92
10a	392	8550	372	9000	380	4100	2.08	0.95
10b	396	8500	375	8600	384	3750	2.27	0.99
11a	392	7200	372	7600	380	4100	1.76	0.95
11b	392	7000	372	7200	382	3400	2.06	0.97

[a] All spectra were recorded in 5×10^{-5}–10^{-4} M benzene solution; wavelength is given in nm.

scribed in Section 4. As discussed in detail in Section 4, a rapid estimate of the lifetime suggested the presence of small amounts of a fluorescent impurity, which was identified with 9-anthrylmethylcyclopentadiene, by thin layer chromatography. Indeed, further purification of the samples caused a drastic reduction in the fluorescence emission. Thus, in all cases the fluorescence intensity is below 5% in the one observed for 9-methylanthracene, the only apparent exception concerning [Rh(η^5-AnCH$_2$C$_5$H$_4$)(PPh$_3$)(η^2-C$_2$H$_4$)$_2$] (**7**), whose further purification resulted to be less efficient than in the other cases. For this reason **7** has not been further considered in the following discussion.

The intensity of fluorescence emission, although being very low in all cases, increases in the following order:

4 < **5** < **10a** < **6** < **11a** < **8** < **9**

However, since it is likely than traces of fluorescent impurities contribute to the spectra of all compounds, a main conclusion is that fluorescence quenching is highly efficient in all cases. The fluorescence quenching is expected to be higher when strong interactions between the involved groups occur. When compared with the qualitative evaluation of the strength of the interaction between the anthrylic and the cyclopentadienyl–metal moieties, as obtained from the above absorption data, the fluorescence quenching data appear to be more or less in a reverse order:

interaction strength form absorption:
5 < **4** < **8** < **6**
fluorescence quenching:
4 > **5** > **6** > **8**

With the aim to gain more insight on the role played by the electron donating and accepting properties of the various components of the supramolecules described in this paper, the influence exerted by the nature of the transition metal centre was explored, at a preliminary stage, by comparing the spectroscopic behaviour of the rhodium(I) derivatives [Rh(η^5-AnCH$_2$C$_5$H$_4$)(η^2-C$_8$H$_{14}$)$_2$] (**10a**) and [Rh(η^5-AnCH$_2$C$_5$H$_4$)(η^4-1,5-C$_8$H$_{12}$)] (**11b**) with that exhibited by the isostructural iridium(I) complexes [Ir(η^5-AnCH$_2$C$_5$H$_4$)(η^2-C$_8$H$_{14}$)$_2$] (**10b**) and [Ir(η^5-AnCH$_2$C$_5$H$_4$)(η^4-1,5-C$_8$H$_{12}$)] (**11b**).

Just looking at the $\varepsilon_{1max}/\varepsilon_{min}$ and $\varepsilon_{1max}/\varepsilon_{2max}$ ratios for the complexes **10a**, **10b**, **11a**, and **11b** (Table 6), one can

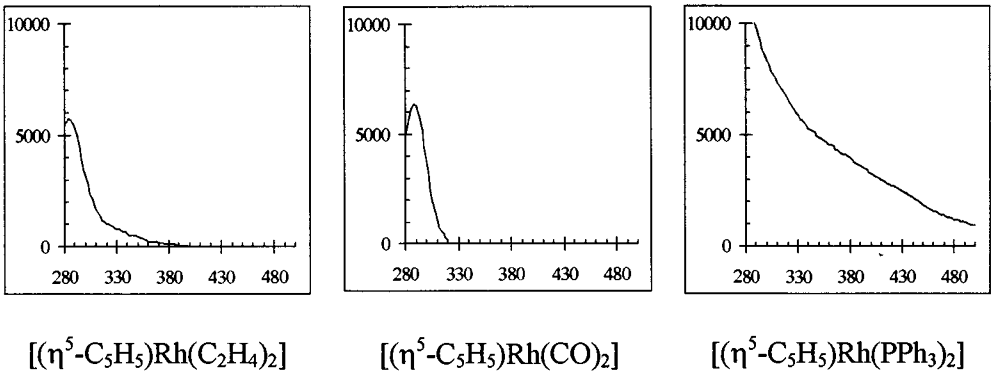


Fig. 5. Absorption spectra (ε vs. λ, nm) of [Rh(η^5-C$_5$H$_5$)(η^2-C$_2$H$_4$)$_2$], [(η^5-C$_5$H$_5$)Rh(CO)$_2$] and [(η^5-C$_5$H$_5$)Rh(PPh$_3$)$_2$], in 5×10^{-5}–10^{-4} M benzene solution.

conclude that: (i) the resolution of the absorption spectrum is higher when cyclooctene is present in the coordination sphere of the metal centre as ancillary ligand and (ii) under the same structural conditions, the absorption spectra of the iridium derivatives are more resolved than those of the rhodium ones. Thus, according to the above discussion, the interaction between the anthrylic and the cyclopentadienyl–metal subunits is higher in the rhodium(I) derivatives than it is in the case of the isostructural iridium(I) complexes and when the cyclooctene, instead of 1,5-cyclooctadiene, completes the coordination sphere of the metal centre. When compared with the qualitative evaluation of the strength of the interaction between the anthrylic and the cyclopentadienyl–metal moieties, as obtained from the absorption data, the fluorescence quenching data obtained for the complexes **10** and **11** appear to be in the following order:

interaction strength form absorption:
11a > 11b > 10a > 10b
fluorescence quenching:
11b > 11a > 10a > 10b

3. Conclusions

Various 9-anthrylmethylcyclopentadienylic derivatives of rhodium(I) and iridium(I) of general formula $[M(\eta^5\text{-AnCH}_2C_5H_4)L_2]$ can be prepared in good yields by reacting 9-anthrylmethylcyclopentadienylthallium(I) with the corresponding metal chlorides. ^{1}H-NMR and IR data of the complexes **4**–**11** indicates that 9-anthrylmethylcyclopentadienyl is a better electron-donor than cyclopentadienyl.

The absorption and fluorescence spectra suggest some preliminary conclusions: (i) the presence of the methylene group as a spacer between the anthryl group and the cyclopentadienyl–metal moieties makes them to interact, the strength of such an interaction depending upon the nature of the ancillary ligands bound to the transition metal centre and (ii) while 9-anthrylmethylcyclopentadiene is an efficient light-emitting molecule, the fluorescence of anthryl group is strongly quenched in all rhodium and iridium complexes. As far as this last point is concerned, it must be underlined that since rhodium and iridium cause similar effects on the fluorescence quenching, an energy transfer mechanism, implicating either the reabsorption of the anthracene emission by the metal centre or a dipolar interaction, should not be the fundamental quenching process involved. Moreover, the absence of a clear correlation between the absorption tail and the fluorescence quenching suggests that intramolecular energy transfer should not be an important parameter. Consequently, the electron transfer between the anthryl fragment and the cyclopentadienyl–metal moiety is a more likely candidate. The occurrence of such an electron transfer is fully justified on a thermodynamic grounding. In fact, on the base of a study of the electrochemical behaviour of some of the complexes **4**–**11** [13][1], it was possible to estimate the free energy change associated with the intramolecular transfer of one electron from the metal–cyclopentadienyl moiety to the photoexcited anthryl group (Scheme 2). Such a free energy change, calculated for the complexes $[Rh(\eta^5\text{-AnCH}_2C_5H_4)(\eta^2\text{-}C_2H_4)_2]$ (**4**) and $[Rh(\eta^5\text{-AnCH}_2C_5H_4)(CO)_2]$ (**5**) through the combination of photophysical and electrochemical quantities, results to have a marked negative value, at 25°C, in both cases ($\Delta G° = -0.24$ eV, for complex **4**; $\Delta G° = -0.73$ eV, for complex **5**), thus indicating that the process outlined in Scheme 2 is thermodynamically favourable [13b].

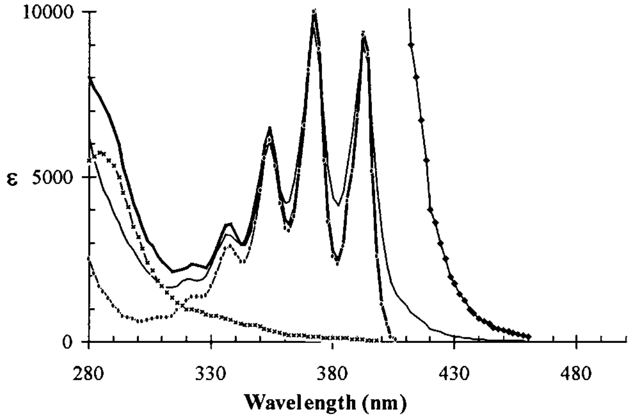


Fig. 6. Comparison of the sum (bold solid line) of the UV–vis spectra of 9-methylanthracene (dots and dashes) and $[Rh(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_2H_4)_2]$ (crosses) with the spectrum of $[Rh(\eta^5\text{-AnCH}_2C_5H_4)(\eta^2\text{-}C_2H_4)_2]$ (**4**) (solid line); (diamonds) amplification (× 10) of the tail of the spectrum of **4**.

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[1] Free energy changes were calculated through the equation:

$$\Delta G° = -E^{0-0'}_{(An)} + e\,(E°_{(RhCpL2+/RhCpL2)} - E°_{(An/An-)}) - \Delta G_S$$

where $E^{0-0'}_{(An)} = 3.2$ eV is the absorption energy of the anthryl group as determined through the UV spectra of the complexes **4** and **5**; $E°_{(RhCpL2+/RhCpL2)}$ and $E°_{(An/An-)}$ are the standard reduction potentials for the rhodium(I) moiety and the anthryl group, respectively, as they were determined through the voltammetric study of **4** and **5** in THF, and have the following figures:

$E°_{(RhCpL2+/RhCpL2)} = +0.85$ V and $E°_{(An/An-)} = -1.89$ V, in the case of **4**

$E°_{(RhCpL2+/RhCpL2)} = +1.00$ V and $E°_{(An/An-)} = 1.94$ V, in the case of **5**

finally, ΔG_S is a corrective term which accounts for the electrostatic free energy change occurring as a consequence of the electron transfer as well as for the passage from THF, solvent in which the electroctochemical measurements were performed, to benzene, solvent in which were carried out the photophysical measurements.

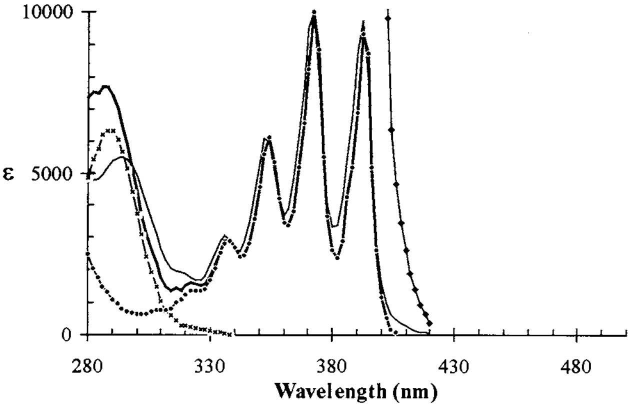


Fig. 7. Comparison of the sum (bold solid line) of the UV–vis spectra of 9-methylanthracene (dots and dashes) and $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ (crosses) with the spectrum of $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(CO)_2]$ (**5**) (solid line); (diamonds) amplification (× 10) of the tail of the spectrum of **5**.

Furthermore, work is still in progress with the aim to clarify further the complex phenomenology associated with the photophysical properties of the metal derivatives reported in this paper.

4. Experimental details

4.1. General

The reactions and manipulations of organometallics were carried out under dinitrogen or argon using standard techniques. All solvents were dried and distilled prior to use following standard procedures. Microanalyses were performed by the Laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa. Melting or decomposition points were determined by a MEL-TEMP II (Aldrich) apparatus and are not corrected. ^{1}H-NMR spectra were run at 200 MHz on a Varian Gemini 200 instrument. IR spectra were obtained by a FTIR Perkin–Elmer 1750 spectrometer. Electron ionisation mass spectra (EI MS) were obtained with a VG Analytical 7070E apparatus.

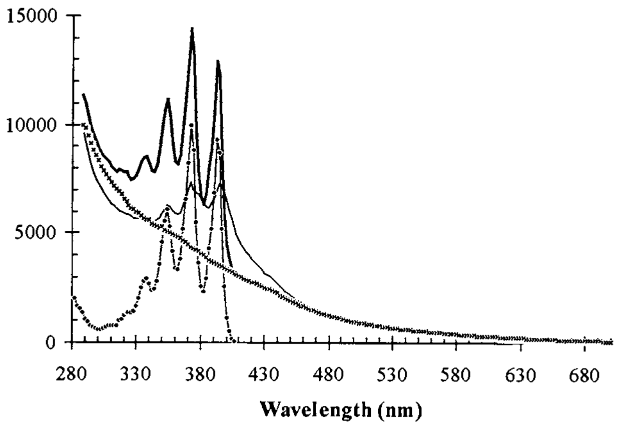


Fig. 8. Comparison of the sum (bold solid line) of the UV–vis spectra of 9-methylanthracene (dots and dashes) and $[Rh(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ (crosses) with the spectrum of $[Rh(\eta^5\text{-}AnCH_2C_5H_4)(PPh_3)_2]$ (**6**) (solid line).

Table 7
Fluorescence emission spectra data for 9-methylanthracene (**MeAn**), 9-anthrylmtehylcyclopentadiene (AnMeCPD) **1**, and complexes **4**–**11** [a]

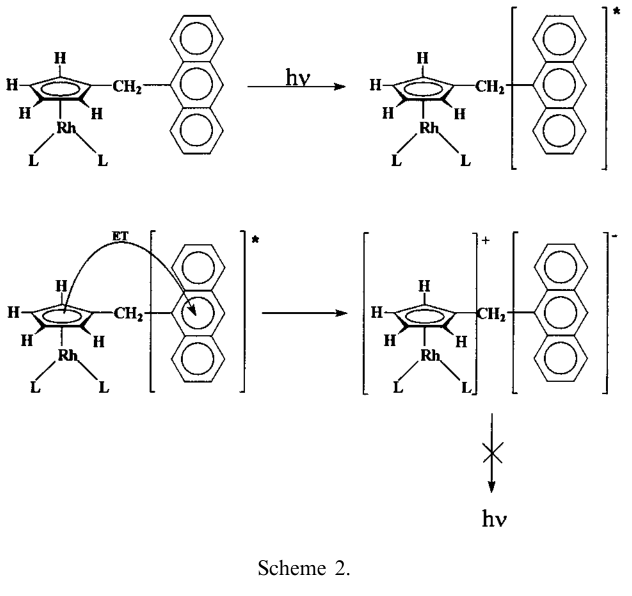
Compound	λ_{max}	I_{max}/I_{365}	I_{rel} [b]	Q (%) [c]
MeAn	392	12.14	100.0	0.0
AnMeCPD **1**	392	11.55	93.1	6.9
4	392	0.05	0.4	99.6
5	390	0.12	1.0	99.0
6	394	0.31	2.5	97.5
7 [c]	392	1.06	8.7	91.3
8	393	0.40	3.3	96.7
9	393	0.61	5.0	95.0
10a	392	0.29	2.4	97.6
10b	392	0.63	5.2	94.8
11a	394	0.34	2.8	97.2
11b	393	0.15	1.2	98.8

[a] Wavelength is given in nm.

[b] The emission intensity of 9-methylanthracene (**MeAn**) was taken as reference, i.e. 100.

[c] The sample contained a few percent of 9-anthrylmethylcyclopentadiene **1**.

9-bromomethylanthracene [14], cyclopentadienylsodium [7], di-μ-chlorotetrakis(carbonyl)dirhodium(I) [15], di-μ-chlorotetrakis(η^2-ethylene)dirhodium(I) [16], chlorotris(triphenylphosphine)rhodium(I) [17], di-μ-chloro-tetrakis(η^2-cyclooctene)dirhodium(I) [18], di-μ-chlorobis(η^4-cycloocta-1,5-diene)dirhodium(I) [19], di-μ-chlorobis(η^4-norbornadiene)dirhodium(I) [20], di-μ-chlorotetrakis(η^2-cyclooctene)diiridium(I) [21], and di-μ-chlorobis(η^4-cycloocta-1,5-diene)diiridium(I) [19], (η^5-cyclopentadienyl)bis(η^2-ethylene)rhodium(I) [22] and (η^5-cyclopentadienyl)dicarbonylrhodium(I) [9] were prepared as reported. Thallium(I) ethoxide (Aldrich),



Scheme 2.

triphenylphosphine (Aldrich), 9-methylanthracene (Aldrich), 1,5-cyclooctadiene (Aldrich), cyclooctene (Aldrich), ethylene (Matheson Gas Products), carbon monoxide (Matheson Gas Products) and 9-chloromethylanthracene (Aldrich) were used as received. Dicyclopentadiene (Fluka) was cracked immediately prior to use.

4.2. X-ray diffraction analysis

Single crystals of [Rh(η^5-AnCH$_2$C$_5$H$_4$)(η^2-C$_2$H$_4$)$_2$] (**4**) suitable for X-ray analysis were obtained by slowly cooling a saturated toluene/pentane solution of such a compound. The crystals were great red–orange prisms. A splinter, obtained by cutting one of them in air, was sealed in a capillary under dinitrogen atmosphere. The measurements were done on a Siemens P4 four circles diffractometer, equipped with graphite monochromatised Mo–K$_\alpha$ radiation. The crystal parameters are listed in Table 8.

Data collection was performed by following the conditions displayed in Table 8 and the redundant set of data was corrected for Lorentz, polarisation and absorption effects by using the ψ-scan method [23], then it was merged. The structure solution was obtained by means of the standard direct methods contained in the TREF procedure of the SHELXTL program [24] and was completed by the usual Fourier transform method. The hydrogen atoms were in part found in the difference Fourier maps and in part introduced in calculated positions. Those of ethylene ligands were kept fixed in the found positions during the next refinement. Some statistical parameters obtained in the final refinement cycles are listed in Table 8.

Single crystals of [Rh(η^5-AnCH$_2$C$_5$H$_4$)(CO)$_2$] (**5**) suitable for X-ray analysis were obtained by slowly cooling a saturated toluene/pentane solution of such a compound. The crystals were well shaped yellow prisms. One of them was selected in air and sealed in a capillary under dinitrogen atmosphere. The measurements were done on a Siemens P4 four circles diffractometer, equipped with graphite monochromatised Mo–K$_\alpha$ radiation. The lattice parameters are listed in the third column of Table 8. Data collection was performed by following the conditions displayed in the same column and the redundant set of data was corrected for Lorentz, polarisation and absorption effects by using the ψ-scan method [23], then it was merged. The structure solution was obtained by means of the standard direct methods contained in the TREF procedure of the SHELXTL program [24] and was completed by the usual Fourier transform method. The hydrogen atoms were in part found in the difference Fourier maps and in part introduced in calculated positions. Some statistical parameters obtained in the final refinement cycles are listed in Table 8.

Table 8
Crystal data and structure refinement for complexes **4** and **5**

Compound	**4**	**5**
Empirical formula	$C_{24}H_{23}Rh$	$C_{22}H_{15}O_2Rh$
Formula weight	414.33	414.25
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	11.112(1)	12.232(1)
b (Å)	12.065(1)	13.463(1)
c (Å)	15.982(2)	13.488(1)
α (°)	99.83(1)	61.25(1)
β (°)	107.86(1)	68.51(1)
γ (°)	107.22(1)	67.45(1)
Volume (Å^3)	1865.6(3)	1752.5(2)
Z	4	4
D_{calc} (Mg m^{-3})	1.475	1.570
Absorption coefficient (mm^{-1})	0.918	0.985
F(000)	848	832
Crystal size (mm^3)	0.64 × 0.12 × 0.12	0.48 × 0.38 × 0.26
θ Range for data collection (°)	2.01–21.24	2.02–25.00
Index ranges	$-1 \leq h \leq 11$, $-11 \leq k \leq 11$, $-16 \leq l \leq 15$	$-1 \leq h \leq 14$, $-13 \leq k \leq 14$, $-15 \leq l \leq 16$
Reflections collected	4910	6862
Independent reflections	4098 [$R_{int} = 0.0286$]	5942 [$R_{int} = 0.0132$]
Completeness to $\theta = 21.24°$ (%)	98.8	96.5
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4098/0/451	5942/0/451
Goodness-of-fit [a] on F^2	1.002	1.015
Final R indices [a] [$I > 2\sigma(I)$]	$R_1 = 0.0414$, $wR_2 = 0.0953$	$R_1 = 0.0343$, $wR_2 = 0.0795$
R indices [a] (all data)	$R_1 = 0.0727$, $wR_2 = 0.1113$	$R_1 = 0.0487$, $wR_2 = 0.0862$
A, B (w) [a]	0.0645, 0.00	0.0460, 0.60
Largest difference peak and hole (e Å^{-3})	1.151 and −0.904	0.564 and −0.438

[a] Goodness-of-fit $= [\Sigma[w(F_o^2 - F_c^2)^2]/(N-P)]^{1/2}$, where N, P are the numbers of observations and parameters, respectively, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ]$ where $Q = [\max(F_o^2, 0) + 2F_c^2]/3$.

4.3. Spectroscopic measurements

The absorption spectra were measured at r.t. in benzene solutions using a Cary 14 spectrophotometer with a resolution of 1 nm. The fluorescence properties at r.t. were measured on an ISS-GREG 200 multi-phase fluorimeter with resolution of 2–4 nm in dinitrogen-saturated solutions at an absorbance of 0.1 at the excitation wavelength, i.e. ca. 365 nm. The emission spectra were not corrected for the instrumental response since they were all similar. The relative values of the fluorescence quantum yields were therefore obtained by comparison with the emission intensity of 9-methylanthracene which has a quantum yield of 0.35 and a lifetime 4.6 ns in cyclohexane [25]. The solvent Rayleigh scattering was used as an internal reference. All data have been normalised to the same absorbance at the excitation wavelength. The relative fluorescence quantum yields observed in most samples (0.01–0.05) indicate fluorescence lifetimes of about 40–200 ps which can be obtained with a minimum of accuracy only if molecular rotation is accounted for, i.e. by the use of a polariser which implies some intensity loss. Consequently, this imposes extremely long measurement periods and the resulting measurements are of limited precision. In the case of too high fluorescence yields (typically of the order of 10%), the fundamental problem is to discriminate between the presence of fluorescent impurities and a high intrinsic emission intensity so that fluorescence lifetime estimate can be sufficient. Preliminary measurements were thus carried out at 40 MHz. In all cases, the lifetime values, obtained by phase and modulation, turned out to be a few ns. Such a long lifetime suggests the presence of a fluorescent impurity which, together with a non negligible scattering component, can yield such an apparent lifetime. Indeed, high resolution TLC analysis of complexes **4**–**11**, performed on Aluminium Oxide 60 (Merck) by using a benzene–pentane mixture (3/7, v/v) as eluant, revealed the presence of very small amounts of 9-anthrylmethylcyclopentadiene **3**. On this basis, further purification of the metallorganic compounds was successfully performed only by extracting the samples with absolute ethanol. Compound **3** being more soluble in such a solvent than complexes **4**–**11** were; the treatment allowed a marked reduction of the impurity content. Consequently, the fluorescence quenching, which in some cases had resulted in relatively lower values, became drastically higher after the purification of the sample by ethanol extraction. The following examples illustrates the observed effects:

Complex	Before purification by ethanol		After purification by ethanol	
	Fluorescence	Quenching	Fluorescence	Quenching
4	2.9	97.1	0.4	99.6
11b	10.1	89.9	1.2	98.8

*4.4. Preparation of 9-anthrylmethylcyclopentadiene **1***

9-Bromomethylanthracene (14.3 g, 53 mmol) was added to a solution of cyclopentadienylsodium (6.08 g, 69.1 mmol) in tetrahydrofuran (180 ml) at 0°C. The resulting mixture was stirred at this temperature for 1.5 h and then filtered. A yellow solution was obtained which was kept to dryness under reduced pressure, at 0°C. The residue was subdivided into 0.5 g portions and each portion was purified by column (internal diameter, 10 mm; length, 300 mm) chromatography on silica gel 60 (230–400 mesh) (Merck), using a 1/1 (v/v) chloroform/hexane mixture as eluant. The first dark yellow band which eluted was collected and kept to dryness under vacuum. The overall yield was: 11 g of 9-anthrylmethylcyclopentadiene (75%) as a dark yellow microcrystalline solid. Found: C, 93.68; H, 6.20. Anal. Calc. for $C_{20}H_{16}$: C, 93.75; H, 6.25%. EI MS, *m*/*z* (relative intensity %): 256 $[M]^+$ (31), 215 (10), 191 (100), 165 (19), 83 (50), 47 (22).

*4.5. Preparation of 9-anthrylmethylcyclopentadienylthallium(I) (**3**)*

A mixture of 9-anthrylmethylcyclopentadiene (2.6 g, 10.1 mmol), thallium(I) ethoxide (975 ml, 13.7 mmol), and absolute ethanol (180 ml) was stirred for 3 h, at r.t. An ochre–yellow solid precipitated which was separated by decanting off the surnatant solution, washed with absolute ethanol (2 × 60 ml), then with dry diethyl ether (2 × 60 ml) and with pentane (2 × 60 ml), and, finally dried under vacuum. A 2.54 g sample of the title compound (54% yield) as a ochre–yellow microcrystalline solid, was obtained. Found: C, 52.00; H, 3.38. Anal. Calc. for $C_{20}H_{15}Tl$: C, 52.13; H, 3.47%.

*4.6. Preparation of (η^5-9-anthrylmethylcyclopentadienyl)bis(η^2-ethylene) rhodium(I) (**4**)*

A mixture of 9-anthrylmethylcyclopentadienylthallium(I) (0.75 g, 1.63 mmol), di-μ-chlorotetrakis(η^2-ethylene)dirhodium(I) (0.32 g, 0.81 mmol), and anhydrous benzene (60 ml) was stirred for 100 min, at r.t., and then filtered. An orange solution was obtained which was kept to dryness under reduced pressure. The residue was dissolved in benzene (2 ml) and the resulting solution was passed through a column (internal diameter, 10 mm; length, 30 mm) of alumina (Aluminium oxide 90, 70–230 mesh, Merck), using benzene as eluant. From the first orange–yellow band which eluted, 0.5 g of the title compound (74% yield), as a yellow microcrystalline solid, was obtained. Found: C, 69.50; H, 5.50. Anal. Calc. for $C_{24}H_{23}Rh$: C, 69.56; H, 5.56%. EI MS, *m*/*z* (relative intensity %): 414 $[M]^+$ (11), 386 $[M-C_2H_4]^+$ (17), 358 $[M-2\ C_2H_4]^+$ (100), 253 (15).

*4.7. Preparation of (η^5-9-anthrylmethylcyclopentadienyl)dicarbonyl-rhodium(I) (**5**)*

A mixture of 9-anthrylmethylcyclopentadienylthallium(I) (0.71 g, 1.54 mmol), di-μ-chlorotetrakis(carbonyl)dirhodium(I) (0.30 g, 0.77 mmol), and benzene (60 ml) was stirred at r.t. for 2 h and then filtered. The solution was kept to dryness under reduced pressure. The residue was dissolved in benzene (2 ml) and purified by column (internal diameter, 10 mm; length, 30 mm) chromatography on alumina (Aluminium oxide 90, 70–230 mesh, Merck), using benzene as eluant. From the first orange–yellow band which eluted, 0.57 g of the title compound (89% yield), as an orange–yellow microcrystalline solid, was obtained. Found: C, 63.70; H, 3.57. Anal. Calc. for $C_{22}H_{15}O_2Rh$: C, 63.77; H, 3.62%. EI MS, *m*/*z* (relative intensity %): 414 $[M]^+$ (17), 386 $[M-CO]^+$ (36), 358 $[M-2\ CO]^+$ (100), 253 (21), 191 (53), 103 (11). IR (Nujol, cm^{-1}): 2953(s), 2919(s), 2854(s), 2042(s), 1979(s), 1461(s), 1377(s), 722(w).

4.8. Preparation of (η⁵-9-anthrylmethylcyclopentadienyl)bis(triphenyl phosphine)rhodium(I) ***(6)***

A mixture of 9-anthrylmethylcyclopentadienylthallium(I) (0.11 g, 0.24 mmol), chlorotris(triphenylphosphine)rhodium(I) (0.22 g, 0.24 mmol), and benzene (20 ml) was stirred at r.t. for 5 h. Afterwards, the mixture was filtered and the resulting solution was kept to dryness under reduced pressure. The residue was dissolved in benzene (2 ml) and purified by column (internal diameter, 10 mm; length, 30 mm) chromatography on alumina (Aluminium oxide 90, 70–230 mesh, Merck), using benzene as eluant. From the first orange band which eluted, 0.16 g of the title compound (77% yield) was obtained as a red–brown microcrystalline solid. Found: C, 76.00; H, 4.98. Anal. Calc. for $C_{56}H_{45}P_2Rh$: C, 76.19; H, 5.10%.

4.9. Preparation of (η⁵-9-anthrylmethylcyclopentadienyl)(η²-ethylene) (triphenylphosphine)rhodium(I) ***(7)***

A mixture of (η^5-9-anthrylmethylcyclopentadienyl)-bis(η^2-ethylene)rhodium(I) (0.11 g, 0.27 mmol), triphenylphosphine (0.07 g, 0.27 mmol) and *p*-xylene (5 ml) was stirred at 130°C for 3.5 h and then filtered. The solution was kept to dryness under reduced pressure. The residue was dissolved in benzene (2 ml) and purified by column (internal diameter, 10 mm; length, 30 mm) chromatography on alumina (Aluminium oxide 90, 70–230 mesh, Merck), using benzene as eluant. From the first orange band which eluted, 0.14 g of the title compound (80% yield) was obtained as a red–brown microcrystalline solid. Found: C, 74.00; H, 5.18. Anal. Calc. for $C_{40}H_{34}PRh$: C, 74.07; H, 5.25%.

4.10. Preparation of (η⁵-9-anthrylmethylcyclopentadienyl)(carbonyl) (triphenylphosphine)rhodium(I) ***(8)***

A mixture of (η^5-9-anthrylmethylcyclopentadienyl)dicarbonyl-rhodium(I) (0.1 g, 0.24 mmol), triphenylphosphine (0.06 g, 0.24 mmol), and benzene (16 ml) was refluxed for 5 h, filtered and then kept to dryness under reduced pressure. The residue was dissolved in benzene (2 ml) and purified by column (internal diameter, 10 mm; length, 30 mm) chromatography on alumina (Aluminium oxide 90, 70–230 mesh, Merck), using a 1/1 (v/v) benzene/hexane mixture as eluant. From the first orange band which eluted, 0.12 g of the title compound (74% yield) was obtained as an orange–red microcrystalline solid. Found: C, 72.18; H, 4.59. Anal. Calc. for $C_{39}H_{30}OPRh$: C, 72.22; H, 4.63%. IR (Nujol, cm^{-1}): 2953(s), 2921(s), 2855(vw), 1951(m), 1461(s), 1377(s), 723(w).

4.11. Preparation of (η⁵-9-anthrylmethylcyclopentadienyl)(η⁴-norborna-diene)rhodium(I) ***(9)***

A mixture of 9-anthrylmethylcyclopentadienylthallium(I) (0.16 g, 0.34 mmol), di-μ-chlorobis(η^4-norbornadiene)dirhodium(I) (0.08 g, 0.17 mmol), and benzene (30 ml) was stirred at r.t. for 3 h, filtered, and then kept to dryness under reduced pressure. A yellow residue was obtained which was dissolved in benzene (2 ml) and purified by column (internal diameter, 10 mm; length, 30 mm) chromatography on alumina (Aluminium oxide 90, 70–230 mesh, Merck), using benzene as eluant. From the first orange band which eluted, 0.12 g of the title compound (76% yield) was obtained as a yellow microcrystalline solid. Found: C, 69.70; H, 5.06. Anal. Calc. for $C_{27}H_{23}Rh$: C, 72.00; H, 5.11%. EI MS, *m*/*z* (relative intensity %): 450 $[M]^+$ (45), 358 $[M-C_7H_8]^+$ (100), 252 (23), 191 (16), 103 (13), 78 (34).

4.12. Preparation of (η⁵-9-anthrylmethylcyclopentadienyl)bis(η²-cyclo-octene)rhodium(I) ***(10a)***

A mixture of 9-anthrylmethylcyclopentadienylthallium(I) (0.35 g, 0.76 mmol), di-μ-chlorotetrakis(η^2-cyclooctene)dirhodium(I) (0.27 g, 0.38 mmol), and benzene (40 ml) was stirred at r.t. for 2.5 h, filtered, and then kept to dryness under reduced pressure. A yellow residue was obtained which was dissolved in benzene (2 ml) and purified by column (internal diameter, 10 mm; length, 30 mm) chromatography on alumina (Aluminium oxide 90, 70–230 mesh, Merck), using benzene as eluant. From the first orange band which eluted, 0.34 g of the title compound (78% yield) was obtained as an orange microcrystalline solid. Found: C, 74.70; H, 7.40. Anal. Calc. for $C_{36}H_{43}Rh$: C, 74.74; H, 7.44%. EI MS, *m*/*z* (relative intensity %): 578 $[M]^+$ (6), 503 (20), 429 (28), 192 (11), 110 (100).

4.13. Preparation of (η⁵-9-anthrylmethylcyclopentadienyl)bis(η²-cyclo-octene)iridium(I) ***(10b)***

A mixture of 9-anthrylmethylcyclopentadienylthallium(I) (0.35 g, 0.77 mmol), di-μ-chlorotetrakis(η^2-cyclooctene)diiridium(I) (0.35 g, 0.38 mmol), and benzene (30 ml) was stirred at r.t. for 2 h, filtered, and then kept to dryness under reduced pressure. A yellow residue was obtained which was dissolved in benzene (2 ml) and purified by column (internal diameter, 10 mm; length, 30 mm) chromatography on alumina (Aluminium oxide 90, 70–230 mesh, Merck), using benzene as eluant. From the first orange band which eluted, 0.35 g of the title compound (68% yield) was obtained as an orange–red microcrystalline solid. Found: C, 64.71; H, 6.40. Anal. Calc. for $C_{36}H_{43}Ir$: C, 64.75; H, 6.44%. EI MS, *m*/*z* (relative intensity %): 668 $[M]^+$ (26), 558 $[M-C_8H_{14}]^+$ (52), 448 $[M-2C_8H_{14}]^+$ (100), 367 (40), 191 (39), 67 (93).

4.14. Preparation of (η^5-9-anthrylmethylcyclopentadienyl)(η^4-cycloocta-1,5-diene)rhodium(I) (**11a**)

A mixture of 9-anthrylmethylcyclopentadienylthallium(I) (0.25 g, 0.55 mmol), di-μ-chlorobis(η^4-cycloocta-1,5-diene)dirhodium(I) (0.14 g, 0.27 mmol), and benzene (30 ml) was stirred at r.t. for 2.5 h, filtered, and then kept to dryness under reduced pressure. A yellow residue was obtained which was dissolved in benzene (2 ml) and purified by column (internal diameter, 10 mm; length, 30 mm) chromatography on alumina (Aluminium oxide 90, 70–230 mesh, Merck), using benzene as eluant. From the first orange band which eluted, 0.22 g of the title compound (85% yield) was obtained as an orange–red microcrystalline solid. Found: C, 72.06; H, 5.72. Anal. Calc. for $C_{28}H_{27}Rh$: C, 72.10; H, 5.79%. EI MS, *m*/*z* (relative intensity %): 466 $[M]^+$ (58), 358 $[M-C_8H_{12}]^+$ (100), 253 (10), 191 (12), 78 (86), 51 (15).

4.15. Preparation of (η^5-9-anthrylmethylcyclopentadienyl)(η^4-cycloocta-1,5-diene)iridium(I) (**11b**)

A mixture of 9-anthrylmethylcyclopentadienylthallium(I) (0.17 g, 0.36 mmol), di-μ-chlorobis(η^4-cycloocta-1,5-diene)diiridium(I) (0.12 g, 0.18 mmol), and benzene (40 ml) was stirred at r.t. for 2.5 h, filtered, and then kept to dryness under reduced pressure. A yellow residue was obtained which was dissolved in benzene (2 ml) and purified by column (internal diameter, 10 mm; length, 30 mm) chromatography on alumina (Aluminium oxide 90, 70–230 mesh, Merck), using benzene as eluant. From the first orange band which eluted, 0.13 g of the title compound (64% yield) was obtained as an orange–red microcrystalline solid. Found: C, 60.50; H, 4.78. Anal. Calc. for $C_{28}H_{27}Ir$: C, 60.52; H, 4.85%. EI MS, *m*/*z* (relative intensity %): 556 $[M]^+$ (100), 448 $[M-C_8H_{12}]^+$ (26), 363 (13), 84 (12).

5. Supplementary material

A full list of atomic parameters and details about the data collection and structure refinement in the form of CIF file have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 124876 and 124877.

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