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Syntheses and crystal structures of ferrocene substituted indenyl complexes

Petra Escarpa Gaede *

TU Berlin Institut für Anorganische und Analytische Chemie, Straße des 17. Juni 135, 10623 Berlin, Germany

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Dedicated to Professor Dr. Herbert Schumann on the occasion of his 65th birthday

Abstract

From the reaction of $FeCl_2$ with the ligand $[C_5H_4CMe_2C_9H_7]^-$, where a cyclopentadienyl and an indene unit are linked by a methylene like bridge, the new complex $[\{\eta^5\text{-}C_5H_4CMe_2(C_9H_7)\}_2Fe]$ (**1**) was obtained. This compound was deprotonated and reacted with $[(cod)RhCl]_2$ (cod: 1,5-cyclooctadiene) to give the two new heterobimetallic complexes $[(\eta^5\text{-}C_5H_4CMe_2C_9H_7)Fe(\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_9H_6)Rh(cod)]$ (**2**) and $[Fe\{(\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_9H_6)Rh(cod)\}_2]$ (**3**). The related species $[(\eta^5\text{-}C_5H_4CMe_2C_9H_7)Fe(\eta^5\text{-}Cp)]$ (**4**) and $[CpFe(\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_9H_6)Rh(cod)]$ (**5**) were synthesized by the reaction of lithioferrocene with dimethylbenzofulvene and $[(cod)RhCl]_2$ in the latter case. $[(\eta^5\text{-}C_9H_6CMe_2C_4H_9)Rh(cod)]$ (**6**) and $[(\eta^5\text{-}C_9H_6CCH_2Me)Rh(cod)]$ (**7**) are side products in the last reaction. All new compounds were characterized by MS and NMR. Single crystals of **4**, **5** and $[(\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_9H_6)Rh_2(cod)_2]$ (**8**) were characterized by X-ray analysis. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ferrocene; Heterobimetallic complexes; X-ray crystal analysis; Indenes

1. Introduction

Bimetallic compounds have attracted a great deal of attention in recent years based on the idea that the concerted effects of two metals in close proximity should result in novel reactions useful in stoichiometric synthesis and in catalysis [1]. The assumption or potential synthetic use of such dinuclear species is a bifunctionalised ligand which prevents formation of monometalated units. With regard to this assumption bridged cyclopentadienyl ligands have been shown to be particularly successful systems because of their strong binding to a large number of metals in different oxidation states [2]. Substitution of one cyclopentadienyl by an indenyl gives an additional electronic and structural effect in these bimetallic compounds. The ligand 2,2-cyclopentadienyl-indenyl-propane has been employed by Green et al. [3], Alt [4] and some other groups [5] in the synthesis of various metal complexes, especially of Group 4 and Group 6. We previously reported on some compounds with this ligand mainly from Group 9 metals [6] and in this paper we extend the chemistry of this bridging ligand with ferrocene derivatives.

2. Results and discussion

The ferrocene derivative $[\{\eta^5\text{-}C_5H_4CMe_2(C_9H_7)\}_2Fe]$ (**1**) can be obtained by the reaction of the monodeprotonated ligand $Li[C_5H_4CMe_2C_9H_7]$ with $FeCl_2$ in good yield. Depending on the batch of the ligand, different ratios of the resulting isomers are formed (Fig. 1). The isomers are caused by the two possible positions of the double bond in the indenyl ring. If the double bond is in the 2-position (B) a chiral center arises resulting in two diastereomers for the BB isomer. The NMR spectra show mainly two sets of signals for the isomeric forms A and B of the ligand. Only the signals of the methyl groups are separated for all isomers.

The indene rings of **1** can be deprotonated with one or two equivalents of butyllithium and react further

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* Tel.: +49-30-31426255; fax: +49-30-31422168.

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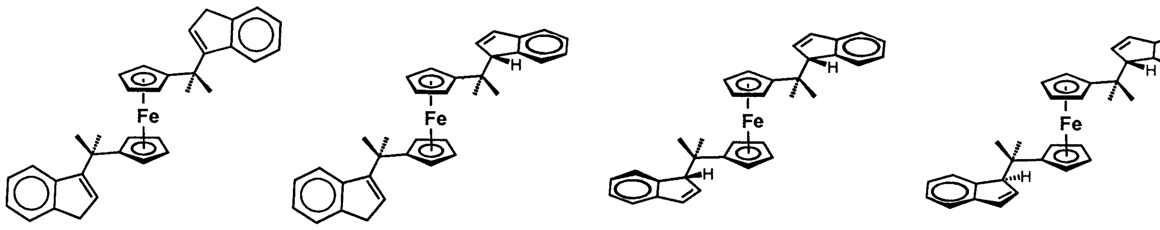
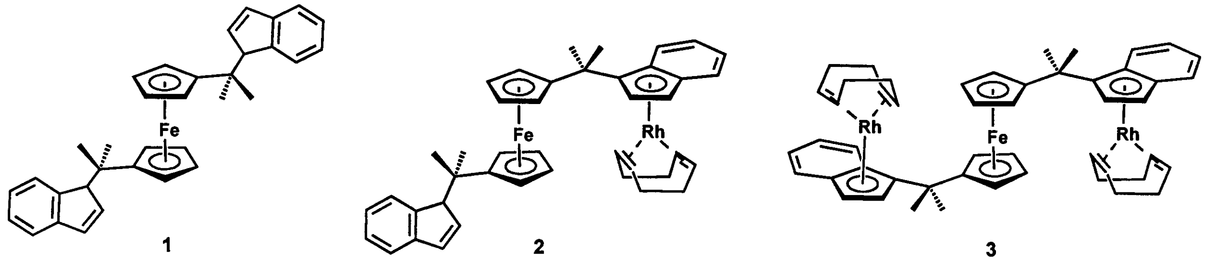


Isomer AA Isomer AB (R,S) Isomer BB (RR, SS) Isomer BB (RS)

Fig. 1. Isomers of complex **1**.



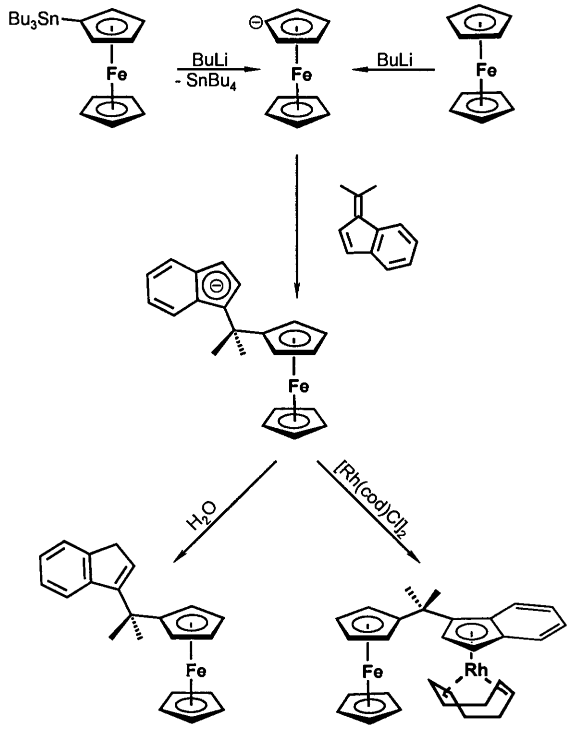
1 **2** **3**

Fig. 2. Structures of **1**, **2** and **3**.

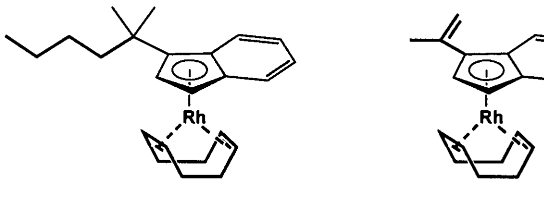
with a metal salt, in our case with $[(cod)RhCl]_2$, to give the compounds $[(\eta^5\text{-}C_5H_4CMe_2C_9H_7)Fe(\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_9H_6)Rh(cod)]$ (**2**) or $[Fe\{(\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_9H_6)Rh(cod)\}_2]$ (**3**), respectively (Fig. 2). Whereas the double deprotonation producing **3** proceeds quite well, the abstraction of only one proton gives a mixture of unreacted **1**, **2** and **3**, which are difficult to separate by chromatography.

To avoid the unselective deprotonation of the indenyl rings we decided to synthesize the ferrocene species $[(\eta^5\text{-}C_5H_4CMe_2C_9H_7)Fe(\eta^5\text{-}Cp)]$ (**4**) with only one linked ligand (Scheme 1).

This can be achieved by the reaction of lithiated ferrocene with dimethylbenzofulvene and subsequent quenching with water. The synthesis of a related complex without methyl groups at the bridging carbon atom starting from ferrocene carboxaldehyde and lithium indenyl followed by reduction with $LiAlH_4$ has been described by Chung et. al. [7]. If $[(cod)RhCl]_2$ is added to the reaction mixture instead, the dinuclear complex $[CpFe(\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_9H_6)Rh(cod)]$ (**5**) results. For both reactions large amounts of ferrocene are found in the reaction mixture. It can be shown that the ferrocene does not originate from unconsumed starting material using $CpFeC_5H_4Sn(Bu)_3$ instead of Cp_2Fe in the reaction with BuLi. The former reacts quantitatively to give monolithiated ferrocene and Bu_4Sn whereas in the direct synthesis of ferrocene with BuLi there is always some unreacted starting material remaining in the reaction mixture. But in the further course of the tin route a lot of ferrocene is formed, probably by a proton exchange reaction between one of the methyl groups of the dimethylbenzofulvene and the lithioferrocene. It is known that the exocyclic double bond of fulvenes can react with lithium alkyls in different ways: nucleophilic addition of the alkyl metal compound [8a], reduction [8b], reductive coupling [8c] or deprotonation of the 6-methyl group [8d]. The rate of the deprotonation reaction does not depend on the



Scheme 1.



6 **7**

Fig. 3. Structures of the side products **6** and **7**.

basicity but on the nucleophilicity of the organolithium alkyl. Due to ferrocene being a bad nucleophil, the proton transfer reaction is favored and the two (cod)Rh-indenyl species [(η^5-$C_9H_6CMe_2C_4H_9$)Rh(cod)] (**6**) and [(η^5-$C_9H_6CCH_2Me$)Rh(cod)] (**7**) (Fig. 3) result as side products in much higher yields than the desired compound **5**.

2.1. *Molecular structures of [(η^5-$C_5H_4CMe_2C_9H_7$)Fe(η^5-Cp)] (**4**), [CpFe(η^5-$C_5H_4CMe_2$-η^5-C_9H_6)Rh(cod)] (**5**), and [(η^5-$C_5H_4CMe_2$-η^5-C_9H_6)$Rh_2(cod)_2$] (**8**)*

Complex **4** crystallizing in the triclinic space group $P\bar{1}$ (Table 1) with the indenyl plane being nearly orthogonal (89.26(12)°) to the C_5H_4-ring, shows the same configuration as all other previously known structurally characterized compounds with this ligand [4,6]. The bond lengths C1–C9, C6–C7, C7–C8 and C8–C9 are in ranges typical for comparable single and double bonds, respectively, indicating for the indenyl the more thermodynamically stable isomeric form. The iron atom is η^5-coordinated to both cyclopentadienyl rings with distances ranging from 2.025(4) (C22) to 2.059(3) Å (C13). Both five-membered rings are nearly coplanar enclosing an angle of only 3.2°. The iron atom is located in the middle between both ring planes with distances of 1.644 and 1.646 Å, respectively. The rings are arranged exactly eclipsed to each other, so that the indenyl plane forms a pseudo, non-crystallographic mirror plane including the atoms C10, C13 and the metal atom. The bridging atom C10 lies in the plane of the indenyl ring but is bent out of the cyclopentadienyl plane with an angle of 6.5°. The molecular structure is shown in Fig. 4.

Complexes **5** and **8** crystallize in the space groups $P2_1/n$ and $P\bar{1}$, respectively (Table 1). The synthesis of [(η^5-$C_5H_4CMe_2$-η^5-C_9H_6)$Rh_2(cod)_2$] (**8**) achieved by adding the double deprotonated ligand $[C_5H_4CMe_2C_9H_6]^{2-}$ to $[(cod)RhCl]_2$ and its spectroscopic characterization is described previously [6]. We were now able to get single crystals of it and to compare the structure with that of the related compound **5**, carrying instead of the CpFe unit, only a second Rh(cod) fragment.

Table 1

Crystal and data collection parameters for **4**, **5**, and **8**

	4	**5**	**8**
Formula weight (g mol^{-1})	342.25	552.32	642.47
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a (Å)	7.3221(2)	8.8851(2)	7.081(2)
b (Å)	9.9448(3)	10.8120(2)	13.092(3)
c (Å)	12.8526(5)	24.9791(2)	14.423(3)
α (°)	81.704(2)	90	89.65(2)
β (°)	74.744(2)	93.1670(10)	82.69(2)
γ (°)	70.273(2)	90	84.16(2)
V ($Å^3$)	848.33(5)	2395.97(7)	1319.4(5)
Z	2	4	2
D_{calc} (g cm^{-3})	1.340	1.531	1.617
μ (Mo–K_α) (cm^{-1})	8.86	13.1	11.75
Theta range (°)	$2,3 \leq 2\theta \leq 54.0$	$3.26 \leq 2\theta \leq 55.0$	$2.84 \leq 2\theta \leq 54.86$
Index range (h, k, l)	$-10 \rightarrow 10$, $-13 \rightarrow 14$, $-18 \rightarrow 9$	$-12 \rightarrow 12$, $-15 \rightarrow 13$, $-29 \rightarrow 35$	$-9 \rightarrow 9$, $-16 \rightarrow 16$, $-18 \rightarrow 18$
Data	6381	17934	12022
Independent observed reflections (R_{int})	3687 (0.0452)	5494 (0.1286)	6011 (0.0397)
Independent reflections	3684	5470	6008
Parameters	296	291	318
$\Delta(\rho)$ (e·$Å^{-3}$)	0.335/−0.262	0.939/−0.758	1.006/−0.674
Goodness-of-fit	0.982	0.999	1.018
R [a]	0.0540 (0.0971) [b]	0.0600 (0.1308) [b]	0.0336 (0.0672) [b]
wR_2 [a]	0.0967 (0.1120) [b]	0.0947 (0.1150) [b]	0.0770 (0.0885) [b]

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)]^2]^{1/2}$, $[F_o > 4\alpha(F_o)]$.

[b] Based on all data.

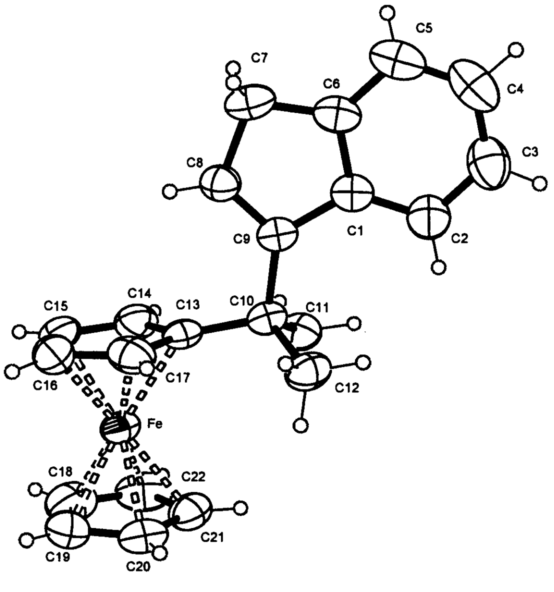


Fig. 4. Molecular structure of **4**.

2.2. Molecular structure of **5**

The conformation of the ligand is very similar to that found in the mononuclear compounds and in [(η^5:η^5-$C_5H_4CMe_2C_9H_6$)$Rh_2(C_2H_4)_4$] [6]. The cyclopentadienyl ring is nearly orthogonal to the indenyl ring, but the angle between the planes is 82.02(2)° and so slightly smaller than that in the case of the two $Rh(C_2H_4)_2$ fragments (88.06°). The ferrocenic part of the structure is very similar to that of the mononuclear compound **4**, only the twisting between the two five-membered rings has grown to 6°. But the steric influence of the larger Rh(cod) unit compared to the $Rh(C_2H_4)_2$ fragment [6] is reflected in the structure. The rhodium atom is slipped out of the five-membered ring center towards C7 (Rh–C7 2.195, Rh–C9 2.276 Å) not only by the usual indenyl effect ($\eta^5 \leftrightarrow \eta^3$) but also by a steric interaction. The methyl group C11 which is directed to the Rh(cod) side is slightly bent down towards the iron atom, reflected by the torsion angle C11–C10–C13–C17 being 9° smaller than usual in the mononuclear species **4**. The indenyl ring is folded twice, the hinge angle along the C7–C9 axis is calculated to be 8.22(54)° and the fold angle between the five-membered (C1, C6–C9) and the six-membered ring (C1–C6) to be 1.54(3)°.

Compared with the structure of **5** the conformation of the bridging ligand in **8** is totally different (Fig. 5). Apart from its coordination planes which are orthogonal (89.97°) the indenylRh(cod) unit is turned along the C10–C9 bond by around 85°. The reason for this might be the greater steric interaction of the two large Rh(cod) units with the methyl groups of the bridge. The distances of the two rhodium atoms to the five-membered ring centres differ by 0.035 Å, 1.9020 (C_5H_4) and 1.9378 Å (indenyl), respectively. A similar effect is observed for the averaged bond lengths to the (cod) ligand being around 0.03 Å longer in the case of the indenyl bound Rh. The fold angle is calculated to be 0.55(25)° and the hinge angle to be 6.03(50)°.

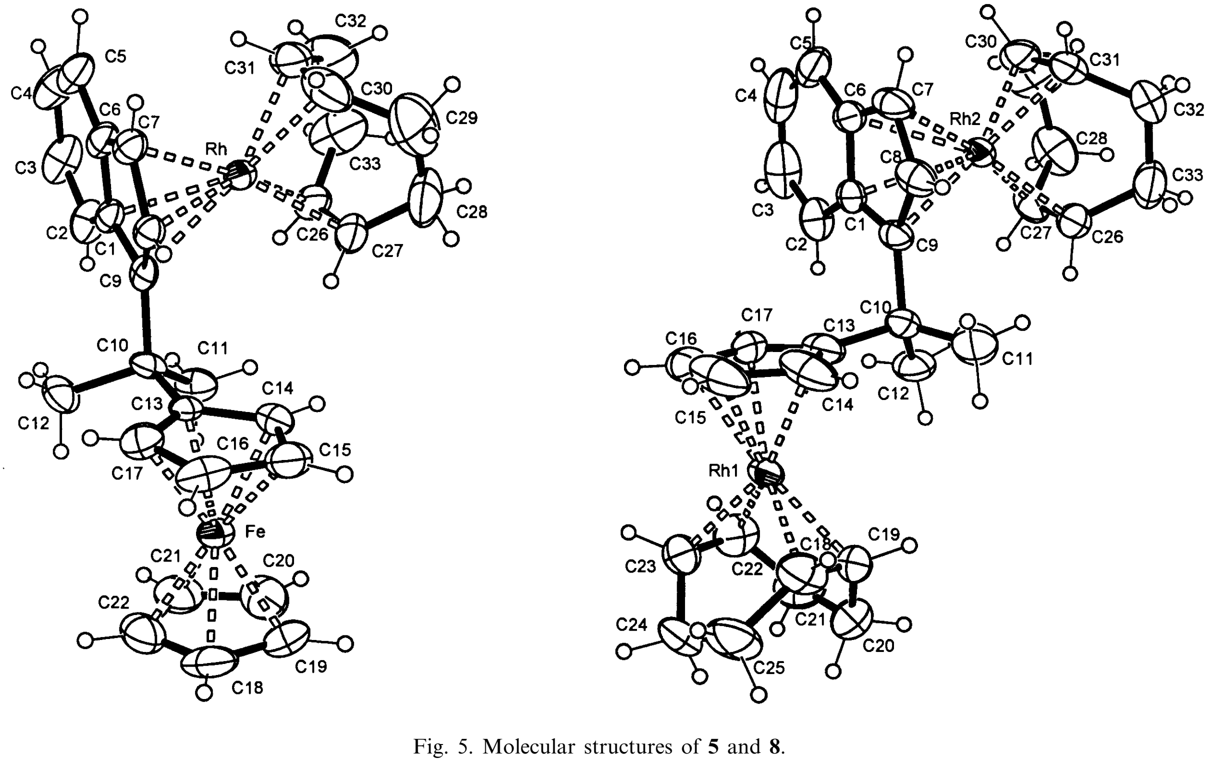


Fig. 5. Molecular structures of **5** and **8**.

Table 2
Selected bond lengths (Å) for **4**, **5**, and **8**

Bond	**4**	**5**	**8**
Fe–C(13–22)	2.035(4)	2.035(6)	
Rh(1)–C(13–17)			2.245(5)
Rh(1)–$C_{(olefine)}$			2.101(5)
Rh(2)–$C_{(olefine)}$		2.140(7)	2.129(4)
Rh(2)–C(7)		2.195(6)	2.207(4)
Rh(2)–C(8)		2.258(6)	2.247(4)
Rh(2)–C(9)		2.276(6)	2.263(3)
Rh(2)–C(1)		2.381(6)	2.368(4)
Rh(2)–C(6)		2.314(6)	2.342(4)
C(1)–C(2)	1.396(4)	1.419(7)	1.410(6)
C(1)–C(6)	1.396(4)	1.422(7)	1.429(5)
C(1)–C(9)	1.490(4)	1.476(7)	1.461(5)
C(2)–C(3)	1.391(5)	1.362(8)	1.369(6)
C(3)–C(4)	1.375(6)	1.405(9)	1.397(8)
C(4)–C(5)	1.371(6)	1.372(8)	1.362(8)
C(5)–C(6)	1.387(5)	1.413(7)	1.413(6)
C(6)–C(7)	1.499(5)	1.450(7)	1.433(6)
C(7)–C(8)	1.501(5)	1.415(7)	1.397(6)
C(8)–C(9)	1.336(4)	1.405(7)	1.415(5)
C(9)–C(10)	1.527(4)	1.536(7)	1.540(5)
C(10)–C(11)	1.537(4)	1.536(7)	1.529(6)
C(10)–C(12)	1.549(4)	1.539(7)	1.522(6)
C(10)–C(13)	1.520(4)	1.522(7)	1.538(5)
C(Cp)–C(Cp)	1.409(6)	1.406(7)	1.405(7)
C(18)–C(19)			1.387(6)
C(22)–C(23)			1.407(6)
C(26)–C(27)		1.389(8)	1.393(6)
C(30)–C(31)		1.404(9)	1.385(6)

Selected bond lengths for all three structures are listed in Table 2. The molecular structures of **5** and **8** are shown in Fig. 5.

3. Conclusion

The compound $C_5H_4CMe_2C_9H_7$ has been established to be a suitable bridging ligand for the synthesis of binuclear complexes. We have shown that ferrocene species with this ligand are potential starting materials for the introduction of further metal units to obtain heterobi- and -trinuclear compounds. The conformation of such dinuclear complexes is affected by the sterical demand of the metal fragments and the ligand bridge.

4. Experimental

Reactions were carried out under nitrogen with conventional Schlenk techniques. All solvents were distilled from Na or K. The NMR spectra were recorded on a Bruker ARX 200 spectrometer in C_6D_6 (^{1}H: 200.1 MHz, ^{13}C: 50.3 MHz). $[(cod)RhCl]_2$ [9], $[CpFeC_5H_4SnBu_3]$ [10], dimethylbenzofulvene [11] and the ligand $C_5H_5CMe_2C_9H_7$ [3a] were prepared by literature methods. Mass spectra (EI, 70 eV) were recorded on a Varian MAT 311A. The X-ray diffraction structural analyses were performed with Mo–K_α radiation ($\lambda = 0.71073$ Å, graphite monochromator) at 293 K using a Siemens SMART CCD area detector diffractometer for **4** and **5** and a CAD4 Data for **8**, respectively. All crystal structures were solved using the direct method (SHELXS-86) and subsequently refined by full-matrix least-squares methods (SHELXL-93 [12]). The positions of all hydrogen atoms could be found for the structure of **4**. All hydrogen atoms in the structures of **5** and **8** were positioned at calculated coordinates with a fixed thermal parameter. The data for structure refinement of **4**, **5** and **8** are listed in Table 1.

4.1. Synthesis of $[(\eta^5\text{-}C_5H_4CMe_2C_9H_7)_2Fe]$ (**1**)

Butyllithium (1.7 ml) ($c = 2.2$ mol l^{-1} in hexane) was added to a solution of the ligand (790 mg) in THF (50 ml) and stirred at room temperature (r.t.) for 3 h. $FeCl_2$ (226 mg) was dissolved in THF (20 ml) and added to the mixture which was then stirred for another 3 h. The reaction mixture turned very dark during this time before the solvent was removed in vacuo. The residue was filtered over a short column of Al_2O_3 with a 5:1 hexane–ether mixture yielding 745 mg (84%) of pure **1** as an orange solid. Isomer AA: ^{1}H-NMR: (ppm, the numbering of the atoms corresponds with that in the crystal structures): δ 4.10 (m, 4H, H_{Cp}), 4.06 (m, 4H, H_{Cp}), 5.83 (t, 2H, $J = 2.1$ Hz, H_8), 2.96 (d, 2H, $J = 2.1$ Hz, H_7), 1.73 (s, 12H, H_{Me}), 7.63 (d, 2H, $J = 8$ Hz, H_2), 7.26 (d, 2H, $J = 8$ Hz, H_5), 7.20 (t, 2H, $J = 8$ Hz, H_3), 7.09 (t, 2H, $J = 8$ Hz, H_4). ^{13}C-NMR (C_6D_6): δ 67.9/67.8 ($4C_{Cp}$), 100.2 ($2C_{Cp}$), 145.2 ($2C_1$), 144.2 ($2C_6$), 154.1 ($2C_9$), 127.3 ($2C_8$), 125.9, 124.3, 124.2, 122.7, 37.0 ($2C_7$), 36.3, 28.6 ($4C_{Me}$). Isomer AB: ^{1}H-NMR: δ 3.85–4.12 (m, 8H, H_{Cp}), 5.80 (t, 1H, $J = 2.1$ Hz, H_8), 2.94 (d, 1H, $J = 2.1$ Hz, H_7), 1.72/1.71/1.29/1.20 (s, 3H, H_{Me}), 7.61 (d, 2H, $J = 8$ Hz, H_2), 7.3–7.0 (m, 7H, H_{3-5}), 6.28 (m, 1H, $H_{7'}$), 6.65 (m, 1H, $H_{8'}$), 3.23 (t, 1H, $J = 2$ Hz, H_9). ^{13}C-NMR: δ 67.9/67.8 ($4C_{Cp}$), 100.7 (C_{Cp}), 100.2 (C_{Cp}), 145.8 ($C_{1'}$), 145.2 (C_1), 145.2 ($C_{6'}$), 144.2 (C_6), 154.1 (C_9), 138.1 ($C_{8'}$), 131.9 ($C_{7'}$), 127.3 (C_8), 126.9, 125.9, 125.7, 124.3, 124.2, 122.7, 121.1, 63.0 ($C_{9'}$), 37.0 (C_7), 37.0, 36.3, 28.6 ($2C_{Me}$), 27.2 (C_{Me}), 25.0 (C_{Me}). Isomer BB: ^{1}H-NMR: δ 3.98 (m, 4 H, H_{Cp}), 3.89 (m, 4 H, H_{Cp}), 6.31(m, 2H, H_7), 6.65 (m, 2H, H_8), 3.26 (t, 2H, $J = 2$ Hz, H_9), 7.0–7.3 (m, 8H), 1.30/1.26/1.22/1.17 (s, 3H, H_{Me}). ^{13}C-NMR: δ 67.0–68.3 ($8C_{Cp}$), 100.7 ($2C_{Cp}$), 145.8 ($2C_1$), 145.2 ($2C_6$), 63.0 ($2C_9$), 138.1 ($2C_8$), 126.9, 125.7, 124.3, 121.1, 131.9($2C_7$), 37.0, 27.3/25.3/27.0/25.3 (C_{Me}). MS (157°C) m/z: 498 [M^+], 383 [$M-(Ind)^+$], 277 [$M-(C_5H_4CMe_2C_9H_7)^+$].

4.2. Synthesis of $[(\eta^5\text{-}C_5H_4CMe_2C_9H_7)Fe(\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_9H_6)\text{-}Rh(cod)]$ (**2**)

Butyllithium (0.18 ml) ($c = 2.2$ mol l^{-1} in hexane) was added to a solution of compound **1** (190 mg) in THF (20 ml) and stirred at r.t. After 2 h $[(cod)RhCl]_2$ (85 mg) was dissolved in THF (20 ml) before it was added to the reaction mixture and stirred for 12 h. The solvent was removed in vacuo. The reaction mixture was first filtered over a short column of Al_2O_3 before it was chromatographed over a longer column with hexane. The separation of the starting material **1**, the product **2** (40 mg, 15% yield) and the byproduct **3** in this order is very poor. ^{1}H-NMR (ppm): δ 4.0–4.2 (m, 8H, H_{Cp}), 5.75 (m, 1H, H_8), 4.48 (m, 1H, H_7), 1.30/1.17/1.26/1.22 (s, 3H, H_{Me}), 7.50 (m, 2H, H_2), 7.0–7.3 (m, 6H, H_{3-5}), 6.28 (dt, 1H, $J = 6 + 2$ Hz, $H_{7'}$), 6.64 (dd, 1H, $J = 6 + 2$ Hz, $H_{8'}$), 3.23 (t, 1H, $J = 2$ Hz, $H_{9'}$), 3.89 (m br, 4H, H_{cod}), 1.87 (m, 4H, H_{cod}), 1.75 (m, 4H, H_{cod}). ^{13}C-NMR: δ 67.0–68.5 (C_{Cp}), 100.7 (C_{Cp}), 101.4 (C_{Cp}), 72.8 ($J_{C\text{–}Rh} = 5$ Hz, C_7), 93.0 ($J_{C\text{–}Rh} = 4.9$ Hz, C_8), 107.8 ($J_{C\text{–}Rh} = 3.8$ Hz, C_9), 145.8($C_{1'}$), 145.3 ($C_{6'}$), 131.8 ($C_{7'}$), 138.1 ($C_{8'}$), 126.9, 125.7, 124.3, 122.5, 122.2, 122.6, 120.6, 120.4, 113.4 ($J_{C\text{–}Rh} = 2.4$ Hz, C_1), 112.3 ($J_{C\text{–}Rh} = 2$ Hz, C_6), 63.5 ($C_{9'}$), 37.0, 36.2, 29.6 ($2C_{Me}$), 29.7, 29.8, 67.8 ($J_{C\text{–}Rh} = 17$ Hz, C_{cod}), 67.4 ($J_{C\text{–}Rh} = 13.4$ Hz, C_{cod}), 32.0 (C_{cod}), 31.2 (C_{cod}). MS (205°C) m/z: 708 [M^+], 600 [$M - (cod)^+$], 494 [$M - Rh(cod)\text{-}3H^+$], 484 [$M - (cod) - (HInd)^+$], 444 [$CpFeC_5H_4CMe_2IndRh^+$], 378 [$Fe\ C_5H_4CMe_2IndRh - H^+$], 323 [$C_5H_4CMe_2IndRh^+$], 267 [$Fe(C_5H_4CMe_2)_2 - H^+$].

4.3. Synthesis of $[Fe\{\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_9H_6)Rh(cod)\}_2]$ (**3**)

Butyllithium (0.15 ml) ($c = 2.5$ mol l^{-1} in hexane) was added to a solution of compound **1** (81 mg) in THF (20 ml) and stirred at r.t. After 2 h $[(cod)RhCl]_2$ (85 mg) was added to the dark reaction mixture and stirred for 12 h. The solvent was removed in vacuo. The reaction mixture was filtered with a 5:1 hexane–ether mixture over a short column of Al_2O_3. The only yellow–orange fraction containing 97 mg (66% yield) of $[Fe\{\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_9H_6)Rh(cod)\}_2]$ (**3**) was eluated. ^{1}H-NMR (ppm): δ 4.0–4,1 (m, 8H, H_{Cp}), 5.77 (dd, 2H, $J = 2.8$ Hz, $J_{H\text{–}Rh} = 2$ Hz, H_8), 4.48 (t, 2H, $J = J_{H\text{–}Rh} = 2$ Hz, H_7), 1.73/1.74/1.63/1.60 (s, 3H, H_{Me}) 7.52 (m, 2H, H_2), 7.0–7.3 (m, 6H, H_{3-5}), 3.94 (m br, 8H, H_{cod}),1.87 (m, 8H, H_{cod}), 1.72 (m, 8H, H_{cod}). ^{13}C-NMR (C_6D_6): δ 68.0/68.2/68.3/68.4 ($2C_{Cp}$), 101.4 ($2C_{Cp}$), 72.8 ($J_{C\text{–}Rh} = 5$ Hz, $2C_7$), 93.0 ($J_{C\text{–}Rh} = 4.9$ Hz, $2C_8$), 107.8 ($J_{C\text{–}Rh} = 3.8$ Hz, $2C_9$), 122.2, 122.6, 120.6, 120.4, 113.4 ($J_{C\text{–}Rh} = 2.4$ Hz, $2C_1$), 112.3 ($J_{C\text{–}Rh} = 2$ Hz, $2C_6$), 36.2, 29.7, 29.6, 67.8 ($J_{C\text{–}Rh} = 17$ Hz, $4C_{cod}$), 67.4 ($J_{C\text{–}Rh} = 13.4$ Hz, $4C_{cod}$), 32.0 ($4C_{cod}$), 31.2 ($4C_{cod}$). MS (257°C) m/z: 918 [M^+], 810 [$M - (cod)^+$], 702 [$M - 2(cod)^+$], 599 [$M - 2(cod) - Rh^+$], 494 [$M - 2Rh(cod) - H_2^+$], 484 [$M - (Ind)Rh(cod) - (cod)^+$], 444 [$CpFeC_5H_4CMe_2IndRh^+$], 378 [$FeC_5H_4CMe_2IndRh - H_2^+$], 323 [$C_5H_4CMe_2IndRh^+$], 267 [$Fe\ (C_5H_4CMe_2)_2 - H^+$].

4.4. Synthesis of $[(\eta^5\text{-}C_5H_4CMe_2C_9H_7)FeCp]$ (**4**)

Butyllithium (2 ml) ($c = 2{,}5$ mol l^{-1} in hexane) was added to a solution of $CpFeC_5H_4Sn(C_4H_9)_3$ (2 g, 4.2 mmol) in THF (25 ml) and stirred at r.t. for 30 min. During this time the color of the solution changed to red and dimethylbenzofulvene (655 mg) was added. After 10 h, the reaction mixture was quenched with water and transferred to a separatory funnel, diethyl ether was added and the aqueous phase rejected. The organic phase was dried with $MgSO_4$, filtered, and the solvent was removed in vacuo. After ferrocene was sublimed yellow–orange crystals of **4** crystallized from the remaining oil. The crystals were separated, washed with hexane and recrystallised from hexane to yield 100 mg (7%) of pure **4**. ^{1}H-NMR (ppm): δ 4.06 (s, 5H, H_{Cp}), 4.05 (t, 2H, $J = 2$ Hz, H_{Cp}), 3.96 (t, 2H, $J = 2$ Hz, H_{Cp}), 5.76 (t, 1H, $J = 2$ Hz, H_8), 2.92 (d, 2H, $J = 2$ Hz, H_7), 1.74 (s, 6H, H_{Me}), 7.64 and 7.24 (d, 1H, $J = 8$ Hz, $H_{2/5}$), 7.20 and 7.08 (t, 1H, $J = 8$ Hz, $H_{3/4}$). ^{13}C-NMR: δ 68.7 ($5C_{Cp}$), 67.1 ($2C_{Cp}$), 67.2 ($2C_{Cp}$), 100.4 ($1C_{Cp}$), 154.1 (C_9), 145.9 (C_1), 144.2 (C_6), 127.3, 125.9, 124.3, 124.2, 122.6, 36.9 (C_7), 36.2, 28.2 ($2C_{Me}$). MS (100°C) m/z: 342 [M^+], 227 [$M - (Ind)^+$], 186 [Cp_2Fe^+], 121 [$CpFe^+$].

4.5. Synthesis of $[(\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_9H_6)FeCpRh(cod)]$ (**5**)

Butyllithium (0.5 ml) ($c = 2.2$ mol l^{-1} in hexane) was added to a solution of Cp_2Fe (190 mg, 1.02 mmol) in ether (25 ml) and stirred at r.t. for 20 h. After 2 h dimethylbenzofulvene (140 mg, 0.9 mmol) and $[(cod)RhCl]_2$ (200 mg, 0.8 mmol) were added and stirred over night. The solvent was removed in vacuo. The residue was filtered with a 5:1 hexane–ether mixture over a short column of Al_2O_3. After removing the solvent, ferrocene (102 mg) was removed by sublimation (45°C, 0.5 mbar). The remaining oil was chromatographed on Al_2O_3 (5% H_2O). $[(\eta^5\text{-}C_9H_6CMe_2C_4H_9)Rh(cod)]$ (**6**) and $[(\eta^5\text{-}C_9H_6CCH_2Me)\text{-}Rh(cod)]$ (**7**) were eluated with hexane in the first two fractions, respectively. With a mixture of hexane–ether, compound **5** (20 mg (5% related to the rhodium salt)) was eluated as an orange fraction. ^{1}H-NMR (ppm): δ 4.02 (s, 5H, H_{Cp}), 3.90 (m, 2H, H_{Cp}), 4.02 (m, 2H, H_{Cp} partly hidden), 5.74 (dd, 1H, $J = 2.8$ Hz, $J_{H\text{–}Rh} = 2$ Hz,

H_8), 4.46 (dd, 1H, $J = 2.8$ Hz, $J_{H-Rh} = 0.6$ Hz, H_7), 1.65 (s, 3H, H_{Me}), 1.76 (s, 3H, H_{Me}), 7.51 (d, 1H, $J = 8$ Hz, H_2), 7.06 (m, 3H, H_{3-5}), 4.03 (m, br, 4H, H_{cod}), 1.90 (m, 4H, H_{cod}), 1.40 (m, 4H, H_{cod}). ^{13}C-NMR: δ 68.7 ($5C_{Cp}$), 67.9 (C_{Cp}), 67.3 (C_{Cp}), 66.8 (C_{Cp}), 66.7 (C_{Cp}), 101.3 (C_{Cp}), 122.5, 122.2, 120.6, 120.3, 113.5 ($J_{C-Rh} = 2.7$ Hz), 112.3 ($J_{C-Rh} = 1.9$ Hz), 107.9 ($J_{C-Rh} = 4$ Hz, C_9), 93.1 ($J_{C-Rh} = 5$ Hz, C_8), 72.9 ($J_{C-Rh} = 5.1$ Hz, C_7), 36.1, 29.7 (C_{Me}), 29.5 (C_{Me}), 68.3 ($J_{C-Rh} = 13.8$ Hz, $2C_{cod}$), 68.1 ($J_{C-Rh} = 13.8$ Hz, $2C_{cod}$), 32.0 ($2C_{cod}$), 31.3 ($2C_{cod}$). MS (156°C) m/z: 552 [M^+], 444 [$M - (cod)^+$], 378 [$M - (cod, CpH)^+$], 323 [$M - (cod, CpFe)^+$].

4.6. Synthesis of [(η^5-$C_9H_6CMe_2C_4H_9$)Rh(cod)] (**6**)

^{1}H-NMR: (δ in ppm): 5.90 (dd, 1H, $J = 2.8$ Hz, $J_{H-Rh} = 2$ Hz, H_8), 4.62 (dd, 1H, $J = 2.8$ Hz, $J_{H-Rh} = 0.7$ Hz, H_7), 1.32 (s, 6H, H_{Me}), 1.8 (m, 6H), 0.76 (t, $J = 7$ Hz, 3H), 7.55 (m, 1H, H_2), 7.06 (m, 3H, H_{3-5}), 3.98 (m, br, 4H, H_{cod}), 1.70 (m, 4H, H_{cod}), 1.10 (m, 4H, H_{cod}). MS (154°C, EI) m/z: 424 [M^+], 325 [$M - (C_7H_{15})^+$].

4.7. Synthesis of [(η^5-$C_9H_6CCH_2Me$)Rh(cod)] (**7**)

^{1}H-NMR (ppm): δ 6.00 (dd, 1H, $J = 3.0$ Hz, $J_{H-Rh} = 1.9$ Hz, H_8), 4.80 (dd, 1H, $J = 3.0$ Hz, $J_{H-Rh} = 0.7$ Hz, H_7), 2.02 (q, 3H, $J = 1.5$ Hz, H_{Me}), 5.34 (m, 1H), 5.15 (dq, $J = 3$ Hz, 1H), 7.51 (m, 1H, H_2), 7.06 (m, 3H, H_{3-5}), 3.77 (m, br, 2H, H_{cod}), 3.63 (m, br, 2H, H_{cod}), 1.80 (m, 4H, H_{cod}), 1.70 (m, 4H, H_{cod}). MS (154°C) m/z: 366 [M^+], 258 [$M - (cod)^+$].

4.8. Synthesis of [(η^5-$C_5H_4CMe_2$-η^5-C_9H_6)$Rh_2(cod)_2$] (**8**)

Butyllithium (1.3 ml) ($c = 1.6$ mol l^{-1} in hexane) was added to a solution of $C_5H_5CMe_2C_9H_7$ (220 mg) in THF (20 ml) and stirred at r.t. After 3 h a THF solution of $[(cod)RhCl]_2$ (490 mg) was added to the red reaction mixture and stirred for an additional 2 h. The solvent was removed in vacuo and the residue was filtered over a short column of Al_2O_3. The first fraction eluted with hexane contained [(η^5-$C_5H_4CMe_2C_9H_7$)Rh(cod)] contaminated with [(η^5-$C_5H_4CMe_2$-η^5-C_9H_6)$Rh_2(cod)_2$] (**8**). The main fraction of **8** was eluted with ether as a yellow–orange band to give **8** (412 mg, 64% yield). ^{1}H-NMR (ppm): δ 4.90 (m, 2H, H_{Cp}), 4.66 (m, 1H, H_{Cp}), 4.60 (m, 1H, H_{Cp}), 5.92 (dd, 1H, $J = 2.8$ Hz, $J_{H-Rh} = 2$ Hz, H_8), 4.53 (d, 1H, $J = 2.8$ Hz, H_7), 1.81 (s, 3H, H_{Me}), 1.68 (s, 3H, H_{Me}), 7.50 (m, 1H, H_2), 7.17 (m, 1H, H_5), 7.05 (m, 2H, $H_{3/4}$), 3.93 (m br, 8H, H_{cod}), 2.23 (m, 8H, H_{cod}), 1.97 (m, 8H, H_{cod}). ^{13}C-NMR: δ 86.0 ($J_{C-Rh} = 4$ Hz, C_{Cp}), 85.7 ($J_{C-Rh} = 3.8$ Hz, C_{Cp}), 84.8 ($J_{C-Rh} = 3.7$ Hz, C_{Cp}), 84.6 ($J_{C-Rh} = 3.7$ Hz, C_{Cp}), 120.7 ($J_{C-Rh} = 4.2$ Hz, C_{Cp}), 122.6, 122.3, 120.5, 120.5, 113.5 ($J_{C-Rh} = 2.7$ Hz, C_1), 112.6 ($J_{C-Rh} = 2$ Hz, C_6), 107.6 ($J_{C-Rh} = 4$ Hz, C_8), 93.0 ($J_{C-Rh} = 5.0$ Hz, C_9), 73.0 ($J_{C-Rh} = 5$ Hz, C_7), 36.8, 32.1 (C_{Me}), 31.3 (C_{Me}), 63.1 ($J_{C-Rh} = 14$ Hz, C_{cod}), 32.9 ($J_{C-Rh} = 3.5$ Hz, C_{cod}), 68.4 ($J_{C-Rh} = 13.4$ Hz, $C_{cod'}$), 68.1 ($J_{C-Rh} = 13.7$ Hz, $C_{cod'}$), 31.4 ($C_{cod'}$), 30.3 ($C_{cod'}$), 27.2 ($C_{cod'}$). MS (140°C) m/z: 642 [M^+], 532 [$M - (cod) - H_2^+$], 426 [$M - 2(cod)^+$].

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 144146, 144145 and 144144 for the compounds **4**, **5**, and **8**, respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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