Transition metal complexes of 2-cyclopentadienyl-2-indenyl-propane

Petra Escarpa Gaede *, Paul H. Moran, Andrea-N. Richarz

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

Abstract

The new complexes $[(\eta^5\text{-CpCMe}_2C_9H_7)Rh(C_2H_4)_2]$ **1**, $[(\eta^5\text{-CpCMe}_2C_9H_7)Rh(CO)_2]$ **2**, $[(\eta^5\text{-CpCMe}_2C_9H_7)Rh(nbd)]$ **4**, $[(\eta^5\text{-CpCMe}_2C_9H_7)Rh(cod)]$ **5**, $[(\eta^5\text{-CpCMe}_2C_9H_7)TiCl_2Cp]$ **6**, $[(\eta^5\text{-CpCMe}_2C_9H_7)Mn(CO)_3]$ **7**, were obtained from the reaction of the monoanion $[CpCMe_2C_9H_7]^-$ with the appropriate metal–halide unit. $[(\eta^5\text{-CpCMe}_2C_9H_7)Co(CO)_2]$ **8** and $[(\eta^5\text{-CpCMe}_2C_9H_7)Fe(CO)_2]_2$ **11** could be synthesized by reacting $CpHCMe_2C_9H_7$ with $Co_2(CO)_8$ and $Fe_2(CO)_9$, respectively. With the dilithiumsalt of the ligand the dinuclear complexes $[(\eta^5:\eta^5\text{-CpCMe}_2C_9H_6)Rh_2(C_2H_4)_4]$ **12** and $[(\eta^5:\eta^5\text{-CpCMe}_2C_9H_6)Rh_2(CO)_4]$ **13**, $[(\eta^5:\eta^5\text{-CpCMe}_2C_9H_6)Rh_2(nbd)^2]$ **14** and $[(\eta^5:\eta^5\text{-CpCMe}_2C_9H_6)Rh_2(cod)^2]$ **15** could be formed. Also some compounds $[(\eta^5\text{-CpCMe}_2)_2(C_9H_6)Rh_2(L_n)_2]$ **16–18** (L = C_2H_4, CO, nbd) with the related ligand $[1,3\text{-}(CpCMe_2)_2(C_9H_6)]^{2-}$ were isolated. Some unsuccessful attempts to synthesize heterobimetallic complexes with the ligand $CpCMe_2C_9H_6$ were described. All new compounds were characterized by MS and NMR. Single crystals of **1**, **5**, **8** and **12** were obtained and characterized by X-ray analysis. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Transition metal; Cyclopentadienyl; Metal center

1. Introduction

Bimetallic complexes have attracted attention because of the belief that molecules containing two closely adjacent metal atoms may permit cooperative effects resulting in unique catalytic applications [1]. Coupling Cp rings is one strategy to maintain metal centers within close range. Variation of the ring linkage allows flexibility in the relative positions of the metals. A wide range of complexes with two linked Cp metal units are known [2]. In a few cases it has been possible to monometallate bis(Cp)ligands, leaving the second, unsubstituted ring free for subsequent chemistry [3]. Substitution of one Cp by an indenyl offers the possibility of selective metallation. The difference in the electronic character between the Cp and the indenyl ring leads to a different environment for the two metals even if they are the same. The ligand 2-cyclopentadienyl-2-indenylpropane [CpCMe₂Ind] was introduced by Green,

Spaleck and Alt and their coworkers to metals of the 4th and 6th Groups to generate mono- and bimetallated compounds [4–7]. In this paper we like to report some further complexes mainly with Group 9 metals with this CpCMe₂Ind ligand.

2. Results and discussion

The ligand $CpHCMe_2C_9H_7$ prepared by literature mode ([4]a) contains $(CpHCMe_2)_2C_9H_6$ as a by-product which has until now not been reported. Separation of both compounds by chromatography is difficult and time consuming. The separation can be obtained more easily through metallation, subsequent complexation and chromatography over a short Al_2O_3 column.

The mononuclear complexes $[(\eta^5\text{-CpCMe}_2C_9H_7)Rh(C_2H_4)_2]$ **1**, $[(\eta^5\text{-CpCMe}_2C_9H_7)Rh(CO)_2]$ **2**, $[(\eta^5\text{-CpCMe}_2C_9H_7)Rh(nbd)]$ **4** (nbd, C_7H_8 norbornadiene), $[(\eta^5\text{-CpCMe}_2C_9H_7)Rh(cod)]$ (cod, C_8H_{12} 1,5-cyclooctadiene) **5**, $[(\eta^5\text{-CpCMe}_2C_9H_7)TiCl_2Cp]$ **6**, $[(\eta^5\text{-CpCMe}_2C_9H_7)$

* Corresponding author.
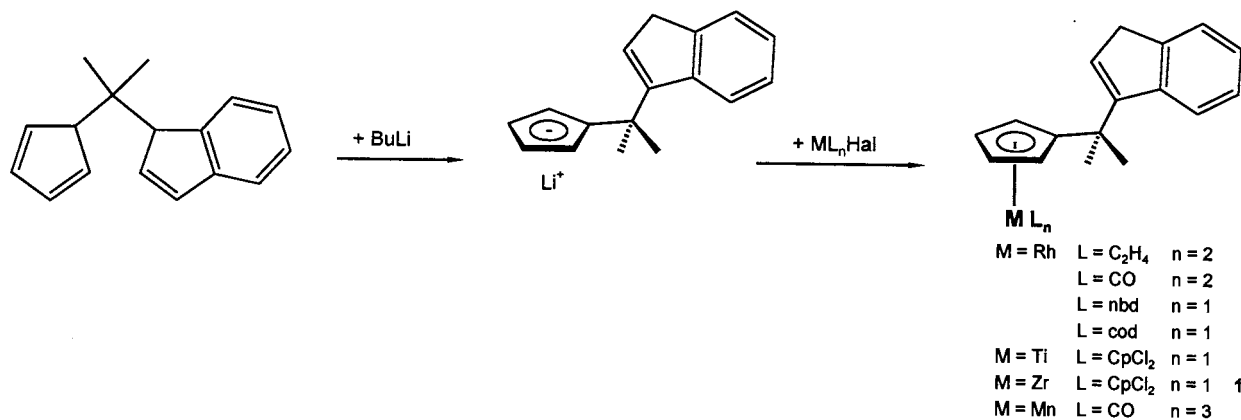
Fig. 1. Scheme for the synthesis of **1**, **2**, **4–7** and **10**.
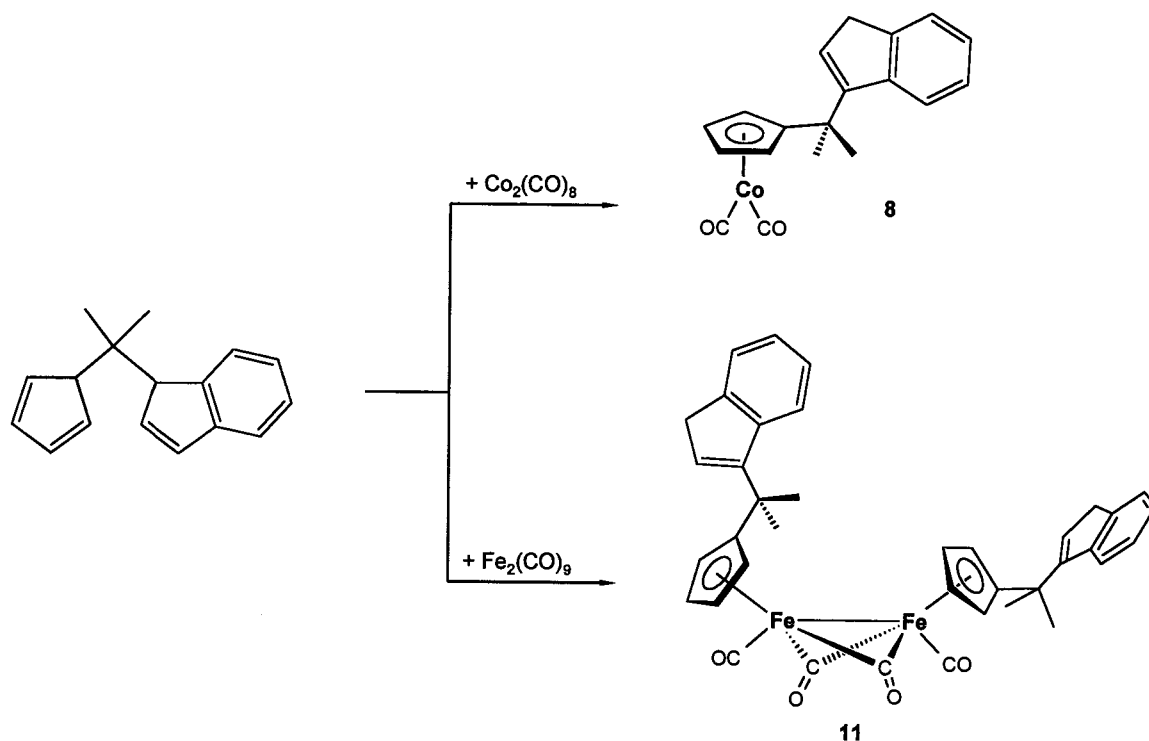
Fig. 2. Scheme for the synthesis of **8** and **11**.

$Mn(CO)_3$] **7**, were prepared by reacting the monoanion [$CpCMe_2C_9H_7$]Li with the appropriate metal–halide unit (Fig. 1). Only in the cases of [(η^5-$CpCMe_2C_9H_7$) $Co(CO)_2$] **8** and [(η^5-$CpCMe_2C_9H_7$)$Fe(CO)_2$]$_2$ **11** was deprotonation not required. The desired complex could be synthesized by reacting $CpHCMe_2C_9H_7$ with $Co_2(CO)_8$ or $Fe_2(CO)_9$ to obtain the corresponding complexes (Fig. 2). The iron species **11** is a dimer with two bridging carbonyl ligands with an IR active band at 1770 cm^{-1}. The expected bridged complex [(μ^2-η^5:η^5-$CpCMe_2C_9H_6$)$Fe_2(CO)_4$] could not be detected. [(η^5-$CpCMe_2C_9H_7$)$Rh(C_2H_4)(CO)$] **3** was obtained from the reaction of **2** with butyllithium and [$Rh(C_2H_4)_2Cl$]$_2$. This reaction was at first carried out to produce the bimetallic complex [(η^5:η^5-$CpCMe_2C_9H_6$)$Rh_2(C_2H_4)_2$

$(CO)_2$]. However, instead of deprotonating the indenyl moeity of **2** the butyllithium reacts, presumably, with the carbonyl ligand to produce an intermediate of unknown nature, which on addition of [$Rh(C_2H_4)_2Cl$]$_2$ substitutes a carbonyl ligand for an ethene, yielding complexes **1** and **3**. Further attempts to isolate or characterize this intermediate (perhaps as a metal oxocarbene) failed. Addition of Me_3OBF_4 to the reaction mixture of **2** and butyllithium or methyllithium does not give any evidence of a neutral carbene complex.

NMR analysis of the monometallated compounds [(η^5-$CpCMe_2C_9H_7$)ML_n] **1–8** and **11** revealed that the indenyl fragment is exclusively present as the thermodynamically more stable 3H-isomer. A previous report

Table 1
^{1}H-NMR data for the mononuclear compounds [(η^5-CpCMe$_2$C$_9$H$_7$)ML$_n$] **1–11** in C$_6$D$_6$

	H$_{12/15}$	H$_{13/14}$	H$_7$	H$_8$	H$_{16}$	H$_{2/5}$	H$_{3/4}$	L$_n$
Rh(C$_2$H$_4$)$_2$ **1**	4.43	4.95	3.01	5.99	1.73	7.46/7.26	7.07/7.16	2.9/1.12
Rh(CO)$_2$ **2**	4.81	5.01	2.95	5.85	1.49	7.34/7.25	7.1/7.06	
Rh(CO)(C$_2$H$_4$) **3**	4.64	5.03	2.98	5.93	1.66	7.46/7.26	7.1/7.16	2.6
Rh(nbd) **4**	5.05	4.96	3.01	5.97	1.67	7.60/7.25	7.19/7.09	3.23/1.02
Rh(cod) **5**	4.64	4.97	3.01	6.02	1.78	7.60/7.25	7.19/7.09	3.99/2.25/1.97
CpTiCl$_2$ **6**	6.50	5.72	3.0	6.11	1.82	7.0	7.0	5.98
Mn(CO)$_3$ **7**	3.80	4.35	2.93	5.80	1.44	7.4	7.15	
Co(CO)$_2$ **8**	4.39	4.49	2.95	5.87	1.50	7.34	7.2	
Mo(CO)$_3$Me **9**	4.41	4.64	2.91	5.73	1.42	7.3	7.1	0.49
CpZrCl$_2$ **10**	6.24	5.73	3.01	6.29	1.82	7.24/7.20	7.20–7.0	5.98
Fe(CO)$_2$ **11**	4.66	3.87	2.98	5.97	1.89	7.3–7.0	7.3–7.0	

([7]c) described the synthesis of both isomers of [(η^5-CpCMe$_2$C$_9$H$_7$)Mo(CO)$_3$Me] **9**, however, this result could not be reproduced and only the thermodynamically more stable isomer could be found. The ^{1}H- and ^{13}C-NMR data for the compounds **1–8** and the known complexes **9** and [(η^5-CpCMe$_2$C$_9$H$_7$)Zr(Cp)] **10** are listed in Tables 1 and 2 (also see Fig. 3).

By reacting the ligand CpHCMe$_2$C$_9$H$_7$ with two equivalents of base in THF, the dianion was obtained, which forms, with the appropriate rhodium halide units, the corresponding dinuclear complexes (Fig. 4). Some species of this type are already known for molybdenum, tungsten [6], zirconium and hafnium [4,5]. In the case of bis-ethene and dicarbonyl rhodium chloride the by-products [(η^5-CpCMe$_2$)$_2$(C$_9$H$_6$)Rh$_2$(C$_2$H$_4$)$_4$] **16**

and [(η^5-CpCMe$_2$)$_2$(C$_9$H$_6$)Rh$_2$(CO)$_4$] **17** were also obtained and could be separated by chromatography from the main products [(η^5:η^5-CpCMe$_2$C$_9$H$_6$)Rh$_2$(C$_2$H$_4$)$_4$] **12** and [(η^5:η^5-CpCMe$_2$C$_9$H$_6$)Rh$_2$(CO)$_4$]**13**, respectively. For the synthesis of [(η^5:η^5-CpCMe$_2$C$_9$H$_6$)Rh$_2$(nbd)^2] **14** and [(η^5:η^5-CpCMe$_2$C$_9$H$_6$)Rh$_2$(cod)] **15** the purified ligand was used and therefore no by-product was obtained in these cases. However, [(η^5-CpCMe$_2$)$_2$(C$_9$H$_6$)Rh$_2$(nbd)^2] **18** could be isolated from the reaction of [(nbd)RhCl]$_2$ with LiCpCMe$_2$C$_9$H$_7$ which was contaminated with the (LiCpCMe$_2$)$_2$C$_9$H$_6$.

All NMR spectra (Tables 3 and 4) for the complexes **12–15** show two sharp singlets for the two methyl groups due to hindered rotation along the C9–C10 bond. In the ^{13}C-NMR spectra of **14** and **15** a additi-

Table 2
^{13}C-NMR data for the mononuclear compounds [(η^5-CpCMe$_2$C$_9$H$_7$)ML$_n$] **1–11** in C$_6$D$_6$

|	C$_{1/6}$	C$_{2/3/4/5}$	C$_7$	C$_8$	C$_9$	C$_{10}$	C$_{11}$	C$_{12/15}$	C$_{13/14}$	C$_{16}$	L$_n$
Rh(C$_2$H$_4$)$_2$ **1**	145.7/144.1	125.9/124.4/ 124.2/122.8	37.1	127.0	153.3	36.4	119.8	86.3	86.4	30.8	37.0
Rh(CO)$_2$ **2**	145.6/143.7	126.0/124.6/ 124.3/122.4	37.2	127.8	151.4	35.4	125.8	85.6	86.8	31.5	192.9
Rh(CO)(C$_2$H$_4$) **3**	144.0/145.7	126.0/124.5/ 124.2/122.7	37.2	127.8	152.3	35.9	123.9	87.0	86.2	31.4	31.4
Rh(nbd) **4**	145.7/144.3	125.9/123.3/ 124.1/122.7	37.2	127.3	153.7	36.5	118.1	84.1	84.0	30.2	28.5/46.9/57.4
Rh(cod) **5**	146.2/144.8	123.2/124.8/ 124.6/126.4	37.6	127.5	154.3	37.1	120.1	86.4	86.0	30.9	33.3/63.5
CpTiCl$_2$ **6**	145.6/143.6	125.6/125.1/ 124.6/122.5	37.2	127.8	152.9	38.9	128.5	120.2	116.2	28.0	119.8
Mn(CO)$_3$ **7**	145.6/143.4	126.0/124.7/ 124.3/122.2	37.0	128.1	151.9	35.4	113.8	79.2	85.8	29.5	226.0
Co(CO)$_2$ **8**	145.6/143.6	122.5/126.0/ 124.6/124.3	37.2	127.8	151.7	35.4	119.7	83.5	82.6	30.4	206.1 (br)
Mo(CO)$_3$Me **9**	146.1/143.6	128.8/125.4/ 124.8/124.3	37.0	128.8	152.2	38.1	137.5	92.9/92.7	91.6/90.6	29.9/26.8	241.4/227.8/−21.1
CpZrCl$_2$ **10**	145.5/141.2	127.0/125.7/ 124.7/124.3	36.9	127.3	141.2	39.6	129.0	118.7	111.6	28.0	115.6
Fe(CO)$_2$ **11**	145.3/143.2	125.5/124.2/ 123.9/121.8	36.7	127.9	152.0	36.0	114.3	88.4	88.0	28.7	
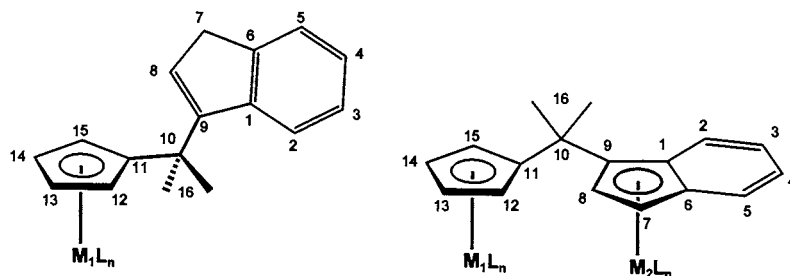
Fig. 3. Numbering scheme for NMR Tables 1–5.
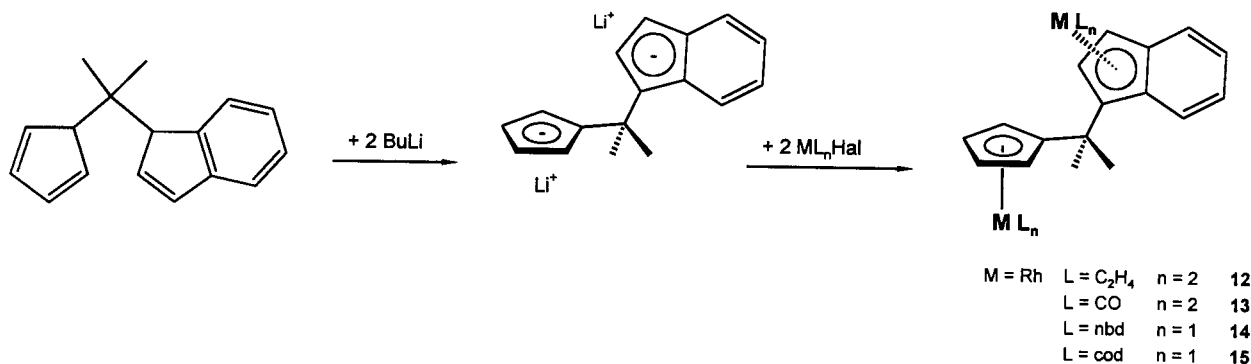
Fig. 4. Scheme for the synthesis of **12–15**.

tional hindered rotation at room temperature (r.t.) of the (nbd) and the (cod) ligand on the rhodium indenyl unit could be observed due to the non equivalent signals for the olefinic carbons. The five carbon atoms of the Cp rings are also inequivalent in the spectra; this implies a relatively rigid conformation over all for the dinuclear compounds.

The structure shown in Fig. 5 could be deduced from their ^{1}H-NMR spectra (Table 5) for the complexes **16**, **17** and **18** from the signals for H_7 and H_8 in the indenyl moiety. The chemical shift around 6 ppm for H_8 indicates an uncoordinated olefinic proton. The coupling constant of 2 Hz with the doublet around 3 ppm is typical for a vicinal coupling constant in a five-membered ring. Due to this fact, a 1,3-substitution for the indenyl must be postulated. C7 represents a chiral carbon atom, which makes all methyl groups diasteriomeric resulting in four distinct singlets in the spectra.

2.1. Molecular structure of [(η^5-CpCMe$_2$C$_9$H$_7$)Rh(C$_2$H$_4$)$_2$] **1**, [(η^5-CpCMe$_2$C$_9$H$_7$)Rh(cod)] **5** and [(η^5-CpCMe$_2$C$_9$H$_7$)Co(CO)$_2$] **8**

From compounds **1**, **5** and **8**, crystals suitable for X-ray diffraction analysis could be grown. Compound **1** crystallized in the monoclinic space group *C2/c* with two different molecules in the asymmetric unit. For compounds **5** and **8** the crystal structure could be solved in the space groups *P2$_1$/a* and *P$\bar{1}$* respectively. All three structures show the same configuration for the

ligand with the indenyl plane nearly orthogonal to the Cp ring. The angles between these planes are 84.50(46), 89.89(46), 89.61(20) and 89.88(24)°, respectively. In all cases the bond lengths C8–C9 are in the typical double bond range and C1–C9, C6–C7 and C7–C8 in the range of a normal single bond indicating the indenyl in the thermodynamically more stable isomer. The metal atoms are η5-coordinated to the Cp-rings with distances to the centers of the rings of 1.948(7), 1.933(6), 1.941(3) and 1.738(4) Å, respectively. The bridging atom C10 which link the Cp to the indenyl ring (all cases) is in the plane of the indenyl ring but bent out of the plane of the Cp ring with angles of 10.7, 8.7, 10.9, 5.1 and 6.4°, respectively. In all three structures the indenyl plane forms a pseudo, non-crystallographic mirror plane including the atoms C10, C11 and the metal atom. The coordinated double bonds of the olefin ligands are parallel to this pseudo mirror plane. A similar geometry was also observed for the carbonyl ligands in **8**. This is probably due to the fact that this represents the thermodynamically most stable rotamer.

Selected bond lengths and angles are listed in Table 6. The molecular structures are shown in Figs. 6–8.

2.2. Molecular structure of [(η^5:η^5-CpCMe$_2$C$_9$H$_6$)Rh$_2$(C$_2$H$_4$)$_4$] **12**

The conformation of the ligand is very similar to this in the mononuclear compounds with the Cp ring being nearly orthogonal [88.06(2)°] to the indenyl ring. Both bis-ethene–rhodium units are η^5-coordinated to the

Table 3
^{1}H-NMR data for the dinuclear compounds $[(\eta^5:\eta^5\text{-CpCMe}_2\text{C}_9\text{H}_6)\text{M}_2(\text{L}_n)_2]$ **12–15** in C$_6$D$_6$

	H$_{12/15}$	H$_{13/14}$	H$_7$	H$_8$	H$_{16}$	H$_{2/5}$	H$_{3/4}$	L$_n$
Rh$_2$(C$_2$H$_4$)$_4$ **12**	4.83	4.35/4.26	4.32	5.87	1.60/1.71	7.51/7.05	7.07/7.0	2.9–2.7, 1.2–1.0
Rh$_2$(CO)$_4$ **13**	5.5/5.32	5.10/4.85	5.78	5.25	1.35/1.10	7.46	6.98	
Rh$_2$(nbd)$_2$ **14**	4.96	4.98/4.89	4.75	5.93	1.61/1.57	7.0	7.05	3.36–3.02, 1.01/0.81
Rh$_2$(cod)$_2$ **15**	4.90	4.66/4.60	4.53	5.96	1.81/1.68	7.50/7.2	7.1	3.94/2.25/1.97
Mo$_2$(CO)$_6$A[a]	5.06/5.30	5.37/5.90	5.53	6.46	1.64/1.78	7.9–7.5	7.4–7.1	
Mo$_2$(CO)$_6$B[a]	4.96/5.25	5.43/5.80	5.53	6.46	1.53/1.84	7.9–7.5	7.4–7.1	
[Mo(CO)$_3$Me]$_2$[b]	5.11/5.27	5.21/5.19	5.61	5.16	1.74/1.68	7.35/7.05	7.15	−0.64/0.37
CpZrCl$_2$Rh(CO)$_2$[c]	6.68/6.20	6.51/6.47	5.60	5.75	1.95/2.08	7.36/7.26	7.11	6.45
CpZrCl$_2$Mn(CO)$_3$[c]	6.69	6.45/6.28	4.66	5.13	1.93/2.07	7.46	7.08	6.45

[a] In CDCl$_3$ at −20°C two conformers are observed [6]. [b] In CDCl$_3$ [6]. [c] In CD$_2$Cl$_2$ ([4]b).

two five membered rings of the ligand. The rhodium bond lengths to the carbon atoms of the Cp ring are within the normal range with an average of 228.3 pm. The η^5-coordination to the indenyl ring shows only a slight tendency towards η^3, as indicated by the longer bond distances of Rh2 to C1 and C6 (241.0 and 237.2 pm, respectively) as well by the longest C–C bond in the indenyl ring being C1–C9 and C6–C7, which should have mostly single bond character in the case of a η^3-coordination. However, the η^5-coordination is clearly shown in the alternation of bond lengths in the six-membered ring (short: 139, long: 143 pm). This Kekúle distortion is caused by the donation of the third π bond to the rhodium atom and the loss of aromaticity in the ring. The indenyl ring is folded twice, the angle between the allyl plane (C7, C8, C9) and the six-membered ring (C1–C6) is calculated to be 7.68(41)° and the angle between the five-membered ring (C1, C6–C9) and

the four uncoordinated carbon atoms C2–C5 to 3.7(4)°. In each bis-ethene–rhodium unit the ethene ligands are non coplanar, the ethene ligands of Rh1 exhibit a torsion angle of 8.5° and the ethenes of Rh2 have a torsion angle of 15.3°.

Selected bond lengths and angles are listed in Table 6. The molecular structure is shown in Fig. 9.

Attempts to synthesize heterobimetalic complexes with this ligand in a two step reaction have not been successful. The reaction of butyllithium with a mononuclear species $[(\eta^5\text{-CpCMe}_2\text{C}_9\text{H}_7)\text{ML}_n]$ followed by the addition of a metal halide unit does not give any evidence of a dinuclear compound, only the starting material and decomposition could be observed. Similar results were obtained for the same reaction of KH instead of BuLi. However, when the reaction mixture was quenched with D$_2$O instead of adding the second metal unit, it could be shown that the corresponding anion of $[(\eta^5\text{-CpCMe}_2\text{C}_9\text{H}_7)\text{ML}_n]$ has been formed on the indenyl ring. The NMR spectra of the isolated product $[(\eta^5\text{-CpCMe}_2\text{C}_9\text{H}_5\text{D}_2)\text{Rh(cod)}]$ **19** shows the replacement of both protons at C7 by two deuteriums. The double exchange of the hydrogen atoms was caused by the excess of KH which favored with its basic character the second substitution.

A further possibility to produce a heterodinuclear complex was the deprotonation of the mononuclear species $[(\eta^5\text{-CpCMe}_2\text{C}_9\text{H}_7)\text{ML}_n]$ by potassium followed by the reaction with a second metal–halide unit. This reaction strategy was tested by reacting **7** with potassium and later addition of [Rh(nbd)Cl]$_2$ in the attempt to obtain $[(\eta^5:\eta^5\text{-CpCMe}_2\text{C}_9\text{H}_6)\text{Rh(nbd)Mn(CO)}_3]$. However, instead of this heterometal species which was obtained only in traces, substitution of the manganese tricarbonyl fragment was observed leading to the main products **4** and **14** in this reaction. This result shows that potassium is an unsuitable base in that case, its potential as a reducing agents is favored in this reaction. The transferred electron destabilized the metal Cp ligand bond and caused it to brake when a second metal unit is offered to the Cp ligand.
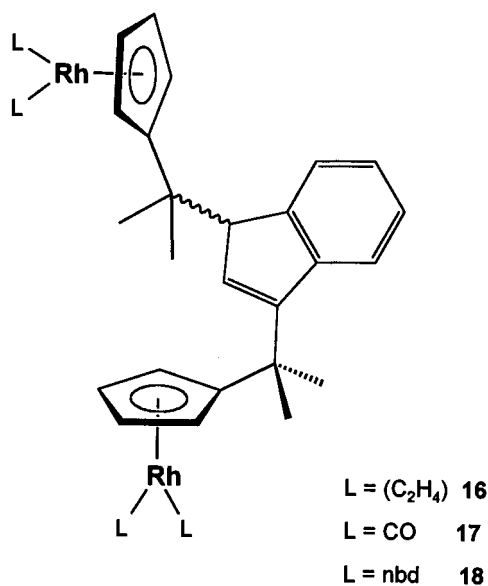

Fig. 5. Structure for the compound type $[(\eta^5\text{-CpCMe}_2)_2(\text{C}_9\text{H}_6)\text{M}_2(\text{L}_n)_2]$ **16–18**.

L = (C$_2$H$_4$) **16**

L = CO **17**

L = nbd **18**

Table 4
^{13}C-NMR data for the dinuclear compounds $[(\eta^5{:}\eta^5\text{-CpCMe}_2\text{C}_9\text{H}_6)\text{M}_2(\text{L}_n)_2]$ **12–15** in C_6D_6

	$C_{1/6}$	$C_{2/3/4/5}$	C_7	C_8	C_9	C_{10}	C_{11}	$C_{12/15}$	$C_{13/14}$	$C_{16/17}$	L_n
$Rh_2(C_2H_4)_4$ **12**	111.1	123.4/122.4/120.5/120.2	75.5	91.6	106.8	36.7	120.9	86.2/85.8	85.1/84.9	31.6/28.3	45.0/36.7
$Rh_2(CO)_4$ **13**		125.6/124.5/120.8/120.3	79.9	93.3	124.2	36.8		89.2/84.8	91.5/91.3	31.5/29.0	
$Rh_2(nbd)_2$ **14**	110.4/109.7	122.2/121.8/121.3/120.0	71.3	92.1	104.5	35.9	119.0	83.5/83.6	83.0/83.4	32.0/30.	28.4/28.5/46.9/57.3, 39.9/37.8/47.7/58.6
$Rh_2(cod)_2$ **15**	113.5/112.6	120.4/122.3/122.6/120.5	73.0	93.0	107.6	36.8	120.7	86.0/85.7	84.8/84.6	32.1/31.3	63.1/32.9, 68.1/68.4, 31.4/30.3/27.3
$[MoMe(CO)_3]_2$[a]		126.2/125.5/125.0/123.6	111.2	114.7	112.0	36.4	126.1	92.6/91.7	91.1/91.2/91.4	31.9/32.1	−21.0/−6.0, 225.9/226.5/226.6/227.2/239.9/240.9
$CpZrCl_2Mn(CO)_3$[b]	105.3/104.3	127.0/126.7/125.6/124.3	69.8	89.1	101.7	37.6	141.1	117.6/0	113.6/111.5	29.7/30.8	116.4/225
$CpZrCl_2Rh(CO)_2$[b]	116.7/117.6	125.0/124.6/119.9/119.4	71.1	97.8	117.3	37.6	140.1	118.2/116.9	114.8/110.3	30.4/30.6	116.4/190.2

[a] In $CDCl_3$ [6]. [b] In CD_2Cl_2 ([4]b).

Table 5
^{1}H-NMR data for the dinuclear compounds $[(\eta^5\text{-CpCMe}_2)_2(C_9H_6)Rh_2(L_n)_2]$ **16–18** in C_6D_6

	H_{Cp}	H_7	H_8	H_{16}	H_2	H_{3-5}	L_n
$Rh_2(C_2H_4)_4$ **16**	4.97/4.45, 4.82/4.30/4.25	3.26	6.08	1.73/1.71, 1.45/1.16	7.33	7.20–7.00	2.9 br, 1.1 br
$Rh_2(CO)_4$ **17**	4.99/4.85, 4.81/4.75/4.70	3.08	5.86	1.43/1.44, 1.17/1.00	7.20	7.20–6.85	
$Rh_2(nbd)_2$ **18**	5.05, 4.98–4.91	Hiden	6.08	1.65/1.39, 1.29/1.13	7.50	7.2–7.0	3.26–3.19, 1.02/0.98

In a further attempt to synthesize a heterobimetallic species, the dianion $Li_2CpCMe_2C_9H_6$ was made and reacted sequentially, in a one-pot reaction, with firstly one equivalent of $[Rh(nbd)Cl]_2$ and finally with one equivalent of $Mn(CO)_5Br$ at $-40°C$. However, after normal workup procedures no species containing manganese could be found.

Our intention to create a new synthetic route to heterobinuclear complexes with bridging ligands in a stepwise reaction failed due to availability of no suitable base. However, the differences in the bonding character between the Cp and the indenyl ring leads to a different electronic environment for the two metal atoms, even if they are the same. So that we can say, that the binuclear complexes $[(\eta^5:\eta^5\text{-CpCMe}_2C_9H_6)M_2L_n]$ poses a intermediate between a homo- and a heterobinuclear compound.

3. 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 Brucker ARX 200 or ARX 400 MHz spectrometer in C_6D_6. MS Spectra were recorded on a modified Varian MAT 311A. The conditions of the X-ray experiment and positional parameters are given in Table 7. All H atom positions were calculated with fixed temperature factors. $[Rh(C_2H_4)_2Cl]_2$ [8], $[Rh(CO)_2Cl]_2$ [8], $[Rh(cod)Cl]_2$ [9], $[Rh(nbd)Cl]_2$ [10], $[Mn(CO)_5Br]$ [11], $CpZrCl_3$ [12] and $CpTiCl_3$ [13] were prepared by literature methods. The X-ray diffraction structural analysis were performed on a Siemens P 21 four circle diffractometer with Mo–K_α radiation ($\lambda = 0.71073$ Å, graphite monochromator). Data were collected at 293 K. All crystal structures were solved using the direct method utilizing SHELX86, they were all subsequently refined using SHELX93. The 2θ value for structure **1** lies 5° under the recommended value of 50° for Mo–K_α radiation as all reflexes above 45° were $< 2\sigma$ and extremely weak. The data for structure refinement of **1**, **5**, **8** and **12** are listed in Table 7.

3.1. Synthesis of $[(\eta^5\text{-CpCMe}_2C_9H_7)Rh(C_2H_4)_2]$ **1**

A 0.65 ml sample of butyllithium (1.6 M) was added to a solution of 220 mg $C_5H_5C(CH_3)_2C_9H_7$ in 20 ml THF and stirred at r.t. After 3 h a THF solution of 194 mg $[Rh(C_2H_4)_2Cl]_2$ was added to the reaction mixture and stirred for a further 2 h. The solvent was removed in vacuo. The reaction mixture was filtered over a short column of Al_2O_3. With hexane 170 mg (45%) of $[(\eta^5\text{-CpCMe}_2C_9H_7)Rh(C_2H_4)_2]$ could be isolated and recrystallized from a hexane/ether solution at $-20°C$ as yellow crystals. ^{1}H-NMR (C_6D_6, δ in ppm): 4.95 (td, 2H, $J = 2.1$ Hz, $J_{H-Rh} = 0.8$ Hz, H_{Cp}), 4.43 (t, 2H, $J = 2.1$ Hz, H_{Cp}), 5.99 (t, 1H, $J = 2.1$ Hz, H_8), 3.01 (d, 2H, $J = 2.1$ Hz, H_7), 1.73 (s, 6H, H_{16}), 7.46 (ddd, 1H, $J = 7.5$ Hz, $J = 1.2$ Hz, $J = 0.8$ Hz, H_2), 7.26 (ddd, 1H, $J = 7.2$Hz, $J = 1.4$ Hz, $J = 0.8$ Hz, H_5), 7.16 (td, 1H, $J = 7.5$ Hz $J = 1.4$ Hz, H_3), 7.07 (td, 1H, $J = 7.2$ Hz, $J = 1.2$ Hz, H_4), 2.90 (d br, 4H, $J \approx 20$ Hz, H_{ethene}), 1.12 (d br, 4H, $J \approx 20$ Hz, H_{ethene}). ^{13}C-NMR: 86.4 ($J_{C-Rh} = 4$ Hz, C_{Cp}), 86.3 ($J_{C-Rh} = 4$ Hz, C_{Cp}), 119.7 ($J_{C-Rh} = 4$ Hz, C_{Cp}), 153.3, 145.7, 144.1, 127.0, 125.9, 124.4, 124.2, 122.8, 37.1, 36.4, 30.8, 37.0 ($J_{C-Rh} = 13.5$ Hz, C_{ethene}). MS (140°C, EI): 378 ($M - H_2$), 352 ($M - C_2H_4$), 324 ($M - 2C_2H_4$).

3.2. Synthesis of $[(\eta^5\text{-CpCMe}_2C_9H_7)Rh(CO)_2]$ **2**

A 0.65 ml sample of butyllithium (1.6 M) was added to a solution of 220 mg $C_5H_5C(CH_3)_2C_9H_7$ in 20 ml THF and stirred at r.t. After 3 h a THF solution of 200 mg $[Rh(CO)_2Cl]_2$ was added to the dark reaction mixture and stirred for 1 h. The solvent was removed in vacuo. The reaction mixture was filtered over a short column of Al_2O_3. With hexane 300 mg (79%) of $[(\eta^5\text{-CpCMe}_2C_9H_7)Rh(CO)_2]$ could be isolated and recrystallized from a hexane solution at $-20°C$ as yellow orange crystals. ^{1}H-NMR (C_6D_6, δ in ppm): 5.01 (td, 2H, $J = 2.2$ Hz, $J_{H-Rh} = 0.4$ Hz, H_{Cp}), 4.81 (td, 2H, $J = 2.2$ Hz, $J_{H-Rh} = 0.8$ Hz, H_{Cp}), 5.85 (t, 1H, $J = 2.2$ Hz, H_8), 2.95 (d, 2H, $J = 2.2$ Hz, H_7), 1.49 (s, 6H, H_{16}), 7.33 (dm, 1H, $J = 7$ Hz, H_2), 7.25 (dm, 1H, $J = 7$ Hz, H_5), 7.16 (m, 1H, H_3), 7.06 (m, 1H, H_4). ^{13}C-NMR:

Table 6
Selected bond distances (Å) for **1**, **5**, **8** and **12**

Bond	1A	1B	5	8	12
M(1)–C(18)	2.15(2)	2.161(13)	2.149(5)	1.713(8)	2.169(7)
M(1)–C(19)	2.13(2)	2.12(2)	2.153(6)	1.753(8)	2.153(7)
M(1)–C(20)	2.14(2)	2.132(14)	2.169(5)		2.155(6)
M(1)–C(21)	2.15(2)	2.161(14)	2.149(5)		2.166(6)
M(1)–C(11–15)	2.30(2)	2.29(2)	2.294(6)	2.121(8)	2.283(7)
C(1)–C(2)	1.43(2)	1.42(2)	1.414(7)	1.419(8)	1.446(8)
C(1)–C(6)	1.44(2)	1.44(2)	1.435(7)	1.438(8)	1.459(7)
C(1)–C(9)	1.52(2)	1.54(2)	1.508(7)	1.520(8)	1.488(8)
C(2)–C(3)	1.42(2)	1.43(2)	1.417(8)	1.433(9)	1.396(9)
C(3)–C(4)	1.44(2)	1.42(2)	1.412(9)	1.402(10)	1.430(11)
C(4)–C(5)	1.41(2)	1.39(2)	1.387(10)	1.404(10)	1.386(11)
C(5)–C(6)	1.39(2)	1.36(2)	1.420(7)	1.419(9)	1.428(8)
C(6)–C(7)	1.52(2)	1.54(2)	1.515(8)	1.523(8)	1.461(9)
C(7)–C(8)	1.55(2)	1.52(2)	1.526(7)	1.515(9)	1.452(8)
C(8)–C(9)	1.37(2)	1.39(2)	1.362(7)	1.370(7)	1.442(8)
C(9)–C(10)	1.56(2)	1.56(2)	1.555(6)	1.550(8)	1.568(7)
C(10)–C(11)	1.56(2)	1.53(2)	1.537(7)	1.559(8)	1.552(8)
C(10)–C(16)	1.56(2)	1.55(2)	1.558(7)	1.556(7)	1.567(8)
C(10)–C(17)	1.56(2)	1.60(2)	1.556(7)	1.570(8)	1.553(8)
C(18)–C(19)	1.43(2)	1.38(2)	1.434(8)		1.430(10)
C(20)–C(21)	1.44(2)	1.44(2)			1.429(10)
C(22)–C(23)			1.428(8)		1.431(11)
C(24)–C(25)					1.420(10)
C(18)–O(1)				1.216(9)	
C(19)–O(2)				1.174(8)	
RH(2)–C(22)					2.170(6)
RH(2)–C(23)					2.174(6)
RH(2)–C(24)					2.175(6)
RH(2)–C(25)					2.179(7)
RH(2)–C(1)					2.410(5)
RH(2)–C(6)					2.372(6)
RH(2)–C(7)					2.216(6)
RH(2)–C(8)					2.284(6)
RH(2)–C(9)					2.330(5)

192.9 ($J_{C–Rh} = 84$ Hz, CO), 86.9 ($J_{C–Rh} = 3.3$ Hz, C_{Cp}), 85.6 ($J_{C–Rh} = 4$ Hz, C_{Cp}), 125.8 ($J_{C–Rh} = 4$ Hz, C_{Cp}), 151.4, 145.6, 143.7, 127.8, 126.0, 124.6, 124.2, 122.4, 37.2, 35.4, 31.5. MS (110°C, EI): 380 (M$^+$), 352 (M − CO), 324 (M − 2CO). IR (KBr) v: 1967(s), 2037(s) cm^{-1}.

3.3. Synthesis of [(η^5-CpCMe$_2$C$_9$H$_7$)Rh(C$_2$H$_4$)(CO)] *3*

A 0.15 ml sample of butyllithium (1.6 M) was added to a solution of 87.5 mg **2** in 20 ml THF and stirred at r.t. The color changed from yellow to red. After 1 h a THF solution of 50 mg [Rh(C$_2$H$_4$)$_2$Cl]$_2$ was added to the reaction mixture, which became immediately dark and was stirred for a further 2 h. The solvent was removed in vacuo. The residue was filtered over a short column of Al$_2$O$_3$. With hexane a mixture of **1** and [(η^5-CpCMe$_2$C$_9$H$_7$)Rh(C$_2$H$_4$)(CO)] could be isolated as a yellow solid. ^{1}H-NMR (C$_6$D$_6$, δ in ppm): 5.03 (td, 2H, $J = 2.1$ Hz, $J_{H–Rh} = 1.4$ Hz, H$_{Cp}$), 4.64 (td, 2H, $J = 2.2$ Hz, $J_{H–Rh} = 0.6$ Hz, H$_{Cp}$), 5.93 (t, 1H, $J = 2.1$ Hz, H$_8$), 2.98 (d, 2H, $J = 2.2$ Hz, H$_7$), 1.66 (s, 6H, H$_{16}$),

7.46 (dm, 1H, $J = 7$ Hz, H$_2$), 7.26 (dm, 1H, $J = 7$ Hz, H$_5$), 7.16 (m, 1H, H$_3$), 7.06 (m, 1H, H$_4$), 2.6 (br, 4H, H$_{ethene}$). ^{13}C-NMR: 87.0 ($J_{C–Rh} = 3.4$ Hz, C_{Cp}), 86.2 ($J_{C–Rh} = 3.8$ Hz, C_{Cp}), 123.9 ($J_{C–Rh} = 4$ Hz, C_{Cp}), 152.3, 145.7, 144.0, 127.8, 126.0, 124.5, 124.2, 122.7, 37.2, 36.4, 31.4, 31.4 ($J_{C–Rh} = 13$ Hz, C_{ethene}). MS (140°C, EI): 380 (M$^+$), 352 (M − C$_2$H$_4$/CO), 324 (M − CO − C$_2$H$_4$). IR (KBr) v: 1970(s), 1935(s) cm^{-1}.

3.4. Synthesis of [(η^5-CpCMe$_2$C$_9$H$_7$)Rh(nbd)] *4*

A 1.3 ml sample of butyllithium (1.6 M) was added to a solution of 440 mg of the mixture of C$_5$H$_5$C(CH$_3$)$_2$C$_9$H$_7$ and (C$_5$H$_5$CMe$_2$)$_2$C$_9$H$_6$ in 20 ml THF and stirred at r.t. After 3 h a THF solution of 460 mg [Rh(nbd)Cl]$_2$ was added to the reaction mixture and stirred for a further 2 h. The solvent was removed in vacuo. The reaction mixture was filtered over a short column of Al$_2$O$_3$. With hexane 70 mg (17%) of [(η^5-CpCMe$_2$C$_9$H$_7$)Rh(nbd)] could be isolated as a yellow solid. ^{1}H-NMR (C$_6$D$_6$, δ in ppm): 5.05 (td, 2H, $J = 2.1$ Hz, $J_{H–Rh} = 0.8$ Hz, H$_{Cp}$), 4.96 (td, 2H, $J = 2.1$ Hz,
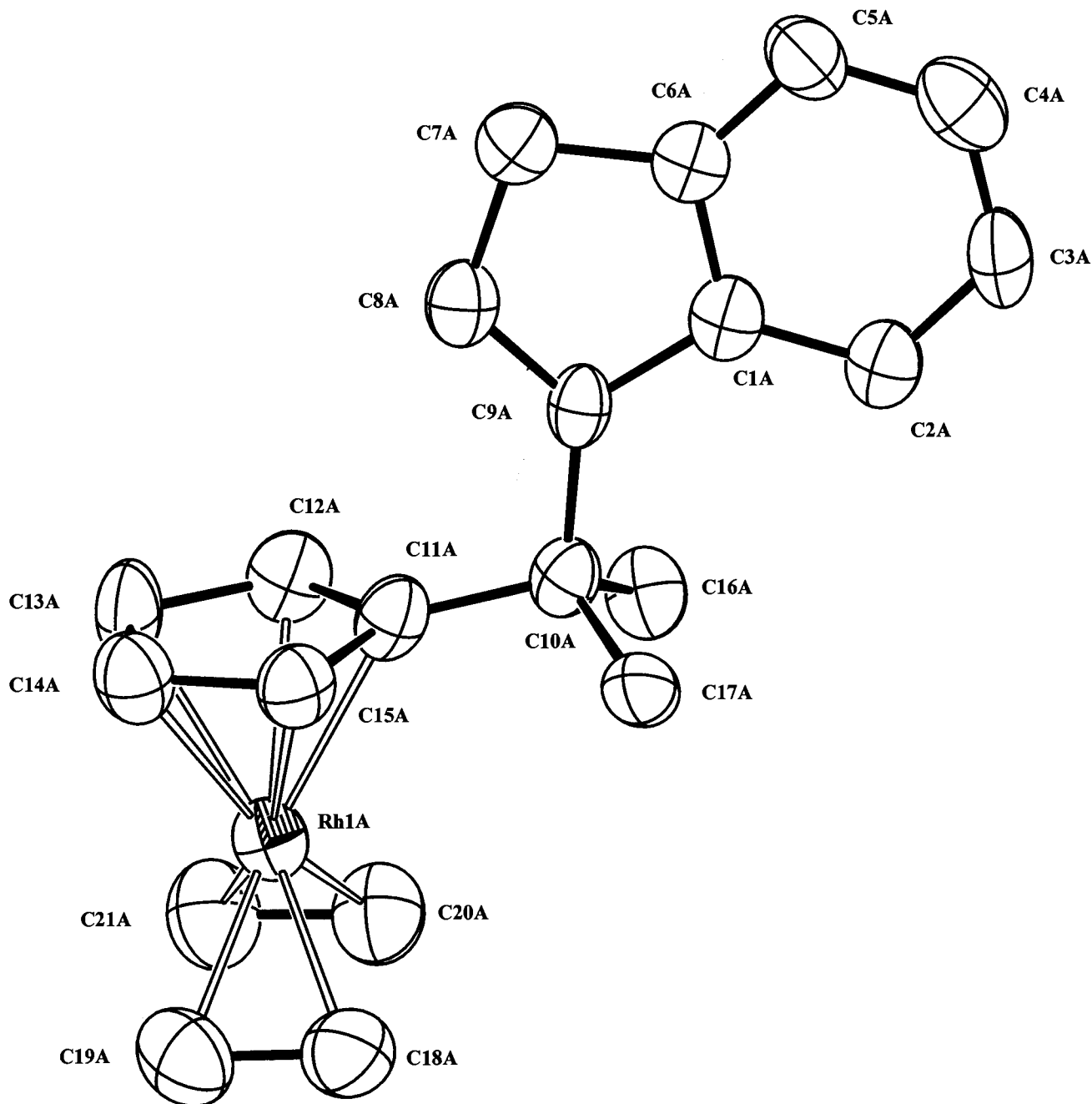
Fig. 6. Molecular structure of **1**.

$J_{H-Rh} = 0.8$ Hz, H_{Cp}), 5.97 (t, 1H, $J = 2$ Hz, H_8), 3.01 (d, 2H, $J = 2$ Hz, H_7), 1.67 (s, 6H, H_{16}), 7.60 (d, 1H, $J = 8$ Hz, H_2), 7.25 (d, 1H, $J = 8$ Hz, H_5), 7.19 (t, 1H, $J = 8$ Hz, H_3), 7.09 (t, 1H, $J = 8$ Hz, H_4), 3.23 (m, 6H), 1.02 (t, 2H, $J = 1.6$ Hz). ^{13}C-NMR: 84.1 ($J_{C-Rh} = 4.2$ Hz, C_{Cp}), 84.0 ($J_{C-Rh} = 4.2$ Hz, C_{Cp}), 118.1 ($J_{C-Rh} = 4.6$ Hz, C_{Cp}), 153.7, 145.8, 144.3, 127.3, 125.9, 124.3, 124.1, 122.7, 37.0, 36.5, 30.1, 57.4 ($J_{C-Rh} = 6.8$ Hz, C_{nbd}), 46.9 ($J_{C-Rh} = 3.4$ Hz, C_{nbd}), 28.5 ($J_{C-Rh} = 10.4$ Hz, C_{nbd}). MS (100°C, EI): 416 (M^+), 324 ($M - nbd$). Using ether, a second band

could be eluted which gave $(\eta^5\text{-CpCMe}_2)_2(C_9H_6)$ $Rh_2(nbd)_2$ **18**, as an orange oil. ^{1}H-NMR (C_6D_6, δ in ppm): 5.05 (m, 2H, H_{Cp}), 4.98–4.91 (m, 6H, H_{Cp}), 6.08 (d, 1H, $J = 2$ Hz, H_8), H_7 overlapping with H_{nbd}, 1.65 (s, 3H, H_{16}), 1.39 (s, 3H, H_{17}), 1.29 (s, 3H, $H_{16'}$), 1.13 (s, 3H, $H_{17'}$), 7.50 (d, 1H, $J = 8$ Hz, H_2), 7.2–7.0 (m, 3H, H_{3-5}), 3.26 (m, 6H, H_{nbd}), 3.19 (m, 6H, H_{nbd}), 1.02 (t, 2H, $J = 1.6$ Hz, H_{nbd}), 0.98 (t, 2H, $J = 1.6$ Hz, H_{nbd}). MS (210°C, EI): 716 (M^+), 624 ($M - nbd^+$) 301 ($CpCMe_2Rh(nbd)^+$), 323 ($CpCMe_2$ $(C_9H_6)Rh^+$).
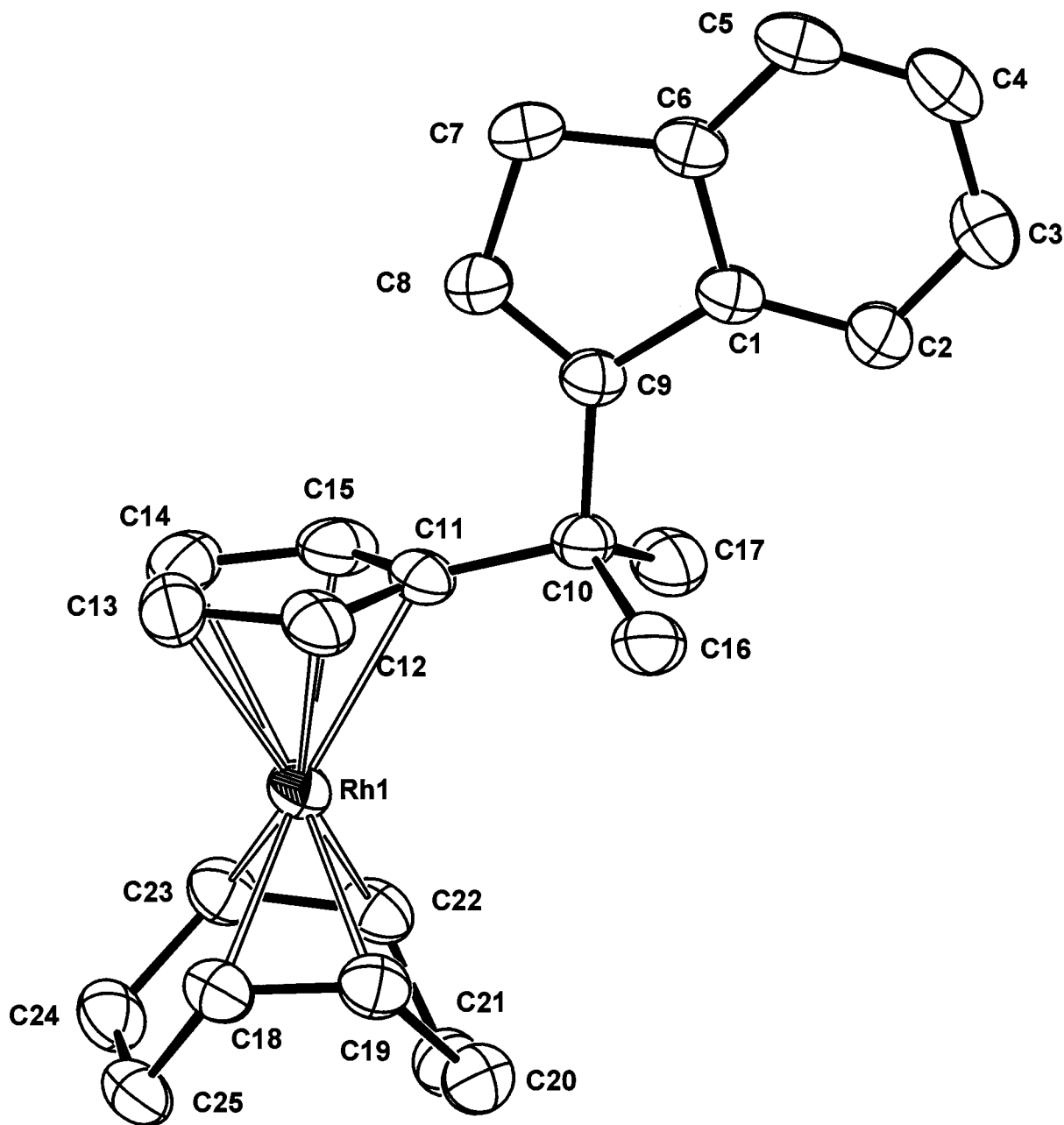
Fig. 7. Molecular structure of **5**.

3.5. Synthesis of [(η⁵-CpCMe₂C₉H₇)Rh(cod)] 5

A 0.65 ml sample of butyllithium (1.6 M) was added to a solution of 220 mg $C_5H_5C(CH_3)_2C_9H_7$ in 20 ml ether and stirred at r.t. After 2 h the reaction mixture was cooled to $-78°C$ and a THF solution of 240 mg [Rh(cod)Cl]₂ was added and stirred for a further 2 h. During this time the reaction was allowed to warm up to r.t. The solvent was removed in vacuo. The reaction mixture was filtered over a short column of Al₂O₃. With hexane 280 mg (65%) of [(η⁵-CpCMe₂C₉H₇)Rh(cod)] could be isolated and recrystallized from an ether solu-

tion at $-4°C$ as yellow crystals. ¹H-NMR (C₆D₆, δ in ppm): 4.64 (td, 2H, $J = 2$ Hz, $J_{H–Rh} = 0.6$ Hz, H_{Cp}), 4.97 (t, 2H, $J = 2$ Hz, H_{Cp}), 6.02 (t, 1H, $J = 2$ Hz, H_8), 3.01 (d, 2H, $J = 2$ Hz, H_7), 1.78 (s, 6H, H_{16}), 7.60 (d, 1H, $J = 8$ Hz, H_2), 7.25 (d, 1H, $J = 8$ Hz, H_5), 7.19 (m, 1H, H_3), 7.09 (m, 1H, H_4), 3.99 (s br, 4H, H_{cod}), 2.25 (m, 4H, H_{cod}), 1.97 (m, 4H, H_{cod}). ¹³C-NMR: 86.4 ($J_{C–Rh} = 4$ Hz, C_{Cp}), 86.0 ($J_{C–Rh} = 3.7$ Hz, C_{Cp}), 120.1 ($J_{C–Rh} = 4$ Hz, C_{Cp}), 154.3, 146.2, 144.8, 127.5, 126.4, 124.8, 124.6, 123.2, 37.6, 37.1, 30.9, 63.5 ($J_{C–Rh} = 14$ Hz, C_{cod}), 33.3 ($J_{C–Rh} = 1.1$ Hz, C_{cod}). MS (120°C, EI): 432 (M⁺), 324 (M − cod⁺).
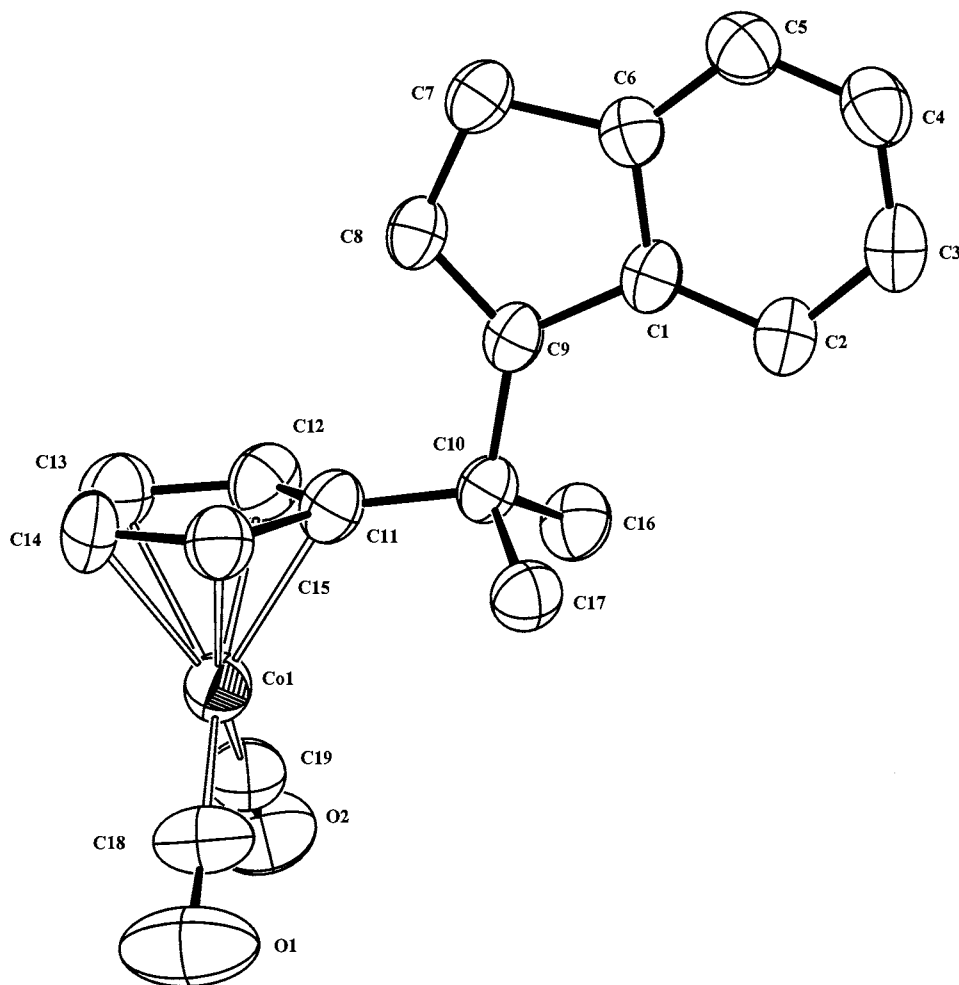
Fig. 8. Molecular structure of **8**.

3.6. Synthesis of [(η⁵-CpCMe₂C₉H₇)TiCl₂Cp] 6

A 0.65 ml sample of butyllithium (1.6 M) was added to a solution of 220 mg $C_5H_5C(CH_3)_2C_9H_7$ in 20 ml THF and stirred at r.t. After 2 h a THF solution of 440 mg TiCpCl₃ was added, the color of the reaction mixture changed immediately to red and was stirred for a further 2 h. The solvent was removed in vacuo. The solid was dissolved in toluene, dropped into hexane and filtered. A total of 145 mg (35%) of [(η⁵-CpCMe₂C₉H₇)TiCpCl₂] was obtained as a white solid. ¹H-NMR (C_6D_6, δ in ppm): 6.50 (t, 2H, $J = 2.6$ Hz, H_{Cp}), 5.72 (t, 2H, $J = 2.6$ Hz, H_{Cp}), 6.11 (t, 1H, $J = 2$ Hz, H_8), 3.0 (d, 2H, $J = 2$ Hz, H_7), 1.82 (s, 6H, H_{16}), 7.0 (m, 4H, H_{2-5}), 5.98 (s, 5H, H_{Cp}). ¹³C-NMR: 119.8 (C_{Cp}), 152.9, 145.6, 143.0, 128.5, 127.8, 125.6, 125.1, 124.6, 122.2, 120.2, 116.2 38.9, 37.2, 28.0. MS (120°C, EI): 369 (M − Cl⁺), 333 (M − 2Cl⁺), 303 (M − Cp − Cl⁺), 268 (M − 2Cl − Cp⁺).

3.7. Synthesis of [(η⁵-CpCMe₂C₉H₇)Mn(CO)₃] 7

A 2.6 ml sample of butyllithium (1.6 M) was added to a solution of 880 mg $C_5H_5C(CH_3)_2C_9H_7$ in 80 ml THF and stirred at r.t. After 2 h a THF solution of 1.1 g [Mn(CO)₅Br] was added and stirred overnight and heated for a further 2 h at 50°C. The solvent was removed in vacuo. The reaction mixture was redissolved in hexane and filtered over a column of Al₂O₃. With hexane Mn₂(CO)₁₀ was eluted first as a bright yellow band. The next fraction, eluted with a mixture of hexane and ether, contained the product contaminated with Mn₂(CO)₁₀, which can be removed by sublimation at 40°C. The residual pale yellow solid was identified as [(η⁵-CpCMe₂C₉H₇)Mn(CO)₃] [yield 126 mg (8.7%)]. ¹H-NMR (C_6D_6, δ in ppm): 4.35 (td, 2H, $J = 2.2$ Hz, H_{Cp}), 3.78 (t, 2H, $J = 2.3$ Hz, H_{Cp}), 5.79 (t, 1H, $J = 2.1$ Hz, H_8), 2.92 (d, 2H, $J = 2.1$ Hz, H_7), 1.43 (s, 6H, H_{16}), 7.40 (m, 2H, $H_{2/5}$), 7.15 (m, 2H, $H_{3/4}$). ¹³C-NMR: 85.8, 79.2, 113.8, 151.9, 145.6, 143.4, 128.1, 126.0, 124.7, 124.3,

37.0, 35.6, 29.5, 126.0 (CO). MS (120°C, EI): 360 (M^+), 276 ($M - 3CO^+$), 160 ($M - 3CO - C_9H_7^+$).

3.8. Synthesis of [(η^5-CpCMe$_2$C$_9$H$_7$)Co(CO)$_2$] 8

A solution of 220 mg of $C_5H_5C(CH_3)_2C_9H_7$ and 340 mg $Co_2(CO)_8$ was heated in 40 ml hexane for 4 h. From this solution [(η^5-CpCMe$_2$C$_9$H$_7$)Co(CO)$_2$] crystallized as orange–brown crystals at -20°C [yield 285 mg (84.8%)]. ^{1}H-NMR (C_6D_6, δ in ppm): 4.49 (br, 2H, H_{Cp}), 4.39 (br, 2H, H_{Cp}), 5.88 (br, 1H, H_8), 2.95 (br, 2H, H_7), 1.50 (s, 6H, H_{16}), 7.34–7.1 (m, 4H, H_{2-5}). ^{13}C-NMR: 83.5, 82.6, 119.7, 151.7, 145.6, 143.6, 127.8, 126.0, 124.6, 124.3, 37.2, 35.4, 30.4, 206 (br, CO). MS (120°C, EI): 336 (M^+), 308 ($M - CO^+$), 280 ($M - 2CO^+$), 265 ($M - 2CO - CH_3^+$).

3.9. Synthesis of [(η^5-CpCMe$_2$)(C$_9$H$_7$)Fe(CO)$_2$]$_2$ 11

A sample of Fe$_2$(CO)$_9$ (364.1 mg) was heated with 220 mg of $C_5H_5CMe_2C_9H_7$ in 20 ml THF to reflux. After 4 h the solvent was removed in vacuo. The reaction mixture was filtered over a small column of
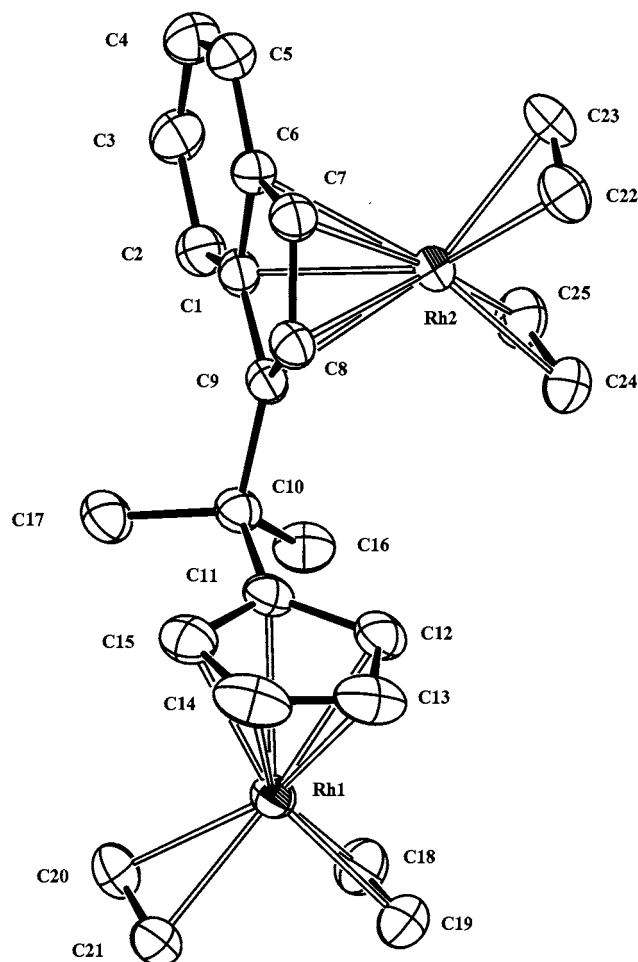

Fig. 9. Molecular structure of **12**.

Al$_2$O$_3$. With hexane a yellow oily fraction was eluted, which contain mostly unreacted ligand, a species with the chemical formula [($C_5H_5CMe_2$)(C_9H_7)Fe(CO)$_3$] and traces of the ferrocene derivative [(η^5-CpCMe$_2$ C_9H_7)$_2$Fe]. A total of 15 mg of [(η^5-CpCMe$_2$) (C_9H_7)Fe(CO)$_2$]$_2$ **11** was eluted with ether and crystallized as a red solid. ^{1}H-NMR (C_6D_6, δ in ppm): 4.66 (m, 4H, H_{Cp}), 3.87 (m, 4H, H_{Cp}), 5.97 (m, 2H, H_8), 2.98 (s br, 4H, H_7), 1.89 (s, 12H, H_{16}), 7.30–7.0 (m, 8H, H_{2-5}). ^{13}C-NMR: 88.4, 88.0, 114.3, 152.0, 145.3, 143.2, 127.8, 125.5, 124.1, 123.9, 121.8, 36.7, 36.0, 28.7. MS (140°C, EI): 550 ($M - C_9H_8^+$), 522 ($M - C_9H_8 - CO^+$), 494 ($M - C_9H_8 - 2CO^+$), 466 ($M - C_9H_8 - 3CO^+$), 438 ($M - C_9H_8 - 4CO^+$), 324 ([CpCMe$_2$Fe]$_2^+$) 277 (CpCMe$_2$C$_9$H$_7$Fe$^+$). IR (KBr) v: 2035(s), 1986(s), 1933(s), 1770(s) cm^{-1}.

3.10. Synthesis of [(η^5:η^5-CpCMe$_2$C$_9$H$_6$)Rh$_2$(C$_2$H$_4$)$_4$] 12

A 0.65 ml sample of butyllithium (1.6 M) was added to a solution of 110 mg the mixture of $C_5H_5CMe_2C_9H_7$ and ($C_5H_5CMe_2$)$_2C_9H_6$ in 20 ml THF and stirred at r.t. After 3 h the dark reaction mixture was cooled to -40°C and a THF solution of 196 mg [Rh(C$_2$H$_4$)$_2$Cl]$_2$ was added and stirred for 10 h and this solution warmed up to r.t. during this time. The solvent was removed in vacuo. The reaction mixture was filtered over Al$_2$O$_3$ to remove decomposition. The products were obtained by chromatography at -25°C over 30 cm of Al$_2$O$_3$. Firstly, 11 mg of **1** was isolated with hexane as a pale yellow band, followed by a second yellow fraction containing 226 mg (84%) of [(η^5:η^5-CpCMe$_2$C$_9$H$_6$)Rh$_2$(C$_2$H$_4$)$_4$] **12**. Using ether 14 mg of [(η^5-CpCMe$_2$)$_2$(C$_9$H$_6$)Rh$_2$(C$_2$H$_4$)$_4$] **16** was obtained as an orange oil. Compound **12** was recrystallized from a ether solution at -20°C as yellow crystals.

Compound **12**: ^{1}H-NMR (C_6D_6, δ in ppm): 4.83 (td, 2H, $J = 2.1$ Hz, $J_{H-Rh} = 0.8$ Hz, H_{Cp}), 4.35 (m, 1H, H_{Cp}), 4.26 (m, 1H, H_{Cp}), 5.87 (dd, 1H, $J = 2.8$ Hz, $J_{H-Rh} = 1.9$ Hz, H_8), 4.32 (dd, 1H, $J = 2.8$ Hz, $J_{H-Rh} = 0.6$ Hz, H_7), 1.60 (s, 3H, H_{16}), 1.71 (s, 3H, H_{17}), 7.51 (dd, 1H, $J = 8.3$ Hz, $J = 1.2$ Hz, H_2), 7.07 (m, 1H, H_5), 7.05 (m, 1H, H_3), 7.0 (m, 1H, H_4), 2.90–2.70 (m br, 8H, H_{ethene}), 1.2–1.0 (m br, 8H, H_{ethene}). ^{13}C-NMR (CDCl$_3$): 86.2 ($J_{C-Rh} = 4$ Hz, C_{Cp}), 85.8 ($J_{C-Rh} = 4$ Hz, C_{Cp}), 85.1 ($J_{C-Rh} = 3.7$ Hz, C_{Cp}), 84.9 ($J_{C-Rh} = 3.7$ Hz, C_{Cp}), 120.9 ($J_{C-Rh} = 4.5$ Hz, C_{Cp}), 123.4, 122.4, 120.5, 120.2, 111.1 ($J_{C-Rh} = 3$ Hz, 2C), 106.8 ($J_{C-Rh} = 4$ Hz), 91.6 ($J_{C-Rh} = 5.2$ Hz), 75.5 ($J_{C-Rh} = 5$ Hz), 36.7, 31.6, 28.3, 45.0 ($J_{C-Rh} = 13.0$ Hz, C_{ethene}), 36.7 ($J_{C-Rh} = 13.3$ Hz, C_{ethene}). MS (140°C, EI): 510 ($M - C_2H_4^+$), 482 ($M - 2C_2H_4^+$), 454 ($M - 3C_2H_4^+$), 426 ($M - 4C_2H_4^+$), 218 (RhC$_9$H$_6^+$).

Compound **16**: ^{1}H-NMR (C_6D_6, δ in ppm): 4.97 (m, 3H, H_{Cp}), 4.45 (m, 2H, H_{Cp}), 4.82 (m, 1H, H_{Cp}), 4.30 (m, 1H, H_{Cp}), 4.25 (m, 1H, H_{Cp}), 6.08 (d, 1H, $J = 2$ Hz,

Table 7
X-ray crystal structure collection and refinement data for **1**, **5**, **8** and **12**

	1	**5**	**8**	**12**
Crystal parameters				
Formula weight (g mol^{-1})	380.32	432.39	336.26	538.33
Crystal system	Monoclinic	Monoclin	Triclinic	Triclinic
Space group	$C2/c$ (no. 15)	$P2_1/a$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a (Å)	30.81(4)	13.964(14)	7.135(5)	8.045(8)
b (Å)	10.367(7)	10.133(9)	9.965(7)	12.62(2)
c (Å)	27.40(3)	14.947(9)	13.006(12)	13.047(10)
α (°)	90	90	89.53(7)	113.72(8)
β (°)	120.51(10)	99.84(7)	81.47(6)	101.97(7)
γ (°)	90	90	69.67(6)	97.28(10)
V (Å^3)	7540(15)	2084(3)	856.6(11)	1154(2)
Z	8	4	2	2
$D_{calc.}$ (g cm^{-3})	1.340	1.378	1.304	1.550
$F(000)$	3136	896	348	544
$\mu(Mo-K_\alpha)$ (cm^{-1})	8.34	7.64	10.05	13.27
Data collection				
θ range (°)	$3 \le 2\theta \le 45$	$2.76 \le 2\theta \le 55.06$	$3.16 \le 2\theta \le 55.02$	$3.56 \le 2\theta \le 54.98$
Index range (h, k, l)	$-33-28, 0-11, 0-29$	$0-18, 0-13, -19-19$	$0-9, -12-12, -16-16$	$0-10, -16-16, -16-16$
Data	5073	4995	4257	5704
Independent observed reflections (R_{int})	4943 (0.0303)	4793 (0.0187)	3938 (0.0369)	5293 (0.0262)
Independent reflections	4907	4789	3934	5276
Parameters	402	238	202	279
Refinement				
$\Delta(\rho)$ (e Å^{-3})	0.856/-0.818	0.639/-0.817	0.585/-0.549	0.683/-0.525
Extinction coefficient	0.0011(2)	0.0155(12)	0.0000	0.0000
GOF	1.022	1.085	1.015	1.030
R[a]	0.0751 (0.1385)[b]	0.0523 (0.0937)[b]	0.0788 (0.1552)[b]	0.0460 (0.0790)[b]
wR_2[a]	0.1844 (0.2562)[b]	0.1230 (0.1590)[b]	0.1875 (0.2665)[b]	0.1027 (0.1325)[b]

[a] $R = \Sigma \|F_o| - |F_c\| / \Sigma |F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)]\}^{0.5}$, $[F_o > 4\sigma(F_o)]$. [b] Based on all data.

H$_8$), 3.26 (d, 1H, $J = 2$ Hz, H$_7$), 1.73 (s, 3H, H$_{16}$), 1.71 (s, 3H, H$_{17}$), 1.45 (s, 3H, H$_{16'}$), 1.16 (s, 3H, H$_{17'}$), 7.33 (d, 1H, $J = 8$ Hz, H$_2$), 7.00–7.20 (m, 3H, H$_{3-5}$), 2.90 (m br, 8H, H$_{ethene}$), 1.1 (m br, 8H, H$_{ethene}$). ^{13}C-NMR (C$_6$D$_6$): 86.8 ($J_{C-Rh} = 4.1$ Hz, C$_{Cp}$), 86.6 ($J_{C-Rh} = 3.8$ Hz, C$_{Cp}$), 86.4 ($J_{C-Rh} = 3.7$ Hz, C$_{Cp}$), 86.3 ($J_{C-Rh} = 4.2$ Hz, C$_{Cp}$), 86.2 ($J_{C-Rh} = 4.1$ Hz, C$_{Cp}$), 86.1 ($J_{C-Rh} = 3.8$ Hz, C$_{Cp}$), 85.7 ($J_{C-Rh} = 3.7$ Hz, C$_{Cp}$), 85.5 ($J_{C-Rh} = 4.2$ Hz, C$_{Cp}$), 119.8 ($J_{C-Rh} = 4.5$ Hz, 2 C$_{Cp}$), 152.7, 147.0, 144.8, 131.2 126.3, 123.9, 122.6, 122.4, 60.3, 37.8, 36.3, 30.8, 30.2, 30.1, 26.1, 37.0 ($J_{C-Rh} = 13.5$ Hz, C$_{ethene}$). MS (160°C, EI): 616 (M $-$ C$_2$H$_4^+$), 588 (M $-$ 2C$_2$H$_4^+$), 560 (M $-$ 3C$_2$H$_4^+$), 532 (M $-$ 4C$_2$H$_4^+$), 429 (M $-$ Rh(C$_2$H$_4$)$_2^+$).

3.11. Synthesis of [(η^5:η^5-CpCMe$_2$C$_9$H$_6$)Rh$_2$(CO)$_4$] 13

A 0.65 ml sample of butyllithium (1.6 M) was added to a solution of 111.4 mg of the mixture of C$_5$H$_5$CMe$_2$C$_9$H$_7$ and (C$_5$H$_5$CMe$_2$)$_2$C$_9$H$_6$ in 20 ml THF and stirred at r.t. After 2 h the dark reaction mixture were cooled to -40°C and a THF solution of 220 mg [Rh(CO)$_2$Cl]$_2$ was added and stirred overnight and this solution warmed up to r.t. during this time. The solvent

was removed in vacuo. The reaction mixture was filtered over Al$_2$O$_3$ to remove decomposition. The products were obtained by chromatography at -25°C over 25 cm of Al$_2$O$_3$. A small amount of **2** was isolated with hexane as a yellow oil, followed by a second yellow fraction which contained [(η^5-CpCMe$_2$)$_2$(C$_9$H$_6$)Rh$_2$(CO)$_4$] **17**. Using ether an orange–brown oil was obtained containing 120 mg (37%) of [(η^5:η^5-CpCMe$_2$C$_9$H$_6$)Rh$_2$(CO)$_4$] **13**.

Compound **13**: ^{1}H-NMR (C$_6$D$_6$, δ in ppm): 5.5 (m br, 1H, H$_{Cp}$), 5.32 (m, 1H, H$_{Cp}$), 5.10 (m, 1H, H$_{Cp}$), 4.85 (m, 1H, H$_{Cp}$), 5.78 (d, 1H, $J = 3$ Hz, H$_7$), 5.25 (dd, 1H, $J = 3$ Hz, $J_{H-Rh} = 2$ Hz, H$_8$), 1.35 (s, 3H, H$_{16}$), 1.10 (s, 3H, H$_{17}$), 7.46 (dd, 1H, $J = 8.3$ Hz, $J = 1.2$ Hz, H$_2$), 6.98 (m, 3H, H$_{3-5}$). ^{13}C-NMR (C$_6$D$_6$): 91.5. ($J_{C-Rh} = 4$ Hz, C$_{Cp}$), 91.2 ($J_{C-Rh} = 4$ Hz, C$_{Cp}$), 89.2 ($J_{C-Rh} = 3.7$ Hz, C$_{Cp}$), 84.8 ($J_{C-Rh} = 3.7$ Hz, C$_{Cp}$), 117.4 ($J_{C-Rh} = 4.5$ Hz, C$_{Cp}$), 93.3 ($J_{C-Rh} = 5.2$ Hz), 79.9 ($J_{C-Rh} = 5$ Hz), 125.6, 124.5, 120.8, 120.3, 119.5, 117.6, 36.8, 31.5, 29.0. MS (190°C, EI): 510 (M $-$ CO$^+$), 482 (M $-$ 2CO$^+$), 454 (M $-$ 3CO$^+$), 426 (M $-$ 4CO$^+$), 218 (RhC$_9$H$_6^+$).

Compound **17**: ^{1}H-NMR (C$_6$D$_6$, δ in ppm): 4.99 (m, 3H, H$_{Cp}$), 4.85 (m, 2H, H$_{Cp}$), 4.81 (m, 1H, H$_{Cp}$), 4.75 (m, 1H, H$_{Cp}$), 4.70 (m, 1H, H$_{Cp}$), 5.86 (d, 1H, $J = 2$ Hz,

H_8), 3.08 (d, 1H, $J = 2$ Hz, H_7), 1.43 (s, 3H, H_{16}), 1.44 (s, 3H, H_{17}), 1.17 (s, 3H, $H_{16'}$), 1.00 (s, 3H, $H_{17'}$), 7.20–6.85 (m, 4H, $H_{2–5}$). MS (160°C, EI): 616 (M − CO$^+$), 588 (M − 2CO$^+$), 560 (M − 3CO$^+$), 532 (M − 4CO$^+$), 429 (M − Rh(CO)$_2^+$).

3.12. Synthesis of [(η^5:η^5-CpCMe$_2$C$_9$H$_6$)Rh$_2$(nbd)$_2$] 14

A 1.4 ml sample of butyllithium (1.6 M) was added to a solution of 250 mg $C_5H_5C(CH_3)_2C_9H_7$ in 20 ml THF and stirred at r.t. After 3 h a THF solution of 520 mg [Rh(nbd)Cl]$_2$ was added to the red reaction mixture and stirred for 2 h. The solvent was removed in vacuo. The reaction mixture was filtered over a short column of Al_2O_3. The first fraction eluted with hexane contained a small quantity of 4 contaminated with [(η^5:η^5-CpCMe$_2$C$_9$H$_6$)Rh$_2$(nbd^2)] 14. The main fraction of 14 was eluted with ether as an orange band with a yield of 424 mg (62%).

Compound 14: ^{1}H-NMR (C$_6$D$_6$, δ in ppm): 4.98 (m, 1H, H_{Cp}), 4.96 (m, 2H, H_{Cp}), 4.89 (m, 1H, H_{Cp}), 5.93 (dd, 1H, $J = 2.8$ Hz, $J_{H–Rh} = 2$ Hz, H_8), 4.75 (d, 1H, $J = 2.8$ Hz, H_7), 1.61 (s, 3H, H_{16}), 1.57 (s, 3H, H_{17}), 7.70 (m, 1H, H_2), 7.17 (m, 1H, H_5), 7.05 (m, 2H, $H_{3/4}$), 3.19 (m, 4H, H_{nbd}), 3.27 (m, 2H, H_{nbd}), 1.01 (t, 2H, $J = 1.6$ Hz, H_{nbd}), 3.36 (m, 2H, $H_{nbd'}$), 3.31 (m, 2H, $H_{nbd'}$), 3.02 (m, 2H, $H_{nbd'}$), 0.81 (t, 2H, $J = 1.6$ Hz, $H_{nbd'}$). ^{13}C-NMR (C$_6$D$_6$): 83.6 ($J_{C–Rh} = 4.3$ Hz, C_{Cp}), 83.5 ($J_{C–Rh} = 4.4$ Hz, C_{Cp}), 83.4 ($J_{C–Rh} = 4.5$ Hz, C_{Cp}), 83.0 ($J_{C–Rh} = 4.5$ Hz, C_{Cp}), 119.0 ($J_{C–Rh} = 4.6$ Hz, C_{Cp}), 122.2, 121.8, 121.3, 120.0, 109.7 ($J_{C–Rh} = 2.5$ Hz), 104.5 ($J_{C–Rh} = 5$ Hz), 92.1 ($J_{C–Rh} = 5.5$ Hz), 71.3 ($J_{C–Rh} = 5$ Hz), 35.9, 32.0, 30.9, 57.3 ($J_{C–Rh} = 6.8$ Hz, C_{nbd}), 46.9 ($J_{C–Rh} = 2.6$ Hz, C_{nbd}), 28.5 ($J_{C–Rh} = 10.6$ Hz, C_{nbd}), 28.4 ($J_{C–Rh} = 10.6$ Hz, C_{nbd}), 58.6 ($J_{C–Rh} = 6.8$ Hz, $C_{nbd'}$), 47.7 ($J_{C–Rh} = 2.6$ Hz, $C_{nbd'}$), 39.8 ($J_{C–Rh} = 10.6$ Hz, $C_{nbd'}$), 37.8 ($J_{C–Rh} = 10.6$ Hz, $C_{nbd'}$). MS (140°C, EI): 610 (M$^+$), 518 (M − (nbd)$^+$).

3.13. Synthesis of [(η^5:η^5-CpCMe$_2$C$_9$H$_6$)Rh$_2$(cod)$_2$] 15

A 1.3 ml sample of butyllithium (1.6 M) was added to a solution of 220 mg $C_5H_5C(CH_3)_2C_9H_7$ in 20 ml THF and stirred at r.t. After 3 h a THF solution of 490 mg [Rh(cod)Cl]$_2$ was added to the red reaction mixture and stirred for 2 h. The solvent was removed in vacuo. The reaction mixture was filtered over a short column of Al_2O_3. The first fraction eluted with hexane contained 5 contaminated with [(η^5:η^5-CpCMe$_2$C$_9$H$_6$)Rh$_2$(cod)^2] 15. The main fraction of 15 was eluted with ether as an orange band with a yield of 412 mg (64%).

Compound 15: ^{1}H-NMR (C$_6$D$_6$, δ in ppm): 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_{16}), 1.68 (s, 3H, H_{17}), 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 (C$_6$D$_6$): 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), 112.6 ($J_{C–Rh} = 2$ Hz), 107.6 ($J_{C–Rh} = 4$ Hz), 93.0 ($J_{C–Rh} = 5.0$ Hz), 73.0 ($J_{C–Rh} = 5$ Hz), 36.8, 32.1, 31.3, 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, EI): 642 (M$^+$), 532 (M − (cod)$^+$), 426 (M − 2(cod)$^+$).

3.14. Synthesis of [(η^5-CpCMe$_2$C$_9$H$_5$D$_2$)Rh(cod)] 19

A 40 mg solution of 5 in THF was added to a solution of 15 mg KH in THF and this was stirred at r.t. The color of the reaction mixture changed from orange over red to brown. After 2 h the reaction mixture was quenched with 0.5 ml of D$_2$O, H$_2$ gas evolution was observed. The solvent was removed in vacuo. The reaction mixture was filtered over a short column of Al_2O_3. Using hexane [(η^5-CpCMe$_2$C$_9$H$_6$D$_2$)Rh(cod$^+$)] was isolated.

Compound 19: ^{1}H-NMR (C$_6$D$_6$, δ in ppm): 4.64 (td, 2H, $J = 2$ Hz, $J_{H–Rh} = 0.6$ Hz, H_{Cp}), 4.97 (t, 2H, $J = 2$ Hz, H_{Cp}), 6.02 (s, 1H, H_8), 1.78 (s, 6H, H_{16}), 7.60 (d, 1H, $J = 8$ Hz, H_2), 7.25 (d, 1H, $J = 8$ Hz, H_5), 7.19 (m, 1H, H_3), 7.09 (m, 1H, H_4), 3.99 (s br, 4H, H_{cod}), 2.25 (m, 4H, H_{cod}), 1.97 (m, 4H, H_{cod}). MS (120°C, EI): 434 (M$^+$), 326 (M − cod).

3.15. Reaction of 7 with potassium and [Rh(nbd)Cl]$_2$

A sample of 140 mg of 7 was refluxed in THF with potassium for 4 h. The solution turned dark during this time. After cooling to r.t. the potassium was filtered from the solution and 90 mg of [Rh(nbd)Cl]$_2$ dissolved in THF were added and stirred for 10 h. After removing the solvents in vacuo, the reaction mixture was filtered over a column of Al_2O_3. With hexane a fraction containing 4 contaminated with 14 was eluted. In the second band washed down with ether a mixture of 14, the starting material 7 and traces of [(η^5:η^5-CpCMe$_2$C$_9$H$_6$)Rh(nbd)Mn(CO)$_3$] were obtained. MS: 554 (M$^+$), 470 (M − 3CO$^+$), 378 (M − 3CO − nbd$^+$).

4. Supporting material

Additional material available from Cambridge Crystallographic Data Centre under the deposit number 100800 comprises atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

References

[1] (a) E.L. Mutterties, R.N. Rhodin, E. Band, C.F. Brucker, W.R. Pretzer, Chem. Rev. 79 (1979) 91. (b) T.J. Marks, Acc. Chem. Res. 25 (1992)57. (c) G. Süss-Fink, G. Meister, Adv. Organomet. Chem. 35 (1993) 41.

[2] (a) T.E. Bitterwolf, J. Organomet. Chem. 312 (1986), 197. (b) P.A. McGovern, K.P.C. Vollhardt, Synlett (1990) 493. (c) H. Werner, H.J. Scholz, R. Zolk, Chem, Ber. 118 (1985) 4531.

[3] H. Werner, Inorg. Chem. Acta 198 (1992) 715.

[4] (a) M.L.H. Green, N. Ishihara, J. Chem. Soc. Dalton Trans. (1994) 657. (b) G.M. Diamond, M.L.H. Green, N.A. Popham, A.N. Chernega, J. Chem. Soc. Chem. Commun. (1994) 727. (c) G.M. Diamond, M.L.H. Green, P. Mountford, N.A. Popham, A.N. Chernega, J. Chem. Soc. Chem. Commun. (1994) 103.

[5] W. Spaleck, M. Antberg, V. Dolle, R. Klein, J. Rohrmann, A. Winter, New J. Chem. 14 (1990) 499.

[6] R. Fierro, T.E. Bitterwolf, A.L. Rheingold, G.P.A. Yap, L.M. Liabe-Sands, J. Organomet. Chem. 524 (1996) 19.

[7] (a) H.G. Alt, J. Su Han, U. Thewalt, J. Organomet. Chem. 456 (1993) 89. (b) H.G. Alt, J. Su Han, R.D. Rogers, J. Organomet. Chem. 454 (1993) 165. (c) H.G. Alt, J. Su Han, R.D. Rogers, J. Organomet. Chem. 445 (1993) 115.

[8] R. Cramer, Inorg. Synth. XV, 14.

[9] J. Chatt, L.M. Venanzi, J. Chem. Soc. (1957) 4735.

[10] E.W. Abel, M.A. Bennet G. Wilkinson, J. Chem. Soc. (1959) 3178

[11] E.W. Abel, G. Wilkinson, J. Chem. Soc. (1959) 1501

[12] Csaszar, L. Hedberg, K. Hedberg, R.C. Burns, A.T.Wen, M.J. McGlinchey, J. Inorg. Chem. (1991) 1371

[13] I.M. Fussing, D. Pletcher, R.J. Whitby, J. Organomet. Chem. 470 (1994) 109.