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New trisubstituted cyclopentadienyl ligands: synthesis, characterisation and catalytic properties of mono and dinuclear cobalt, rhodium, iron and ruthenium complexes

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Abstract

The synthesis of a set of dialkyl 4-alkoxycarbonylcyclopenta-1,3-diene-1,2-diacetates (**1a**–**e**) is described. Their coordinating abilities as anions have been investigated in relation to the formation of new sandwich, half-sandwich and dinuclear complexes and their structural features. We report here the preparation and characterisation of some complexes such as a mononuclear half-sandwich cobalt(1,5-COD) complex which has shown to be a very efficient catalyst for the cyclocotrimerisation reaction of alkynes and nitriles to pyridines. Half-sandwich rhodiumdicarbonyl complexes containing trisubstituted cyclopentadienyl ligands with ester chains of different length have been employed successfully as catalysts for hydroformylation of styrene. Finally ligands **1a**–**e** have been used for the synthesis of ferrocenes and dinuclear carbonyl complexes of iron and ruthenium. The structures of the complexes 1,5-cyclooctadiene[1-methoxycarbonyl-3,4-di(methoxycarbonylmethylene)cyclopentadienyl]cobalt [Co(MDMCp)-COD] (**9**), dicarbonyl[1-methoxycarbonyl-3,4-di(methoxycarbonylmethylene)cyclopentadienyl]rhodium [Rh(MDMCp)$(CO)_2$] (**2a**) and of a new ferrocene complex [Fe$(MDMCp)_2$] (**15a**) have been determined by X-ray diffraction methods.

Keywords: Substituted cyclopentadiene; Cyclopentadienyl complexes: cobalt, rhodium, iron, ruthenium; Alkyne cyclisation; Hydroformylation

1. Introduction

Derivatives of cyclopentadiene form one of the most important and versatile classes of ligands in the metallorganic chemistry. In their substituted or unsubstituted form they are able to stabilise metals in both high or low oxidation states through $\eta^1-\eta^5$ bonding modes [1]. The functionalisation of the cyclopentadienyl ring can alter significantly the steric and electronic properties of the corresponding complexes [2].

In the last few years, significant efforts have been devoted to work out smooth synthetic procedures for the preparation of new multiple functionalised cyclopentadienyl ligands and their sandwich and half-sandwich metal complexes [2–4].

Several synthetic strategies are available for the synthesis of substituted mono- and di-η^5-cyclopentadienyl metal complexes. Two main experimental approaches can be distinguished: the former is based on the direct use of suitable substituted cyclopentadienyl rings which are caused to react with transition metal complexes according to the procedure for the synthesis of sandwich and half-sandwich complexes [5]; the latter is based on the introduction of substituents in the ring after preparation of a cyclopentadienyl metal complex. This includes metallation reactions and electrophilic aromatic substitution reactions [6].

Recently we developed a new multistep procedure to prepare a cyclopentadiene derivative substituted by one

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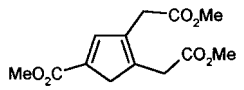
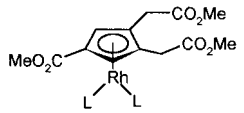
methoxycarbonyl and two methoxycarbonylmethylene functions (**1a**, HMDMCp) [7].



1a, HMDMCp

Our procedure consists of a palladium-catalysed ring-forming oxidative carbonylation of benzyl methyl 2,2-diprop-2-ynylmalonate, followed by the elimination of the benzyloxycarbonyl group and double bond isomerisation. The cyclopentadienyl anion (**1a**) was caused to react with rhodium complexes [{RhCl(L)$_2$}$_2$], [L = CO, C_2H_4, 1,5-cyclooctadiene (COD)], yielding the corresponding η^5-cyclopentadienyl complexes (**2a**–**a**″).



2a L = CO
2a' L = C_2H_4
2a" L-L = COD

Complexes **2a**′ and **2a** are efficient catalysts for the alkyne-nitrile cyclocotrimerisation to pyridines and for the hydroformylation of styrene and 1-hexene, respectively, showing a higher activity compared with the corresponding unsubstituted cyclopentadienylrhodium complexes [7].

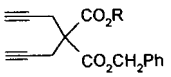
Herein we report the results concerning the synthesis and characterisation of a mononuclear half-sandwich cobalt complex containing ligand **1a**. Its catalytic activity was tested in cyclocotrimerisation reactions of alkynes and nitriles to pyridines. Moreover our synthetic procedure gave easy access to a set of trisubstituted cyclopentadienyl ligands with C_1 to C_{12} ester chains and their corresponding η^5-cyclopentadienylrhodiumdicarbonyl complexes, which were tested as catalysts for the hydroformylation of styrene. Trisubstituted cyclopentadienyl ligands of the type **1a**–**e** were also used in the synthesis of ferrocenes and dinuclear carbonyl complexes of iron and ruthenium.

The crystal structures of the complexes 1,5-cyclooctadiene[1 - methoxycarbonyl - 3,4 - di(methoxycarbonylmethylene)cyclopentadienyl]cobalt [Co(MDMCp)COD], (**9**), dicarbonyl[1methoxycarbonyl-3,4-di-(methoxycarbonylmethylene)cyclopentadienyl]rhodium [Rh(MDMCp)(CO)$_2$] (**2a**), and of a new ferrocene complex [Fe(MDMCp)$_2$] (**15a**) are also reported.

2. Results and discussion

2.1. Ligand synthesis

The synthetic procedure yielding dimethyl 4-methoxycarbonylcyclopenta-1,3-diene-1,2-diacetate was appropriately adapted in order to obtain trisubstituted cyclopentadiene derivatives containing suitable ester groups. For this purpose we prepared alkyl benzyl 2,2-diprop-2-ynylmalonate (**3a**–**d**) which underwent palladium-catalysed oxidative carbonylation to cyclic ester derivatives.



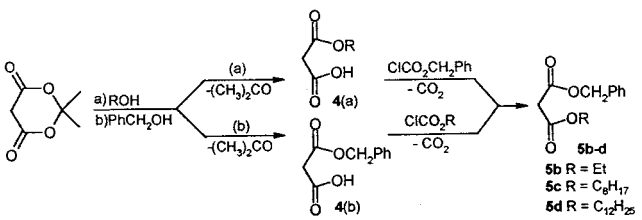
3a: R = Me
3b: R = Et
3c: R = C_8H_{17}
3d: R = $C_{12}H_{25}$

The presence of a smoothly hydrolisable ester benzyl group favoured decarboxylation followed by double bond isomerisation to a trisubstituted cyclopentadiene derivative. Product **3a** was obtained as reported [7] starting from the commercially available methyl benzyl malonate. Substrates **3b**–**d** could be prepared through two alternative ways (Scheme 1) both starting from 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum acid).

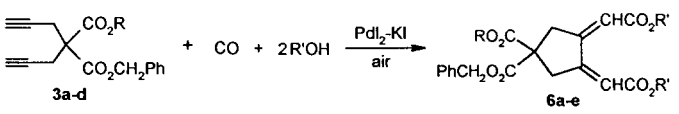
Procedure (a) allows the synthesis of a variety of malonic benzyl-alkyl diesters. Alternatively procedure (b), if the alkyl chloroformate is not commercially available, diester **5** can be prepared from the acid chloride of **4**(b).

The overall yields of isolated malonic diesters **5b**–**d** (R = Et, C_8H_{17}, $C_{12}H_{25}$) based on the starting Meldrum acid were ca. 35–40%. The propynylation of benzyl alkyl malonates (**5a**–**d**) was carried out according to the procedure reported previously [7] with yields of **3a**–**d** ranging from 83 to 72%.

The subsequent oxidative carbonylation was based on our procedure described previously [7]. Reactions and yields are shown in Scheme 2.

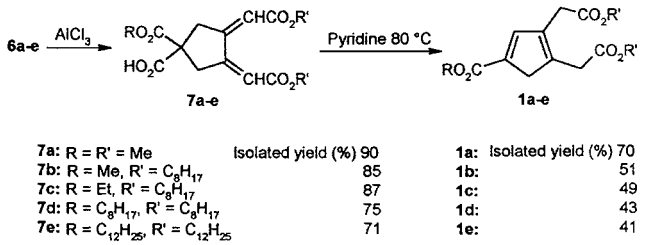


Scheme 1.



		Isolated yield (%)
6a:	R = R' = Me	68
6b:	R = Me, R' = C_8H_{17}	62
6c:	R = Et, R' = C_8H_{17}	63
6d:	R = C_8H_{17}, R' = C_8H_{17}	52
6e:	R = $C_{12}H_{25}$, R' = $C_{12}H_{25}$	41

Scheme 2.



7a: R = R' = Me	Isolated yield (%) 90	**1a:**	Isolated yield (%) 70
7b: R = Me, R' = C_8H_{17}	85	**1b:**	51
7c: R = Et, R' = C_8H_{17}	87	**1c:**	49
7d: R = C_8H_{17}, R' = C_8H_{17}	75	**1d:**	43
7e: R = $C_{12}H_{25}$, R' = $C_{12}H_{25}$	71	**1e:**	41

Scheme 3.

The results show that the carbonylation reaction is efficient and general for linear alcohols with chains from C_1 to C_{12}. Elimination of the benzyl group followed by decarboxylation and isomerization reactions to products **1a**–**e** were carried out according to a reported procedure [8] (Scheme 3).

This multistep process enabled the synthesis of new trisubstituted cyclopentadiene derivatives functionalized with aliphatic ester chains of variable length and steric hindrance.

Alternatively a more direct synthetic way to prepare cyclopentadienes **1** was worked out, based on a two stage process consisting of the introduction of two propynyl groups into Meldrum acid, followed by oxidative carbonylation in methanol in the presence of 10% Pd–C and KI. A mixture of two isomers **8a** (78:22 molar ratio, GC) was obtained in 38% isolated yield (Scheme 4).

Isomerization of **8a** led to product **1a** (70% isolated yield). Such a procedure, however, works in reasonable yield only for methyl esters.

2.2. Synthesis of the metal complexes

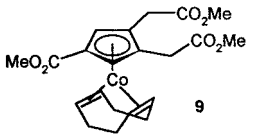
Cyclopentadiene derivatives **1a**–**e** were used as precursors of ligands for metallorganic complexes.

2.2.1. Mononuclear cobalt complex

Cyclopentadiene derivative **1a** was converted into cyclopentadienyl anion (MDMCp) and caused to react with $CoCl(PPh_3)_3$ in the presence of 1,5-cyclooctadiene. Complex **9** (39% yield) was obtained as an air stable red orange solid according to Eq. (1).

$$\mathrm{LiMDMCp} + \mathrm{CoCl(PPh_3)_3} + \text{1,5-COD} \rightarrow \underset{\mathbf{9}}{\mathrm{Co(MDMCp)(COD)}} + \mathrm{LiCl} + 3\mathrm{PPh_3} \quad (1)$$

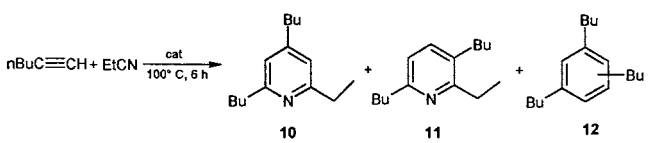
IR, ^{1}H- and ^{13}C-NMR data of complex **9** shows a close analogy to those of the corresponding rhodium complex described previously [7] and an X-ray analysis confirms the proposed structure.



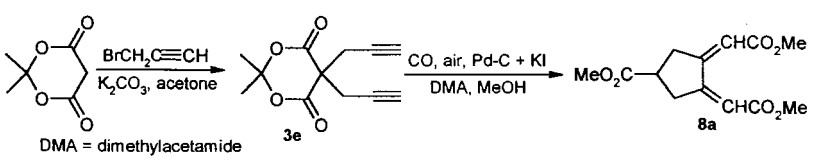
A view of the structure is shown in Fig. 1 together with the atomic labelling system; selected bond distances and angles are given in Table 1. The cobalt atom interacts in a η^5-fashion with the substituted cyclopentadienyl ring of ligand **1a** and completes its coordination through two η^2-interactions with the double bonds of the COD ligand. The distance of cobalt from the centroid M(1) of the Cp is 1.714(2) Å and those from the midpoints M(2) and M(3) of the two double bonds are 1.905(3) and 1.900(2) Å, respectively. The cobalt atom is practically coplanar with M(1), M(2) and M(3). The mean planes through the Cp ring and through the C(14)C(15)C(18)C(19) atoms are almost parallel, the dihedral angle being 1.9(1)°. The methoxycarbonyl substituent is practically coplanar with the Cp ring, whereas the two methoxycarbonylmethylene substituents point on the same side almost perpendicularly to the ring and approaching to one another with a short O(4)···O(5) contact of 3.252(2) Å.

The C(1)–C(6) bond involving the methoxycarbonyl substituent on the Cp ring is approximately parallel to both double bonds of complexed COD.

Catalytic activities and selectivities of various cobalt and rhodium complexes containing unsubstituted and substituted cyclopentadienyl ligands were compared utilising test reaction 2. The homogeneous cyclocotrimerization of 1-hexyne and propionitrile to pyridines (Eq. (2)) was carried out catalytically in the presence of complex **9** under the reaction conditions used for complex $[(MDMCp)Rh(C_2H_4)_2]$ [7] and for other analogous experiments reported in the literature [9].



(2)



Scheme 4.

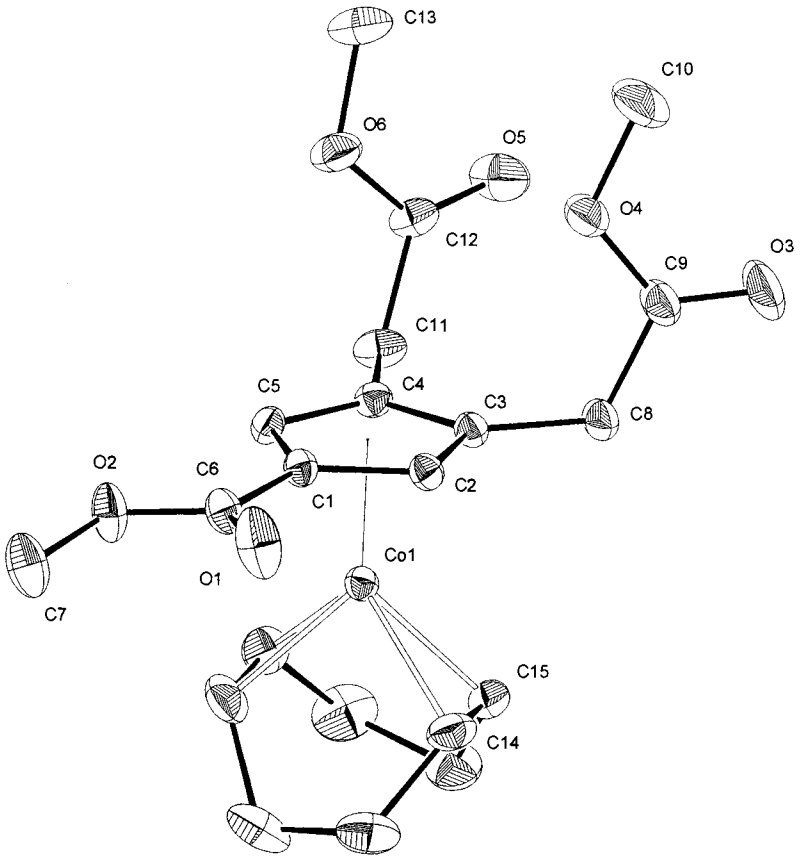


Fig. 1. ORTEP view of the structure of the complex **9** together with the atomic numbering scheme. The ellipsoids for the atoms are drawn at 30% probability level.

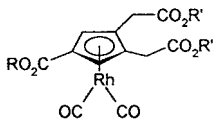
In Table 2 the activity and selectivity data are summarised along with those obtained using the reported rhodium complex, unsubstituted (cyclopentadienyl)cobalt complex [CpCo(COD)] and (cyclopentadienyl)rhodium complex [CpRh(COD)] as catalysts, respectively.

Differences in product distribution and yields are due to the influence of the substituents in the cyclopentadienyl ring and the neutral ligands. In the context of pyridine syntheses from alkynes and nitrile catalysed homogeneously by (cyclopentadienyl)cobalt complexes, it was found that electron-withdrawing groups on the cyclopentadienyl ring significantly increase the activity. A good linear correlation between the ^{59}Co chemical shift and the catalytic properties was found [10] for all the monosubstituted cyclopentadienyl ligands investigated. Compounds of this type having electron-withdrawing substituents are more active in catalysis than the parent compounds [11]. Exceptions are multisubstituted cyclopentadienyl ligands such as $1,2(Me_3Si)_2C_5H_3$ and Ph_4C_5H which gave both high regioselectivity and activity [11]. This is probably due to steric effects on the catalytically active species. Sterically demanding substituents force a parallel orientation of substituents and COD double bonds. In our case these features are present: the catalytic properties of the trisubstituted (cyclopentadienyl)cobalt confirm that a relationship between electron distribution at the cobalt and the activity of the complex in the synthesis of pyridine derivatives is present. It can be observed that complex **9** containing electron-withdrawing substituents gave the highest yield. The corresponding rhodium complex did not give an appreciable yield under the same conditions. To achieve a similar activity, the rhodium complex needs a different neutral ligand (C_2H_4 instead of COD) and higher temperature (130°C). Actually the chelating COD ligand behaves as a 'blocking' system for the (cyclopentadienyl)rhodium complex in the pyridine synthesis, while a weaker stabilising neutral ligand such as C_2H_4 is able to provide the propagating catalytic species. The selectivities obtained with the cobalt complexes are higher than those obtained with the rhodium complex, cyclization to pyridines (**10** and **11**) being mainly preferred to the trimerization of the alkyne (**12**) [9,11].

2.2.2. Mononuclear rhodium complexes

Mono η^5-cyclopentadienylrhodiumdicarbonyl was prepared according to the reported procedure [7] using ligand **1a** ($R = R' = Me$). Crystals of complex **2a**

[Rh(MDMCp)(CO)$_2$] suitable for a X-ray analysis were grown in *n*-hexane at low temperature.



2a R = R' = Me
2b R = Me, R' = C_8H_{17}
2d R = R' = C_8H_{17}

The structure, in agreement with the proposed one, is shown in Fig. 2 together with the atomic labelling system; selected bond distances and angles are given in Table 3. The rhodium atom interacts in a η^5-fashion with the substituted cyclopentadienyl ring of the ligand **1a** and with two terminal carbonyl groups. The distance of rhodium with the centroid M(1) of the Cp is 1.912(7) Å. The rhodium atom is coplanar with M(1) and the C(14) and C(15) atoms of the carbonyls. As in **9** the methoxycarbonyl substituent is practically coplanar with the Cp ring, whereas the two methoxycarbonylmethylene substituents point on the same side almost perpendicularly to the ring and approaching to one another with a short O(3)···O(6) contact of 3.24(1) Å.

Complexes **2b** (R = Me, R′ = C_8H_{17}) and **2d** (R = R′ = C_8H_{17}) were analogously synthesised in 37 and 32% yield, respectively. IR spectral data show two stretching frequencies (symmetric and antisymmetric) of the carbonyl groups. It is well-known [12] that for such systems the values of ν_{CO} reflect variations in electron densities on the metal. Complexes **2a** [7], **2b** and **2d** show identical ν_{CO} values (see Section 3) confirming that the electronic densities on the metal centres are practically comparable. Such complexes were used as catalysts for the hydroformylation reaction of styrene (Eq. (3)) to estimate a possible steric influence of the C_8 ester chains on the activity and selectivity of the process under practically comparable electronic factors (Table 4).

$$PhCH{=}CH_2 + CO + H_2 \xrightarrow{\textbf{2a,b,d}} \underset{\textbf{13}}{PhCH(CH_3)CHO} + \underset{\textbf{14}}{PhCH_2CH_2CHO} \quad (3)$$

Analogous activities and practically quantitative yields were obtained for the three complexes under the adopted conditions. It can be observed that the presence of the three C_8 octyl chains does not substantially modify the selectivity. From the X-ray structure of **2a** it can be inferred that the ester chains of the two acetyl groups point perpendicularly to the cyclopentadienyl ring plane. This steric situation is probably maintained in solution too. The spatial disposition adopted by the chains in solution does not present a real steric hindrance to olefin coordination on the metal and therefore can not influence the regiospecific formation of a linear or branched alkylrhodium intermediate. A slight difference in the selectivity was observed when the three ester groups were not the same, however. Thus a small change in the substituents of complex **2b** with one methyl and two octyl ester chains probably favoured a preferential coordination of the olefin to the catalytic centre with a shift of the selectivity towards the branched aldehyde. The electronic effects play a more important role in the transition state, which probably includes a slippage or haptotropic shift of the cyclopentadienyl ligand to avoid an unfavorable 20-electron configuration [13,14]. Apparently the three substituents

Table 1
Selected bond lengths (Å) and angles (°) for **9** [a]

Bond distances			
Co1–C1	2.095(2)	C4–C11	1.507(2)
Co1–C2	2.106(2)	C14–C15	1.398(3)
Co1–C3	2.126(2)	C1–C19	1.393(3)
Co1–C4	2.108(2)	C6–O1	1.205(2)
Co1–C5	2.054(2)	C6–O2	1.340(2)
Co1–M1	1.714(2)	C7–O2	1.441(3)
Co1–M2	1.905(3)	C8–C9	1.501(3)
Co1–M3	1.899(2)	C9–O3	1.189(3)
C1–C2	1.419(2)	C9–O4	1.322(3)
C1–C5	1.433(2)	C10–O4	1.437(3)
C2–C3	1.421(2)	C11–C12	1.510(3)
C3–C4	1.412(2)	C12–O5	1.192(3)
C4–C5	1.428(2)	C12–O6	1.329(2)
C1–C6	1.461(2)	C13–O6	1.444(3)
C3–C8	1.503(2)		
Bond angles			
M1–Co1–M2	134.4(1)	O4–C9–C8	113.9(2)
M1–Co1–M3	134.5(1)	C4–C11–C12	112.1(2)
M2–Co1–M3	91.1(1)	O5–C12–O6	123.8(2)
O1–C6–O2	123.2(2)	O5–C12–C11	124.8(2)
O1–C6–C1	124.8(2)	O6–C12–C11	111.4(2)
O2–C6–C1	111.9(2)	C6–O2–C7	116.5(2)
C9–C8–C3	117.0(2)	C9–O4–C10	115.8(2)
O3–C9–O4	123.1(2)	C12–O6–C13	117.4(2)
O3–C9–C8	122.9(2)		

[a] M1 is the centroid of the Cp ring. M2 is the midpoint of the C14–C15 double bond of the COD ligand. M3 is the midpoint of the C18–C19 double bond of the COD ligand.

Table 2
Reaction of 1-hexyne with propionitrile at 100°C for 6 h [a]

Catalytic complex	Yield (%) [b]		Selectivity (%) [b]	
	10+**11**	**12**	**10**/(**10**+**11**)	(**10**+**11**)/(**10**+**11**+**12**)
CpCo(COD) [c]	65 (55) [d]	22	59	75
(MDMCp)-Co(COD) **9**	88 (77) [d]	8	52	92
$CpRh(C_2H_4)_2$ [e]	67	18	56	79
(MDMCp)-$Rh(C_2H_4)_2$ [e]	78	15	44	84

[a] 1-Hexyne (1.05 ml, 9.2 mmol), propionitrile (3.62 ml), catalytic complexes (0.092 mmol), EtCN:*n*-BuC≡CH molar ratio = 5.5; *n*-BuC≡CH: Co-catalyst = 100.
[b] By GLC, based on starting alkyne.
[c] Conversion 90%.
[d] Isolated yields.
[e] Temperature = 130°C.

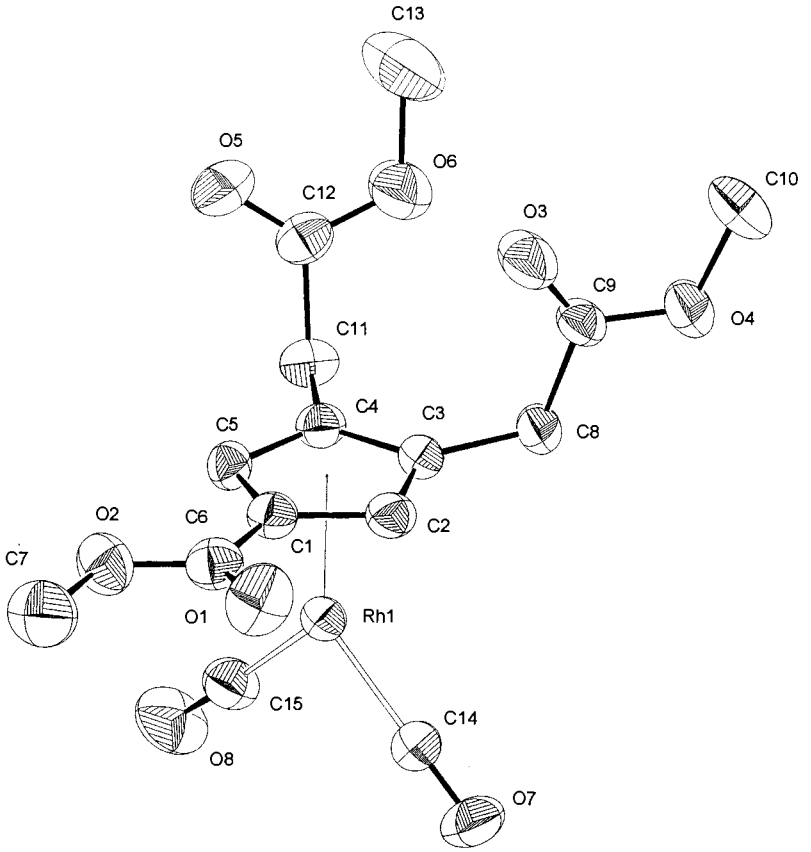


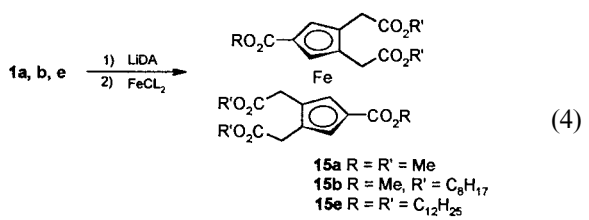
Fig. 2. ORTEP view of the structure of the complex **2a** together with the atomic numbering scheme. The ellipsoids for the atoms are drawn at 30% probability level.

on the ring do not produce a particular hindrance on the metallic centre and on its surroundings.

The synthesis and structural characterisation of sandwich and dinuclear iron and ruthenium complexes containing trisubstituted cyclopentadienyl ligands have also been pursued.

2.2.3. Ferrocenes

For the synthesis of ferrocenes we started with cyclopentadiene **1a** which was transformed in its anion using lithium diisopropylamide. The anion was caused to react with dry $FeCl_2$ according to the (eq. (4)). Ferrocene **15a** was obtained in 35% isolated yield.



(4)

15a R = R' = Me
15b R = Me, R' = C_8H_{17}
15e R = R' = $C_{12}H_{25}$

Using the same procedure we obtained ferrocenes **15b** (R = Me, R′ = C_8H_{17}) and **15e** (R = R′ = $C_{12}H_{25}$) in 28 and 15% isolated yield, respectively. The low yields obtained have to be attributed to losses in purification. ^{1}H-NMR data at room temperature gave evidence about the steric arrangement of the cyclopentadienyl ligands of these complexes. Only one signal was observed for the four hydrogen of the two cyclopentadienyl rings. This equivalence points out a complete rotational freedom of the two rings. Moreover the hydrogens of the two methylene groups bonded to each ring are diastereotopic, two doublets with geminal coupling constants of 16.3 Hz being present.

The structure of complex [Fe(MDMCp)$_2$] (**15a**) determined by X-ray study, is shown in Fig. 3 together with the atomic labelling system; selected bond distances and angles are given in Table 5. The ferrocene type complex has an imposed crystallographic C_i symmetry with the inversion center on the Fe atom and can be considered as a sandwich complex with a staggered conformation. The distance of the centroid of the substituted Cp from the Fe atom is 1.648(2) Å and the η^5 interaction is symmmetrical as the Fe–C distances range from 2.037(2) to 2.050(3) Å. As in **9** and **2a**, the methoxycarbonyl substituent is practically coplanar with the Cp ring, whereas the two methoxycarbonylmethylene substituents point on the same side almost perpendicularly to the ring and approaching to one another with a short O(3)···O(6) contact of 3.221(4) Å.

2.2.4. Dinuclear complexes: Fe and Ru complexes

Cyclopentadiene derivative **1a** (HMDMCp) was caused to react with $Fe_2(CO)_9$ (Eq. (5)) and $Ru_3(CO)_{12}$ (Eq. (6)) in the presence of norbornene as hydrogen acceptor according to procedures adapted from the literature [15]. Complexes $[(MDMCp)Fe(CO)_2]_2$ (**16**) and $[(MDMCp)Ru(CO)_2]_2$ (**17**) respectively were obtained.

$$2HMDMPc + Fe_2(CO)_9 + C_7H_{10} \xrightarrow[\text{(reflux)}]{n\text{-heptane}} \underset{\mathbf{16},\ 40\%\ \text{yield}}{3[(MDMCp)Fe(CO)_2]_2} + 5CO + C_7H_{12} \quad (5)$$

Table 3
Selected bond lengths (Å) and angles (°) for **2a** [a]

Bond distances			
Rh1–C1	2.285(6)	O2–C7	1.464(10)
Rh1–C2	2.235(8)	O3–C9	1.158(9)
Rh1–C3	2.289(7)	O4–C9	1.322(8)
Rh1–C4	2.274(7)	O4–C10	1.43(2)
Rh1–C5	2.215(6)	O5–C12	1.178(9)
Rh1–M1	1.912(7)	O6–C12	1.29(1)
Rh1–C14	1.860(8)	O6–C13	1.48(2)
Rh1–C15	1.837(10)	C1–C6	1.476(8)
C1–C2	1.419(9)	C3–C8	1.509(9)
C1–C5	1.415(9)	C4–C11	1.505(9)
C2–C3	1.403(8)	C8–C9	1.503(12)
C3–C4	1.412(9)	C11–C12	1.488(12)
C4–C5	1.434(8)	O7–C14	1.113(10)
O1–C6	1.170(10)	O8–C15	1.152(13)
O2–C6	1.325(10)		
Bond angles			
C15–Rh1–M1	134.9(3)	O4–C9–C8	110.3(6)
C14–Rh1–M1	135.0(3)	O3–C9–C8	125.5(7)
C14–Rh1–C15	90.1(4)	O3–C9–O4	124.2(7)
O2–C6–C1	111.1(7)	C4–C11–C12	111.4(6)
O1–C6–C1	124.6(7)	O6–C12–C11	113.2(8)
O1–C6–O2	124.3(7)	O5–C12–C11	124.1(7)
C3–C8–C9	111.7(6)	O5–C12–O6	122.7(8)
C6–O2–C7	113.8(7)	Rh1–C14–O7	179.4(7)
C9–O4–C10	116.6(7)	Rh1–C15–O8	177.5(8)
C12–O6–C13	116.8(10)		

[a] M1 is the centroid of the Cp ring.

Table 4
Reaction of styrene with CO and H_2 (1:1 vol/vol, 70 bar) in toluene (5 ml) at 100°C for 3 h, Rh-catalyst 0.059 mmol, olefin 11.72 mmol

Rh-catalyst	Olefin conversion (%) [a]	Selectivity (%) [a]		
		13	**14**	**13/14**
2a	99	58	42	1.38
2b	98	64	36	1.78
2d	98	59	41	1.44

[a] By GLC, based on starting styrene.

$$6HMDMPc + 2Ru_3(CO)_{12} + 3C_7H_{10} \xrightarrow[\text{(reflux)}]{n\text{-heptane}} \underset{\mathbf{17},\ 42\%\ \text{yield}}{3[(MDMCp)Ru(CO)_2]_2} + 12CO + C_7H_{12} \quad (6)$$

The infrared spectra restricted to the carbonyl region (1700–2200 cm^{-1}) of complexes **16** and **17** were recorded in the solid state (KBr) and in liquid solution (CH_2Cl_2). A comparison of these values with the exhaustive IR data reported in the literature [16] show a very strict analogy with the bands of the isomorphous and isostructural complexes $[CpFe(CO)_2]_2$ and $[CpRu(CO)_2]_2$ and other parent complexes of iron and ruthenium in the *cis* geometry with two bridging and two terminal CO groups (molecular symmetry C_{2v}) (Scheme 5, Table 6).

The two coordinated cyclopentadienyl rings and their substituents exhibit coincident ^1H- or ^{13}C-NMR single sharp signals in $CDCl_3$ or CD_3COCD_3 at room temperature for complexes **16** and **17**. The NMR equivalence of the two ligands and the finding that the IR carbonyl bands in solution are analogous with those in the solid state, except for slight shifts of the frequencies, confirm that the *cis* carbonyl-bridged dimer is present as the predominant form of **16** and **17** also in solution. Reactions of HCpMDM with $Fe_2(CO)_9$ and $Ru_3(CO)_{12}$ likewise proceed in selective homogeneous fashion yielding complexes **16** and **17** in the less common *cis* geometry. As the steric bulk of the cyclopentadienyl ligand increases, the stability of the *cis* bridged isomer decreases to the point that with $[(C_5Me_5)M(CO)_2]_2$ and $[(C_5Me_4CF_3)M(CO)_2]_2$ (M = Fe, Ru) [17], only the *trans* bridged isomer is observed. Some dinuclear carbonyl metal complexes containing multiply substituted cyclopentadienyl ligands exhibit a *cis* carbonyl-bridged dinuclear structure either in the solid state or in solution, however, *trans* carbonyl-bridged and *cis* and *trans* non bridged dimers being absent [15,18].

In conclusion the syntheses and characterisations of metal complexes containing a new trisubstituted cyclopentadienyl ligand (**1a**–**d**) has been described. The mononuclear complexes of cobalt **9** and rhodium **2a**, **2b** and **2d** have displayed an interesting catalytic activity. The ligands used also allow the selective preparation of dinuclear complexes of iron and ruthenium in their *cis* form and sandwich complexes of iron. X-ray analyses elucidate the structural features of some of these complexes.

3. Experimental

Melting points were determined by an Electrothermal Melting Point apparatus and are uncorrected. Elemen-

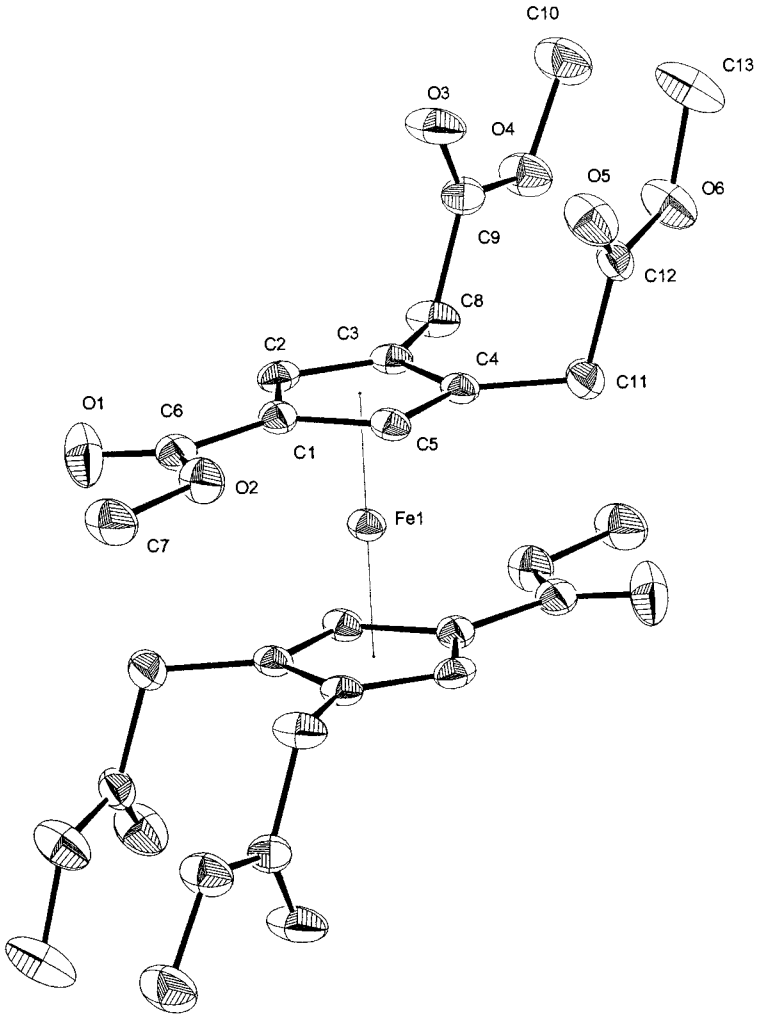


Fig. 3. ORTEP view of the structure of the complex **15a** together with the atomic numbering scheme. The ellipsoids for the atoms are drawn at 30% probability level.

tal analyses were carried out with a Carlo Erba model EA 1108 elemental analyzer. GLC analyses were performed on HR 3800 Dani Instrument using a methylsilicone (OV101) stationary phase, capillary column (25 m). Products and starting substrates were quantitatively determined by GLC using the internal standard method. Merk silica gel 60 (230–400 mesh), Florisil (100–200 mesh, Floridrin Co., USA) and Fluka 507 neutral alumina (100–125 mesh) were used for preparative column chromatography. ^{1}H- and ^{13}C-NMR spectra were run on AC 300 Bruker instruments using the frequence of Me_4Si as reference. Mass spectra were obtained with a Finnigan Mat SSQ 710 at variable ionizing voltage. GC-MS analyses were made using a HP-5890 Series II (Hewlett–Packard) gaschromatograph, equipped with a HP-5971 Series MSD and a split-splitless injector. IR spectra were recorded on Nicolet 5PC FT-IR spectrometer.

3.1. Materials

Solvents were purified by standard methods [19] and stored on molecular sieves (Type 4Å, 1/8 pellets, Union Carbide). 2-Propynylbromide, malonic esters 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum acid), nitriles, alkylchloroformates, oxalylchloride, other acetylenic and olefinic derivatives and $Fe_2(CO)_9$ and $Ru_3(CO)_{12}$ were commercial products. Rhodium complexes $[RhCl(CO)_2]_2$ [20], $[RhCl(CH_2{=}CH_2)_2]_2$ [21], $[CpRh(CH_2{=}CH_2)_2]$ [22] and cobalt complexes $CoCl(PPh_3)_3$ [23] and CpCo(COD) [24] were prepared according to the literature methods.

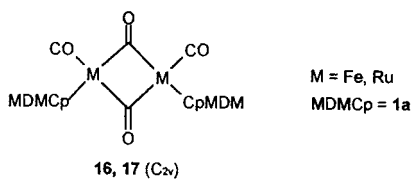
3.2. Synthesis of benzyl alkyl 2,2-dipropynylmalonate *3a–d*

Preparations of **3a** and **1a** was previously described [7]. Substrates **3b–d** were prepared as follows.

Table 5
Selected bond lengths (Å) and angles (°) for **15a** [a]

Bond distances			
Fe1–C1	2.037(2)	O2–C7	1.442(3)
Fe1–C2	2.042(3)	O3–C9	1.189(3)
Fe1–C3	2.046(3)	O4–C9	1.336(3)
Fe1–C4	2.050(3)	O4–C10	1.438(4)
Fe1–C5	2.049(3)	O5–C12	1.194(3)
Fe1–M1	1.648(2)	O6–C12	1.328(3)
C1–C2	1.428(4)	O6–C13	1.440(5)
C1–C5	1.429(5)	C1–C6	1.484(4)
C2–C3	1.421(4)	C3–C8	1.504(4)
C3–C4	1.428(5)	C4–C11	1.507(5)
C4–C5	1.411(3)	C8–C9	1.501(4)
O1–C6	1.200(5)	C11–C12	1.518(4)
O2–C6	1.338(4)		
Bond angles			
O2–C6–C1	111.0(2)	O4–C9–C8	110.0(2)
O1–C6–C1	124.8(3)	O3–C9–C8	126.2(3)
O1–C6–O2	124.2(3)	O3–C9–O4	123.8(3)
C3–C8–C9	114.4(2)	C4–C11–C12	108.9(3)
C6–O2–C7	116.5(2)	O6–C12–C11	111.9(3)
C9–O4–C10	117.0(2)	O5–C12–C11	124.7(3)
C12–O6–C13	115.0(3)	O5–C12–O6	123.4(3)

[a] M1 is the centroid of the Cp ring.



Scheme 5.

3.2.1. Preparation of malonic acid mono benzyl ester *4b*

A solution of 2,2-dimethyl-1,3-dioxane-4,6-dione (25 g, 0.174 mol), benzylic alcohol (36 ml, 0.347 mol) in toluene (100 ml) was reacted under reflux for 24 h. The cooled mixture was poured into a Na_2CO_3 solution (5% w in water). The aqueous phase was extracted with Et_2O and the combined organic layers were acidified with 1 N HCl. The organic product was extracted with EtOAc and dried with Na_2SO_4. Monoester of malonic acid was recovered as a white solid (16.98 g, 50% yield) m.p. 49–50°C. IR (KBr) ν cm^{-1}: 3212 (s), 1741 (s), 1704 (s). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 3.47 (s, 2H, CH_2), 5.20 (s, 2H, CH_2), 7.35 (br s, 5H, aromatics), 9.60 (br s, 1H, OH).

Other alkyl monoesters of malonic acid **4a** could be prepared analogously.

3.2.2. Preparation of ethyl benzyl and octyl benzyl malonates

In a dry Schlenk flask (100 ml) **4b** (1.94 g, 0.01 mol) and triethylamine (1.39 ml, 0.01 mol) were dissolved in THF (30 ml). The cooled mixture (4°C) was added with alkylchloroformate ($R = C_2H_5$, 0.96 ml, 0.01mmol; $R = C_8H_{17}$ 1.96 ml, 0.01 mmol) and stirred for 30 min. The mixture was filtered and the solution was concentrated under vacuum to obtain colourless liquid ($R = C_2H_5$ 1.49 g, 67% yield). MS (EI, m/z): 222 (M^+, 5), 194 (3), 107 (71), 91 (100). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.22 (t, 3H, $J = 7.1$ Hz, Me), 3.39 (s, 2H, CH_2), 4.14 (q, 2H, $J = 7.1$ Hz, OCH_2), 5.17 (s, 2H, CH_2), 7.33 (br s, 5H, aromatics); ($R = C_8H_{17}$ 1.99 g, 65% yield). MS (EI, m/z): 306 (M^+, 3), 194 (7), 107 (100), 91 (90). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, 3H, $J = 7.0$ Hz, Me), 1.23–1.29 (m, 10H, 5 CH_2), 1.59–1.62 (m, 2H, CH_2), 3.41 (s, 2H, CH_2), 4.11 (t, 2H,

Table 6
Vibrational frequencies of carbonyls (ν_{CO} (cm^{-1})) for $[CpM(CO)_2]_2$ complexes

M	Cp	Solvent	Terminal CO		Bridge CO	Ref.
Fe	C_5H_5	Hexane [a]	2005	1961	1794.5	[16]
Ru	C_5H_5	Heptane [b]	2010	1965	1794	[16]
Ru	C_5H_5	$CHCl_3$ [b]	2009	1968	1768	[16]
Ru	C_5H_5	CS_2 [a]	2004	1960	1785	[16]
Ru	MeC_5H_4	Heptane [b]	2006	1960	1790	[16]
Ru	MeC_5H_4	$CHCl_3$ [b]	2003	1959	1779	[16]
Ru	$[C_5H_4CH(NMe_2)]_2$	Heptane [b]	2002	1964	1793	[16]
Ru	C_9H_7 [c]	$CHCl_3$ [b]	2003	1961	1779	[16]
Fe	MDMCp [d]	KBr [b]	2004	1963	1779	[e]
Fe	MDMCp [d]	CH_2Cl_2 [b]	2008	1970	1786	[e]
Ru	MDMCp [d]	KBr [b]	2005	1960	1783	[e]
Ru	MDMCp [d]	CH_2Cl_2 [b]	2014	1973	1787	[e]

[a] At low temperature.
[b] At room temperature.
[c] Indenyl.
[d] 1-Metoxycarbonyl-3,4-di(metoxycarbonylmethylene)cyclopentadienyl.
[e] This work.

$J = 7.0$ Hz, OCH_2), 5.17 (s, 2H, CH_2), 7.33 (br s, 5H, aromatics).

3.2.3. Preparation of dodecyl benzyl malonate

In a dry flask (100 ml) to **4**(a) ($R = C_{12}H_{25}$, 4.21 g, 21.7 mmol) dissolved in toluene (30 ml) was added oxalylchloride (5.25 ml, 60 mmol) under argon. After stirring at 35°C for 24 h the mixture was concentrated under vacuum. The residue was diluted with THF (15 ml) and added with 1-dodecanol (3.64 g, 19.5 mmol) and triethylamine (1.72 ml, 19.5 mmol). The mixture was stirred at room temperature (r.t.) for 24 h. After the usual work up, product **5** ($R = C_{12}H_{25}$) was recovered and purified by silica gel flash column chromatography (hexane: EtOAc = 7:3 as eluent). A pale yellow oil was obtained (3.23 g, 8.9 mmol, 46% yield).). MS (EI, m/z): 362 (M^+, 3), 194 (10), 107 (92), 91 (100). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.89 (t, 3H, $J = 7.0$ Hz, Me), 1.24–1.30 (m, 18H, 9 CH_2), 1.58–1.61 (m, 2H, CH_2), 3.41 (s, 2H, CH_2), 4.12 (t, 2H, $J = 7.0$ Hz, OCH_2), 5.17 (s, 2H, CH_2), 7.33 (br s, 5H, aromatics).

*3.3. Propynylation of malonic esters: synthesis of **3a–e***

Propynylations of benzyl-alkyl malonates were carried out according to the procedure previously reported [7]. The yields and characterisations of products **3b–e** are the following.

Compound **3b** ($R = C_2H_5$) yellow oil, yield 80%. MS (EI, m/z): 298 (M^+, 6), 259 (4), 213 (7), 91 (100); IR (neat), ν cm^{-1}: 3300 (w), 2117 (w), 1733 (s), 1300 (m), 1212 (m); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.16 (t, 3H, $J = 7.1$ Hz, Me), 2.12 (t, 2H, $J = 2.7$ Hz, 2 HC≡), 3.01 (d, 4H, $J = 2.7$ Hz, 2 CH_2C≡), 4.16 (q, 2H, $J = 7.1$ Hz, CH_2), 5.20 (s, 2H, OCH_2Ph), 7.33 (br s, 5H, aromatics).

Compound **3c** ($R = C_8H_{17}$) yellow oil, yield 75%; MS (CI, m/z): 383 (MH^+,29); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, 3H, $J = 7.1$ Hz, Me), 1.20–1.26 (m, 10H, 5 CH_2), 1.52–1.55 (m, 2H, CH_2), 1.99 (t, 2H, $J = 2.7$ Hz, 2 HC≡), 3.01 (d, 4H, $J = 2.7$ Hz, 2 CH_2C≡), 4.08 (t, 2H, $J = 7.0$ Hz, OCH_2), 5.18 (s, 2H, OCH_2Ph), 7.32 (br s, 5H, aromatics).

Compound **3d** ($R = C_{12}H_{25}$) after purification by flash chromatography silica column (CH_2Cl_2: hexane = 7:3), yellow oil 72% yield. MS (CI, m/z): 439 (MH^+, 33); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.88 (t, 3H, $J = 7.1$ Hz, Me), 1.23–1.27 (m, 18H, 9 CH_2), 1.52–1.55 (m, 2H, CH_2), 2.00 (t, 2H, $J = 2.6$ Hz, 2 HC≡), 3.01 (d, 4H, $J = 2.6$ Hz, 2 CH_2C≡), 4.09 (t, 2H, $J = 7.0$ Hz, OCH_2), 5.19 (s, 2H, OCH_2Ph), 7.32 (br s, 5H, aromatics).

Compound **3e** yellow solid m.p. 128–129°C, 88% yield. MS (EI, m/z): 220 (M^+, absent), 205 (6), 162 (18), 89 (67), 43 (100); IR (KBr) ν cm^{-1}: 2999 (m), 2124 (w), 1735 (s); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.82, 1.83 (2s, 6H, 2 Me), 2.17 (t, 2H, $J = 2.6$ Hz, 2 HC≡), 2.86 (d, 4H, $J = 2.6$ Hz, 2 CH_2C≡).

3.4. Carbonylation reaction: synthesis of benzyl alkyl 3,4-di(alkoxycarbonylmethylene)cyclopentane

*3.4.1. Products **6b–e***

In a general procedure a 250 ml stainless-steel autoclave was loaded with **3b–e** (4.60 mmol) dissolved in a mixture of the selected alcohol and dimethoxyethane (DME), (50 and 30 ml, respectively) 10%Pd–C (0.082 g, 0.23 mmol) and KI (0.57 g, 3.40 mmol). The autoclave was pressurised with air (6 bar) and CO (18 bar) and heated at 65°C under stirring for 60 h. The brown mixture was filtered and the solution was distilled under vacuum for eliminating DME and the alcohol in excess.

In particular the preparation of the single products:

Product **6b** ($R = Me$, $R' = C_8H_{17}$); substrate **3a** (1.25 g, 4.60 mmol), 1-octanol (50 ml) and DME (30 ml) were caused to react with CO and air in the presence of 10% Pd–C (0.082 g, 0.23 mmol) and KI (0.57 g, 3.40 mmol). Chromatographic purification through silica gel column (9:1 CH_2Cl_2–hexane as eluent) gave **6b** (1.63 g, 62% yield) as a pale yellow oil. MS (CI, m/z): 599 (MH^+, 100); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.88 (t, 6H, $J = 7.1$ Hz, 2 Me), 1.22–1.31 (m, 20H, 10 CH_2), 1.62–1.67 (m, 4H, 2 CH_2), 3.51, 3.58 (2dd, ABX system, 4H, $J = 19.0$, $J = 2.4$ Hz, 2 CH_2=), 3.65 (s, 3H, OMe), 4.12 (t, 4H, $J = 7.0$ Hz, 2 OCH_2), 5.16 (s, 2H, CH_2Ph), 6.31 (t, 2H, $J = 2.4$ Hz, CH=), 7.31 (br s, 5H, aromatics).

Product **6c** ($R = Et$, $R' = C_8H_{17}$); substrate **3b** (0.657 g, 2.20 mmol), 1-octanol (25 ml) and DME (15 ml) were caused to react with CO and air in the presence of 10% Pd–C (0.04 g, 0.11 mmol) and KI (0.274 g, 1.65 mmol). Chromatographic purification through a silica gel column (9:1 CH_2Cl_2–hexane as eluent gave **6c** (0.845 g, 63% yield) as a pale yellow oil. MS (CI, m/z): 613 (MH^+, 100); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.88 (t, 6H, $J = 7.1$ Hz, 2 Me), 1.13 (t, 3H, $J = 7.1$ Hz, Me), 1.26-1.32 (m, 20H, 10 CH_2), 1.65–1.67 (m, 4H, 2 CH_2), 3.58, 3.65 (2dd, ABX system, 4H, $J = 19.0$, $J = 2.4$ Hz, 2 CH_2=), 4.08–4.16 (three superimposed q, 6H, 3 CH_2), 5.17 (s, 2H, CH_2Ph), 6.32 (t, 2H, $J = 2.4$ Hz, 2 CH=), 7.31 (br s, 5H, aromatics).

Product **6d** ($R = R' = C_8H_{17}$); substrate **3c** (1.025 g, 2.68 mmol), 1-octanol (30 ml) and DME (18 ml) were caused to react with CO and air in the presence of 10% Pd–C (0.048 g, 0.134 mmol), KI (0.334 g, 2.01 mmol). Chromatographic purification through a silica gel column (9:1 hexane–EtOAc as eluent) gave **6d** (0.967 g, 52% yield) as a yellow oil. MS (CI, m/z): 697 (MH^+, 100); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, 9H, 3 Me), 1.23–1.31 (m, 30H, 15 CH_2), 3.51, 3.58 (2dd, ABX system, 4H, $J = 19.0$, $J = 2.4$ Hz, 2 CH_2=), 4.05 (t, 2H, $J = 7.0$ Hz, CH_2), 4.12 (t, 4H, $J = 7.0$ Hz, 2 CH_2), 5.16 (s, 2H, CH_2Ph), 6.31 (t, 2H, $J = 2.4$ Hz, 2 HC=), 7.29 (br s, 5H, aromatics).

Product **6e** ($R = R' = C_{12}H_{25}$); substrate **3d** (1.00 g, 2.30 mmol),1-dodecanol (45 ml) and DME (27 ml) were caused to react with CO and air in the presence of 10% Pd–C (0.041 g, 0.115 mmol) and KI (0.286 g, 1.73 mmol). Chromatographic purification through silica gel column (9:1 hexane–EtOAc as eluent) gave **6e** (0.81 g, 41% yield) as a yellow oil. MS (CI, m/z): 865 (MH^+, 62); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, 9H, three superimposed triplet, 3Me), 1.21–1.29 (m, 54H, 27 CH_2), 1.60–1.64 (m, 6H, 3 CH_2), 3.51, 3.58 (2dd, ABX system, 4H, $J = 19.0$, $J = 2.4$ Hz, 2 CH_2=), 4.05 (t, 2H, $J = 7.0$ Hz, CH_2), 4.12 (t, 4H, $J = 7.0$ Hz, 2 CH_2), 5.15 (s, 2H, CH_2Ph), 6.31 (t, 2H, $J = 2.4$ Hz, 2 HC=), 7.30 (br s, 5H, aromatics).

Product **8a** ($R = R' = Me$); substrate **3e** (1.54 g, 7.0 mmol) in MeOH (80 ml) were caused to react with CO and air in the presence of 10% Pd–C (0.37 g, 0.35 mmol) and KI (0.87 g, 5.25 mmol). Chromatographic purification through a silica gel column (1:1 hexane–acetone as eluent) gave **8a** (0.90 g, 38% yield). MS (CI, m/z): 269 (MH^+, 100); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 3.50–3.62 (m, 5H, CH, 2 CH_2), 3.67 (s, 3H, OMe), 3.76 (s, 6H, 2 OMe), 6.33 (t, 2H, $J = 2.4$ Hz, 2CH=).

3.5. Hydrolysis of benzyl esters to 7b–c and decarboxylation and isomerisation; synthesis of 1b–c

The hydrolisis reactions were carried out in the presence of $AlCl_3$ following a known procedure [8]. The monobasic acid was added with dry pyridine (20 ml) in a Schlenk tube under argon. The mixture was stirred for 7 h at 80°C and extracted with CH_2Cl_2. The organic layer was washed with an aqueous solution of $NaHCO_3$ and dried over Na_2SO_4.

Product **1b** ($R = Me$, $R' = C_8H_{17}$) was obtained from **7b** (0.821 g, 1.62 mmol). After purification through silica gel column chromatography (8:2 hexane–EtOAc as eluent) **1b** (0.383 g, 51% yield) was recovered as a yellow oil. MS (CI, m/z): 465 (MH^+, 70); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.86 (t, 6H, $J = 7.1$ Hz, 2 Me), 1.24–1.28 (m, 20H, 10 CH_2), 1.57–1.60 (m, 4H, 2 CH_2), 3.35 (s, 2H, CH_2), 3.41 (s, 4H, 2 CH_2), 3.74 (s, 3H, OMe), 4.05 (t, 4H, $J = 7.0$ Hz, 2 OCH_2), 7.31 (s, 2H, CH=).

Product **1c** ($R = Et$, $R' = C_8H_{17}$) was obtained from **7c** (0.57 g, 1.1 mmol). After purification through silica gel column chromatography (8:2 hexane–EtOAc as eluent) **1c** (0.258 g, 49% yield) was recovered as a yellow oil. MS (CI, m/z): 479 (MH^+, 72); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.88 (t, 6H, $J = 7.1$ Hz, 2 Me), 1.26–1.29 (m, 23 H, 10 CH_2, Me), 1.59–1.62 (m, 4H, 2 CH_2), 3.37 (s, 2H, CH_2), 3.43 (s, 4H, 2 CH_2), 4.07 (t, 4H, $J = 7.0$ Hz, 2 OCH_2), 4.22 (q, 2H, $J = 6.9$ Hz, OCH_2), 7.32 (s, 1H, CH=).

Product **1d** ($R = R' = C_8H_{17}$) was obtained from **7d** (0.97 g, 1.6 mmol). After purification through silica gel column chromatography (85:15 hexane–EtOAc as eluent) **1d** (0.387 g, 43% yield) was recovered as a yellow oil. MS (CI, m/z): 563 (MH^+, 100); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, 9H, 3 Me), 1.25–1.29 (m, 30 H, 15 CH_2), 1.59–1.63 (m, 6H, 3 CH_2), 3.36 (s, 2H, CH_2), 3.41 (s, 4H, 2 CH_2), 4.07, 4.15 (2t, 6H, $J = 7.0$ Hz, 3 OCH_2), 7.32 (s, 1H, CH=).

Product **1e** ($R = R' = C_{12}H_{25}$) was obtained from **7e** (0.35 g, 0.45 mmol). After purification through silica gel column chromatography (9:1 hexane–EtOAc as eluent) **1e** (0.135 g, 41% yield) was recovered as a yellow oil. MS (CI, m/z): 731 (MH^+, 75); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, 9H, 3 Me), 1.23–1.27 (m, 54H, 27 CH_2), 1.59–1.63 (m, 6H, 3 CH_2), 3.36 (s, 2H, CH_2), 3.41 (s, 4H, 2 CH_2), 4.07, 4.15 (2t, 6H, $J = 7.0$ Hz, 3 OCH_2), 7.31 (s, 1H, CH=).

3.6. Synthesis of (η^4-1,5-cyclooctadiene) [η^5-1-methoxycarbonyl-3,4-di(methoxycarbonylmethylene)-cyclopentadienyl]cobalt [Co(MDMCp)(1,5-cod)] (9)

The preparation of complex **9** was adapted from the literature [25]. LiMDMCp was prepared according to the reported procedure [7] from lithium diisopropylamide and HMDMCp at 0°C in THF: Under argon atmosphere at r.t. the Li(MDMCp) (1.029 g, 3.84 mmol) in THF (15 ml) was added to a solution of $CoCl(PPh_3)_3$ (3.15 g, 3.57 mmol) and 1,5 COD (0.580 g, 5,36 mmol) in toluene (30 ml) in a Schlenk tube (100 ml). After stirring for 1 h at r.t. the mixture was heated at 80°C for 1 h. The reaction mixture was filtered through a short column of alumina (activity grade III). The filtrate was concentrated to ca. 10 ml and after addition of hexane (20 ml) the solution was allowed to stand overnight then was filtered again to eliminate PPh_3 precipitated. The filtered products were separated through an alumina (activity grade III) chromatographic column (1.5 × 15 cm). An orange band was eluted by a 8:2 = hexane:EtOAc mixture. The fraction containing the product was concentrated almost to dryness. The oily residue was dissolved in hexane–CH_2Cl_2 (3/1, vol/vol) and was kept in refrigerator to separate a red-brown solid (0.60 g, 38% yield). This was recrystallised from the same solvent, m.p. 78°C. Anal. Found: C, 58.00; H, 6.21. $C_{21}H_{27}O_6Co$ Calc.: C, 58.06; H, 6.22%. MS (EI, m/z): 434 (50), 327 (87), 326 (100), 296 (54), 59 (56). IR (KBr) ν cm^{-1}: 2989 (w), 2934 (m), 2871 (w), 2827 (w), 1734 (s), 1705 (s), 1443 (m), 1229 (s), 1224 (s), 1141 (m), 1012 (m), 769 (w); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.55–1.67 (m, 4H, 4CH COD), 2.29–2.34 (m, 4H, 4CH COD), 3.28 (br s, 4H, 4CH= COD), 3.34 (AB system 4H, $J = 15.7$ Hz, $2CH_2CO$), 3.65 (s, 6H, 2 OMe), 3.88 (s, 3H, OMe), 4.39 (s, 2H, 2 CH= Cp); ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 31.55 (4 CH_2 cod), 32.27 (2 CH_2 Cp), 51.38 (OMe), 70.44 (4 CH= COD), 84.93 (2 CH= Cp), 85.69 (1qC), 95.92 (2 qC), 167 20 (CO); 170.36 (2 CO).

3.7. Synthesis of bis(carbonyl)η⁵[1-alkoxycarbonyl-3,4-di(alkoxycarbonylmethylene) cyclopentadienyl]rhodium (2b, 2d)

Complexes **2b** and **2d** were prepared following the synthetic procedure already reported for **2a** [7].

Complex **2b** (R Me, R′ = C_8H_{17}). Under argon atmosphere in a Schlenk tube (50 ml) at 0°C lithium salt of cyclopentadienyl **1b** (0.272 g, 0.59 mmol) in dry THF (5 ml) was added slowly to a degassed solution of $[Rh(CO)_2Cl]_2$ (0.115 g, 0.30 mmol) in dry THF (7 ml). The brown mixture was stirred at r.t. for 16 h. The complex was separated by column chromatography on Florisil (activated at 100°C for 2 h under vacuum) using pentane:THF = 9:1 as eluent. Complex **2b** was isolated as an orange-red wax (0.120 g, 0.19 mmol) 32% yield. Anal. Found: C, 55.91; H, 6.90; $C_{29}H_{34}O_8Rh$ Calc: C, 55.95; H, 6.91%. MS (CI, m/z): 623 (MH^+, 10), 596 (25), 595 (100), 567 (40); IR (neat) ν cm^{-1}: 2928 (w), 2856 (w), 2051 (s), 1987 (s), 1739 (s), 1714 (s), 1447 (m), 1218 (m); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.88 (t, 6H, J = 6.0 Hz, 2 Me), 1.25–1.29 (m, 20H, 10 CH_2), 1.59–1.64 (m, 4H, 2 CH_2), 3.42 (AB system, 4H, J = 16.1 Hz, 2CH_2) 3.76 (s, 3H,OMe), 4.10 (t, 4H, J = 6.8 Hz, 2 OCH_2), 5.96 (s, 2H, CH= Cp).

Complex **2d** (R = R′ = C_8H_{17}) Analogously to preparation of **2b**, lithium salt of cyclopentadienyl **1d** (0.378 g, 0.67 mmol) was caused to react with $[Rh(CO)_2Cl]_2$ (0.130 g, 0.33 mmol) giving after separation through a Florisil chromatographic column (pentane:THF = 95:5 as eluent) **2d** (0.152 g, 0.21 mmol) 31% yield as an orange-red oil. Anal. Found: C, 59.94; H, 7.90; $C_{36}H_{57}O_8Rh$ Calc: C, 60.00; H, 7.92%. MS (CI, m/z). 721 (MH^+, 11); IR (neat) ν cm^{-1}: 2927 (w), 2857 (w), 2051 (s), 1988 (s), 1740 (s), 1437 (m), 1210 (m); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, 9H, J = 7.0 Hz, 3Me), 1.23–1.28 (m, 30H, 15 CH_2), 1.57–1.61 (m, 6H, 3 CH_2), 3.42 (AB system, 4H, J = 16.0 Hz, 2CH_2) 3.76 (s, 3H,OMe), 4.09 (t, 4H, J = 6.8 Hz, 2 OCH_2), 5.96 (s, 2H, CH= Cp); ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 14.0 (Me), 22.5, 25.8, 25.9, 28.4, 28.5, 29.1, 30.8, 31.7, 32.4 (CH_2), 64.6 (OCH_2), 87.6 (CH), 96.2 (qC), 105.7 (qC), 163.1 (CO), 169.8 (CO), 188.7 (d, J = 84.6 Hz, Rh–CO).

3.8. Synthesis of bis-η⁵[1,1′-di(alkoxycarbonyl)-3,3′,4,4′-tetra(alkoxycarbonylmethylene) cyclopentadienyl]iron 15a [(MDMCp)₂Fe], (15b, 15e)

Preparation of complex **15a** (R = R′ = Me). In a dry Schlenk tube (50 ml) under argon containing LiMDMCp (0.162 g, 0.59 mmol) dissolved in dry THF (10 ml) and cooled at 0°C was added slowly $FeCl_2$ (0.037 g, 0.29 mmol) (dried according the literature methods [26]) in dry THF (5 ml). The brown mixture was stirred at r.t. for 24 h then concentrated to dryness. The residue was added with CH_2Cl_2 (10 ml) and filtered to eliminate $FeCl_2$ unreacted. The complex **15a** was isolated by silica gel column chromatography (1:1 hexane–EtOAc as eluent) (0.060 g, 0.1 mmol 35% yield as an orange solid recrystallised from pentane, m.p. 183–184°C. Anal. Found: C, 52.84; H, 5.06; $C_{26}H_{30}O_{12}Fe$ Calc.: C, 52.88; H, 5.08%. MS (CI, m/z): 591 (MH^+, 40), 590 (100), 589 (60), 558 (53); IR (KBr) ν cm^{-1}: 2956 (w), 1739 (s), 1714 (s), 1441 (m), 1226 (m), 1088 (w); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 3.23 (AB system 8H, J = 16.3 Hz, 4 CH_2), 3.65 (s, 12H, 4 OMe), 3.81 (s, 6H, 2 OMe), 4.79 (s, 4H, CH= Cp); ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 31.57 (CH_2), 51.71 (Me), 72.36 (qC), 73.54 (CH Cp), 84.2 8qC), 169.55 (CO), 170.19 (CO).

Preparation of complex **15b** (R = Me, R′ = C_8H_{17}). Following the same procedure adopted for **15a** substrate **1b** (0.30 g, 0.65 mmol) was transformed in lithium salt and caused to react with dry $FeCl_2$ (0.041 g, 0.33 mmol). Purification by silica gel column chromatography (85:15 hexane–THF as eluent) gave complex **15b** (0.041 g, 0.09 mmol, 28% yield) as an orange–red wax. Anal. Found: C, 65.95; H, 8.75, $C_{54}H_{86}O_{12}Fe$ Calc: C, 65.99; H, 8.76%. MS (CI, m/z): 983 (MH^+, 80); IR (neat) ν cm^{-1}: 2954 (w), 1740 (s), 1713 (s), 1441 (m), 1225 (m). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, 12H, J = 7.0 Hz, 4 Me), 1.24–1.28 (m, 40 H, 20 CH_2), 1.56–1.60 (m, 8H, 4 CH_2), 3.21 (AB system 8H, J = 16.2 Hz, 4 CH_2), 3.80 (s, 6H, 2 OMe), 4.03 (t, 8H, J = 6.9 Hz, 4 OCH_2), 4.78 (s, 4H, 4CH= Cp); ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 14.12 (Me), 22.61, 25.41, 28.52, 29.27, 29.71, 31.73 (CH_2), 51.71 (OMe), 65.25 (OCH_2), 72.34 (qC), 73.56 (CH Cp), 84.21 (qC), 168.05 (CO), 170.08 (CO).

Preparation of complex **15e** (R = R′ = $C_{12}H_{25}$). Following the same procedure adopted for **15a** substrate **1e** (0.506 g, 0.69 mmol) was transformed in lithium cyclopentadienyl salt and caused to react with dry $FeCl_2$ (0.044 g, 0.34 mmol). Purification by silica gel column chromatography (9:1 hexane–THF as eluent) gave complex **15e** (0.081 g, 0.05 mmol, 15% yield) as an orange–red wax. Anal. Found: C, 72.88; H, 10.69, $C_{92}H_{162}O_{12}Fe$ Calc: C, 72.92; H, 10.70%. MS (CI, m/z): 1515 (MH^+, 100), 1414 (78); IR (neat) ν cm^{-1}: 2956 (w), 1740 (s), 1714 (s), 1441 (m), 1224 (m); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.89 (t, 18H, J = 7.0 Hz, 6 Me), 1.28–1.32 (m, 108H, 54 CH_2), 1.62–1.66 (m, 12H, 6 CH_2), 3.31 (AB system 8H, J = 16.3 Hz, 4 CH_2), 4.05 (t, 8H, J = 6.8 Hz, 4 OCH_2), 4.28 (t, 4H, J = 6.9 Hz, 2 OCH_2) 4.81 (s, 4H, 4CH= Cp).

3.9. Synthesis of bis[dicarbonyl-η⁵-methoxycarbonyl-3,4-di(mehoxycarbonylmethylene) cyclopentadienyliron] (16) [Fe(MDMCp)(CO)₂]₂ and bis[dicarbonyl-η⁵-methoxycarbonyl-3,4-di(mehoxycarbonylmethylene)-cyclopentadienylruthenium] (17) [Ru(MDMCp)(CO)₂]₂

Preparation of complex **16**. A 250 ml three-necked flask was equipped with a magnetic stirring bar, reflux

condenser and a Schlenk filter tube that was attached to another sealed 250 ml three-necked flask fitted with an argon inlet and serum stoppers. The apparatus was dried, degassed via successive argon vacuum cycles and charged in turns under argon with heptane (100 ml) HMDMCp (0.760 g, 2.83 mmol) and norbornene (1.076 g, 11.43 mmol). Under stirring the solution was cooled to −78°C and $Fe_2(CO)_9$ (1.915 g, 5.26 mmol) was introduced. The mixture was heated at the reflux temperature under stirring for 48 h. Then the cooled solution was concentrated under vacuum at about 1/5 of its initial volume and the precipitate was collected by filtration. The brown-red solid was chromatographed through a Florisil (1.5 × 20 cm) column (6:4 hexane–EtOAc as eluent) and the solid was recrystallised in CH_2Cl_2–hexane (1:3, v/v) solution giving complex **16** (1.59 g, 2.10 mmol) in 40% yield as a red solid m.p. 127–129°C. Anal. Found: C, 47.47; H, 3.95; $C_{30}H_{30}O_{16}Fe_2$ Calc: C, 47.49; H, 3.96%. MS (CI, positive ions m/z): (M^+, absent), 590 (3), 559 (6), 269 (38), 237 (100), 209 (96); (CI, negative ions m/z): (M^-, absent), 379 (20), 352 (100). MS (EI, positive ions m/z): (M^+, absent), 647 (8), 591 (100); (EI, negative ions, m/z): (M^-, absent), 730 (16), 702 (24), 590 (25), 379 (100), 352 (56); IR (KBr) ν cm^{-1}: 2956 (w), 2004 (s), 1963 (m), 1808 (w sh), 1779 (s), 1741 (s), 1718 (s), 1450 (m), 1436 (m), 1350 (m), 1270 (s), 648 (m); (CH_2Cl_2, 2100–1700 cm^{-1} region) ν cm^{-1}: 2008 (s), 1970 (m), 1818 (w sh), 1786 (s), 1742 (s), 1721 (m); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 3.39, 3.52 (2d, AB system 8H, $J = 17.1$ Hz, 4 CH_2), 3.67 (s, 12H, 4 OMe), 3.95 (s, 6H, 2 OMe), 5.17 (s, 4H, 4 CH= Cp); ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 31.75 (CH_2), 52.34 (OMe), 52.58 (OMe), 66.75 (CH=), 93.87 (qC), 102.39 (qC), 164.94 (CO), 170.26 (CO).

Preparation of complex **17**. To a suspension of $Ru_3(CO)_{12}$ (0.637 g, 1.00 mmol) in heptane (100 ml) under argon was added HMDMCp (0.813 g, 3.00 mmol) and norbornene (0.31 g, 3.3 mmol). The reaction mixture was heated at reflux an vigorously stirred for 7 h. The solvent was evaporated under vacuum to 1/5 of its initial volume and after cooling a black solid was filtered and washed with hexane. The solid was dissolved in CH_2Cl_2–hexane (1/2 vol/vol) and precipitated again by concentration under vacuum. The mixture was cooled to −10°C and a brown solid was separated. This was purified through a neutral alumina (water deactivated) column chromatography (1.5 × 30 cm) (EtOAc–hexane eluent solution varying from 2:8 to 4:6 v/v). The 4:6 fraction was concentrated under vacuum giving complex 17 (0.534 g, 0.63 mmol) 42% yield as a yellow solid that was recrystallised from a CH_2Cl–hexane (1/2 v/v) solution yielding yellow crystals m.p. 122–124°C. Anal. Found: C, 42.42; H, 3.53; $C_{30}H_{30}O_{16}Ru_2$ Calc: C, 42.45; H, 3.54%. MS dinuclear complex **17** shows different combinations of ruthenium isotopes (CI, m/z): 854 (16), 852 (36), 850 (59), 848 (55), 846 (52), 844 (20), 842 (20), 428 (9), 427 (44), 425 (100), 423 (54), 422 (11), 399 (26), 397 (58), 396 (42), 395 (18); IR (KBr) ν cm^{-1}: 2956 (w), 2005 (s), 1960 (m), 1783 (w sh), 1762 (s), 1739 (s), 1711 (s), 1420 (m), 1414 (m), 1343 (m), 1283 (s), 648 (m); (CH_2Cl_2 2100–1700 cm^{-1} region) ν cm^{-1}: 2014 (s), 1973 (m), 1820 (w sh), 1787 (s), 1742 (s), 1721 (m); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 3.33, 3.47 (2d, AB system 8H, $J = 17.2$ Hz, 4 CH_2), 3.68 (s, 12H, 4 OMe), 3.85 (s, 6H, 2 OMe), 5.76 (s, 4H, 4 CH= Cp); ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 31.98 (CH_2), 52.41 (OMe), 52.58 (OMe), 69.57 (CH=), 97.66 (qC), 106.40 (qC), 163.33 (CO), 170.37 (CO).

3.10. Catalytic synthesis of pyridines

A Carius tube (25 ml) fitted with a Rotaflo teflon tap was charged under argon atmosphere with complex **9** (0.040 g, 0.092 mmol), propionitrile (3.62 ml, 50.6 mmol) and 1-hexyne (1.05 ml, 9.2 mmol). The reactor was heated in a silicone oil bath (Fischer) at 100°C for 6 h under stirring. Gas chromatographic yields based on the starting alkynes amounted to 88% (1.773 g, 8.096 mmol) of two isomeric pyridine derivatives (**10**:**11** = 52: 48) and 8% (0.181 g, 0.736 mmol) of alkyne trimers. The same procedure and amounts of substrates were used with cyclopentadienylcobalt-(1,5-cyclooctadiene (0.021 g, 0.092 mmol) as catalyst. Yields of 65% (1.309 g, 5.98 mmol) of two isomeric pyridine derivatives (**10**:**11** = 59:41) and 22% (0.498 g, 2.024 mmol) of alkyne trimers were determined by GLC.

3.11. Hydroformylation reactions

The hydroformylation reactions were carried out in a 50 ml stainless-steel autoclave (Parr) fitted with magnetic bar and thermostatted (±1°C) in a silicone oil bath (Fischer). In a typical run complex **2a** (0.025 g, 0.059 mmol) distilled styrene (1.22 g, 11.76 mmol) and degassed dry toluene were introduced into the autoclave under N_2. The autoclave cooled at −60°C was evacuated and then pressurised at r.t. with H_2–CO mixture (1/1) at 70 bar. The reaction mixture was stirred at 100°C for 3 h. After cooling the product mixture was recovered by usual work up and analysed by GLC. A yield of 99% (1.556 g, 11.65 mmol) of aldehydes **13** and **14** (**13**:**14** = 58:42) was obtained. The hydroformylation reaction was carried out analogously with complexes **2b** and **2d** using the same molar amounts. The yields were 98% (1.540 g, 11.53 mmol) of aldehydes **13** and **14** (**13**:**14** = 64:36) and 98% (1.540 g, 11.53 mmol) of aldehydes **13** and **14** (13:14 = 59:41), respectively.

Table 7
Crystal data and structure refinement for **9**, **2a**, and **15a**

	9	**2a**	**15a**
Formula	$C_{21}H_{27}O_6Co$	$C_{15}H_{15}O_8Rh$	$C_{26}H_{30}FeO_{12}$
Formula weight	434.36	426.18	590.35
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.288(4)	9.808(3)	7.944(3)
b (Å)	10.201(5)	12.304(5)	12.383(5)
c (Å)	9.584(3)	7.941(3)	7.656(3)
α (°)	84.31(3)	95.77(2)	103.63(3)
β (°)	68.08(2)	99.73(2)	114.64(3)
γ (°)	65.94(3)	111.70(3)	81.91(2)
V (Å^3)	1015.7(7)	863.6(5)	664.5(5)
Z	2	2	1
D_{calc} (g cm^{-3})	1.420	1.639	1.475
$F(000)$	456	428	308
Crystal size	$0.26\times0.27\times0.37$	$0.21\times0.17\times0.27$	$0.15\times0.28\times0.31$
μ (cm^{-1})	8.79	83.58	6.32
Reflections collected	5940	3258	3885
Observed reflections	5030 [$I>2\sigma(I)$]	3049 [$I>2\sigma(I)$]	1752 [$I>2\sigma(I)$]
Final R indices [$I>2\sigma(I)$]	$R_1=0.0397$ [a], $wR_2=0.1153$ [b]	$R_1=0.0637$ [a], $wR_2=0.1771$ [b]	$R_1=0.0415$ [a], $wR_2=0.0958$ [b]
R indices (all data)	$R_1=0.0473$ [a], $wR_2=0.1205$ [b]	$R_1=0.0659$ [a], $wR_2=0.1848$ [b]	$R_1=0.1099$ [a], $wR_2=0.1279$ [b]

[a] $R_1=\Sigma\|\|F_o|-|F_c\|/\Sigma|F_o|$.
[b] $wR_2=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

3.12. Crystal structure determination of complexes *9*, *2a* and *15a*

The intensity data of **9**, **2a** and **15a** were collected at r.t. on a Philips PW 1100 (**9** and **15a**) and a Siemens AED (**2a**) single-crystal diffractometers using a graphite monochromated Mo–K_α radiation (**9** and **15a**) and Cu–K_α radiation (**2a**) and the $\theta/2\theta$ scan technique. Crystallographic and experimental details for the structures are summarised in Table 7.

A correction for absorption was made for complex **2a** [maximum and minimum value for the transmission coefficient was 1.000 and 0.704] and for **9** [maximum and minimum value for the transmission coefficient was 1.000 and 0.743] [27].

The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) (SHELX-97) [28] first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms.

The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms. In the final cycles of refinement a weighting scheme for **15a** was $w=1/[\sigma^2F_o^2+(0.0879\ P)^2]$, for 2a was $w=1/[\sigma^2F_o^2+(0.1570\ P)^2+0.6791\ P]$ and for **9** was $w=1/[\sigma^2F_o^2+(0.0786\ P)^2+\ 0.0983\ P]$ where $P=(F_o^2+2F_c^2)/3$ was used.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC, no. 148800 for compound **2a**, no. 148801 for compound **9**, no. 148802 for compound **15a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Rd, Cambridge, CB2 1EZ (fax +44-1223-336033 or e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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