ELSEVIER

Journal of Organometallic Chemistry 488 (1995) 47–53

Journal of Organometallic Chemistry

A new cyclopentadiene and its use as a ligand for catalytically active rhodium complexes ☆

Mirco Costa *, Francisco Santos Dias, Gian Paolo Chiusoli, Gian Luca Gazzola

Dipartimento di Chimica Organica e Industriale dell'Università, Viale delle Scienze, 43100 Parma, Italy

Received 19 May 1994

Abstract

Dimethyl 4-methoxycarbonylcyclopenta-1,3-diene-1,2-diacetate has been prepared from benzyl methyl malonate by reaction with 2-propynyl bromide, followed by palladium-catalyzed ring-forming oxidative carbonylation and by elimination of the benzyloxycarbonyl group and double bonds isomerization. The anion of the diacetate readily reacts with transition metal complexes, to give the corresponding cyclopentadienyl derivatives. We describe here some complexes, obtained from $[\{RhCl(L)_2\}_2]$ [L = CO, C_2H_4, or 1,5cyclooctadiene (COD)], which are efficient catalysts for the alkyne-nitrile co-cyclization to pyridines and for the hydroformylation of styrene and 1-hexene.

Keywords: Rhodium; Hydroformylation; Cyclization; Cyclopentadienyl complexes; Catalysis

1. Introduction

Cyclopentadienyl ligands are well known in organometallic chemistry and catalysis [1]. Substituted cyclopentadienes, such as the pentamethylcyclopentadienyl [2] and the alkoxycarbonylcyclopentadienyls [3], are ligands with special properties. We wondered whether our recently developed technique of oxidative carbonylation-aromatization [4] could offer a new way to prepare cyclopentadiene derivatives symmetrically substituted by alkoxycarbonyl and alkoxycarbonylmethylene functions.

2. Results and discussion

We devised a process with the steps shown below.

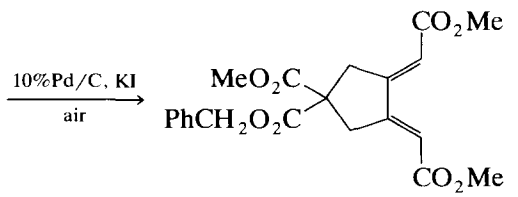
(1) Propynylation of benzyl methyl malonate (Eq. 1).

$$CH_2(CO_2Me)(CO_2CH_2Ph) + 2BrCH_2C{\equiv}CH \xrightarrow[K_2CO_3]{\text{acetone(reflux)}} \xrightarrow[-2KBr]{} (HC{\equiv}CCH_2)_2C(CO_2Me)(CO_2CH_2Ph)$$

1 (83% yield) (1)

(2) Oxidative carbonylation of compound **1** with carbon monoxide in methanol (Eq. 2).

1 + 2CO + 2MeOH



(2)

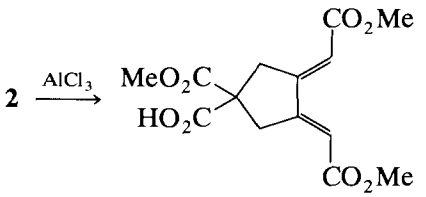
2 (70% yield)

(3) Deprotection of the benzyl group with decarboxylation and isomerization to **4** (Eq. 3).

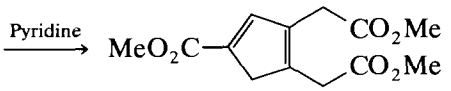
☆ Dedicated to Prof. Fausto Calderazzo in recognition of his fundamental contributions to organometallic chemistry.

* Corresponding author.

SSDI 0022-328X(94)00020-4



3 (92% yield)



4 (72% yield)

The first step was carried out using conventional procedures [5] although this particular product had not been reported previously.

The second step was based on our procedure for the oxidative carbonylation of alkynes [4]. Compound **1** was subjected to reaction with carbon monoxide in methanol at 45°C under moderate pressure of CO (6 bar) and air (2 bar), using 10% Pd/C and an excess of KI (25–30 mol KI per mol of Pd).

Finally, deprotection of the benzyl group was carried out according to a reported procedure [6] and the mixture was heated in pyridine to obtain the decarboxylated and isomerized product as a white solid (**4**). Because of the presence of the three chains, containing methoxycarbonyl groups, compound **4** has no tendency to undergo Diels-Alder reaction with itself. The overall isolated yield based on the starting methyl benzyl malonate was ca. 42% (using distilled or crystallized products for each step).

The cyclopentadiene derivative **4** was readily transformed into a cyclopentadienyl ligand through its anion, hereafter indicated as MDMCp. To evaluate its properties, we chose some cyclopentadienylrhodium complexes which had been found to be active in catalytic processes and prepared the corresponding complexes with our ligand. These complexes were fully characterized through elemental analysis, and ^1H, ^{13}C NMR, IR and mass spectroscopies.

$[\{Rh(CO)_2Cl\}_2]$ + **4** → [(MDMCp)Rh(CO)$_2$]

5 50% isolated yield, yellow-red solid, m.p. 34–35°C (from hexane at −20°C)

$[\{Rh(CH_2CH_2)_2Cl\}_2]$ + **4** → [(MDMCp)Rh(CH$_2$CH$_2$)$_2$]

6 47% isolated yield, yellow solid, m.p. 52–54°C (from hexane at −20°C)

$[\{Rh(COD)Cl\}_2]$ + **4** → [(MDMCp)Rh(COD)]

7 47% isolated yield, yellow solid, m.p. 60–62°C (from hexane at −20°C)

Spectral data clearly indicate that complexes **5–7** have the structure expected for a π-cyclopentadienyl metal complex. The diacetate **4**, with one electron-withdrawing group and another two symmetrically positioned alkoxycarbonylmethylene groups on the cyclopentadienyl ring (C_2 symmetry), gives relatively simple ^1H and ^{13}C NMR spectra in complexes **5–7**.

A more detailed ^1H NMR study of complex **6** in $CDCl_3$ has shown a temperature-dependence (−70°C, +60°C), without line broadening, of the chemical shifts of the cyclopentadienyl ring protons [H(2), H(5) δ: 5.45 (−70°C), 5.52 (+60°C), $\Delta\delta = -0.07$ ppm] and of a pair of the protons of the two methylene groups, the other pair of protons being unaffected by temperature [H(6), H(6′), δ: 3.40 (−70°C), 3.38 (+60°C), $\Delta\delta = 0.02$ ppm; H(7), H(7′), δ: 3.20 (−70°C), 3.20 (+60°C), $\Delta\delta$ = 0.00 ppm]. A similar behaviour, involving the signals of protons H(2), H(5) and H(3), H(4) of a complex containing a monosubstituted cyclopentadienyl ring with one electron-withdrawing group and ethylene as a neutral ligand, has already been reported [7]. This was attributed to a departure from purely π-delocalized bonding of the cyclopentadienyl system, which causes unequal barriers for rotation of the cyclopentadienyl ring. At lower temperature the population of the molecule in the lowest energy conformation states becomes progressively greater, and this is reflected in the ^1H NMR spectra. In our case, in spite of the presence of the two bulky symmetrical substituents in place of H(3) and H(4), this behaviour is also strictly followed, suggesting that the preferred rotamer in solution may be one containing a localized structure ($\eta^3 + \eta^2$) as shown in Fig. 1 [8].

Complexes **5–7** are remarkably more stable to air and elevated temperatures than the parents containing an unsubstituted cyclopentadienyl ring. For example, the dicarbonyl derivative **5** decomposes only after 5 h at 150°C in dimethyl sulfoxide.

With complexes [(MDMCp)Rh(CH$_2$CH$_2$)$_2$] (**6**) and [(MDMCp)Rh(CO)$_2$] (**5**) we tested two reactions, namely the synthesis of a pyridine ring [9] from 1-hexyne and propionitrile (Eq. 4, Table 1) and the hydroformylation of styrene [10] (Eq. 5, Table 2) and of 1-hexene [10] (Eq. 6, Table 3). The pyridine synthesis with cyclopentadienylrhodium complexes has been studied recently in detail [11], and it was found that electron-withdrawing substituents increase the yield. Hydroformylation with cyclopentadienylrhodium carbonyls

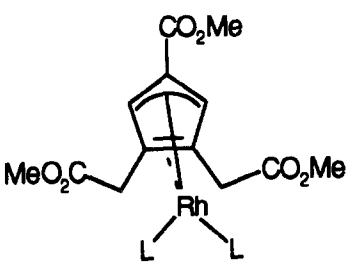


Fig. 1.

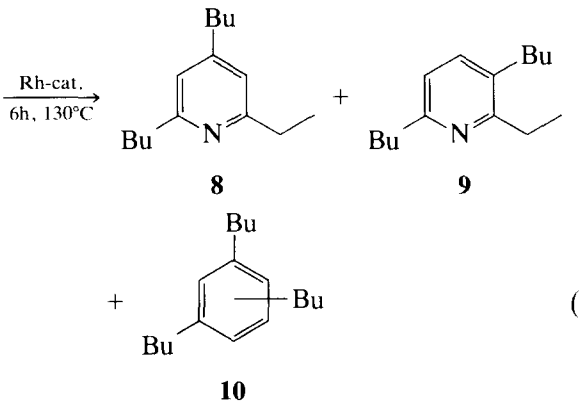
Table 1
Reaction of 1-hexyne with propionitrile at 130°C for 6 h; 1-hexyne (0.91 ml, 0.651 g, 7.93 mmol), propionitrile (3.1 ml), Rh-catalyst 0.079 mmol; EtCN/*n*-BuC≡CH molar ratio = 5.5; *n*-BuC≡CH/Rh-cat. molar ratio = 100

L in $[LRh(C_2H_4)_2]$	Yield (%) [a]		Selectivity (%) [a]	
	8 + 9	**10**	$\frac{\mathbf{8}}{\mathbf{8+9}}$	$\frac{\mathbf{8+9}}{\mathbf{8+9+10}}$
(MDMCp)	78	15	44	84
(MeO_2CCp)	68	19	43	82
Cp	67	18	56	79
Cp [c]	75	18	56	80
Me_5C_5 [d]	37	25	81	60

[a] By GLC, based on starting alkyne; conversion was practically complete. [b] (MeO_2CCp) = methoxycarbonylcyclopentadienyl. [c] 130°C, 15 h; data from Ref. [11]. [d] 130°C, 24 h; data from Ref. [11].

occurs at best using polymer-attached $\{CpRh(CO)_2\}$, which possesses remarkable stability [12].

n-BuC≡CH + EtCN



(4)

Table 2
Reaction of styrene with CO and H_2 in the presence or absence of PPh_3; Rh catalyst 0.058 mmol, olefin 11.72 mmol

Lin $[LRh(CO)_2]$	Temp. (°C)	Time (h)	Total pressure (bar) (CO/H_2) [a]	Solvent (ml)	Mol PPh_3 / Mol Rh	Yield [b] (%) **11 + 12**	Selectivity (%) **11**	**12**
(MDMCp)	100	3	70	Tol(5) [c]	0	99	42	58
(MeO_2CCp)	100	3	70	Tol(5)	0	94	27	73
Cp	100	3	70	Tol(5)	0	92	42	58
(MDMCp)	80	3	56	Tol(5)	5	98	6	94
(MeO_2CCp)	80	3	56	Tol(5)	5	99	1	99
Cp	80	3	56	Tol(5)	5	25 [d]	1	99
(MDMCp)	60	10	56	Tol(5)	5	100	3	97
(MDMCp)	60	1	56	Tol(1) MeOH(4)	5	94	5	95
(MeO_2CCp)	60	1	56	Tol(1) MeOH(4)	5	85	1	99

[a] $CO/H_2 = 40/60$. [b] By GLC, based on starting olefin. [c] Tol = toluene. [d] 27% conversion based on starting olefin.

Table 3
Reaction of 1-hexene with CO and H_2 in the presence or absence of PPh_3; Rh catalyst 0.054 mmol, olefin 10.8 mmol or 21.6 mmol

L in $[LRh(CO)_2]$	Temp (°C)	Time (h)	Total pressure (bar) (CO/H_2)	Mol olefin / Mol Rh	Toluene (ml)	Mol PPh_3 / Mol Rh	Yield [a] (%) **13 + 14 + 15**	Selectivity [a] (%) **13**	**14**	**15**
(MDMCp) [b]	100	3.5	70 (1/1)	400	6	0	90	44	44	12
(MeO_2CCp)	100	3.5	70 (1/1)	400	6	0	85	44	51	5
Cp	100	5.0	70 (1/1)	400	6	0	87	38	55	7
(MDMCp)	80	3.0	42 (4/6)	200	5	5	91	25	75	–
(MeO_2CCp)	80	3.0	42 (4/6)	200	5	5	90	26	74	–
Cp	80	6.0	42 (4/6)	200	5	5	29 [c]	25	75	–
(MDMCp)	60	12.0	56 (4/6)	200	5	5	75	25	75	–

[a] By GLC, based on starting olefin. [b] Polymer-supported $[CpRh(CO)_2]$ gave a 98.3% yield and a linear-to-branched aldehyde ratio of 1.69 at 110°C and ca. 100 bar [12]. [c] 34% conversion of 1-hexene.

Table 1 shows that the selectivity obtained with the new ligand is slightly higher than that obtained using the cyclopentadienyl without substituents, or with a carbomethoxy group as substituent, cyclization to pyridine (derivatives **8** and **9**) being preferred to trimerisation of the alkyne (**10**). Compound **9** is preferred to **8** both with (MDMCp) and with (MeO_2CCp).

$$PhCH{=}CH_2 + CO/H_2 \xrightarrow{\text{Rh-cat.}} \underset{\mathbf{11}}{PhCH_2CH_2CHO} + \underset{\mathbf{12}}{PhCH(Me)CHO} \quad (5)$$

The hydroformylation of styrene (Table 2) with [(MDMCp)$Rh(CO)_2$] (**5**) as catalyst, and with a reference catalyst without substituents or with a methoxycarbonyl group as a substituent on the cyclopentadienyl ring, shows comparable activity at 100°C. By contrast, on decreasing the temperature to 80°C and adding PPh_3, catalyst **5** and that having a methoxycarbonyl as a substituent maintained a high reactivity and selectivity towards the branched aldehyde, while the catalyst without substituents on the cyclopentadienyl ring lost efficiency, even though a high selectivity was retained. Addition of a polar solvent such as MeOH further increased the activity of catalyst **5**. The catalyst could be recovered unaltered (see the hydroformylation reactions in the Experimental Section).

$$n\text{-}BuCH{=}CH_2 + CO/H_2 \xrightarrow{\text{Rh-cat.}} \underset{\mathbf{13}}{n\text{-}BuCH(Me)CHO} + \underset{\mathbf{14}}{n\text{-}Bu(CH_2)_2CHO} + \underset{\mathbf{15}}{n\text{-}PrCH(Et)CHO} \quad (6)$$

Similar considerations apply to the hydroformylation of 1-hexene (Table 3) which gives the linear aldehyde preferentially with added PPh_3. The efficiency of our ligand, even at low temperature, is likely to be caused not only by electronic effects but also by steric effects, which could favour the "slippage" mechanism generally believed to be involved in reactions of cyclopentadienyl ligands, and particularly studied with indenyl ligands [13].

Both in the case of pyridine synthesis [9,11] and of hydroformylation [10,12] the reactions with the rhodium complex of our ligand were complete in a shorter time and occurred at lower temperature than those with the unsubstituted cyclopentadienylrhodium complexes. The results are even better than those obtained with methoxycarbonylcyclopentadienylrhodium, which is the best among the cyclopentadienylrhodium compounds recently reported for the synthesis of pyridines [11]. In addition, cyclopentadiene **4** has the advantage of greater chemical and thermal stability, particularly towards dimerisation, and this may favour its use for preparation of a hydroformylation catalyst as an alternative to the polymer-supported catalyst [12]. The examples here reported suggest that MDMCp may have potential for many other reactions, and with other metals. Further work is being carried out to prepare other catalytic systems.

3. Experimental details

Melting points were determined by a Buchi 530 apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba Model EA 1108 Elemental Analyzer. GLC analyses were performed on a HR 3800 Dani Instrument equipped with a flame ionization detector using a methylsilicone (OV101 stationary phase) capillary column (25 m). Quantitative determination of products and starting materials were carried out by GLC using the internal standard method. Merk silica gel 60 (230–400 mesh), Florisil (100–200 mesh, Floridin Company USA) and Fluka 507C neutral alumina (100–125 mesh) were used for preparative column chromatography. ^1H and ^{13}C NMR spectra were run on AC100, CXP200 and AMX400 Bruker Instruments using Me_4Si as an internal standard. Mass spectra were obtained with a Finnigan 1020 and Finnigan Mat SSQ710 at 70 eV ionizing voltage. IR spectra were recorded on Perkin Elmer 298 or Nicolet 5PC FT-IR spectrometers.

3.1. Materials

Solvents were purified by standard methods [14] and stored on molecular sieves (Type 4A, 1/8 pellets, Union Carbide). 2-Propynyl bromide, malonic esters, nitriles and other acetylenic and olefinic derivatives were commercial products. Rhodium complexes [{$RhCl(CO)_2$}$_2$] [15], [{$RhCl(CH_2{=}CH_2)_2$}$_2$] [16], [{RhCl(COD)}$_2$] [17], [$CpRh(CH_2CH_2)_2$] [18], [$CpRh(CO)_2$] [19] and [$(MeO_2CCp)Rh(CO)_2$] [20] were prepared according to literature methods.

3.2. Propynylation of malonic esters [5]: synthesis of benzyl methyl 2,2-dipropynylmalonate 1

Benzyl methyl malonate (20.9 g, 0.1 mol), K_2CO_3 (30 g, 0.22 mol) and dry acetone (180 ml) were placed in a three-necked 500 ml round bottomed flask equipped with a water condenser, a dropping funnel and a mechanical stirrer. 2-Propynyl bromide (47.6 g, 0.4 mol) dissolved in acetone (40 ml) was rapidly added at room temperature. The mixture was heated under reflux for 65 h with vigorous stirring. After cooling, the solid was filtered off, acetone was distilled off under reduced pressure, then water (200 ml) was added. The organic product was extracted with Et_2O (4 × 50 ml)

and dried over Na_2SO_4. The diacetylene derivative was distilled under vacuum and a pure solid product **1** (23.5 g, 0.083 mol) m.p. 48–50°C was obtained in 83% yield. IR (film): 3272, 3269, 2955, 2123, 1799, 1500, 1439, 1211, 1185, 1081, 1059, 973, 854, 736, 681 cm^{-1}. ^1H (100 MHz) NMR ($CDCl_3$): δ 2.02 (t, $J = 2.6$ Hz, 2H, 2=CH), 3.06 (d, $J = 2.6$ Hz, 4H, $2CH_2$), 3.68 (s, 3H, OMe), 5.19 (s, 2H, CH_2O), 7.32 (s, 5H, Ph). MS(*m/e*): 284 (M^+, 18), 245(100), 225(17), 214(18), 111(22), 103(31), 89(96), 79(62), 69(27), 65(26), 63(38).

3.3. Carbonylation reaction: synthesis of benzyl methyl 3,4-di(methoxycarbonylmethylene)cyclopentane-1,1-dicarboxylate 2

A 250 ml stainless-steel autoclave (Sotelem) was loaded with **1** (1.00 g, 3.536 mmol) dissolved in MeOH (60 ml) and with 10%Pd/C (18.7 mg, 0.0177 mmol), KI (73.0 mg, 0.443 mmol) under air, then it was pressurized with air (2 bar) and CO (6 bar) and heated at 45°C for 36 h with stirring. The brown mixture was filtered and the residue was washed with AcOEt. GC analysis showed that two carbonylated isomers, one of which was predominant, were formed in an 80% yield (1.137 g, 2.83 mmol). Separation by column chromatography on SiO_2 (hexane : AcOEt = 6 : 4) and crystallization of the oil resulting from MeOH at −20°C gave **2** (*E*, *E*) as a pure white solid in 70% yield (1.011 g, 0.251 mmol), m.p. 99–100°C. IR (KBr): 3456, 2965, 1767, 1740, 1728, 1710 1667, 1440, 1378, 1297, 1240, 1227, 1176, 1083, 881, 742 cm^{-1}. ^1H (200 MHz) NMR ($CDCl_3$): δ 3.55, 3.62 (2dd (ABX system), $J = 19.0$, 2.4 Hz, 4H, $2CH_2$), 3.67 (s, 3H, OMe), 3.76 (s, 6H, 2OMe), 5.18 (s, 2H, OCH_2), 6.32 (t, $J = 2.4$ Hz, 2H, 2=CH), 7.29–7.35 (m, 5H, Ph). ^{13}C (25 MHz) NMR ($CDCl_3$): δ 39.40 ($2CH_2$), 51.61 (2OMe), 52.87 (OMe), 58.12 (1qC), 67.47 (OCH_2), 113.35 (2=CH), 127.98, 128.35, 128,53 (5 aromatic CH), 135.28 (1qC), 155.00 (2qC), 166.32(CO), 170.54(2CO), 171.15(CO). MS (*m/e*): 402 (M^+,12), 343(45), 235(22), 207(29), 175(15), 91(100), 59(6).

3.4. Hydrolysis of the benzyl ester to methyl 3,4-di-(methoxycarbonylmethylene)cyclopentane-1,1-carboxylic acid carboxylate 3

The reaction was carried out in the presence of $AlCl_3$, following a procedure reported in the literature [6]. A white solid (m.p. 179–180°C) corresponding to the acid **3** (*E*, *E*) derived from hydrolysis of the benzyl ester **2** was obtained in 92% yield. IR (KBr): 3298, 2962, 1768, 1741, 1711, 1658, 1445, 1378, 1305, 1266, 1225, 1187, 1124, 880, 695, 668 cm^{-1} ^1H (200 MHz) NMR (CD_3COCD_3): δ3.48, 3.57 (2dd, (ABX system), $J = 19.2$, 2.4 Hz, $J = 19.2$, 2.2 Hz, 4H, $2CH_2$), 3.69 (s, 6H, 2OMe), 3.71 (s, 3H, OMe), 6.47–6.49 (m, 2H, 2=CH). MS (*m/e*): 312 (M^+, 8), 280(6), 268(4), 253(61), 237(31), 236(48), 208(100), 206(33), 193(28), 177(37), 175(32), 161(50), 149(96), 117(35), 59(28).

3.5. Decarboxylation and isomerization: synthesis of dimethyl 4-methoxycarbonylcyclopenta-1,3-diene-1,2-di acetate 4

To the monobasic acid obtained from **2** (0.718 g, 2.27 mmol) was added dry pyridine (20 ml) in a Schlenk tube under N_2. The mixture was stirred for 4 h at 80°C, then cooled, poured into a 10% HCl (250 ml) at 0°C and extracted with CH_2Cl_2 (4 × 50 ml). The organic layer was washed with an aqueous solution of $NaHCO_3$, and dried over Na_2SO_4. Product **4** was crystallized as a white solid (m.p. 53–54°C) from petroleum ether (35–50°C) in 78% yield (0.474 g, 1.771 mol). Anal. Found: C, 58.16; H, 6.00. $C_{13}H_{16}O_6$ Calc.: C, 58.21; H, 6.01%. IR (film): 2968, 1760, 1718, 1561, 1445, 1368, 1210, 1094, 1015, 745 cm^{-1}. ^1H (100 MHz) NMR ($CDCl_3$): δ 3.39 (brs, 2H, CH_2), 3.43–3.44 (m, 2H, CH_2), 3.45 (s, 2H, CH_2), 3.690, 3.694 (2s, 6H, 2OMe), 3.77 (s, 3H, OMe), 7.32 (t, $J = 1.3$ Hz, 1H, =CH). ^{13}C (25 MHz) NMR ($CDCl_3$): δ 33.12(CH_2), 34.31(CH_2), 44.55(CH_2), 51.58(OMe), 52.40(2OMe), 135.37(1qC), 136.07(1qC), 142.21(1qC), 144.83(=CH), 170.77(CO), 170.96(2CO). MS (*m/e*): 268 (M^+, 16), 237(21), 236(21), 208(76), 177(70), 176(41), 149(100), 121(21), 118(25), 117(48), 91(44), 59(22).

3.6. Synthesis of bis(carbonyl)[1-methoxycarbonyl-3,4-di(methoxycarbonylmethylene) cyclopentadienyl]rhodium [(MDMCp)Rh(CO)$_2$] 5

To a dry 50 ml Schlenk tube under N_2, were added dry THF (5 ml), diisopropylamine (0.4 ml, 2.55 mmol), previously distilled from KOH and stored on K_2CO_3, and butyllithium (hexane solution 1.6 M, 2 ml, 3.2 mmol) at 0°C. The solution was stirred for 10 min at 0°C and H(MDMCp) (0.615, g, 2.29 mmol), dissolved in dry THF (10 ml), was dropped into the lithium isopropylamide solution at 0°C. After stirring at 25°C for 1 h the mixture was evaporated under vacuum to eliminate the solvent and diisopropyl amine. The residue was dissolved in dry THF (10 ml), cooled at 0°C and a degassed solution of [{$Rh(CO)_2Cl$}$_2$] (0.445 g, 2.29 mmol) in dry THF (10 ml) was added slowly. The brown mixture was stirred at room temperature for 16 h. The complex was separated under N_2 by column chromatography on Florisil, previously activated at 100°C for 2 h, using pentane : THF (80 : 20) as eluent. The pure complex (checked by IR) was isolated after solvent removal under vacuum, (0.488 g, 1.15 mmol, 50% yield) as a yellow red wax. The complex was crystallized from hexane at −20°C as a yellow red solid; m.p. 34–35°C. Anal. Found: C, 42.20; H, 3.52, $C_{15}H_{15}O_8Rh$ Calc.: C, 42.27; H, 3.55%. IR (film):

3107, 2956, 2825, 2048, 1982, 1736, 1715, 1460, 1219, 1095, 1020, 995, 775 cm^{-1}. ^1H (400 MHz) NMR (C_6D_6, room temperature): δ 2.97, 3.02 (2d (AB system), J = 16.2 Hz, 4H, $2CH_2$), 3.31 (s, 6H, 2OMe), 3.41 (s, 3H, OMe), 5.88 (s, 2H, 2=CH); (CD_3COCD_3, room temperature): δ 3.55 (s, 4H, $2CH_2$), 3.64 (s, 6H, 2OMe), 3.69 (s, 3H, OMe), 6.03 (s, 2H, 2=CH); ($CDCl_3$, room temperature): δ 3.41, 3.70 (2d (AB system), J = 16.2 Hz, 4H, $2CH_2$), 3.72 (s, 6H, 2OMe), 3.75 (s, 3H, OMe), 5.95 (s, 2H, 2=CH). ^{13}C (25 MHz) NMR ($CDCl_3$, room temperature): δ 32.31 ($2CH_2$), 51.87 (OMe), 52.43 (2OMe), 87.82 (d, J = 2.9 Hz, 2C, 2=CH), 96.52 (d, J = 4.4 Hz, 1qC, CCO_2Me), 106.11 (d, J = 3.5 Hz, 2qC, $2CCH_2$), 163.62 (CO_2Me), 170.37 ($2CO_2Me$), 187.21 (CO), 190.57(CO). MS, direct introduction by DEP, CI (methane), positive ions, (m/e): 427 ($M + 1^+$, 6), 426 (M^+, 8), 400(16), 399(75), 398(50), 372(15), 371(76), 370(42), 297(12), 269(19), 238(22), 237(100), 236(24), 209(56), 59(5).

3.7. Synthesis of bis(ethylene)[1-methoxycarbonyl-3,4-di(methoxycarbonylmethylene) cyclopentadienyl]rhodium [(MDMCp)Rh (CH_2CH_2)$_2$] 6

Following the procedure adopted for the carbonyl derivative, [{$Rh(C_2H_4)_2Cl$}$_2$] (0.390 g, 1.0 mmol) was caused to react under N_2 with of Li(MDMCp) (2.49 mmol) in dry THF (30 ml). The mixture was heated under reflux for 30 min and stirred for 16 h at room temperature. After purification by column chromatography on Florisil under N_2 as previously described using pentane : THF (80 : 20) as eluent, a yellow oil was obtained, which on standing in hexane at −20°C gave a yellow solid (m.p. 52–54°C) in 47% yield (0.40 g, 0.939 mmol). Anal. Found: C, 47.86; H, 5.39. $C_{17}H_{23}O_6Rh$ Calc.: C, 47.89; H, 5.40%. IR (KBr): 3060, 2994, 2953, 1734, 1704, 1437, 1261, 1215, 1199, 766 cm^{-1}. ^1H (400 MHz) NMR (C_6D_6, room temperature): δ 1.39 (brs, 4H, 4=CH ethylene), 2.71 (brs, 4H, 4=CH ethylene), 2.94, 3.15 (2d, (AB system), J = 15.9 Hz, 4H, $2CH_2$, 3.33 (s, 6H, 2OMe), 3.49 (s, 3H, OMe), 5.54 (s, 2H, 2=CH); ($CDCl_3$, room temperature): δ 1.42 (brs, 4H, 4=CH, ethylene), 2.69 (brs, 4H, 4=CH, ethylene), 3.23, 3.40 (2d (AB system), J = 15.9 Hz, 4H, $2CH_2$), 3.69 (s, 6H, 2OMe), 3.78 (s, 3H, OMe), 5.53 (s, 2H, 2=CH).

Analogously to those of [{$CpRh(C_2H_4)_2$}$_2$] the proton signals of the ^1H NMR spectra of the complex with substituted cyclopentadienes are sensitive to temperature. For instance in complex **6**, at 60°C the proton signals of ethylene coalesced to a broad singlet at 2.04 ppm, while at −70°C the same protons gave two doublets at 1.37 ppm and 2.65 ppm with a coupling constant of 12.5 Hz. ^{13}C (25 MHz) NMR ($CDCl_3$) room temperature: δ 32.13 ($2CH_2$), 44.26 (d, J = 13.3 Hz, 2=CH_2), 51.70 (OMe), 52.28 (2OMe), 64.28 (d, J = 22.9 Hz, 2=CH_2), 89.85 (d, J = 3.7 Hz, 2=CH), 91.42 (d, J = 4.4 Hz, 1qC, CCO_2Me), 101.05 (d, J = 3.6 Hz, 2qC, CCH_2), 165.32 (CO), 170.48 (2CO). MS, direct introduction by DEP, CI (methane), positive ions, (m/e): 426 (M^+, 9), 413(10), 400(26), 399(88), 398(92), 373(12), 372(51), 370(100), 339(18), 312(20), 254(10), 59(5).

3.8. Synthesis of (1,5-cyclooctadiene)[1-methoxycarbonyl-3,4-di(methoxycarbonylmethylene)cyclopentadienyl]-rhodium [(MDMCp)Rh(COD)] 7

Following the previously reported procedure, di-μ-chloro-bis(η^4-1,5-cyclooctadiene)dirhodium (0.479 g, 0.97 mmol) was caused to react under N_2 with Li(MDMCp) (2.32 mmol) in dry THF (30 ml). The mixture was heated under reflux for 30 min and stirred at room temperature for 16 h. After purification by column chromatography on Florisil under N_2 using pentane : THF (80 : 20) as eluent, a yellow oil was obtained, which, on standing in hexane at −20°C, gave a yellow solid (m.p. 60–62°C) in 47% of yield (0.437 g, 0.913 mmol). Anal. Found: C, 52.69; H, 5.64. $C_{21}H_{27}O_6Rh$ Calc.: C, 52.72; H, 5.65%. IR (KBr): 2995, 2970, 2941, 2882, 2830, 1742, 1705, 1440, 1265, 1230, 1140, 765 cm^{-1}. ^1H (400 MHz) NMR (C_6D_6, room temperature): δ 1.82–1.96 (m, 4H, 4CH(COD)), 2.14–2.22 (m, 4H, 4CH(COD)), 3.02, 3.22 (2d (AB system), J = 15.8 Hz, 4H, $2CH_2$), 3.35 (s, 6H, 2OMe), 3.56 (s, 3H, OMe), 3.84 (brs, 4H, 4=CH(COD)), 5.63 (s, 2H, 2=CH); ($CDCl_3$, room temperature): δ 1.87–1.95 (m, 4H, 4CH(COD)), 2.10–2.18 (m, 4H, 4CH(COD)), 3.26, 3.43 (2d (AB system), J = 15.8 Hz, 4H, $2CH_2$), 3.69 (s, 6H, 2OMe), 3.77 (s, 3H, OMe), 3.79 (brs, 4H, 4=CH (COD)), 5.48 (s, 2H, 2=CH). ^{13}C (25 MHz) NMR ($CDCl_3$, room temperature): δ 32.26 ($4CH_2$), 32.51 ($2CH_2$), 51.53(OMe), 52.24(2OMe), 69.92 (d, J = 13.9 Hz, 4=CH(COD)), 88.87 (d, J = 3.7 Hz, 2=CH), 91.41 (d, J = 3.3 Hz, 1qC, CCO_2Me), 101.23 (d, J = 2.7 Hz, 2qC, $2CCH_2$), 165.45(CO), 170.81(2CO), MS, direct introduction by DEP, CI (methane), positive ions (m/e): 480 ($M + 2^+$, 30), 479 ($M + 1^+$, 100), 478 (m, 94), 419(8), 370(17), 59(8).

We did not observe any coupling between ^{103}Rh and the two protons of the cyclopentadienyl.

3.9. Catalytic synthesis of pyridines

A Pyrex Carius tube (25 ml) fitted with a Rotaflo teflon tap was charged under N_2 with complex **6** (33.8 mg, 0.0793 mmol), propionitrile (3.1 ml, 2.39 g 43.6 mmol) and 1-hexyne (0.91 ml, 0.651 g 7.92 mmol). The Carius tube was heated in a silicone oil bath (Fischer) at 130°C for 6 h under stirring. After cooling to room temperature, the unreacted alkyne and nitrile were removed under reduced pressure. The residue, containing pyridines and alkyne trimerization products,

was chromatographed on a column of neutral alumina using diethyl ether as eluent and analyzed by GLC and ^{1}H NMR spectroscopy. Pyridines and neutral derivatives were isolated by acid-base separation. Their properties were consistent with those reported in the literature [9]. Yields, based on the starting alkyne, amounted to 78% (0.677 g, 3.093 mmol) of two isomers (**8**:**9** = 44:56) containing the pyridine ring and 15% (0.0975 g, 0.396 mmol) of alkyne trimers. The same procedure and amount of substrates were used with cyclopentadienyl(bisη^2-ethylene) rhodium (18.0 mg, 0.0793 mmol) as catalyst. Yields of 67% (0.582 g, 2.656 mmol) of two isomers **8**:**9** = 56:44) containing the pyridine ring and 18% (0.117 g, 0.476 mmol) of alkyne trimers were determined by GLC.

3.10. Hydroformylation reactions

The hydroformylation reactions were performed in a 50 ml stainless-steel autoclave (Parr) equipped with magnetic stirrer and thermostatted (±1°C) in a silicone oil bath (Fischer). Yield and regioselectivity of **11** and **12** were determined by GLC using internal standards. In a typical run, complex **5** (0.025 g, 0.0586 mmol), distilled styrene (1.22 g, 11.76 mmol), and previously degassed dry toluene (5 ml), were introduced into the autoclave under N_2. The autoclave was closed, cooled to −60°C, evacuated, and then pressurized at room temperature with dihydrogen and carbon monoxide (60:40) at 70 bar. The reaction mixture was stirred at 100°C for 3 h, After cooling to −50°C the gases were removed and the reaction products were collected in a Schlenk tube with toluene under N_2 and compared to authentic samples by GLC. A 99% yield (1.556 g, 11.61 mmol) of aldehydes **11** and **12** (**11**:**12** = 42:58) was obtained. After a similar experiment, the solvent and the products were completely distilled off under reduced pressure and the residue was recovered with $CDCl_3$. ^{1}H NMR and IR spectra confirmed that complex **5**, used as catalyst, was unchanged. The same residue, heated at 150°C in DMSO for 5 h, was only partially decomposed. The other hydroformylation reactions of styrene or 1-hexene with [$(MeO_2CCp)Rh(CO)_2$] or [$CpRh(CO)_2$] as catalysis in the presence or absence of PPh_3, were carried out similarly.

Acknowledgements

This work was carried out within the framework of Progetto Finalizzato Chimica Fine 2 of the Italian Consiglio Nazionale delle Ricerche. Centro Interfacoltà di Misure of the University of Parma provided the facilities for NMR and mass spectra. F.S.D. was recipient of a grant from the Brazilian Government.

References

[1] N.J. Coville, K.E. DuPlooy and W. Pickl, *Coord. Chem. Rev.*, *116* (1992) 1; E. Watts, *Organomet. Chem.*, *10* (1982) 283; D.W. Macomber, W.P. Hart and M.D. Rausch, *Pure Appl. Chem.*, *58* (1986) 617.

[2] J.W. Kang and P.M. Maitlis, *Organomet. Chem.*, *26* (1971) 393; W.P. Fehlhammer, W.A. Herrmann and K. Oefele, in G. Brauer (ed.), *Handbuch der Praparative Anorganischen Chemie*, 3rd ed., Enke Verlag, Stuttgart, 1981,p. 1799.

[3] R. Cramer and J.J. Mrowca, *Inorg. Chim. Acta*, *5* (1971) 528; M.D. Arthurs, M. Sloan, M.G.B. Drew and S.M. Nelson, *J. Chem. Soc., Dalton Trans.*, (1975) 1794; M.D. Arthurs and S.M. Nelson, *J. Coord. Chem.*, *13* (1983) 29.

[4] G.P. Chiusoli, M. Costa and S. Reverberi, *Synthesis* (1989) 262; B. Gabriele, M. Costa, G. Salerno and G.P. Chiusoli, *J. Chem. Soc., Perkin Trans.*, *1* (1994) 83.

[5] The improved procedure reported here was kindly communicated to us by Dr. A. Liebarria, CSIR, Barcelona.

[6] T. Tsuji, T. Kataoka, M. Yoshioka, Y. Sendo, Y. Nishitani, S. Hirai, T. Maeda and W. Nagata, *Tetrahedron Lett.*, (1979) 2793.

[7] M. Arthurs, S.M. Nelson and M.G.B. Drew, *J. Chem. Soc., Dalton Trans.*, (1977) 779.

[8] M.J. Bennett, M.R. Churchill, M. Gerlach and R. Mason, *Nature*, *201* (1964) 1318; F.A. Cotton, *Discussions Faraday Soc.*, *47* (1969) 79.

[9] H. Bonnemann and W. Brijoux in R. Ugo (ed.), *Aspect of Homogeneous Catalysis*, Vol. 5, Reidel, Dordrecht, 1984, p. 77.

[10] D. Evans, J.A. Osborn and G. Wilkinson, *J. Chem. Soc., A* (1968) 3133; R.L. Pruett and J.A. Smith, *J. Org. Chem.*, *34* (1969) 327; J. Falbe, *New Syntheses with Carbon Monoxide*, Springer, Berlin, 1980; D. Neibecker and R. Réau, *Angew. Chem., Int. Ed. Engl.*, *28* (1989) 500; L. Marko, in R. Ugo (ed.), *Aspects of Homogeneous Catalysis*, Vol. 2, Reidel, Dordrecht, 1974, p. 3. and references therein.

[11] P. Cioni, P. Diversi, G. Ingrosso, A. Lucherini and P. Ronca, *J. Mol. Cat.*, *40* (1987) 337, and references therein; P. Diversi, L. Ermini, G. Ingrosso and A. Lucherini, *J. Organomet. Chem.*, *447* (1993) 291.

[12] B.H. Chang, R.H. Grubbs and C.H. Brubaker, Jr., *J. Organomet. Chem.*, *172* (1979) 81.

[13] F. Basolo, *Polyhedron*, *9* (1990) 1503, and references therein; A. Ceccon, A. Gambaro, S. Santi and A. Venzo, *J. Mol. Cat.*, *69* (1991) L1; A.K. Kakkar, N.J. Taylor, T.B. Marder, J.K. Shen, N. Hallinan and F. Basolo, *Inorg. Chim. Acta*, *198–200* (1992) 219.

[14] D.D. Perrin and W.L.F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon Press, NY, 1988.

[15] J. McCleverty and G. Wilkinson, *Inorg. Synth.*, *8* (1966) 211.

[16] R. Cramer, *Inorg. Synth.*, *15* (1974) 14.

[17] A. Van der Ent and A.L. Onderlinden, *Inorg. Synth.*, *14* (1973) 93.

[18] R.B. King, *Inorg. Chem.*, *2* (1963) 528.

[19] E.O. Fischer and K. Bittler, *Z. Naturforsch.*, *16B* (1961) 225.

[20] W.P. Hart, D.W. Macomber and M.D. Rausch, *J. Am. Chem. Soc.*, *102* (1980) 1196.