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(η^6-Cyclohepta-1,3,5-triene)(η^4-cycloocta-1,5-diene)iron(0) complex as attractive precursor in catalysis

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Dedicated to Professor Martin Bennett on the occasion of his retirement.

Abstract

The catalytic activity of the complex Fe(η^6-CHT)(η^4-COD), (CHT = 1,3,5-cycloheptatriene; COD = 1,5-cyclooctadiene), **1**, has been evaluated in some reference reactions such as the hydroformylation of 1-hexene and styrene and the cyclotrimerisation of a wide range of terminal and internal acetylenes. The title complex has been found to be a convenient catalytic precursor and it resulted more active than other iron catalysts in the investigated reactions. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Hydroformylation; Alkyne cyclotrimerisation; Cycloolefin complexes; Aldehydes; Arenes

1. Introduction

The design and preparation of efficient catalysts represent crucial issues of organotransition metal chemistry. According to the literature, a possible way to obtain active catalysts is to synthesise complexes containing unsaturated organic ligands, such as cycloolefins, bonded to the metal. Ni(η^4-COD)$_2$, (COD = 1,5-cyclooctadiene) [1], [RhCl(η^4-COD)]$_2$ [2], Ru(η^6-cycloocta-1,3,5-triene)(η^4-COD) [3], are well-known examples of compounds that have played an important role in organometallic chemistry and catalysis as very reactive starting materials. In such compounds the organic molecules can be easily displaced from the metal, thus making available coordination sites that are required for substrate activation of stoichiometric and catalytic reactions.

The complex Fe(η^6-CHT)(η^4-COD), (CHT = 1,3,5-cycloheptatriene), **1**, containing only cycloolefins bonded to the metal, belongs in this class. Complex **1** was synthesised by us via co-condensation of iron atoms with COD at −196°C followed by condensation of CHT in a Metal Vapour Synthesis (MVS) apparatus and its reactivity with small molecules as CO and P(OMe)$_3$ was also studied [4]. It can be now obtained in larger amount (10 g for run) using a new MVS reactor, elsewhere described [5], making possible a more detailed study about its chemical properties. Complex **1** is an attractive compound in catalysis and its activity was examined in well known processes such as the hydroformylation of olefins [6–12] and the cyclotrimerisation of acetylenes [13,14], previously investigated using other iron complexes.

2. Results and discussion

2.1. Hydroformylation reactions

1-Hexene and styrene, two olefins largely studied in hydroformylation reactions [15,16], have been used as substrates. The runs have been performed in toluene as solvent, at 100°C and 100 atm CO/H$_2$ (1/1) total pressure using a substrate/catalyst molar ratio = 150 (Table 1).

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Table 1
Hydroformylation of 1-hexene and styrene catalysed by Fe(η^6-CHT)(η^4-COD) (**1**) [a]

Substrate	Reaction time (h)	Conv. (%)	Reaction mixture composition (%) [b]					Regio-selectivity (%)	Chemo-selectivity [c]
			$\mathbf{H_1}$	$\mathbf{H_2}$	**N**	**B**	**C**		
	6	60	40	–	36	24	–	20 [d]	1
1-Hexene	12	84	16	–	50	34	–	19 [d]	1
	24	96	4	–	58	38	–	21 [d]	1
			S		$\mathbf{N_s}$	$\mathbf{B_s}$			
	6	18	82		5	13		44 [e]	
Styrene	12	34	66		9	25		47 [e]	
	24	65	35		17	48		48 [e]	
	48	98	2		26	72		47 [e]	

[a] Reaction conditions: Substrate (17.6 mmol); catalyst (0.117 mmol); 1:1 CO–H_2 pressure, 100 atm; temperature, 100°C; solvent, toluene (10 ml).
[b] $\mathbf{H_1}$ = 1-Hexene; $\mathbf{H_2}$ = 2-Hexene; **N** = Heptanal; **B** = 2-Methylhexanal; **C** = 2-Ethylpentanal; **S** = Styrene; $\mathbf{N_S}$ = 3-Phenylpropanal; $\mathbf{B_S}$ = 2-phenylpropanal.
[c] $\{[N]+[B]\}/\{[N]+[B]+[C]+[H_2]\}$.
[d] $100 \times \{[N]-[B]\}/\{[N]+[B]\}$.
[e] $100 \times \{[Bs]-[Ns]\}/\{[Ns]+[Bs]\}$.

2.1.1. Hydroformylation of 1-hexene

Under hydroformylation conditions 1-hexene, $\mathbf{H_1}$, can give the normal aldehyde heptanal, **N**, and the branched aldehyde 2-methylhexanal, **B**, as reaction products. The internal olefins 2-hexene, $\mathbf{H_2}$, and 3-hexene, $\mathbf{H_3}$, deriving from the isomerisation of $\mathbf{H_1}$, the 2-ethylpentanal, **C**, deriving from the hydroformylation of $\mathbf{H_2}$ and/or $\mathbf{H_3}$, and hexane, deriving from the hydrogenation of the olefins, are also formed as outcome of by reactions (Scheme 1).

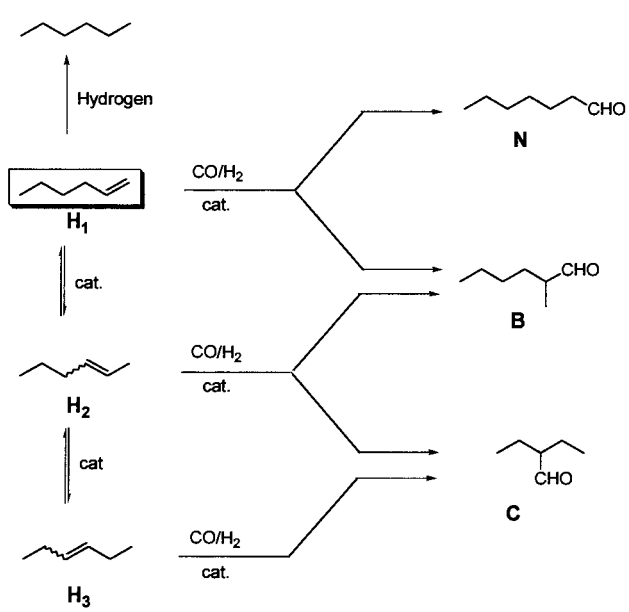
Among the possible products, only heptanal, **N**, and 2-methylhexanal, **B**, are formed with **1** (Table 1) with complete chemoselectivity and with regioselectivity, $100 \times \{[\mathbf{N}]-[\mathbf{B}]\}/\{[\mathbf{N}]+[\mathbf{B}]\}$, of ca. 20%. Hexane and 2- or 3-hexene have not been detected in the reaction products, pointing out the absence of hydrogenation or isomerisation reactions. Under the adopted conditions, conversion 60% and 96% is obtained after 6 and 24 h, respectively.

2.1.2. Hydroformylation of styrene

The hydroformylation of styrene, **S**, gives the 3-phenylpropanal, $\mathbf{N_S}$, and the 2-phenylpropanal, $\mathbf{B_S}$. Compared with 1-hexene, the conversion of styrene to aldehydes is lower being of 18% after 6 h and of 65% after 24 h. The branched aldehyde $\mathbf{B_S}$ is the main product and the regioselectivity, $100 \times \{[\mathbf{B_S}]-[\mathbf{N_S}]\}/\{[\mathbf{N_S}]+[\mathbf{B_S}]\}$, representing the regiomeric excess of the branched aldehyde, is 47%. Ethylbenzene, deriving from the hydrogenation of styrene, was not detected in the reaction products.

In agreement with literature reports [15,16], the regioselectivity in the hydroformylation of styrene is the reverse of that with 1-hexene ($[\mathbf{B_S}] > [\mathbf{N_S}]$, for styrene; $[\mathbf{N}] > [\mathbf{B}]$, for 1-hexene), the formation of the branched aldehyde as main component in the hydroformylation of styrene being ascribed to the different stability of the metal-alkyl intermediates [16].

Iron compounds are generally considered very poor hydroformylation catalysts [12,17–22]; however, the results obtained using complex **1** as precursor, mainly in the hydroformylation of 1-hexene, were quite promising. In order to better evaluate the peculiarity of complex **1**, the hydroformylation of 1-hexene and styrene has been also performed using $Fe(CO)_5$, a traditional iron hydroformylation catalyst [17,22]. The results are reported in Table 2 and compared with those obtained using **1** as precursor.



Scheme 1.

Table 2
Comparison between the catalytic activity of Fe(η^6-CHT)(η^4-COD) (**1**), and $Fe(CO)_5$ in the hydroformylation of 1-hexene and styrene [a]

Substrate	Catalyst	Conv. (%)	Reaction mixture composition (%) [b]					Chemo-selectivity [c]	Turnover frequency [d] (TOF, h^{-1})
			H_1	H_2	N	B	C		
1-Hexene	Fe(η^6-CHT)(η^4-COD)	96	4	–	58	38		1	6
	$Fe(CO)_5$	68	32	11	35	21	1	0.82	3.6
			S		N_s	B_s			
Styrene	Fe(η^6-CHT)(η^4-COD)	65	35		17	48		4.1	
	$Fe(CO)_5$	9	91		3	6		0.6	

[a] Reaction conditions: Substrate (17.6 mmol); catalyst (0.117 mmol); 1:1 CO–H_2 pressure, 100 atm; temperature, 100°C; time, 24 h; solvent, toluene (10 ml).
[b] $\mathbf{H_1}$ = 1-Hexene; $\mathbf{H_2}$ = 2-Hexene; **N** = Heptanal; **B** = 2-Methylhexanal; **C** = 2-Ethylpentanal. **S** = Styrene; $\mathbf{N_S}$ = 3-Phenylpropanal; $\mathbf{B_S}$ = 2-phenylpropanal.
[c] {[N]+[B]}/{[N]+[B]+[C]+[H_2]}.
[d] TOF = mol aldehyde/mol catalyst × h.

It appears from the reported data that complex **1** is more active than $Fe(CO)_5$ under the adopted reaction conditions. Such difference is more evident in the case of styrene where the TOF numbers are 4.1 h^{-1} and 0.6 h^{-1} in the presence of complex **1** and $Fe(CO)_5$, respectively.

It is worth knowing that theoretical investigations on hydroformylation reactions [23] indicate that, in the Reppe synthesis catalysed by $Fe(CO)_5$, an effective catalyst should be CO deficient hydrido species such as $H_2Fe(CO)_3$ and $HFe(CO)_3^-$. Such species could be probably involved in the above hydroformylation reactions and it appears that they can be more easily formed starting from complex **1**, containing weakly bonded ligands, and where, moreover, hydrogen atom migrations between the cycloolefinic ligands and the iron are likely to occur [24].

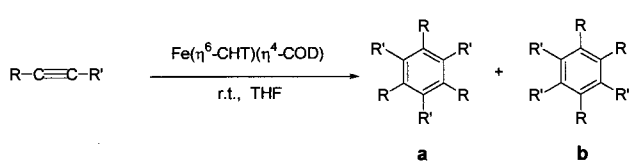
2.2. Cyclotrimerisation of alkynes

Complex **1** easily catalyses the cyclotrimerisation of a wide range of terminal and internal alkynes to benzene derivatives (Scheme 2).

The reactions, performed in THF as solvent at room temperature, afford the cyclotrimerisation products in high yield and complete chemoselectivity (Table 3).

1-Hexyne, the simplest alkyne used, is completely converted into a 1:1 mixture of 1,3,5- and 1,2,4-tri-*n*-butylbenzene, **2a** and **2b**, in 46 h. Under the same reaction conditions, the conversion of 3-methyl-1-pentyne to 1,3,5- and 1,2,4-tri-*sec*-butylbenzene, **3a** and **3b** (**3a**: **3b** = 53: 47), is 70% (run 6), the lower reactivity probably being due to the steric effect of the methyl group in α position to the triple bond that hinders the coordination of the alkyne to the metal. With 4-methyl-1-hexyne, 5-methyl-1-heptyne and 6-methyl-1-octyne, in which the methyl group is shifted successively further from the triple bond, the conversion into the corresponding cyclotrimers 1,3,5- and 1,2,4-tri-(2-methylbutyl)benzene, **4a** and **4b**, 1,3,5- and 1,2,4-tri-(3-methylpentyl)benzene, **5a** and **5b**, and 1,3,5- and 1,2,4-tri-(4-methylhexyl)benzene, **6a** and **6b**, increases to that of 1-hexyne (runs 7, 8 and 9; conv. 85, 90, and 100%, respectively). In the mixtures the regioisomers **a** and **b** are present in ratio of ca. 1:1.

tert-Butylacetylene, which has a bulky group near to the triple bond, exhibits a low reactivity (run 10, conv. 45% to 1,3,5- and 1,2,4-tri-*tert*-butylbenzene, **7a** and



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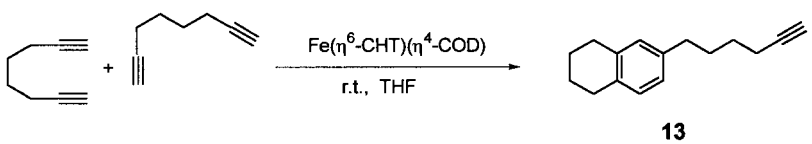
2 : R = H, R' = $(CH_2)_3CH_3$
3 : R = H, R' = $CH(CH_3)C_2H_5$
4 : R = H, R' = $CH_2CH(CH_3)C_2H_5$
5 : R = H, R' = $(CH_2)_2CH(CH_3)C_2H_5$
6 : R = H, R' = $(CH_2)_3CH(CH_3)C_2H_5$
7 : R = H, R' = $C(CH_3)_3$
8 : R = H, R' = $Si(CH_3)_3$
9 : R = H, R' = C_6H_5
10 : R = R' = CH_3
11 : R = R' = C_2H_5
12 : R = R' = C_6H_5

Scheme 2.

Table 3
Catalytic cyclotrimerisation of terminal and internal alkynes promoted by Fe(η^6-CHT)(η^4-COD) (**1**), according to Scheme 2 [a]

Run	Alkyne	Conv. (%)	Products [b]
5	1-Hexyne	100	1,3,5-Tri-*n*-butylbenzene (**2a**), (50) and 1,2,4-tri-*n*-butylbenzene (**2b**) (50)
6	3-Methyl-1-pentyne	70	1,3,5-Tri-*sec*-butylbenzene (**3a**) (53) and 1,2,4-tri-*sec*-butylbenzene (**3b**) (47)
7	4-Methyl-1-hexyne	85	1,3,5-Tri(2-methylbutyl)benzene (**4a**) (45) and 1,2,4-tri(2-methylbutyl)benzene (**4b**) (55)
8	5-Methyl-1-heptyne	90	1,3,5-Tri(3-methylpentyl)benzene (**5a**) (52) and 1,2,4-tri(3-methylpentyl)benzene (**5b**) (48)
9	6-Methyl-1-octyne	100	1,3,5-Tri(4-methylhexyl)benzene (**6a**) (48) and 1,2,4-tri(4-methylhexyl)benzene (**6b**) (52)
10	*tert*-Butylacetylene	45	1,3,5-Tri-*tert*-butylbenzene (**7a**) (30) and 1,2,4-tri-*tert*-butylbenzene (**7b**) (70)
11	Trimethylsilylacetylene	85	1,3,5-Trimethylsilylbenzene (**8a**) (5) and 1,2,4-Trimethylsilylbenzene (**8b**) (95)
12	Phenylacetylene	75	1,3,5-Triphenylbenzene (**9a**) (65) and 1,2,4-Triphenylbenzene (**9b**) (35)
13 [c]	2-Butyne	100	Hexamethylbenzene (**10**) (100)
14 [d]	3-Hexyne	50	Hexaethylbenzene (**11**) (100)
15 [e]	Diphenylacetylene	20	Hexaphenylbenzene (**12**) (100)

[a] Reaction conditions: Alkyne (29.25 mmol); Fe(η^6-CHT)(η^4-COD), 0.05 g (0.195 mmol); THF (5 ml); time 46 h; room temperature.
[b] The regioisomeric composition (**a** and **b**%) was determined by GC-MS and ^{1}H-NMR analyses.
[c] Carried out for 28 h.
[d] The conversion to **11** is quantitative at reflux for 30 h.
[e] The conversion to **12** is quantitative at reflux for 50 h.



Scheme 3.

Table 4
Cyclotrimerisation of 2-butyne with iron complexes

Catalyst	2-Butyne/catalyst (mol/mol)	*T* (°C)	Reaction time (h)	Conv. (%)	Turnover frequency (TOF, h^{-1})	Reference
$Fe(COT)_2$	158	25	24	18	1.2	[27]
$Fe(HMB)_2$	90	45	42	16	0.35	[28]
Fe(CHT)(COD)	150	25	28	100	5.4	–

7b, **7a**:**7b** = 30:70). In contrast, a high conversion (85%) to 1,3,5- and 1,2,4-tri-trimethylsilylbenzene, **8a** and **8b**, (**8a**:**8b** = 5:95) has been found with trimethylsilylacetylene (run 11), probably because the trimethylsilyl group makes the triple bond more reactive. Phenylacetylene is fairly reactive [25] and furnishes a mixture of 1,3,5- and 1,2,4-triphenylbenzene, **9a** and **9b** (**9a**:**9b** = 65:35) with conversion 75% (run 12).

As far as the oligomerisation of internal alkynes is concerned, 2-butyne cyclotrimerises quantitatively to hexamethylbenzene (**10**), in 28 h at room temperature (run 13). The conversion of 3-hexyne to hexaethylbenzene, **11**, is 50% at room temperature after 46 h (run 14), and becomes quantitative when working at the solvent boiling point (65°C) for 30 h. Diphenylacetylene is less reactive than the aliphatic acetylenes, the conversion to hexaphenylbenzene (**12**), being 20% after 46 h at room temperature (run 15) and quantitative at reflux after 50 h.

Complex **1** also catalyses the selective cyclodimerization of 1,7-octadiyne to the alkynylbenzocycloalkene derivative **13**, with a conversion of 65% in 46 h at room temperature (Scheme 3). No other product was formed in the course of the reaction, which was quantitative after 4 days.

In the previous reports on alkyne cyclotrimerisation reactions promoted by iron precursors, compounds such as iron carbonyls [26], bis(cyclooctatetraene)iron, $Fe(COT)_2$ [27], bis(hexamethylbenzene)iron(0), $Fe(HMB)_2$ [28], iron atoms [29], (η^6-toluene)(η^2-olefin)$_2$iron complexes [30] were used, the $Fe(COT)_2$ and the $Fe(HMB)_2$ being largely the most effective catalytic precursors. Comparison of the activity of these two systems with the title complex, Fe(η^6-CHT)(η^4-COD), in the cyclotrimerisation of 2-butyne under quite similar reaction conditions (Table 4) shows that complex **1** is the most active with TOF number of 5.4 h^{-1} versus 1.2 h^{-1} and 0.35 h^{-1} for $Fe(COT)_2$ and $Fe(HMB)_2$, respectively.

3. Conclusions

It appears from the reported results that the complex Fe(η^6-CHT)(η^4-COD) (**1**), is an efficient catalytic precursor for olefin hydroformylation and alkyne cyclotrimerisation, being more active than previously studied iron complexes. As often observed in cycloolefin transition metal chemistry [1–3], the cyclolefin ligands in **1** are probably easily removed, even under mild conditions, in the presence of additional organic substrates, accounting for the good catalytic activity exhibited by **1** in the reported reactions.

These results make of interest a broader study of the chemical properties and the catalytic activity of complex **1**.

4. Experimental

4.1. General

All operations were performed under dry argon. Solvents were purified by conventional methods, distilled and stored under argon. 1-Hexene and styrene were distilled before use. The commercial acetylenes were degassed and stored under argon. 3-Methyl-1-pentyne was prepared in 70% yield by reduction of 1-bromo-3-methyl-1,2-pentadiene with lithium aluminium hydride, according to the Miginiac procedure [31]. 4-Methyl-1-hexyne (70% yield), 5-methyl-1-heptyne (80% yield) and 6-methyl-1-octyne (60% yield) were prepared by bromination–dehydrobromination of the corresponding 1-alkenes. The olefins were treated with equimolecular amounts of bromine and the crude products reacted with sodium amide in mineral oil at 160°C [32]. $Fe(CO)_5$ (Aldrich product) was used as received. The complex (η^6-cyclohepta-1,3,5-triene)(η^4-cycloocta-1,5-diene)iron, (**1**), was prepared using a new reactor elsewhere described [4,5]. In a typical experiment iron vapours (20 g) were co-condensed with cycloocta-1,5-diene (50 ml) and cyclohepta-1,3,5-triene (30 ml) furnishing red–brown crystals of **1** (10 g; yield 22% with respect to vaporised iron).

^{1}H-NMR spectra were recorded on a Varian Gemini 200 instrument at 200 MHz. Chemical shifts were determined relative to internal $Si(CH_3)_4$ ($\delta = 0$ ppm); coupling constants J are in Hz. The aromatic protons have been numbered as shown in Fig. 1.

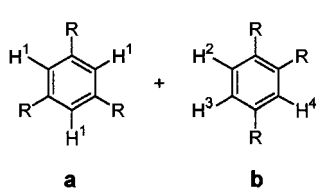


Fig. 1.

GC-MS spectra were recorded on a Perkin–Elmer Q-Mass 910 spectrometer connected with a Perkin–Elmer gas chromatograph, equipped with a 'split-splitless' injector, using a SiO_2 capillary column and helium as carrier gas. The GLC analyses were performed on a Perkin–Elmer 8600 gas chromatograph, equipped with a 'in column' injector and a flame ionisation detector (FID), using a SiO_2 'Wide Bore' column (DB1, 30 m × 0.53 mm, 5 μm) and helium as carrier gas. Microanalyses were carried out by the Laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa, Italy.

4.2. Hydroformylation of 1-hexene and styrene with Fe(η^6-cyclohepta-1,3,5-triene)(η^4-cycloocta-1,5-diene) (**1**), and $Fe(CO)_5$; general procedure

A solution of substrate (17.6 mmol), catalyst (0.117 mmol), internal standard (2 ml) in toluene (5 ml), (cooled to −20°C when the catalyst is complex **1**), was introduced by suction into an evacuated 50 ml stainless steel autoclave. Carbon monoxide was introduced, the autoclave was stirred and heated at 100°C and hydrogen was rapidly introduced up to 100 atm total pressure (1:1 $CO–H_2$). The progress of the reaction was checked by removing liquid samples through a tap and analysing them by GLC. Benzene and *o*-xylene were used as internal standards in the hydroformylation of 1-hexene and styrene, respectively.

4.3. Cyclotrimerisation of alkynes to substituted benzenes with Fe(η^6-cyclohepta-1,3,5-triene)(η^4-cycloocta-1,5-diene) (**1**)

Only the reaction with 1-hexyne (run 5, Table 3) is described in detail, the experimental procedure being the same with the other alkynes.

A 25 ml, round-bottomed flask, containing a solution of complex **1** (0.05 g, 0.195 mmol) in THF (5 ml) cooled to −20°C, was charged with 1-hexyne (3.4 ml, 29.25 mmol). The mixture was stirred at room temperature (r.t.), the progress of the reaction being monitored by GLC. After 46 h the 1-hexyne had disappeared completely. The solvent was evaporated giving a crude oily product that was chromatographed on alumina (Merck product, activity II-III, 70-230 mesh) using THF as eluent and successively purified by vacuum distillation ($T_{bp} = 95–98$°C, 17 mmHg). A mixture of 1,3,5-tri-*n*-butylbenzene (**2a**), and 1,2,4-tri-*n*-butylbenzene, **2b** (**2a**:**2b** = 50:50) was obtained (2.35 g, yield 97%).

GC-MS (m/z): 246 [M^+]. ^{1}H-NMR ($CDCl_3$): δ 0.95 (18H, t, $J = 7.7$, CH_2CH_3); 1.35 (12H, m, $CH_2CH_2CH_3$); 1.55 (12H, m, $CH_2CH_2C_2H_5$); 2.55 (12H, t, $J = 7.6$, $PhCH_2CH_2$); 6.80 (3H, s, H^1, **2a**); 6.92

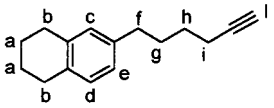


Fig. 2.

(2H, m, $H^3 + H^4$, **2b**); 7.04 (1H, d, $J_{23} = 6.5$, H^2, **2b**). Lit. [33].

*4.3.1. 1,3,5-Tri-sec-butylbenzene (**3a**), and 1,2,4-tri-sec-butylbenzene (**3b**), from 3-methyl-1-pentyne (run 6, Table 3, **3a**:**3b** = 53:47)*

GC-MS (m/z) = 246 [M^+]. ^{1}H-NMR ($CDCl_3$): δ 0.81 (18H, t, $J = 7.6$, CH_2CH_3); 1.20 (18H, d, $J = 7.8$, $CHCH_3$); 1.57 (12H, m, $CHCH_2CH_3$); 2.53 (4H, m, PhC*H*, **3a** + **3b**); 2.95 (2H, m, PhC*H*, **3b**); 6.78 (3H, s, H^1, **3a**); 6.95 (m, 2H, $H^3 + H^4$, **3b**); 7.11 (1H, d, $J_{23} = 6.5$, H^2, **3b**). Lit. [34].

*4.3.2. 1,3,5-Tri(2-methylbutyl)benzene (**4a**) and 1,2,4-tri(2-methylbutyl)benzene (**4b**), from 4-methyl-1-hexyne (run 7, Table 3, **4a**:**4b** = 45:55)*

GC-MS (m/z) = 288 [M^+]. ^{1}H-NMR ($CDCl_3$): δ 0.75–1.05 (36H, m, $CHCH_3 + CH_2CH_3$); 1.20–1.60 (18H, m, $CHCH_3 + CH_2CH_3$); 2.30 (6H, m, PhC*H*H); 2.60 (6H, m, PhCH*H*); 6.73 (2.7H, s, H^1, **4a**); 6.88 (m, 2.2H, $H^3 + H^4$, **4b**); 7.0 (1.1H, d, $J_{23} = 6.5$, H^2, **4b**). Anal. Calc. for $C_{21}H_{36}$: C, 87.41; H, 12.59. Found: C, 87.29; H, 12.40%. Lit. [33].

*4.3.3. 1,3,5-Tri(3-methylpentyl)benzene (**5a**), and 1,2,4-tri(3-methylpentyl)benzene (**5b**), from 5-methyl-1-heptyne (run 8, Table 3, **5a**:**5b** = 52:48)*

GC-MS (m/z) = 330 [M^+]. ^{1}H-NMR ($CDCl_3$): δ 0.9 (36H, m, $CHCH_3 + CH_2CH_3$); 1.10–1.95 (30H, m, $CH_2CH(CH_3)CH_2CH_3$); 2.5 (12H, m, PhCH_2); 6.78 (3H, s, H^1, **5a**); 6.92 (m, 2H, $H^3 + H^4$, **5b**); 7.0 (1H, d, $J_{23} = 6.5$, H^2, **5b**). Anal. Calc. for $C_{24}H_{42}$: C, 87.19; H, 12.81. Found: C, 87.01; H, 12.63. Lit [33].

*4.3.4. 1,3,5-Tri(4-methylhexyl)benzene (**6a**), and 1,2,4-tri(4-methylhexyl)benzene (**6b**) from 6-methyl-1-octyne (run 9, Table 3, **6a**:**6b** = 48:52)*

GC-MS (m/z) = 372 [M^+]. ^{1}H-NMR ($CDCl_3$): δ 0.8 (36H, m, $CHCH_3 + CH_2CH_3$); 1.0–1.70 (42H, m, $CH_2CH_2CH(CH_3)CH_2CH_3$); 2.5 (12H, t, $J = 7.7$, $PhCH_2CH_2$); 6.8 (3H, s, H^1, **6a**); 6.95 (m, 2H, $H^3 + H^4$, **6b**); 7.05 (1H, d, $J_{23} = 6.5$, H^2, **6b**). Anal. Calc. for $C_{27}H_{48}$: C, 87.02; H, 12.98. Found: C, 86.89; H, 12.81%.

*4.3.5. 1,3,5-Tri-tert-butylbenzene (**7a**), and 1,2,4-tri-tert-butylbenzene (**7b**), from tert-butylacetylene (run 10, Table 3, **7a**:**7b** = 30:70)*

GC-MS (m/z) = 246 [M^+]. ^{1}H-NMR ($CDCl_3$): δ 1.30 (12.6H, s, CMe_3, **7b**); 1.34 (16.2H, s, CMe_3, **7a**); 1.54 (12.6H, s, CMe_3, **7b**); 1.57 (12.6H, s, CMe_3, **7b**); 7.12 (1.4H, dd, $J_{32} = 8$, $J_{34} = 2$, H^3, **7b**); 7.20 (1.8H, s, H^1, **7a**); 7.51 (1.4H, d, H^2, **7b**); 7.62 (1.4H, d, H^4, **7b**). Lit. [30,35].

*4.3.6. 1,3,5-Trimethylsilylbenzene (**8a**), and 1,2,4-trimethylsilylbenzene (**8b**), from trimethylsilylacetylene (run 11, Table 3, **8a**:**8b** = 5:95)*

GC-MS (m/z) = 294 [M^+]. ^{1}H-NMR ($CDCl_3$): δ 0.23 (17.1H, s, SiMe_3, **8b**); 0.26 (2.7H, s, SiMe_3, **8a**); 0.42 (17.1H, s, SiMe_3, **8b**); 0.45 (17.1H, s, SiMe_3, **8b**); 6.75 (0.3H, s, H^1, **8a**); 7.49 (1.9H, dd, $J_{32} = 7.5$, $J_{34} = 1.5$, H^3, **8b**); 7.66 (1.9H, d, H^2, **8b**); 7.84 (1.9H, d, H^4, **8b**). Anal. Calc. for $C_{15}H_{30}Si_3$: C, 61.14; H, 10.26. Found: C, 61.03; H, 10.11%. Lit. **8a** [25].

*4.3.7. 1,3,5-Triphenylbenzene (**9a**), and 1,2,4-triphenylbenzene (**9b**), from phenylacetylene (run 12, Table 3, **9a**:**9b** = 65:35)*

GC-MS (m/z) = 306 [M^+]. ^{1}H-NMR (C_6D_6): δ 6.85–7.30 (30H, m, C_6H_5, **9a** + **9b**); 7.35 (0.7H, d, $J_{23} = 5$, H^2, **9b**); 7.49 (0.7H, m, H^3, **9b**); 7.65 (0.7H, d, $J_{34} = 1.8$, H^4, **9b**); 7.74 (3.9H, s, H^1, **9a**). Lit. [25,36].

*4.3.8. Hexamethylbenzene (**10**), from 2-butyne (run 13, Table 3)*

MS (m/z) = 162 [M^+]. ^{1}H-NMR ($CDCl_3$): δ 2.21 (s, CH_3). M.p. = 162°C.

*4.3.9. Hexaethylbenzene (**11**), from 3-hexyne (run 14, Table 3)*

MS (m/z) = 246 [M^+]. ^{1}H-NMR ($CDCl_3$): δ 1.27 (18H, t, $J = 8$, CH_2CH_3); 2.75 (12H, q, CH_2CH_3). M.p. = 130°C. Lit. [37].

*4.3.10. Hexaphenylbenzene (**12**), from diphenylacetylene (run 15, Table 3)*

MS (m/z) = 534 [M^+]. ^{1}H-NMR ($CDCl_3$): δ 6.81 (s, C_6H_5). M.p. = 462°C. Lit. [37].

*4.3.11. 2-(5-Hexynyl)-5,6,7,8-tetrahydronaphthalene (**13**), from 1,7-octadiyne*

GC-MS (m/z) = 212 [M^+]. ^{1}H-NMR ($CDCl_3$, Fig. 2): δ 1.57 (2H, m, H^h); 1.72 (2H, m, H^g); 1.78 (4H, m, H^a); 1.93 (1H, t, $J_{li} = 2.5$, H^l); 2.20 (2H, dt, $J_{ih} = 7.5$, H^i); 2.55 (2H, t, $J_{fg} = 7.8$, H^f); 2.74 (4H, m, H^b); 6.87 (1H, s, H^c); 6.89 (1H, d, $J_{ed} = 7$, H^e), 6.96 (1H, d, H^d). Lit. [38].

References

[1] B. Bogdanovic, M. Kroner, G. Wilke, Annalen 669 (1966) 1.
[2] J. Chatt, L. Venanzi, Nature (London) 177 (1956) 852.
[3] P. Pertici, G. Vitulli, Comments Inorg. Chem. 11 (1991) 175.
[4] P. Pertici, C. Breschi, G. Uccello Barretta, F. Marchetti, G. Vitulli, J. Organomet. Chem. 502 (1995) 95.

[5] G. Vitulli, E. Pitzalis, R. Lazzaroni, P. Pertici, P. Salvadori, O. Salvetti, S. Coluccia, G. Martra, Mat. Sci. Forum 195 (1995) 93.
[6] P. Pino, F. Piacenti, M. Bianchi, in: I. Wender, P. Pino (Eds.), Organic Syntheses via Metal Carbonyls, vol. II, Wiley, New York, 1977, pp. 43–231.
[7] B. Cornils, in: J. Falbe (Ed.), New Syntheses with Carbon Monoxide, Springer-Verlag, Berlin, 1980, pp. 1–225.
[8] C. Botteghi, S. Gladiali, V. Bellagamba, R. Ercoli, A. Gamba, Chim. Ind. (Milan) 62 (1980) 604.
[9] C. Botteghi, S. Gladiali, V. Bellagamba, R. Ercoli, A. Gamba, Chim. Ind. (Milan) 62 (1980) 757.
[10] C. Botteghi, S. Gladiali, V. Bellagamba, R. Ercoli, A. Gamba, Chim. Ind. (Milan) 63 (1981) 29.
[11] I. Tkatchenko, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 8, Pergamon Press, Oxford, 1982, pp. 115–159.
[12] M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpaintner. J. Mol. Catal. 104 (1995) 17 and refs. therein.
[13] See as example, K.P.C. Vollhardt, Angew. Chem. Int. Ed. Engl. 23 (1984) 539.
[14] D.B. Grotjahn, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon Oxford, 1995, p. 741 and refs. therein.
[15] R. Lazzaroni, P. Pertici, S. Bertozzi, G. Fabrizi, J. Mol. Catal. 58 (1990) 75 and refs. therein.
[16] R. Lazzaroni, A. Raffaelli, R. Settambolo, S. Bertozzi, G. Vitulli, J. Mol. Catal. 50 (1989) 1 and refs. therein.
[17] B.L. Booth, R.N. Haszeldine, J. Chem. Soc. (C) (1966) 1447.
[18] J. Tsuji, Y. Mori, Bull. Chem. Soc. Jap. 42 (1969) 527.
[19] E. Cesarotti, A. Fusi, R. Ugo, G.M. Zanderighi, J. Mol. Catal. 4 (1978) 205.
[20] A. Fusi, E. Cesarotti, R. Ugo, J. Mol. Catal. 10 (1981) 231.
[21] B.-H. Chang, P.C. Coil, M.J. Brown, K.W. Barnett, J. Organomet. Chem. 270 (1984) C23.
[22] K.H. Whitmire, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 7, Pergamon, Oxford, 1995, pp. 85–87 and refs. therein.
[23] V. Bellagamba, R. Ercoli, A. Gamba, J. Organomet. Chem. 235 (1982) 201.
[24] A.J. Deeming, G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 4, Pergamon, Oxford, 1982, p. 463.
[25] J.E. Hill, G. Bolaich, P.E. Fanwick, I.A. Rothwell, Organometallics 12 (1993) 2911.
[26] W. Hubel, C. Hoogzand, Chem Ber. 93 (1960) 103.
[27] A. Carbonaro, A. Greco, G. Dall'Asta, J. Org. Chem. 33 (1968) 3948.
[28] S.R. Weber, H.H. Brintzinger, J. Organomet. Chem. 127 (1977) 45.
[29] L.H. Simons, J.J. Lagowski, J. Organomet. Chem. 249 (1983) 195.
[30] A. Funhoff, H. Schäufele, U. Zenneck, J. Organomet. Chem. 345 (1988) 331.
[31] F. Bernadou, D. Mesnard, L. Miginiac, J. Chem. Res. (S) (1978) 106; (M) (1978) 150.
[32] L. Lardicci, C. Botteghi, E. Benedetti, J. Org. Chem. 31 (1966) 1534.
[33] A.M. Caporusso, G. Giacomelli, L. Lardicci, J. Org. Chem. 42 (1977) 914.
[34] G. Giacomelli, A.M. Caporusso, L. Lardicci, J. Chem. Soc. Perkin I (1977) 1333.
[35] C.J. Pouchert, J. Behnke, The Aldrich Library of ^{13}C- and ^{1}H-FT-NMR Spectra, Ed. I, vol. 2, Aldrich, USA, 1993, p. 20/B.
[36] C.J. Pouchert, J. Behnke, The Aldrich Library of ^{13}C- and ^{1}H-FT-NMR Spectra, Ed. I, vol. 2, Aldrich, USA, 1993, p. 30/B.
[37] A.K. Jhingan, W.F. Maier, J. Org. Chem. 52 (1987) 1161.
[38] G. Vitulli, S. Bertozzi, R. Lazzaroni, P. Salvadori, J. Mol. Catal. 45 (1988) 155.