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Journal of Organometallic Chemistry 518 (1996) 213–219

Journal
of Organometallic
Chemistry

Cluster catalysis trends in the hydrogenation and isomerization behaviour of 1-hexene with trinuclear or tetranuclear diorganophosphido and hydrido bridged rhenium carbonyl clusters with respect to the change of the organyl substituent from phenyl to parafluorophenyl

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Received 21 December 1995

Abstract

Hydrogenolysis of $\text{Re}_2(\mu\text{-P}(p\text{-XC}_6\text{H}_4)_2)_2(\text{CO})_8$ ($X = \text{H}, \text{F}$) in xylene solution at 220°C yielded the following twofold unsaturated trinuclear and unifold unsaturated tetranuclear hydrido diorganophosphido bridged rhenium carbonyl clusters with delocalized π -bonds in each metal framework: $\text{Re}_3(\mu_3\text{-H})_2(\mu\text{-P}(p\text{-XC}_6\text{H}_4)_2)_3(\text{CO})_6$ ($X = \text{H}, \text{I}; X = \text{F}, \text{II}$), $\text{Re}_4(\mu\text{-H})_2(\mu\text{-P}(p\text{-XC}_6\text{H}_4)_2)_4(\mu_4\text{-P}(p\text{-XC}_6\text{H}_4))(\text{CO})_8$ ($X = \text{H}, \text{III}; X = \text{F}, \text{IV}$) as well as $\text{Re}_4(\mu\text{-H})(\mu\text{-P}(p\text{-XC}_6\text{H}_4)_2)_3(\mu_4\text{-P}(p\text{-XC}_6\text{H}_4))_2(\text{CO})_8$ ($X = \text{H}, \text{V}; X = \text{F}, \text{VI}$). The cluster complexes were characterized and identified by the following analytical methods: elementary analysis, ^1H , ^{31}P NMR, $\nu(\text{CO})$ FTIR data and X-ray structure analysis. The molecular structure of compound **II** is described. To determine catalytic properties of the cluster complexes, they were dissolved in dioxan and the substrate 1-hexene ($c = 2 \text{ mol l}^{-1}$). The homogeneous catalysts **I–V** hydrogenate and isomerize 1-hexene without any cluster fragmentation. Their maximum activity is obtained at a temperature of 170–180°C in the presence of a hydrogen pressure of 30 bar (room temperature). From a series of investigations under these reaction conditions, the following results were obtained: **II** and **IV** containing *p*-fluorophenyl substituents ($-I$ effect) prefer substrate hydrogenation, all other cluster complexes prefer substrate isomerization. Other factors such as the different cluster type and the unsaturation of the metal framework with their influence on the catalytic product formation are discussed. **V** shows the highest total activity (turnover number = 1328 h^{-1}) with respect to both hydrogenation and isomerization.

Keywords: Rhenium carbonyl cluster derivatives; Catalysts; Hydrogenation; Isomerization; Catalysis

1. Introduction

Polynuclear transition metal complexes containing framework shaping metal–metal bonds of at least trinuclear linkage, the so-called metal clusters, have been of great interest as potential homogeneous catalysts for more than 20 years [1]. Their catalytic efficiency requires an unsaturated organic substrate to pass a sequence of organometallic intermediates during the catalytic cycle without decomposition of the metal framework. According to Laine [2] this criterion is fulfilled if the turnover number (ton) of a catalytic cycle is independent of the catalyst concentration or if the determined rate law of the reaction process contains the term

$(c_{\text{cat}})^1$. Examples of cluster catalysis confirmed by such criteria are very rare [1b,3,4]. Recently, it was shown that the cluster complex $\text{Pt}_3\text{Ru}_6(\mu_3\text{-H})(\mu\text{-H})(\mu_3\text{-PhC}_2\text{Ph})(\text{CO})_{20}$ hydrogenates diphenylacetylene into *Z*-stilbene (ton = 31 h^{-1}) with a selectivity of 100% [5]. Surprisingly, this happens without decomposition in spite of a natural tendency to segregate spontaneously. The contrary was observed using the electron-precise and homonuclear cluster $\text{Rh}_4(\text{CO})_{12}$ as a catalyst for the hydroformylation of cyclohexene into cyclohexanecarboxaldehyde ($\text{C}_6\text{H}_{11}\text{CHO}$). For the catalytic cycle of this oxoprocess an absence of the metal framework fragmentation in $\text{Rh}_4(\text{CO})_{12}$ was suggested by kinetic measurements at 398 K [6], whereas the in situ IR spectroscopic measurements, conducted later, show the fragmentation during which the formation of the inter-

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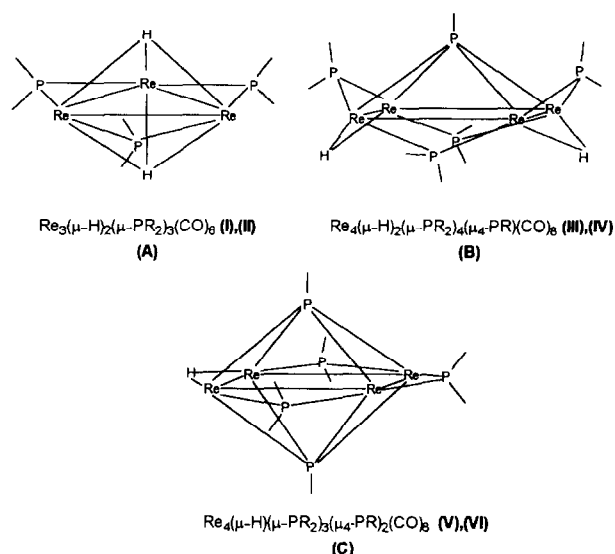
mediate $C_6H_{11}CORh(CO)_4$ occurs [7]. Analogous metal cluster fragmentations occurred with other substrates such as cyclohexene, 3,3-dimethylbut-1-ene, ethene, 1-hexene, 1-octene, cyclopentene and cyclooctene [8–10].

Until now, only a limited number of unsaturated cluster complexes have been used for hydrogenation studies with the substrates 1-hexene and cyclohexene. Worth mentioning are $Os_3(\mu-H)_2(CO)_{10}$ with 46 valence electrons (ve) and $Re_3(\mu_3-H)_2(\mu-PPh_2)_3(CO)_6$ with 44 instead of 48 ve which are present in an unsaturated three-membered transition metal ring [1b,4,11,12]. Examples of homogeneous catalysts containing rhenium are rare, most of them are mononuclear complexes [13]. The investigations of the hydrogenation process with the twofold unsaturated compound **I** were now continued with the substrate 1-hexene. For this purpose the derivative $Re_3(\mu_3-H)_2(\mu-P(p-XC_6H_4)_2)_3(CO)_6$ ($X = F$, **II**) has been synthesized as well as the tetranuclear compounds $Re_4(\mu-H)_2(\mu-P(p-XC_6H_4)_2)_4(\mu_4-P(p-XC_6H_4))_2(CO)_8$ ($X = H$, **III**; $X = F$, **IV**) and $Re_4(\mu-H)(\mu-P(p-XC_6H_4)_2)_3(\mu_4-P(p-XC_6H_4))_2(CO)_8$ ($X = H$, **V**; $X = F$, **VI**) which are unfold unsaturated and contain 62 instead of 64 ve after the EAN rule formalism. All electron deficient cluster complexes **I–V** always contain a metal framework with a delocalized π bond and possess, therefore, other necessary free coordination sites for the uptake of substrates. Furthermore, they were found to fulfil the requirements mentioned above, namely the cluster complex stability, in spite of the fact that they need severe reaction conditions during the hydrogenation process to become activated. In this report, the extent of isomerization and hydrogenation of 1-hexene is analysed in ton values for the named cluster complexes, with the exception of **VI** which is not obtained in the required quantity.

2. Results and discussion

2.1. Preparation

In xylene solution $Re_2(\mu-P(p-XC_6H_4)_2)_2(CO)_8$ ($X = H, F$) [13,14] reacts in a steel autoclave with hydrogen ($p_{H_2} = 3$ bar) at 220°C within 2 days to form the coloured cluster complexes: **I** (yellow), **III** (violet), **V** (brown) ($X = H$) and **II** (orange), **IV** (violet), **VI** (brown) ($X = F$) respectively. The total yield of the products which were separated in previously given order using the PLC procedure was 50% ($X = H$) and 24% ($X = F$) with respect to the starting material. In each case the trinuclear cluster complex represents the major product (25% **I**, 12% **II**). Such hydrogenolysis give the individual compounds **I–VI** only in moderate yields, although the reaction conditions were optimized [14,15]. From the elementary analysis of each compound, correct values of the C, H and P content were

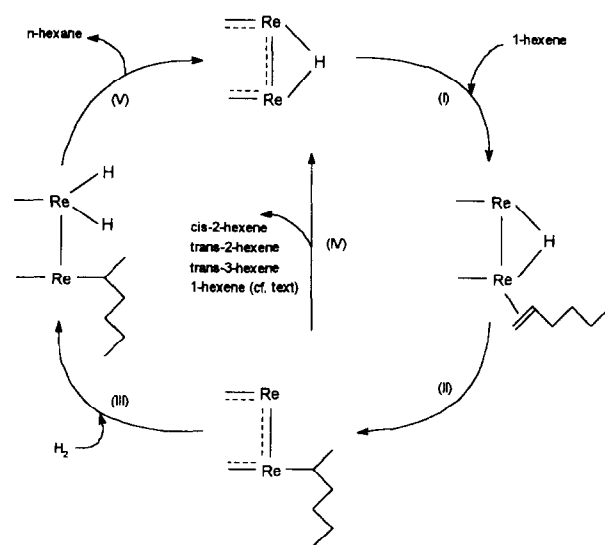


Scheme 1. Structure types of cluster complexes **I–VI**.

obtained. The identification of **I–VI** was ascertained by 1H , ^{31}P NMR and $\nu(CO)$ FTIR data as well as single crystal X-ray structure analysis (**I** [16a]; **III** [16b]; **V** [16c]) (see Experimental details). In Scheme 1 the common structure type of the trinuclear cluster complexes **I–II** is illustrated as **A**, whereas the tetranuclear ones **III–IV** are assigned to **B** and **V–VI** to **C** referring to the different ways in which the phosphorus bridges the metal framework.

2.2. Crystal structure

Compound **II** crystallizes with one molecule of toluene solvent in the asymmetric unit. Its molecular structure (Fig. 1) shows a triangular ring of rhenium



Scheme 2. Principal catalytic cycle of catalytic hydrogenation with catalyst **III**.

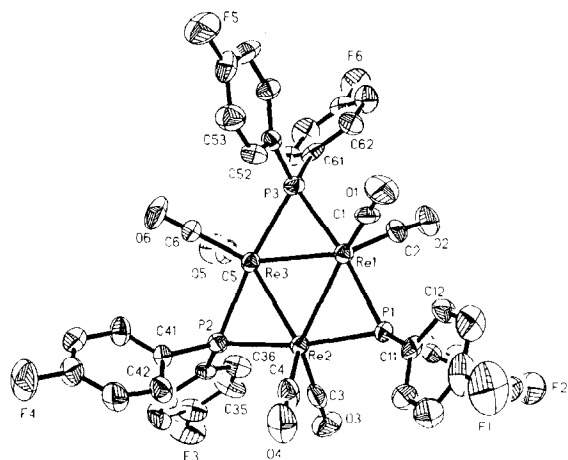


Fig. 1. The molecular structure of complex **II**. H atoms and toluene molecule omitted for clarity. Displacement ellipsoids are plotted at the 50% probability level.

atoms which is edge-bridged by three *p*-fluorophenylphosphido groups and capped by two μ_3 -H ligands. The geometry is principally the same as was found earlier for the unsubstituted phenyl compound **I** [16] or the corresponding cyclohexyl compound [17]. The Re_3P_3 core of the molecule is almost planar, with the largest deviation for an atom from the best plane being 0.05 Å. The three Re–Re bonds differ slightly in length by a maximum of 0.016 Å, but their mean value of 2.733(1) Å is the same as for **I** (2.730(1) Å), indicating the expected largely delocalized multiple-bond character for this 44 ve compound **II**. The Re–P and P–C bond distances and the Re–P–Re bond angles are equal within their standard deviations, and their average values (Re–P 2.385(3), P–C 1.836(12) Å, Re–P–Re 69.9(1)°) do not differ from those of compound **I** (2.369(6), 1.836(14) Å, 70.3(1)°) or from the cyclohexyl compound (2.385(7), 1.875(27) Å, 70.5(2)°). The positions of the bridging hydrogen atoms could not be determined by means of X-ray analysis but were ascertained by the ^1H NMR data. From the X-ray data of **I–III** it can be concluded that the structural parameters discussed are not dependent on the different electronic properties of the diorgano group attached to the phosphorus bridging atoms. This ligand change applies to the redox properties of **I** and **II**.

2.3. Properties

The cluster complexes **I–V** (resistant to air and higher temperatures) used as catalysts, as well as the cluster complex **VI**, were carefully examined using cyclic voltammetric measurements to characterize the change from the phenyl to the *p*-fluorophenyl groups in the diorganophosphido bridges (–I effect) and its effect on the electrochemical properties. According to the MO theory, the frontier orbitals, for example the centred and

edge-bridged ones, in triangular cluster complexes such as $\text{Co}_3(\mu\text{-PH}_2)_3(\text{CO})_6$ (related to **I–II**), are mainly metal orbitals modified by symmetry-adapted orbitals of the phosphorus bridging group [18]. Hence, **I–VI** might be sensitive to an oxidation process, changing the substituent from $\text{X} = \text{H}$ to $\text{X} = \text{F}$ in all three mentioned cluster types. This exchange is expected to hinder the oxidation owing to an increase in the electron withdrawing effect in *p*- XC_6H_4 . According to this notion, there is either an increase in the value of the first reversible one electron transfer E^f (mV) or in that of the first irreversible oxidation step $E_{\text{p,a}}^f$ (mV): $E^f = 1031$ in $\text{Re}_3(\mu_3\text{-H})_2(\mu\text{-PR}_2)_3(\text{CO})_6$ (R = cyclohexyl), 1199 (R = Ph, **I**) and 1576 (R = *p*- FC_6H_4 , **II**) and (in tetranuclear metal cluster complexes) $E_{\text{p,a}}^f = 716$ (R = Ph, **III**), 929 (R = *p*- FC_6H_4 , **IV**) and 1120 (R = Ph, **V**) as well as 1149 (R = *p*- FC_6H_4 , **VI**) [15]. This observed tendency runs parallel to a decrease in λ_{max} (nm) if the MLCT charge transfer band at the long wavelength edge of the uv–vis spectra is considered: 348 (R = cyclohexyl), 343 (R = Ph, **I**) [15], 332 (R = *p*- FC_6H_4 , **II**) in the trinuclear cluster complexes on the one hand, and in the tetranuclear complexes 557 (R = Ph, **III**) and 553 (R = *p*- FC_6H_4 , **IV**) on the other hand [15].

For the subsequently examined catalytic hydrogenation of 1-hexene to *n*-hexane, which in general can be dominated either by the so-called hydride route with an oxidative addition reaction of hydrogen, or by the competitive olefin route with the π complex formation as the most time-consuming partial reaction [19], referring to the redox behaviour of the catalysts **I–V** the following can be expected with respect to the change of ton values. Going from **II** to **I** and **IV** to **III** an improved electron donor capability is involved and the oxidative addition reaction of hydrogen is facilitated in the same direction. This order becomes reversed if the π complex formation between the catalysts and the substrate 1-hexene is decisive because **II** and **IV** ($\text{X} = \text{F}$) are stronger Lewis acids than **I** and **III**. Consequently, the ton values are expected to increase from **I** to **II** and **III** to **IV**. This will be shown later (see Section 2.4).

2.4. Catalysis

Cluster complexes **I–V**, available from hydrogenolysis at 220°C, were dissolved in 2 M solutions of 1-hexene in dioxan (with the catalyst/substrate ratio ranging from 1:6000 (**I**) to 1:12000 (**V**)). All solutions, prepared in a Duran glass tube, were transferred into an autoclave and heated under a hydrogen pressure of 10 bar (adjusted at room temperature) in steps of 10°C starting from 120°C and reaching a maximum temperature of 200°C. The samples were collected at regular time intervals and subjected to GC analysis (*n*-hexane, *trans*-2-hexene, *cis*-2-hexene and *trans*-3-hexene), FTIR

and ^{31}P NMR. The results of these investigations suggested that the catalysts become active at 140°C and reach a maximum activity at 170°C (**I**, **II**; type **A**) or 180°C (**III**, **IV**, **V**; types **B**, **C**). In the course of the catalytic process the cluster complexes did not decompose. This was ascertained by accompanied FTIR measurements and through their complete recovery from the reaction solution. To find optimum reaction conditions, the dependence between the catalytic activity of the clusters and hydrogen pressure was determined by adjusting the pressure to 5, 10, 20, 30 and 40 bar at room temperature. The associated reaction temperature was either 170°C or 180°C. From the five catalysts examined, all have shown a maximum activity at 30 bar with the exception of **III**, which reaches maximum reactivity above 40 bar.

Based on these preliminary tests, the hydrogenation of 1-hexene in a 2 M dioxan solution was carried out with the catalysts **I–V** at a hydrogen pressure of 30 bar and the above-mentioned temperatures. The ton values obtained are listed in Table 1. The catalysts were recovered and Laine's criterion [2] was fulfilled in all cases. By a threefold use of the catalytic mixture of no loss of catalytic activity was observed. In separate experiments with catalyst **I**, the substrate isomerization was at first determined under 30 bar argon instead of hydrogen without changing the other reaction parameters. As opposed to the reference experiment under hydrogen pressure, the substrate isomerization decreased to about one-third. Furthermore, no formation of *n*-hexane was detected. Another aim was to recognize an intermediate of the substrate coordination by heating under reflux **III** and **IV** in 1-hexene. Accompanying FTIR spectra showed a small shift of 2–3 cm^{-1} of the $\nu(\text{CO})$ absorption bands but no change in their number, shape or intensity. Although this seems to be a hint for the formation of a hexyl group by insertion of the substrate 1-hexene into a $\mu\text{-H}$ bond, the postulated intermediate (see Scheme 1,(ii)) could not be isolated using PLC separation procedures. Only the starting material was recovered. Finally, some attempts to prove the existence of this species in solution by ^{31}P NMR measurements remained unsuccessful.

From all results obtained, the following conclusions can be drawn: (1) the total reactivity (as a sum of ton values of the substrate hydrogenation and isomerization) increases in the case of the trinuclear as well as the tetranuclear catalysts, provided the substituent at the phosphorus bridge is changed from phenyl to *p*-fluorophenyl. The highest total reactivity for $\text{ton} = 1328 \text{ h}^{-1}$ is obtained by using **V** as catalyst. The change of the substituent increases the number of hydrogenation cycles, but is accompanied by a decrease in the number of isomerization cycles; (2) all values of the $\text{ton}_{\text{hydr.}}/\text{ton}_{\text{isom.}}$ ratio are equal in the series of the phosphorus-bridged catalysts **I**, **II**, **V**. The extent of isomerization is smaller in the absence of hydrogen.

The findings were interpreted by considering the main reaction steps of an hydrogenation process of the unfold unsaturated catalyst $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ [3,11]. On this basis, a catalytic cycle (see Scheme 1) contains five individual steps: (i) coordination of 1-hexene by an equilibrium reaction forming a π complex followed by (ii) irreversible insertion of the olefin into the transition metal $\mu\text{-H}$ bond, (iii) oxidative addition of hydrogen or (iv) competitive isomerization by β -hydride elimination (major product *trans*-2-hexene) and finally (v) reductive elimination of *n*-hexane by simultaneous regeneration of the key-species. From the observed ton values follows that the change of a substituent at the phosphorus bridge from **I** to **II** and **III** to **IV** is combined with an increasing hydrogenation activity and a simultaneous decrease in the isomerization activity in each pair. The larger amount of hexane results in favour of the olefin route in the hydrogenation process as follows. The catalysts **II** and **IV**, as opposed to those of **I** and **III**, are clearly stronger Lewis acids (see Section 2.3). Consequently, **II** and **IV** are enabled to promote the π complex formation with the substrate 1-hexene in the equilibrium reaction (i), this subsequent addition complex reacts to form an intermediate with a more stable σ -bonded hexyl group (ii) which demands a more hindered β -elimination for thermodynamic reasons (iv). All these reaction steps are relatively more time-consuming than an oxidative addition of hydrogen (iii) contributing to the increase of the *n*-hexane formation

Table 1
Catalytic activity of cluster complexes **I–V**

		I	II	III	IV	V
<i>n</i> -Hexane	turnover (%)	28.6	56.4	23.8	63.5	21.6
	ton (h^{-1})	184	630	288	750	377
<i>cis</i> -2-Hexene	turnover (%)	17.9	4.5	18.8	7.7	16.8
	ton (h^{-1})	115	51	228	91	292
<i>trans</i> -2-Hexene	turnover (%)	40.4	8.3	39.6	21.1	35.1
	ton (h^{-1})	260	92	480	250	612
<i>trans</i> -3-Hexene	turnover (%)	9.2	—	6.0	5.1	2.7
	ton (h^{-1})	60	—	73	60	47
$\text{ton}_{\text{total}}$ (h^{-1})		619	773	1069	1151	1328
$\text{ton}_{\text{hydr.}}/\text{ton}_{\text{isom.}}$		0.4	4.4	0.4	1.9	0.4

obtained. If this assumption were wrong, the hydride route with the oxidative addition of hydrogen would be decisive for the product formation and thus would lead to the reciprocal dependence of the ton values, namely $\text{I} > \text{II}$ and $\text{III} > \text{IV}$, for the formation of *n*-hexane owing to a better availability of σ -electron density in each series of catalysts. Indeed, for the catalyst $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$, partial step (iii) is the most time-consuming step in the hydrogenation process of 1-hexene, but the hydrogenation conditions to obtain *n*-hexane ($p_{\text{H}_2} = 1$ bar, $T = 50^\circ\text{C}$, $\text{ton} < 5 \text{ h}^{-1}$) cannot be compared [11].

Under the severe reaction conditions required, the thermodynamically favoured isomere *trans*-2-hexene is obtained as the major isomerization product. In this context it is assumed that according to the current investigations of β -elimination of a coordinated hexyl-moiety in deuteration experiments, only small amounts of 1-hexene are recovered by pathway (iv) [20]. The severe reaction conditions might also be responsible for the identical $\text{ton}_{\text{hydr.}}/\text{ton}_{\text{isom.}}$ ratio for the catalysts **I**, **III** and **V** which shows that kinetically controlled selectivity is absent. In spite of this, selectivity cannot be totally excluded owing to the different values of 4, 4 and 1, 9 going from **II** (type **A**) to **IV** (type **B**), both being more active in hydrogenation. The observed reactivity changes are not only a function of a substituent exchange from $\text{X} = \text{H}$ against F but, in addition, also a function of the increasing number of rhenium nuclei from 3 to 4, which is accompanied by a simultaneous reduction of the electronically unsaturated state of the metal framework. Furthermore, this correlates with the change from $\mu_3\text{-H}$ to $\mu\text{-H}$ by converting structure type **A** to type **B** and finally with the number of $\mu\text{-H}$, $\mu\text{-PPh}_2$ and $\mu_4\text{-PPh}$ by converting type **B** to type **C**. In the last case, i.e. the transition from **III** to **V**, a sterically less hindered hydrido bridge is present. In this series of catalysts, the electrochemical data would be expected to show the enhanced reactivity which may be accompanied by an additional opening of an Re–Re bond during the hydrogenation cycle in **V**, in addition to the stereochemical advantage mentioned. According to our present knowledge, the following factors show an important influence on the catalytic activity. First the type of hydrido bridge, second the easily accessible free coordination sites (especially at the catalytical active metal–metal-edge in combination with a moderate electronically unsaturated state) and third the type of phosphorus bridge (with electronically modified substituents) as coligands.

3. Experimental details

All reactions were carried out in solvents free of oxygen which were dried according to literature methods, distilled and stored under argon atmosphere. 1-hexene was distilled and stored under argon atmosphere

before its use as hydrogenation substrate. It contained 2% of *n*-hexane, which had to be taken into consideration when compiling the hydrogenation results. The reaction products were characterized by $\nu(\text{CO})$ FTIR spectroscopy (Nicolet P510), ^1H and ^{31}P NMR spectroscopy (Bruker WR 300).

Hydrogenolysis and catalytic hydrogenation were carried out in a 200 ml steel autoclave (DIN 1.4980) equipped with a manometer and a heating jacket with a PT-100 thermometer. The reaction mixture was transferred into a Duran glass tube which was then placed into the autoclave. The autoclave was closed, flushed with hydrogen three times and the desired hydrogen pressure was then adjusted at room temperature.

Hydrogenation products were identified by gas chromatography using the retention times and calibration standards. The yield was calculated from the chromatogram by use of the 100% method. Analysis parameters: gas chromatograph: Perkin–Elmer (model 8420); integrator: Hitachi (model D 2000); column: Chrompack Al_2O_3 capillary column (plot/fused silica), length 50 m, diameter 0.32 mm; components of the reaction mixture: 1-hexene, *cis/trans*-2-hexene, *trans*-3 hexene, *n*-hexane, dioxan (solvent); injection volume: 0.2 gml⁻¹; GC parameters: 150 kPa N_2 pressure; 60 kPa H_2 pressure; 110 kPa synthetic air; injector temperature 220°C; furnace temperature 160°C; detector temperature 210°C; integration interval 10 min after each injection².

Chemicals: HPPPh_2 was purchased from Strem, $\text{Re}_2(\text{CO})_{10}$ and 1-hexene were purchased from Janssen. $\text{HP}(p\text{-FC}_6\text{H}_4)_2$ and $\text{Re}_2(\mu\text{-PR}_2)_2(\text{CO})_8$ ($\text{R} = \text{Phenyl}$, $p\text{-FC}_6\text{H}_4$) were prepared according to literature methods [14,15]. PLC plates (silica gel 60 F_{254} , 20 cm \times 20 cm, thickness 1 mm) were purchased from Merck.

3.1. Preparation of the compounds $\text{Re}_3(\mu_3\text{-H})_2(\mu\text{-PR}_2)_3(\text{CO})_6$ ($\text{R} = \text{Phenyl}$ **I, $p\text{-FC}_6\text{H}_4$ **II**), $\text{Re}_4(\mu\text{-H})_2(\mu\text{-PR}_2)_4(\mu_4\text{-PR})(\text{CO})_8$ ($\text{R} = \text{Phenyl}$ **III**, $p\text{-FC}_6\text{H}_4$ **IV**) and $\text{Re}_4(\mu\text{-H})(\mu\text{-PR}_2)_3(\mu_4\text{-PR})_2(\text{CO})_8$ ($\text{R} = \text{Phenyl}$ **V**, $p\text{-FC}_6\text{H}_4$ **VI**)**

3.1.1. $\text{R} = \text{Phenyl}$

250 mg $\text{Re}_2(\mu\text{-PR}_2)_2(\text{CO})_8$ (0.26 mmol) were stirred in 10 ml of xylene under a hydrogen pressure of 3 bar in an autoclave at 220°C for 50 h. In order to isolate the products, the solvent was removed in vacuo. The residue was dissolved in dichloromethane and filtered over silica gel to separate the polar decomposition products. The filtrate was evaporated to dryness, dissolved in a small

¹ 50 μl of the hydrogenation mixture was added to 1000 μl of dioxan and analysed.

² An interruption of 30 min between two analyses was required to ensure a complete elution of solvent.

amount of dichloromethane and separated by PLC (solvent: dichloromethane–*n*-hexane = 1 : 3). When the solvent had reached the upper edge of the PLC plate the lid of the chromatography tank was lifted a few millimetres. Continuous evaporation of the solvent created an increase in the separation efficiency so that complete separation of compounds was possible. The compounds obtained are listed in the order of their decreasing retention factor R_f : **I** 55.0 mg (24.7%); **III** 13.2 mg (5.6%); **V** 13.5 mg (6.0%).

3.1.2. $R = p\text{-FC}_6\text{H}_4$

250 mg $\text{Re}_2(\mu\text{-PR}_2)_2(\text{CO})_8$ (0.26 mmol) were stirred in 10 ml of xylene under a hydrogen pressure of 3 bar in an autoclave at 210°C for 50 h. The separation procedure was undertaken as described above, but during the PLC treatment the solvent mixture dichloromethane–*n*-hexane = 1 : 5 was used. The compounds obtained are listed in order of their decreasing retention factor R_f : **II** 25.2 mg (12.3%); **IV** 10.6 mg (4.5%); **VI** 1.7 mg (0.7%).

3.2. Spectroscopic data

Elementary analysis: **I** ($\text{C}_{42}\text{H}_{32}\text{P}_3\text{Re}_3$, $M_r = 1284.25$), C, 39.20% (calc. 39.28); H, 2.64 (2.51); **II** ($\text{C}_{42}\text{H}_{26}\text{F}_6\text{P}_3\text{Re}_3$, 1298.11); C, 33.25 (33.31); H, 1.91 (1.79); **III** ($\text{C}_{62}\text{H}_{47}\text{O}_8\text{P}_5\text{Re}_4$, 1819.75); C, 40.84 (40.92); H, 2.75 (2.60); **IV** ($\text{C}_{62}\text{H}_{38}\text{F}_9\text{O}_8\text{P}_5\text{Re}_4$, 1981.66), C, 37.72 (37.58); H, 2.05 (1.93); **V** ($\text{C}_{56}\text{H}_{41}\text{O}_8\text{P}_5\text{Re}_4$, 1741.63); C, 38.52 (38.62); H, 2.51 (2.37); **VI** ($\text{C}_{56}\text{H}_{33}\text{F}_8\text{O}_8\text{P}_5\text{Re}_4$, 1885.55); C, 35.74 (5.67); H, 1.89 (1.76).

δ values ^1H NMR-spectra (CDCl_3 , standard TMS): **I** 7.6–7.2 (m, 30 H, Ph), –18.2 (q, 2H, $\mu_3\text{-H}$, $^2J_{\text{PH}} = 7.3$

Table 2
Crystal data and refinement details for **II**

Formula	$\text{C}_{42}\text{H}_{26}\text{F}_6\text{O}_6\text{P}_3\text{Re}_3 \cdot \text{toluene}$
M_w	1484.3
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	11.825(3)
b (Å)	12.311(3)
c (Å)	18.260(4)
α (deg)	103.02(2)
β (deg)	100.44(2)
γ (deg)	104.91(2)
V (Å ³)	2420.6(10)
Z	2
D_c (g cm ⁻³)	2.036
μ (mm ⁻¹)	7.65
$F(000)$	1400
Diffractometer	Siemens R3m
Radiation	Mo K α
Scan type	ω -2 θ , $3 < 2\theta < 55^\circ$
$R1, wR2$	0.057, 0.116
min/max ΔF	–1.13/1.16 e Å ⁻³ near atom position

Table 3
Selected bond lengths (Å) and angles (deg) for **II**

Re(1)–P(1)	2.382(3)
Re(1)–P(3)	2.385(3)
Re(1)–Re(2)	2.7261(11)
Re(1)–Re(3)	2.7324(9)
Re(2)–P(2)	2.382(3)
Re(2)–P(1)	2.386(3)
Re(2)–Re(3)	2.7424(9)
Re(3)–P(2)	2.387(3)
Re(3)–P(3)	2.388(3)
P(1)–Re(1)–P(3)	170.53(10)
P(1)–Re(1)–Re(2)	55.18(7)
P(3)–Re(1)–Re(2)	115.44(8)
Re(2)–Re(1)–Re(3)	60.32(2)
P(2)–Re(2)–P(1)	169.92(10)
Re(1)–Re(2)–Re(3)	59.95(3)
P(2)–Re(3)–P(3)	169.03(10)
Re(1)–Re(3)–Re(2)	59.73(3)
Re(1)–P(1)–Re(2)	69.74(8)
Re(2)–P(2)–Re(3)	70.21(8)
Re(1)–P(3)–Re(3)	69.84(8)

Hz); **II** 7.5 (s, 12 H, PhF), 7.1 (t, 12 H, PhF, $^3J_{\text{FH}} = 8$ Hz), –18.3 (q, 2 H, $\mu_3\text{-H}$, $^2J_{\text{PH}} = 7$ Hz); **III** 7.6–6.6 (m, 45H, Ph), –10.8 (s, 2 H, $\mu\text{-H}$); **IV** 7.3–6.9 (m, 36 H, PhF), –10.9 (s, 2H, $\mu\text{-H}$); **V** 7.5–6.8 (m, 40 H, Ph), –4.4 (t, 1 H, $\mu\text{-H}$, $^2J_{\text{PH}} = 7$ Hz); **VI** 7.5–6.9 (m, 32 H, PhF), –4.5 (t, 1 H, $\mu\text{-H}$, $^2J_{\text{PH}} = 7$ Hz).

δ values ^{31}P NMR-spectra (CDCl_3 , standard 85% H_3PO_4): **I** 198.2 (s, 3 P, $\mu\text{-P}$); **II** 195.3 (s, 3 P, $\mu\text{-P}$); **III** 207.3 (t, 2 P, $\mu\text{-P}$, $^2J_{\text{PP}} = 60$ Hz), 59.4 (t, 2 P, $\mu\text{-P}$, $^2J_{\text{PP}} = 31$ Hz), –52.2 (dt, 1 P, $\mu_4\text{-P}$, $^2J_{\text{PP}} = 60$ Hz, 31 Hz); **IV** 203.8 (t, 2 P, $\mu\text{-P}$, $^2J_{\text{PP}} = 60$ Hz), 57.7 (t, 2 P, $\mu\text{-P}$, $^2J_{\text{PP}} = 31$ Hz), –53.8 (dt, 1 P, $\mu_4\text{-P}$, $^2J_{\text{PP}} = 60$ Hz, 31 Hz); **V** 176.7 (d, 2 P, $\mu\text{-P}$, $^2J_{\text{PP}} = 50$ Hz), 170.2 (t, 1 P, $\mu\text{-P}$, $^2J_{\text{PP}} = 50$ Hz), 24.7 (s, 2 P, $\mu_4\text{-P}$); **VI** 169.5 (d, 2 P, $\mu\text{-P}$, $^2J_{\text{PP}} = 51$ Hz), 165.6 (t, 1 P, $\mu\text{-P}$, $^2J_{\text{PP}} = 51$ Hz), 18.5 (s, 2 P, $\mu\text{-P}$).

IR data for $\nu(\text{CO})$ absorption bands (cm^{-1}) in CH_2Cl_2 : **I** 1981 vs, 1933 s; **II** 1983 vs, 1937 s; **III** 1983 vs, 1929 s; **IV** 1987 vs, 1933 s; **V** 1975 vs, 1937 s, 1908 m; **VI** 1981 vs, 1938 s, 1914 m.

3.3. Catalytic hydrogenation of 1-hexene

20 ml of a 2 M solution of 1-hexene in dioxane were added with the catalyst and stirred at 180°C (**III**, **IV**, **V**) or 170°C (**I**, **II**) under a hydrogen pressure of 30 bar in an autoclave for 10 h. The catalyst **V** needed only 7 h of hydrogenation time to avoid total conversion of the substrate. The following amounts of catalysts were used: **I** 8.0 mg (6.23×10^{-6} mol); **II** 5.0 mg (3.59×10^{-6} mol); **III** 6.0 mg (3.3×10^{-6} mol); **IV** 6.7 mg (3.38×10^{-6} mol); **V** 5.7 mg (3.28×10^{-6} mol). Catalyst **VI** could not be obtained in the required quantity so that no catalytic data are available.

The ton values were calculated by the following equation:

$$\text{ton} = \frac{\text{turnover} \times \text{amount of 1-hexene (mol)}}{\text{amount of catalyst (mol)} \times \text{hydrogenation time (h)}}$$

3.4. X-ray data collection, structure solution and refinement

An orange crystal, size $0.10 \times 0.21 \times 0.48 \text{ mm}^3$, was used for data collection at $T = 296 \text{ K}$. Lattice parameters were refined from 30 reflections $15 < 2\theta < 34^\circ$. 11521 intensities were collected $3 < 2\theta < 55^\circ$, $-15 < h < 15$, $-16 < k < 15$, $0 < l < 23$; three standard reflections were recorded every 400 and showed only random deviations. Lp correction, empirical absorption correction via psi-scans, min/max transmission 0.580/0.990, after merging ($R_{\text{int}} = 0.044$) 11170 unique intensities. The structure was solved by direct and conventional Fourier methods, full-matrix least squares refinement based on F^2 and 571 parameters; all but H-atoms and toluene carbons refined anisotropically; hydrogen atoms were refined at idealized positions with riding model, and the positions of the two $\mu\text{-H}$ atoms were not determined. The programs used for structure solution and refinement were SHELXTL-PLUS [21] SHELXL-93 [22] respectively. Lists of atomic coordinates, anisotropic displacement parameters, hydrogen atom coordinates and complete bond lengths and angles are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 404280.

References

- [1] (a) F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 5th ed., 1988. (b) D.F. Shriver, H.D. Kaesz and R.D. Adams, *The Chemistry of Metal Cluster Complexes*, VCH, New York, 1990. (c) D.M.P. Mingos and J.D. Wales, *Introduction to Cluster Chemistry*, Prentice Hall, Englewood Cliffs, NY, 1990. (d) B.C. Yates, *Catalytic Chemistry*, Wiley, New York, 1992. (e) G. Schmid, *Cluster and Colloids*, VCH, New York, 1994. (f) G. Süss-Fink, *Angew. Chem.*, 106 (1994) 71.
- [2] R.M. Laine, *J. Mol. Catal.*, 14 (1982) 137.
- [3] B. Walther, *Z. Chem.*, 29 (1989) 117.
- [4] E.L. Muetterties and M.J. Krause, *Angew. Chem.*, 95 (1983) 135.
- [5] R.D. Adams, Z. Li, P. Swepston, W. Wu and J. Yamamoto, *J. Am. Chem. Soc.*, 114 (1992) 10657.
- [6] N. Rosas, C. Marquez, H. Hernandez and R. Gomez, *J. Mol. Catal.*, 48 (1988) 59.
- [7] C. Fyhr and M. Garland, *Organometallics*, 12 (1993) 1753.
- [8] (a) M. Garland, *Dissertation*, No. 8585, ETH-Zürich 1988. (b) M. Garland, I.T. Horváth, G. Bor and P. Pino, *Proc. Herbstversammlung Schweiz. Chem. Ges.*, (1987) 108.
- [9] M. Garland and G. Bor, *Inorg. Chem.*, 28 (1989) 410.
- [10] M. Garland, *Organometallics*, 12 (1993) 535.
- [11] (a) J.B. Keister and J.R. Shapley, *J. Am. Chem. Soc.*, 98 (1976) 1065. (b) J.B. Keister and J.R. Shapley, *J. Organomet. Chem.*, 85 (1975) C29.
- [12] H.-J. Haupt, P. Balsaa and U. Flörke, *Angew. Chem.*, 100 (1988) 280.
- [13] (a) W.A. Herrmann, *J. Organomet. Chem.*, 382 (1990) 1. (b) T.J. Henly, *Coord. Chem. Rev.*, 93 (1989) 269.
- [14] H. Schnieder, *Dissertation*, Paderborn, 1990.
- [15] U. Jüptner, *Dissertation*, Paderborn, 1993.
- [16] (a) H.-J. Haupt, U. Flörke and P. Balsaa, *Acta Crystallogr. Sect. C.*, 44 (1988) 61. (b) H.-J. Haupt, U. Flörke, N. Klouras and M. Woiciechowski, *Acta Crystallogr. Sect. C.*, 46 (1990) 2096. (c) H.-J. Haupt and U. Flörke, *Z. Kristallogr.*, 192 (1990) 278.
- [17] H.-J. Haupt, U. Flörke and H. Schnieder, *Acta Crystallogr. Sect. C.*, 47 (1991) 2531.
- [18] T.A. Albright, S.-K. Kang, A.M. Arif, A.J. Bard, R.A. Jones, J.K. Leland and S.T. Schwab, *Inorg. Chem.*, 27 (1988) 1246.
- [19] H. Brunner, *Chem. Z.*, 14 (1980) 177.
- [20] C.P. Casey and L.M. Petrovich, *J. Am. Chem. Soc.*, 117 (1995) 6007.
- [21] G.M. Sheldrick, *SHELXTL-PLUS Structure determination software programs*, 1990 (Siemens Analytical X-ray Instr. Inc., Madison, WI, USA).
- [22] G.M. Sheldrick, *SHELXL-93 Program for crystal structure refinement*, 1993 (University of Göttingen, Germany).