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IV*. THE REACTIONS OF $M(CO)_2(PPh_3)_3$ COMPLEXES (M = Fe, Ru) AND THE HYDROGENATION AND ISOMERIZATION OF ALKENES CATALYZED BY $RuL(CO)_2(PPh_3)_2$ ($L = H_2$, PPh_3)

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Summary

The complexes $M(CO)_2(PPh_3)_3$ (I, M = Fe; II, M = Ru) readily react with H_2 at room temperature and atmospheric pressure to give *cis*-$M(H)_2(CO)_2(PPh_3)_2$ (III, M = Fe; IV, M = Ru). I reacts with O_2 to give an unstable compound in solution, in a type of reaction known to occur with II which leads to *cis*-$Ru(O_2)(CO)_2(PPh_3)_2$ (V). Even compound IV reacts with O_2 to give V with displacement of H_2; this reaction has been shown to be reversible and this is the first case where the displacement of H_2 by O_2 and that of O_2 by H_2 at a metal center has been observed. III and IV are reduced to $M(CO)_3(PPh_3)_2$ by CO with displacement of H_2; $Ru(CO)_3(PPh_3)_2$ is also formed by treatment of IV with CO_2, but under higher pressure. Compounds II and IV react with $CH_2{=}CHCN$ to give $Ru(CH_2{=}CHCN)(CO)_2(PPh_3)_2$ (VI) which reacts with H_2 to reform the hydride IV.

cis-$Ru(H)_2(CO)_2(PPh_3)_2$ (IV) has been studied as catalyst in the hydrogenation and isomerization of a series of monoenes and dienes. The catalysts are poisoned by the presence of free triphenylphosphine. On the other hand the ready exchange of H_2 and O_2 on the "$Ru(CO)_2(PPh_3)_2$" moiety makes IV a catalyst not irreversibly poisoned by the presence of air. It has been found that even $Ru(CO)_2(PPh_3)_3$ (II) acts as a catalyst for the isomerization of hex-1-ene at room temperature under an inert atmosphere.

Introduction

We recently described convenient syntheses of the complexes $M(CO)_2(PPh_3)_3$ (I, M = Fe; II, M = Ru) and *cis*-$M(H)_2(CO)_2(PPh_3)_2$ (III, M = Fe; IV, M = Ru) [1].

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The reactions of the zerovalent ruthenium complex II have already been briefly studied [2], and it has been shown that II probably loses one phosphine in solution, since rapid addition of various ligands L occurs to give the complexes Ru(L)-$(CO)_2(PPh_3)_2$ (L = O_2, C_2H_4, PhC_2Ph). Complex II is known to absorb H_2 in solution, but the product was not characterized [2]. Compound II thus exhibits a reactivity notably greater than that observed for $Ru(CO)_3(PPh_3)_2$ [3] and for related phosphineruthenium(0) derivatives [4], and this is what one would expect on the basis of the enhanced basicity of the metal and of the steric requirements of the bulky phosphines [5,6]. As a continuation of our studies on the reactivity of phosphineruthenium complexes in low oxidation states [1,7], we report here our results on the reactions of compounds I—IV towards small molecules and alkenes. We have also investigated the catalytic properties of IV in the hydrogenation and isomerization of alkenes. Very recently it was reported that IV is the probable catalyst in the homogeneous hydroformylation of alkenes catalyzed by $Ru(CO)_3(PPh_3)_2$ and in the hydrogenation of hex-1-ene at 50 atm of H_2 and 150°C, in which no isomerization of the alkene was observed [8].

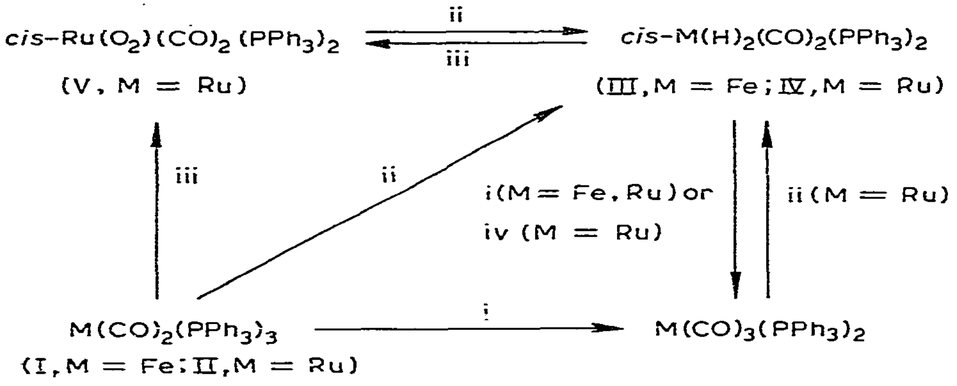
Results

Reactions with small molecules

Compounds I and II react with CO and H_2 giving products of the same stereochemistry (see Scheme 1). By reaction with CO the complexes $M(CO)_3(PPh_3)_2$, having apical phosphines and equatorial CO ligands can be readily obtained [9,10]. I and II absorb hydrogen to give III and IV; compound IV can also be obtained from $Ru(CO)_3(PPh_3)_2$ and H_2, but this requires high pressure and temperature [3a]. In all cases the same isomer having both the CO molecules and the hydrogens in a *cis* position is isolated [1,3a].

Like the ruthenium complex II [2], compound I absorbs oxygen when in solution. The reaction in toluene at 0—5°C gave a complex that is unstable in solution but can be isolated, it has an IR spectrum comparable to that of *cis*-$Ru(O_2)(CO)_2(PPh_3)_2$ [2] (ν(CO) 2005s—1935s; $\nu(FeO_2)$ 905m cm^{-1} in Nujol). We have been unable to grow crystals suitable for an X-ray structural determina-

SCHEME 1



Reagents: i, CO; ii, H_2; iii, O_2; iv, CO_2

tion of this compound [11], which could represent the first example of an iron complex containing a side-on bonded dioxygen.

In the reactions of I and II with O_2 triphenylphosphine oxide was detected among the products. When II (0.05 mmol) and PPh_3 (1.30 mmol) (Ru/PPh_3 1/26) in benzene (15 ml) reacted with O_2 at 40°C and atmospheric pressure, only 8—9% of the phosphine was oxidized to triphenylphosphine oxide in 6 h. Compound I was even less active in this reaction.

Even compound IV reacts with O_2 at atmospheric pressure to give V, with displacement of H_2. The reaction is reversible, but the reversal requires a slight hydrogen pressure. To our knowledge this is the first example of a reversible exchange between H_2 and O_2 on a metal center, a reaction reminiscent of the reversible exchange between H_2 and N_2 on $Ru(H)_4(PPh_3)_3$ [12].

H_2 is also displaced in III and IV by CO, to give the $M(CO)_3(PPh_3)_2$ complexes (M = Fe, Ru). $Ru(CO)_3(PPh_3)_2$ is also formed, although much more slowly, when the hydride IV is treated with CO_2 under pressure (15 atm) at 70—75°C. In this case only traces of hydrogen are detected in the gas phase. When the reaction with CO_2 was carried out even under hydrogen pressure, a significant amount of CO was also produced, while the ruthenium complex was recovered unchanged. However some triphenylphosphine oxide was also observed among the products, and thus the reduction of carbon dioxide may be partly by triphenylphosphine as well as by hydrogen.

Compound IV reats with acrylonitrile to give $Ru(CH_2{=}CHCN)(CO)_2(PPh_3)_2$ (VI) (eq. 1).

$$\mathrm{Ru(H)_2(CO)_2(PPh_3)_2} \underset{\mathrm{H_2}}{\overset{\mathrm{CH_2{=}CHCN}}{\rightleftharpoons}} \mathrm{Ru(CH_3{=}CHCN)(CO)_2(PPh_3)_2} \qquad (1)$$

The analogous reaction with *cis*-$Fe(H)_2(CO)_2(PPh_3)_2$ gave a product with an IR spectrum comparable to that of VI, but with poor elemental analyses. Compound VI was also obtained by treatment of II with $CH_2{=}CHCN$ [2,13], a reaction which confirmed its formulation. On the other hand the reaction of I with $CH_2{=}CHCN$ gave a product comparable to VI, but again elemental analyses were not satisfactory (see experimental). Compound VI shows a *cis* configuration of the carbonyl groups (ν(CO) 1980s—1920s cm^{-1} in Nujol) and the expected low frequency shift of ν(CN) on complexation (ν(CN) 2195mw). The acrylonitrile derivative reacts with hydrogen at atmospheric pressure to reform the hydride IV *. In none of these reactions could we detect propionitrile among the products by gas-chromatographic analyses, and this is probably due to oligomerization of the nitrile residue, as observed during the catalytic reactions (see later). The alkene is also displaced from VI by molecular oxygen, with formation of V, while prolonged reaction of VI with chloroform gives the white *cis*-$Ru(CO)_2(PPh_3)_2Cl_2$.

Catalytic reactions

(a) Hydrogenation and isomerization of monoenes. After hydrogenation of hex-1-ene at atmospheric pressure and 45°C and with *cis*-$Ru(H)_2(CO)_2(PPh_3)_2$

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* An analogous reaction was observed with the impure acrylonitrile iron derivative, compound III being obtained.

TABLE 1

HYDROGENATION OF ALKENES WITH *cis*-$Ru(H)_2(CO)_2(PPh_3)_2$ AS CATALYST, IN BENZENE (15 ml), 75°C, 17 atm H_2 for 7 h

mmol cat.	Alkene (mmol)	Alkane (mol%) [a]	*trans*-Hex-2-ene (mol%) [a]	*cis*-Hex-2-ene (mol%) [a]	*trans/cis* Hex-2-ene
7.32×10^{-2} [b]	hex-1-ene (25.46)	1.2	15.1	4.3	3.5
7.32×10^{-2}	hex-1-ene (25.46)	9.9	70.5	12.9	5.5
3.66×10^{-2}	hex-1-ene (25.46)	7.6	69.0	14.3	4.8
1.83×10^{-2}	hex-1-ene (25.46)	5.0	71.9	13.5	5.3
7.32×10^{-2}	hex-2-ene (25.46) [c]	21.0	58.6 [d]	12.1 [d]	4.9
7.32×10^{-2} + 7.29×10^{-1} PPh_3	hex-1-ene (25.46)	6.7	15.6	23.9	0.7
7.32×10^{-2} + 7.29×10^{-1} PPh_3	hex-2-ene (25.46) [c]	5.8	66.1 [e]	8.2 [e]	8.1
7.32×10^{-2}	cyclohexene (26.63)	15.0			
7.32×10^{-2}	cyclooctene (20.58)	35.0			
3.66×10^{-2}	cyclooctene (20.58)	24.3			
7.32×10^{-2}	styrene (26.63)	7.8			
3.66×10^{-2}	styrene (26.63)	5.2			

[a] (mol product/initial mol of the alkene) × 100. [b] At 45°C and 1 atm H_2. [c] 14.2% *trans* and 85.8%. *cis*; *trans/cis* 0.17. [d] mol% of hex-1-ene: 8.4. [e] mol% of hex-1-ene: 19.9.

(IV) as catalyst, only traces of n-hexane are detected, while the alkene is extensively isomerized to hex-2-ene (Table 1). By increasing the hydrogen pressure to 17 atmospheres, the overall conversion to these products is notably higher, although the amount of n-hexane formed, which increases with increasing catalyst concentration, is always much less than that of the isomerized product. Thus the rate of isomerization is higher than that of hydrogenation in these conditions. The isomerization of hex-1-ene does not require the presence of hydrogen, since it can also be observed under an inert atmosphere (Table 2). At 55°C ca. 50% of hex-1-ene is isomerized to hex-2-ene in 7 h, the extent of reaction decreases with decreasing temperature. The rate of formation of *trans*-hex-2-ene is greater than that of the *cis* isomer, and the ratio *trans/cis* is generally lower than that in reactions conducted under hydrogen (Table 1). In the presence of free triphenylphosphine, rates and conversions are both drastically reduced (Table 2 and Fig. 1).

On the other hand dinitrogen does not inhibit the isomerization, in contrast to the effect observed for the isomerization of pent-1-ene catalyzed by $Ru(H)_2(PPh_3)_3$ [14]. The product composition and the reaction rate profile were practically unchanged when the isomerization of hex-1-ene at 55°C was conducted under argon.

When hex-2-ene (14.2% *trans* and 85.8% *cis*) was isomerized under nitrogen (Table 2) only a slight increase in the amount of the *trans* isomer was observed, while hex-1-ene was also found among the products, but in small quantities. When the same mixture of hex-2-enes was hydrogenated under the usual conditions (Table 1) a relatively high conversion to n-hexane and to hex-1-ene took place. In the presence of free triphenylphosphine, the hydrogenation of hex-1-ene and hex-2-ene to n-hexane is significantly reduced (Table 1). These results indicate that, (i) an internal olefin reacts with the catalyst in a way comparable to that of an external one, and (ii) in the hydrogenation and isomerzation reac-

TABLE 2

ISOMERIZATION OF HEX-1-ENE AND HEX-2-ENE (25.46 mmol) WITH *cis*-$Ru(H)_2(CO)_2(PPh_3)_2$ as CATALYST, IN BENZENE (15 ml), 1 atm N_2 for 7 h

T(°C)	mmol catalyst	*trans*-Hex-2-ene (mol%) [a]	*cis*-Hex-2-ene (mol%) [a]	*trans*/*cis*-Hex-2-ene
35	7.32×10^{-2}	16.0	4.0	4.0
45	7.32×10^{-2}	20.5	6.6	3.1
50	7.32×10^{-2}	32.8	19.2	1.7
55	7.32×10^{-2}	33.9	19.4	1.7
55	7.32×10^{-2} $+ 7.29 \times 10^{-1}$ PPh_3	15.3	3.8	4.0
55	7.32×10^{-2} [b]	26.3 [c]	73.7 [c]	0.4
55	7.30×10^{-2} [d]	28.3	32.5	0.9

[a] (mol product/initial mol of the alkene) × 100. [b] In this experiment hex-2-ene (14.2% *trans* and 85.8% *cis*; *trans*/*cis* 0.17) was the starting alkene. [c] mol% of hex-1-ene: ca. 1.5%. [d] $Ru(CO)_2(PPh_3)_3$ (II) as catalyst.

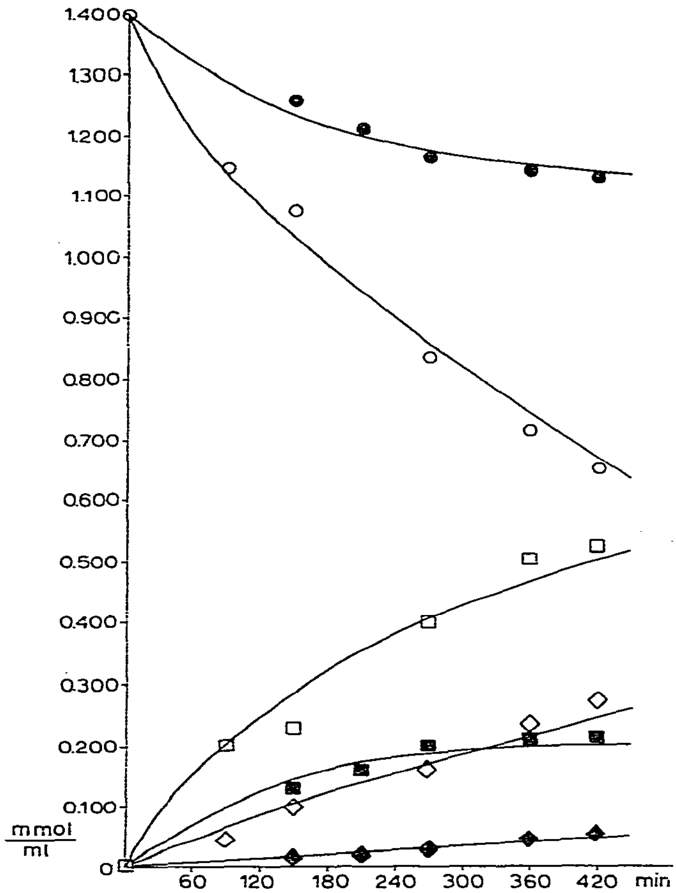


Fig. 1. Isomerization of hex-1-ene (25.46 mmol) with *cis*-$Ru(H)_2(CO)_2(PPh_3)_2$ (7.32×10^{-2} mmol) as catalyst in benzene (15 ml), 55°C, 1 atm N_2: ○ hex-1-ene, □ *trans*-hex-2-ene, ◇ *cis*-hex-2-ene. ●, ■ and ◆ refer to the same reaction conducted in the presence of PPh_3 (7.29×10^{-1} mmol).

tions the dissociation of triphenylphosphine is an important step in the catalytic cycle.

The first point was confirmed by the reactions conducted on cyclic olefins (Table 1). Cyclohexene and cyclooctene were hydrogenated to the corresponding alkane with conversions comparable to those observed for hex-2-ene. A lower degree of hydrogenation was observed when styrene was employed as substrate: in this case significant amounts of polymers were formed. With acrylonitrile no propionitrile was detected, and only polymers were produced.

We have also briefly studied the isomerization in a nitrogen atmosphere of hex-1-ene with $Ru(CO)_2(PPh_3)_3$ (II) as catalyst. With this catalyst the reaction is faster than that observed with *cis*-$Ru(H)_2(CO)_2(PPh_3)_2$ (IV) (Table 1 and Fig. 2). The ratio of *cis*- to *trans*-hex-2-ene is also higher.

(b) Hydrogenation and isomerization of dienes. Some selectivity in the hydrogenation of dienes to monoenes was noted (Table 3). While with 1,3-cyclooctadiene only cyclooctene and cyclooctane were obtained, with 1,5-cyclooctadiene the diene is also isomerized in large amount to the corresponding 1,3-diene and

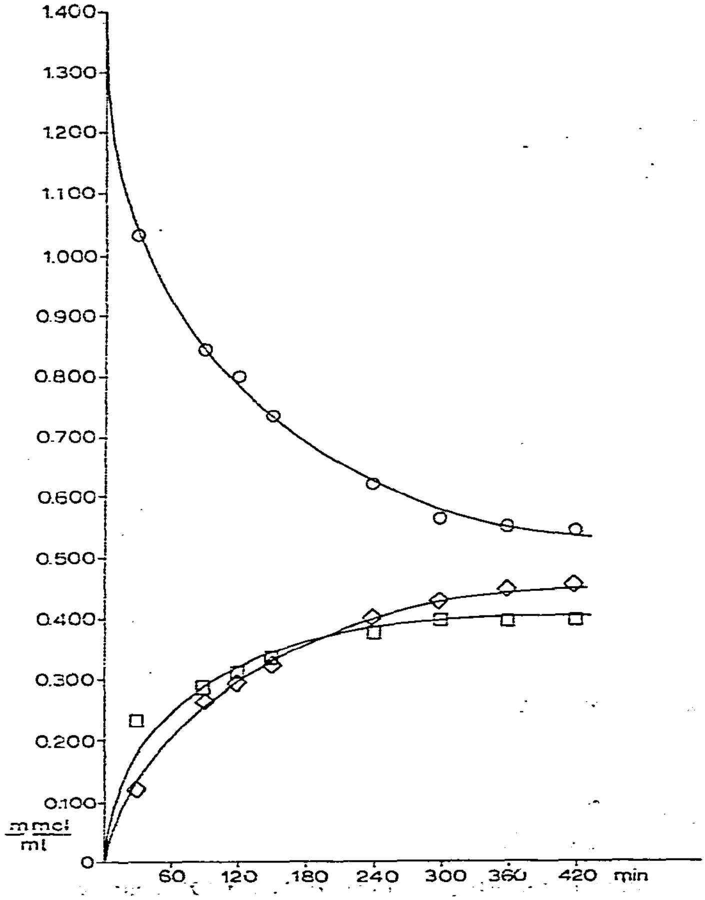


Fig. 2. Isomerization of hex-1-ene (25.46 mmol) with $Ru(CO)_2(PPh_3)_3$ (7.30×10^{-2} mmol) as catalyst, in benzene (15 ml), 55°C, 1 atm N_2: ○ hex-1-ene, □ *trans*-hex-2-ene, ◇ *cis*-hex-2-ene.

TABLE 3

HYDROGENATION OF DIENES WITH *cis*-$Ru(H)_2(CO)_2(PPh_3)_2$ (7.32×10^{-2} mmol), in benzene (15 ml), 75°C, 17 atm H_2 for 7 h

Diene (mmol)	Cyclooctene or hex-1-ene ^{a}	Cyclooctane or n-hexane ^{a}	1,3-Cycloocta-diene ^{a}	*trans*-hex-2-ene ^{a}	*cis*-hex-2-ene ^{a}
1,3-Cyclooctadiene (21.98)	18.6	4.6	—	—	—
1,5-Cyclooctadiene (21.98)	8.6	0.9	28.2 ^{b}	—	—
1,3-Hexadiene (25.4)	4.0	1.4	—	5.1	1.7

^{a} (mol product/initial mol of the diene) × 100. ^{b} Ca. 21% of another product was detected by GLC, immediately after 1,3-cyclooctadiene, and probably it is the 1,4 isomer.

another product, that could be the 1,4-isomer, though this has not been confirmed. The linear conjugated 1,3-hexadiene, gave a mixture of hex-1-ene and hex-2-enes containing small quantities of n-hexane.

In the catalytic experiments described above, the unchanged catalyst, *cis*-$Ru(H)_2(CO)_2(PPh_3)_2$ (IV), was always recovered at the end of the reactions. We also studied some of these reactions using *cis*-$Fe(H)_2(CO)_2(PPh_3)_2$ as catalyst. Although in some cases a significant catalytic activity was evident, extensive decomposition of the catalyst was observed, and no detailed studies have been carried out.

When $Ru(CO)_2(PPh_3)_3$ (II) was employed as catalyst, we were unable to characterise a well defined product.

Conclusions

The complexes $M(CO)_2(PPh_3)_3$ (M = Fe, Ru) show a reactivity comparable to that of $M(PPh_3)_3$ (M = Ni, Pd, Pt) [6]. The most striking difference is the ability of the former to activate molecular hydrogen. This can be taken as an evidence of the greater basic character of iron and ruthenium, in spite of the presence of two carbonyl groups alongside the phosphine ligands in these complexes. A possible mechanism for the hydrogenation and hydroformylation of alkenes with $Ru(CO)_3(PPh_3)_2$ as catalyst has previously been proposed, involving the intermediate formation of *cis*-$Ru(H)_2(CO)_2(PPh_3)_2$ (IV) [8]. Our results substantiate the suggestion that dissociation of triphenylphosphine is an important step in the reactions [8]. At high hydrogen pressure and temperature (50 atm and 150°C) hex-1-ene is hydrogenated but not isomerized [8]. Under our conditions (17 atm and 75°C) elimination of the alkene becomes more favorable than the hydrogen transfer to the coordinated alkyl in the intermediate $Ru(H)(alkyl)(CO)_2(PPh_3)_2$. The inability of *cis*-$Ru(H)_2(CO)_2(PPh_3)_2$ to discriminate between internal and external olefins may be associated with a low degree of crowding of the ligands in the active species, "$Ru(H)_2(CO)_2(PPh_3)$". On the other hand an alternative mechanism should be operative when $Ru(CO)_2(PPh_3)_3$ (II) is employed as catalyst and a π-allyl hydrido intermediate can be proposed to explain the isomerization of the alkene [15].

Experimental

The complexes $M(CO)_2(PPh_3)_3$ and *cis*-$M(H)_2(CO)_2(PPh_3)_2$ (M = Fe, Ru) were prepared as previously described [1]. Reactions were carried out under nitrogen (unless otherwise stated), using well dried solvents. Elemental analyses were carried out by the Analytical Laboratories of Milan University. The IR and ^{1}H NMR spectra were recorded on Perkin—Elmer model 457 spectrophotometer and on a Varian NV-14 instrument operating at 60 MHz. GLC and GSC measurements were carried out by use of Carlo Erba Fractovap Models C and M gas chromatographs, using a 2 m column filled with silica gel for gas analyses, a 2.4 m column filled with 30% weight Carbowax 1500 on Chromosorb W 60—80 mesh for cyclohexene, cyclooctene, styrene and cyclooctadienes analyses (these analyses have been carried out by internal standardisation with n-hexane), a 6 m column filled with 10% weight β,β'-oxydipropionitrile on Chromosorb P 60—80 mesh, DMCS treated on which $AgNO_3$ has been dispersed (4 m) and with 10% weight Carbowax 400 on Chromosorb P 60—80 mesh DMCS treated (2 m) for the hexenes analyses.

With this column *trans*-hex-2-ene appears as a shoulder of hex-1-ene, while the other peaks are well separated; repeated analyses of solutions with known composition have shown that the calculated mol% for hex-1-ene and *trans*-hex-2-ene (Tables 1,2 and 3) is subject to an uncertainty of ±3%. The olefins were distilled under nitrogen and chromatographated on alumina and under nitrogen immediately before use. High-pressure reactions were carried out in a 100 ml stainless steel autoclave. The reagents were placed under nitrogen in a glass liner constructed to fit the autoclave. After cooling with dry-ice/acetone, the autoclave was evacuated and filled with nitrogen at atmospheric pressure four times. The temperature was then allowed to rise to room temperature, and the autoclave was charged with the required gas under pressure. Magnetical stirring was begun and the autoclave was heated to the desired temperature. In the experiments conducted at atmospheric pressure, a sample of the solution was periodically removed with a syringe from a serum cap of the glass reactor, and analysed by GLC.

(1) Reactions of $Fe(CO)_2(PPh_3)_3$ (I) and $Ru(CO)_2(PPh_3)_3$ (II) with CO. Syntheses of $M(CO)_3(PPh_3)_2$ ($M = Fe, Ru$)

To benzene (20 ml) previously saturated with CO for 1 h, I or II (0.1 g) was added. The brown-red I or the yellowish II suspensions were stirred for 3 h with CO bubbling through. The final yellow solutions were evaporated to dryness in vacuo The yellow solid residues were washed with n-hexane and filtered off. They were shown to be the $M(CO)_3(PPh_3)_2$ complexes by their IR spectra which were identical to those of authentic samples [9,10]. When oxygen was not carefully excluded compound V was formed together with $Ru(CO)_3(PPh_3)_2$.

(2) Reactions of $Fe(CO)_2(PPh_3)_3$ (I) and $Ru(CO)_2(PPh_3)_3$ (II) with H_2. Syntheses of *cis*-$Fe(H)_2(CO)_2(PPh_3)_2$ (III) and *cis*-$Ru(H)_2(CO)_2(PPh_3)_2$ (IV)

(1) To benzene (35 ml) previously saturated with H_2 for 1 h, I (0.462 g) was added. The dark-red solution was stirred for 5 h as H_2 was bubbled through. The solution was evaporated to dryness in vacuo and the oily residue was crystallised by addition of ethanol. The crystals were filtered off and washed with ethanol. The pale-brown compound was crystallised from benzene/n-hexane under nitrogen and shown to be *cis*-$Fe(H)_2(CO)_2(PPh_3)_2$ (III) by its IR spectrum, which was identical to that of an authentic sample [1].

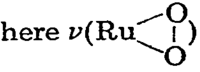
(b) To benzene (25 ml) previously saturated with H_2 for 1 h, II (0.115 g) was added. The yellow suspension was stirred for 4 h as H_2 was bubbled through. The solution was evaporated to dryness in vacuo and the oily residue was crystallised by addition of ethanol; the crystals were filtered off, and washed repeatedly with ethanol and n-hexane. The pale-brown compound was shown to be *cis*-$Ru(H)_2(CO)_2(PPh_3)_2$ (IV) by its IR and ^1H and ^1H NMR spectra, which were identical to those of an authentic sample [1].

(3) Reaction of cis-$Ru(H)_2(CO)_2(PPh_3)_2$ (IV) with O_2. Synthesis of cis-$Ru(O_2)(CO)_2(PPh_3)_2$ (V)

IV (0.07 g), benzene (20 ml) and O_2 (3 atm) were placed in the autoclave as above described. The reaction was allowed to proceed for 4 h at room temperature with magnetical stirring. The gas was analysed by GSC at the start and at the end of the reaction, and the presence of H_2 was detected only at the end. The autoclave was vented, then the solution transferred from the glass liner into a flask and evaporated to dryness in vacuo. The solid residue was shown to be pure V by its IR spectrum. The same reaction can also be carried out at atmospheric pressure by bubbling oxygen through a suspension of IV (0.08 g) in benzene (20 ml) for 3 h. The final solution was evaporated to a small volume and on addition of n-hexane compound V separated. It was filtered off and identified by its m.p. and IR spectrum which were identical to those of the compound obtained by treatment of $Ru(CO)_2(PPh_3)_3$ with O_2 in benzene [2].

(4) Reaction of cis-$Ru(O_2)(CO)_2(PPh_3)_2$ (V) with H_2. Synthesis of cis-$Ru(H)_2(CO)_2(PPh_3)_2$ (IV)

The reaction was carried out as described in (3) by using V (0.07 g), benzene (20 ml) and hydrogen (3 atm). GSC analyses of the gas at the start did not show the presence of O_2, but this was detected after 4 h of reaction. The solid residue after evaporation of the solution was shown to be a ca. 50% mixture of IV and V by its IR spectrum.

Besides the carbonyl stretching frequencies region, the 700—800 cm^{-1} region was particularly useful where  $\nu(\mathrm{Ru}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\langle|}})$ and δ(Ru—H) [1] could be readily distinguished.

(5) Reactions of cis-$Fe(H)_2(CO)_2(PPh_3)_2$ (III) and cis-$Ru(H)_2(CO)_2(PPh_3)_2$ (IV) with CO. Syntheses of $M(CO)_3(PPh_3)_2$ ($M = Fe, Ru$)

The reactions were carried out as described in (3) using III or IV (0.07 g), benzene (20 ml) and CO (3 atm and room temperature, IV; 15 atm and 70°C, III). After 4 h the presence of H_2 in the gas phase was detected by GSC. The solid residues after evaporation of the solutions were shown to be nearly pure $Fe(CO)_3(PPh_3)_2$ or $Ru(CO)_3(PPh_3)_2$, with only small amounts of III and IV, by their IR spectra, which were identical to those of authentic samples [9,10]. The same reaction occurred when we studied the catalytic isomerization of hex-1-ene under the standard conditions, viz. at 55°C under CO, in order to see whether the catalytic reaction was poisoned by the latter. However, the final product contained substantial amounts of unreacted IV as well as $Ru(CO)_3(PPh_3)_2$. No isomerization of hex-1-ene was observed under these conditions.

(6) Reactions of cis-$Ru(H)_2(CO)_2(PPh_3)_2$ (IV) with CO_2 and CO_2/H_2 Synthesis of $Ru(CO)_3(PPh_3)_2$

The reaction was carried out as described in (3) by using IV (0.07 g), benzene (20 ml) and CO_2 (15 atm). GSC analysis of the gas at the start did not show the presence of CO or H_2, and only traces of H_2 were observed after 4 h of reaction at 75°C. Similar results were obtained on increasing the CO_2 pressure (60 atm) and the reaction time (90 h); the solid residue, after evaporation of the solution and careful crystallisation from benzene/n-hexane was shown to be nearly pure $Ru(CO)_3(PPh_3)_2$ by IR spectroscopy. When the same reaction was carried out as above, but with a CO_2 (15 atm)/H_2 (15 atm) mixture, carbon monoxide was detected by GSC in the gas phase at the end of the reaction. The presence of unchanged *cis*-$Ru(H)_2(CO)_2(PPh_3)_2$ in the final product was confirmed by IR spectroscopy. Increasing the CO_2 (45 atm) and H_2 (50 atm) pressure and the reaction time (24 h) caused no significant increase in the amount of carbon monoxide.

(7) cis-$Ru(CH_2{=}CHCN)(CO)_2(PPh_3)_2$ (VI)

(a) IV (0.156 g) and $CH_2{=}CHCN$ (0.8 ml) were allowed to react in benzene (10 ml) for 21 h, under stirring. The solution was evaporated to a small volume and n-hexane was added. The white precipitate was filtered off under nitrogen, washed with a little ethyl ether, n-hexane and dried in vacuo, m.p. 166°C (Found: C, 66.5; H, 4.5; N, 1.9. $C_{41}H_{33}NO_2P_2Ru$ calcd.: C, 67.0; H, 4.5; N, 1.9%). In some preparations, part of the product precipitated from the solution at the end of the reaction.

(b) The same product was obtained from II using the experimental conditions above, m.p. 165°C. When the same reactions were carried out on I or III, a dark yellow compound, which was soluble in benzene but precipitated out by n-hexane, was obtained, (ν(CN) 2195mw, ν(CO) 1955s—1880s cm^{-1} (Nujol)) (Found: C, 68.0—70.6; H, 4.9—5.6; N, 1.9—1.8. $C_{41}H_{33}FeNO_2P_2$ calcd.: C, 71.4; H, 4.8; N, 2.0%.) Attempted crystallisations under nitrogen from benzene/n-hexane gave products with even less satisfactory analyses.

(8) Reactions of $Ru(CH_2{=}CHCN)(CO)_2(PPh_3)_2$ (VI)

With $CHCl_3$. VI (0.135 g) was dissolved in $CHCl_3$ (15 ml) and the solution was left under stirring for 6 h. The solution was evaporated to a small volume and addition of n-hexane gave a pale-brown precipitate. This was filtered off, washed with a little benzene and crystallised from chloroform/n-hexane. A white product was obtained, and shown to be *cis*-$Ru(CO)_2(PPh_3)_2Cl_2$ by its IR spectrum, which was identical to that of an authentic sample [16].

With H_2. VI (0.1 g) was added to benzene (20 ml) previously saturated with H_2. The solution was stirred for 7 h while H_2 was bubbled through. The solution was evaporated to small volume, and addition of n-hexane gave a pale brown precipitate, which was shown to be IV by its IR spectrum. The reaction with H_2 was also carried out on impure *cis*-$Fe(CH_2{=}CHCN)(CO)_2(PPh_3)_2$ under the same conditions (18 h of reaction). The formation of III was confirmed by IR spectroscopy.

With O_2. When the reaction was carried out as above but using O_2 instead of H_2 and for 4 h, compound V was obtained.

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