Journal of Organometallic Chemistry, 456 (1993) 255-262

JOM 23610

Linked *bis*(μ-phosphido) and related ligands for metallic clusters

IX *. Heterogeneous hydrogenation of 1-octene using phosphido-stabilized di- and triruthenium metal clusters on a silica support. A case for an intact supported cluster as a catalyst

Mark D. Soucek [1], Huh-Sun Chiou [2] and Evan P. Kyba [3]

Department of Biochemistry and Chemistry, The University of Texas, Austin, TX 78712 (USA)

(Received September 18, 1992; in revised form February 8, 1993)

Abstract

The homogeneous and heterogeneous hydrogenation of 1-octene was studied using phosphido-stabilized ruthenium clusters as catalysts. All four phosphido-stabilized ruthenium clusters $Ru_2(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]$ (**1**), $Ru_3(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2$ (**2**), $Ru_2(CO)_6[1,2\text{-}(\mu\text{-}P^tBu_2C_6H_4]$ (**3**), and $Ru_3(CO)_6[1,2\text{-}(\mu\text{-}P^tBu_2C_6H_4]_2$ (**4**) were found to be active hydrogenation and isomerization catalyst precursors, but no hydrogenolysis was observed even at elevated temperatures. The polar environment of the Cab-o-sil (silica) support activated the triruthenium cluster **2** in comparison with the homogeneous hydrogenation of 1-octene. Addition of a Lewis acid ($Et_2O:BF_3$) to the homogeneous hydrogenation of 1-octene resulted in modestly higher catalytic activity of **2**. Compound **2** was quantitatively recovered from the Cab-o-sil support intact after hydrogenating 1-octene at 140°C for several hours.

1. Introduction

There has been considerable interest in stabilizing low oxidation ruthenium clusters as catalysts or catalyst precursors [2]. Such species have been utilized in the hydrogenolysis of alkanes [3], ammonia synthesis [4], the hydrodesulfurization of fossil fuels [5], hydroformylation [6], as well as selective hydrogenation of various substrates [7]. A common source of low oxidation state ruthenium clusters is triruthenium dodecarbonyl, activation of which often involves fragmentation, resulting in metal carbonyl species that are volatile under reaction conditions [8]. The typical solutions to this problem have been to prevent fragmentation by the incorporation of bridging ligands such as phosphides, sulfides and oxides [9], or by depositing neutral ruthenium carbonyl catalysts onto solid supports such as silica, in which surface siloxy groups oxidatively add to the cluster and/or displace carbonyl ligands [10].

A general strategy for stabilizing multinuclear transition metal clusters employed by many groups in homogeneous catalysis has been to bridge the metal bonds with phosphido units (R_2P^-) [11]. We have reported several examples of the stabilizing effect of the 1,2-bis(alkyl- or arylphosphido)benzene moiety on metal–metal bonds [1,12]. Recently, the syntheses of a series of 1,2-bis(alkyl- or arylphosphido)benzene triruthenium and diruthenium clusters have been reported [13]. This account describes the unique behavior of the di-bis(phenylphosphido)benzene-ligand triruthenium cluster **2**, and related species under homogeneous and heterogeneous catalytic conditions. The hydrogenation and/or isomerization of an alkene was chosen as a model system because of its relative simplicity and the availability of pertinent literature for comparison [14].

Correspondence to: Dr. M.D. Soucek and Dr. E.P. Kyba.

* For Part VIII, see ref. 1.

[1] Present address: Langley Research Center, NASA, Hampton, VA 23665, USA.

[2] Present address: Hoechst-Celanese, Corpus Christi, TX 78469.

[3] Present address: Conner Research Center, Alcon Laboratories Inc., Fort Worth, TX 76134, USA.

0022-328X/93/$6.00

2. Results

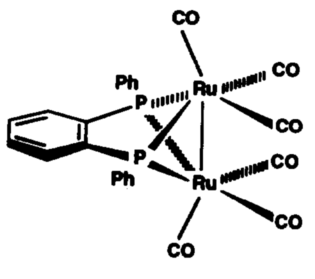
The four phosphido-stabilized ruthenium clusters **1**–**4** [13] were studied as hydrogenation catalysts for 1-octene in a continuous flow heterogeneous catalysis system. The complexes were supported on high surface area silica and dihydrogen carrier gas at a pressure of 1 atm was employed. Tables 1 and 2 summarize the results of the hydrogenation of 1-octene using the dinuclear complex **1** and the trinuclear complex **2**, respectively. At 25°C, hydrogenation and isomerization products were observed both for **1** and **2**. The conversion of 1-octene into octane ranged from 5.4% (25°C) to 27.7% (100°C) for **1** and from 8.6% (25°C) to 80.7% (140°C) for **2**. At 100°C, the average turnover numbers were 34 mol alkene/h · mol catalyst for **1** and 37 for **2**, assuming all the supported material is available for catalysis. At room temperature, the major difference between the di- and triruthenium catalysts was the ratio of hydrogenation to isomerization products. The diruthenium compound **1** produced a 1 : 1 ratio, and the triruthenium compound **2** produced a 1 : 2 ratio. As the temperature was increased, *trans*-2-octene was observed as the major product for **1**, whereas octane was observed to be the major product for **2**.

TABLE 1. Percentage yields of products in the heterogeneous catalytic hydrogenation of 1-octene using complex **1**

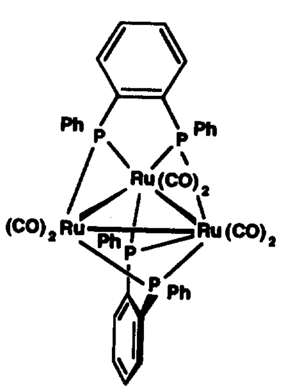
Run	Temperature (°C)	1-octene	octane	*trans*-2-octene	*cis*-2-octene
1	25	89.4	5.4	2.7	2.4
2	25	82.8	8.4	4.6	3.5
1	40	77.0	8.2	7.2	7.6
2	40	67.9	9.0	10.4	12.0
1	60	48.9	12.0	17.3	21.7
2	60	39.3	20.9	21.6	20.1
1 [a]	80	14.2	11.5	44.8	23.5
2 [b]	80	11.8	12.2	47.4	25.2
1 [c]	100	5.4	25.1	28.0	16.4
2 [d]	100	3.0	27.7	30.3	18.5

[a] Other internal alkenes were found; 6.1% *cis*-3-octene and *trans*-3-octene along with trace amounts of 4-octenes; [b] Other internal alkenes were found; 3.4% *cis*-3-octene and *trans*-3-octene along with trace amounts of 4-octenes; [c] other internal alkenes were found; 25.0% *cis*-3-octene and *trans*-3-octene along with trace amounts of 4-octenes; [d] other internal alkenes were found; 20.6% *cis*-3-octene and *trans*-3-octene along with trace amounts of 4-octenes.

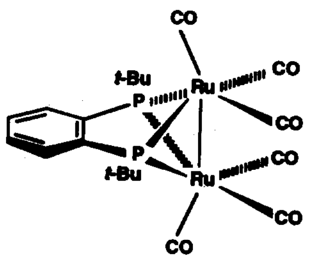
Tables 3 and 4 summarize the results of the hydro-



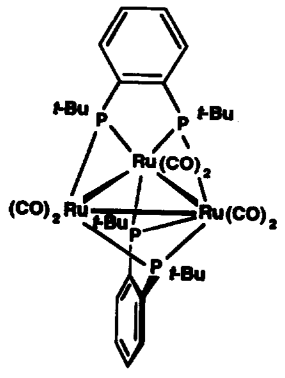
1



2



3



4

TABLE 2. Percentage yields of products in the heterogeneous catalytic hydrogenation of 1-octene using complex **2**

Run	Temperature (°C)	1-octene	octane	*trans*-2-octene	*cis*-2-octene
1	25	73.2	8.6	11.3	6.1
2	25	72.4	11.8	9.5	5.4
1	40	53.5	10.4	24.9	10.6
2	40	31.3	13.9	39.7	14.3
1	60	36.2	16.1	33.3	13.8
2	60	17.6	27.9	39.4	14.0
1	100	3.9	72.9	15.1	5.4
2	100	3.8	71.4	17.5	6.6
1	140	1.7	84.5	7.9	3.2
2	140	1.5	80.7	9.2	3.7

TABLE 3. Percentage yields of products in the heterogeneous catalytic hydrogenation of 1-octene using complex **3**

Run	Temperature (°C)	1-octene	octane	*trans*-2-octene	*cis*-2-octene
1	25	91.8	4.3	2.1	1.8
2	25	82.1	9.4	4.6	3.2
1	40	86.1	4.9	4.3	4.5
2	40	67.9	9.0	10.4	12.0
1	60	60.9	19.1	13.1	16.4
2	60	39.3	10.9	21.6	20.1
1	80	14.2	21.5	40.8	23.5
2	80	11.8	12.2	47.4	25.2
1	100	5.4	39.2	35.2	17.4
2	100	6.5	35.7	41.4	16.4

genation of 1-octene using the dinuclear complex **3** and the trinuclear complex **4**, respectively. Both the t-butyl-substituted clusters **3** and **4** exhibited a 1:1 hydrogenation to isomerization ratio at room temperature. As the temperature was increased, *trans*-2-octene was observed as the major products for the diruthenium **3** and the octane was observed to be the major product for the triruthenium **4**. The conversion of 1-octene into octane ranged from 4.2% (25°C) to 35.7% (100°C) for **3** and from 12.2% (25°C) to 97% (140°C) for **4**. At 100°C, the turnover number for **3** was 23 mol alkene/h mol catalyst, and 22 for **4** assuming, as above, that all the supported material was available for catalysis.

TABLE 4. Percentage yields of products in the heterogeneous catalytic hydrogenation of 1-octene using complex **4**

Run	Temperature (°C)	1-octene	octane	*trans*-2-octene	*cis*-2-octene
1	25	76.1	12.2	5.3	5.3
2	25	70.4	9.1	11.5	7.9
1	40	0.0	47.4	38.1	14.5
2	40	0.0	42.6	41.3	16.0
1	60	15.9	45.3	23.2	15.4
2	60	8.6	61.2	17.8	9.1
1	100	0.0	95.0	–	–
2	100	0.0	97.0	–	–

TABLE 5. Percentage yields of products as a function of temperature cycling in the heterogeneous catalytic hydrogenation of 1-octene using complex **2**

Run	Temperature (°C)	1-octene	octane	*trans*-2-octene	*cis*-2-octene
1	25	83.5	9.5	4.1	2.9
2	140	0.5	80.2	10.8	8.7
3	25	80.1	10.5	5.5	3.9
4	140	1.6	81.4	7.4	3.2
5	25	89.3	6.7	2.3	1.7

Post-catalysis recovery of complexes **1**–**4** was also investigated. Only **2** could be recovered intact after catalysis, with nothing being extracted with toluene in the case of the others. The structure of the recovered cluster was verified by HPLC, IR, ^{31}P NMR, and mass spectroscopy. By HPLC, **2** was recovered quantitatively within experimental error (93 ± 7%).

Further experiments focused on the nature of the catalytic species. First it was determined that the Cab-o-sil from which cluster **2** was recovered, exhibited no discernible activity upon subjecting it to the standard catalysis conditions. Second, the supported complex **2** was put through two and one half cycles of heating from 25 to 140°C. The results of this temperature ramp experiment are shown in Table 5. Only modest changes were observed in the catalytic activity at 25°C after the catalyst was heated to 140°C the first or second time.

The homogenous hydrogenation of 1-octene in the presence of cluster **2** was investigated also. Subjecting 1-octene to **2** in toluene at 54 atm H_2 in a static reactor resulted in complete conversion of 1-octene into octane (120°C, 2 h). Only 40% of the cluster was recovered, however. At 2 atm H_2, the hydrogenation of 1-octene using **2** (120°C, 17 h) resulted in only partial conversion of 1-octene into octane (10.4%) and 90% of the catalyst was recovered. In addition to octane, isomerization products were also observed [*trans*-2-octene (2.5%), and *cis*-2-octene (2.3%)].

The effect of a Lewis acid upon the hydrogenation of 1-octene was studied in order to simulate the polar environment of the supported catalyst (silica). Addition of 1 equivalent of $Et_2O:BF_3$ under the above conditions (2 atm, H_2), resulted in a modest increase in activity (14.6% octane, 4.5% *trans*-2-octene, 3.5% *cis*-2-octene), with an 82% recovery of **2** as determined by HPLC.

3. Discussion

In comparison with previous studies [8] the phosphido stabilized ruthenium carbonyl clusters were more active hydrogenation catalysts than dodecacarbonyltriruthenium. It was our observation that when supported $Ru_3(CO)_{12}$ was warmed much above room temperature under the reaction conditions described above, a metal mirror began to form on the walls of the glass reactor tube. Thus we did not investigate this catalyst in any detail. While the silica-supported phosphido-stabilized ruthenium clusters **1**–**4** promoted hydrogenation as well as isomerization at ambient temperatures (25°C), silica-supported $Ru_3(CO)_{12}$ was found to promote only isomerization of 1-hexene at even higher temperatures (30–50°C) [14]. Overall, the triruthenium clusters **2** and **4** were more active catalyst precursors than the diruthenium counterparts, **1** and **3**. The triruthenium clusters led preferentially to hydrogenation, especially at higher temperatures, whereas the diruthenium clusters were more selective towards isomerization, especially at higher temperatures. Both **1** and **3** exhibit about the same overall activity, indicating little effect of the substituent on the phosphido center on catalytic activity.

We have established that the adsorption of **2** onto high-surface area silica is reversible, even after hours of functioning as a working catalyst at elevated temperatures. Extraction of the silica-supported catalyst with toluene followed by HPLC analysis revealed that a complete recovery, within experimental error, had been effected. By contrast, the t-butyl analog **4** could not be extracted similarly. Presumably, the phenyl substituents render **2** less basic than **4**, with its t-butyl groups. This can be inferred by the comparison of the solution IR spectra of these complexes with those of the silica bound species. Thus, the IR spectrum **2** in the carbonyl stretching region is only modestly affected by the presence or absence of silica, whereas adsorption of **4** onto Cab-o-sil has a pronounced effect on this IR region (Figs. 1–4). The rationale is that **4** is so strongly hydrogen-bonded via the metal carbonyls that the carbonyl stretching modes are substantially affected and that this strong binding disfavors extraction into a nonpolar solvent, whereas with the less basic **2**, such is not the case.

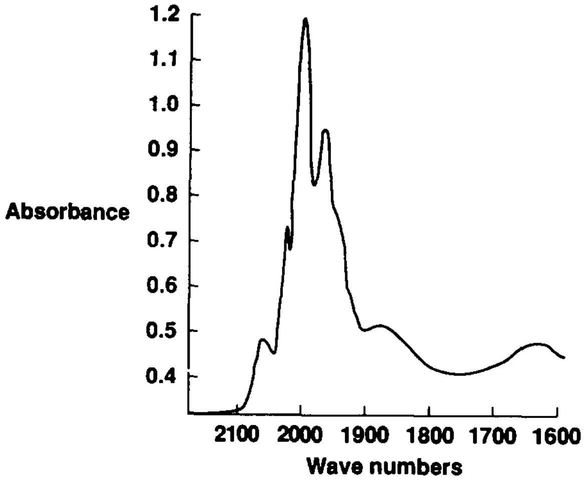


Fig. 2. Solid phase IR spectrum of 2 adsorbed onto Cab-o-sil.

Of particular interest is the mode of catalyst activation of the triruthenium species. There are very few cases of transition metal cluster catalytic processes that do not involve the prior loss of a ligand or a fragmentation into smaller, coordinatively unsaturated complexes that are the actual catalysts [15]. Pittman *et al.*, have reported a phosphinidene-bridged tetracobalt complex that effected hydroformylation of α-olefins, apparently without fragmentation, although the loss of a carbonyl ligand in an activation step was conceivable [16]. Bonnet *et al.* [17a] have described a triruthenium complex, $(\mu\text{-H})_2Ru_3(CO)_6[\mu\text{-PPhCH}_2P(Ph)]_2$, similar to **2** and **4**, except that the two supporting phosphorus chelating ligands were phosphino-phosphido rather than bis(phosphido) as in our case. This triruthenium complex was found to hydrogenate cyclohexanone in solu-

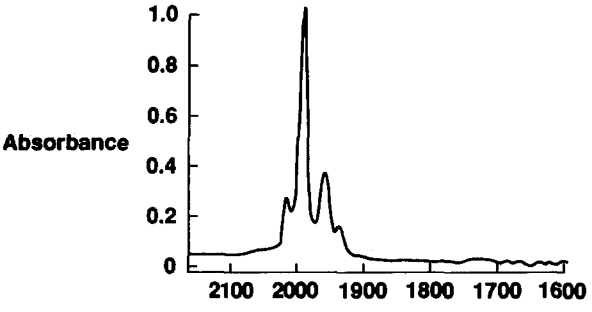


Fig. 1. Solution phase (CH_2Cl_2)IR spectrum of 2.

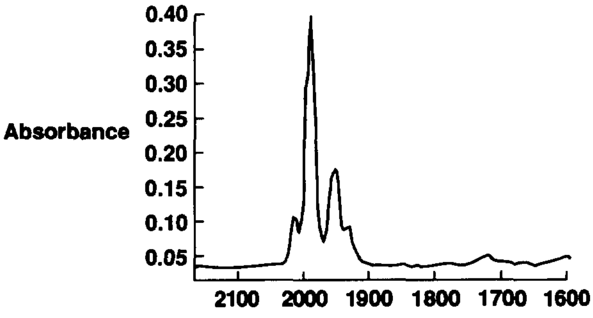


Fig. 3. Solution phase (Ch_2Cl_2)IR spectrum of 4.

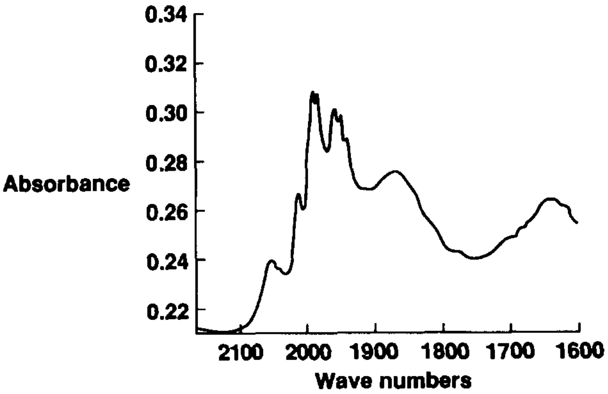


Fig. 4. Solid phase IR spectrum of 4 adsorbed onto Cab-o-sil.

tion at elevated temperatures and pressures of dihydrogen, followed by recovery of the catalyst unchanged [17a]. Similarly, the trinuclear cluster, $(\mu\text{-H})_2Ru_3(CO)_6(\mu\text{-CO})(\mu_3\text{-O})(\mu\text{-}\eta^2\text{-dppm})_2$, was found to hydrogenate 1-hexene homogeneously without any prior fragmentation [17b,c].

Cluster **2** has the fortuitous combination of physical properties, including stability and reactivity that allowed us to observe readily catalysis by the supported cluster and at the same time to isolate the starting **2**, following reactions at up to 140°C for several hours in an atmosphere of dihydrogen. We have described elsewhere that **2** can be heated in mesitylene for hours at 165°C in an argon atmosphere without decomposition [13], and thus expected that fragmentation might be prevented even on a silica support. Since the heterogeneous catalysis reactions were carried out in a flow system, however, the loss of a CO ligand would be irreversible, since it would be swept away with the carrier gas and reactant, dihydrogen. Because the cluster is recovered quantitatively by extraction, it appears that neither fragmentation nor CO ligand loss is involved in the activation of the cluster towards catalysis.

Because it was possible that a very small amount of surface bound **2** was decomposing to an unknown, catalytically active species, the loss of which was undetectable within our experimental uncertainty, we conducted an experiment in which the catalytic activity was measured at 25°C and 140°C over two and one half cycles. Since some catalysis is observed at 25°C, heating the catalyst to 140°C should cause much more decomposition to the catalytic intermediate, which would be expected to give a much higher apparent reactivity upon cooling back down to 25°C (Table 5). In fact, the variation of reactivity, as well as the product ratios for the three measurements at 25°C, was about what might be expected for different catalyst preparations, rather than the same one cycled to 140°C twice, if small amounts of decomposition materials were responsible for catalysis. Thus it appears that the data are in accord with the surface-bound catalyst being the intact cluster activated in some way so as to open a coordination site.

Given the product ratios obtained using **4** (Table 4) instead of **2** (Table 2), it seems reasonable that similar catalyst activation has occurred. It is clear that surface-bound **4** is considerably more reactive than **2** but since it not extractable, one can only refer to the structural similarity of the two to suggest a mode of activation. The situation is considerably more clouded with the binuclear complexes **1** and **3**. It is known that both are thermally unstable. In solution even at temperatures of 80°C in benzene solution in the dark **1** undergoes slow decomposition to give **3** in 60% yield along with uncharacterized polymeric material. What is clear is that whatever the catalytic species that are formed from these binuclear complexes, they are not those obtained from the trinuclear species (**2** and **4**), since hydrogenation is much reduced relative to isomerization with the former.

In none of the four catalyst precursors does the treatment of the surface-bound complexes at elevated temperatures in the presence of an atmosphere of dihydrogen lead to the complete hydrogenolysis of the ligands to form ruthenium metal as it does with $Ru_3(CO)_{12}$. The latter leads to substantial amounts of hydrogenolysis of the hydrocarbon substrate, and in fact a metal mirror on the reactor surface, whereas the former give no evidence of this.

No catalytic hydrogenation of 1-octene was observed in solution by **2** until a temperature of about 100°C was reached, and the reaction was slow even at 115°C. This is in contrast to the supported catalyst, where significant reactivity is observed at 25°C, primarily towards isomerization. Thus it is clear that the deposition of **2** on Cab-o-sil in some way activates the cluster so that the required open coordination site is created without the irreversible loss of a ligand or cluster fragmentation. The interaction could be either electrophilic, *i.e.*, ruthenium-bound carbonyl ligands hydrogen-bonding to surface hydroxyl groups [18] or nuceophilic, *i.e.*, carbonyl ligands attacked at carbon by surface hydroxyl or siloxy groups. Regardless of the mode of interaction between the cluster and the surface, it must be reversible in the case of **2** in order to allow recovery by solvent extraction. More than likely, the electrophilic or nucleophilic interaction described above facilitates the deligation of one of the bridging phosphido groups or the rupture of a metal-metal bond, to open up a coordination site for initiation of a catalytic cycle. If it were the latter process, it probably would involve the unique ruthenium atom located on the C_2 axis rather than one of the pair of doubly phosphido-bridged metal centers. Any further speculation regarding catalyst activation is unwarranted due to the current lack of any other evidence regarding the nature of the catalytic species.

4. Conclusions

The deposition of 1,2-bis(phosphidobenzene)-ligated ruthenium carbonyl clusters on a high surface area silica support (Cab-o-sil) activates such species toward reaction with alkene and dihydrogen ligands, resulting in isomerization and hydrogenation being observed, with the latter process being highly favored at elevated temperatures. The triruthenium cluster, $Ru_3(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2$ (**2**), could be recovered quantitatively after several hours in a flow system with dihydrogen as a carrier gas and reactant at 140°C (235 turnovers), thus providing strong evidence that no ligand loss or cluster fragmentation occurs as an initiation step prior to catalytic action. With all four ruthenium complexes, the 1,2-bis(phosphidobenzene) ligands are not hydrogenolysed even at elevated temperatures, based on comparison of product ratios from these catalyst precursors to those from $Ru_3(CO)_{12}$.

5. Experimental section

IR spectra were obtained either with NaCl solution cells or Cab-o-sil pressed onto a tantalum mesh support on a Matteson Cygnus 100 FTIR under a N_2 or Ar atmosphere. Gas chromatography was performed on a Hewlett Packard HP 5880A using a 50 m OV-1 capillary column and an FID. Integration was by an internal standardization program within the 5880A integrator. The detector response ratio was verified by the direct method. NMR spectra (^1H and ^{31}P) were obtained on a QE-300 with a 10 mm multinuclear probe. Analytical HPLC determinations were performed on a Waters ALC 204 instrument with a silica μ-Porasil 10 μ, 3.9 mm I.D. × 30 cm column fitted with a UV detector (280 nm), and quantitation by a Hewlett-Packard 3390A integrator. Retention times were matched with alkenes purchased from Wiley Chemical Company (*cis*-2-octene, *trans*-2-octene, *trans*-3-octene, *cis*-3-octene, *trans*-4-octene, *cis*-4-octene). The bulk substrate (1-octene) was also purchased from Wiley Chemical with a purity of 99.99%. Dihydrogen gas was purchased from Big Three Gas and was further purified by an oxisorb 11 filter made by MG Scientific Gases.

The M-5 grade Cab-o-sil was dried *in vacuo* at 200°C for 14 hours. The ruthenium complexes **1–4** were prepared and purified as previously described [13]. Catalyst precursors were deposited on the Cab-o-sil by means of a modified incipient wetness technique [4a]. The complexes (12.5 mg) were dissolved in toluene (15–20 ml) and added to 500 mg of Cab-o-sil. The slurry was evaporated to dryness on a rotary evaporator and then gently heated to 40°C *in vacuo* overnight. The tube furnace to control the temperature of the supported catalytic reactions was a Research Inc. dual elliptical radiant heater equipped with infrared lamps, and temperature-controlled (±1°C) by a Eurotherm Doric Trendicator 402 digital control board.

5.1. General method for the reaction of 1-octene with dihydrogen at atmospheric pressure in a flow reactor

The supported catalyst was transferred onto a fritted glass tube reactor with a 10 mm I.D. The system was purged with a 40 ml/min flow of H_2 for 1.5 h, after which the flow rate was adjusted to 4.0 ml/min using a bubble flow meter. The H_2 carrier gas flow was directed through a saturator containing 1-octene for 1.5 h to reach equilibrium. Multiple aliquots of 1 ml were drawn through a septum from a continuous effluent flow at each temperature. The average of each is reported in Tables 1–4. The run designations (1 and 2) on Tables 1–4 were from different batches of catalyst.

5.2. Recovery of complex 2 following a heterogeneous catalysis run

The fritted glass tube reactor containing the supported catalyst was removed from the heterogeneous catalysis apparatus and the ends were sealed with rubber septa. For this particular reaction, the total catalytic turnover number was 235 mol 1-octene/mol **2**, assuming all the supported complex was available for catalysis. The reaction vessel was evacuated and backfilled with dry N_2. The catalyst was washed with 3 × 5.00 ml of toluene and this solution was directly analyzed via HPLC. The detector response factor (extinction coefficient) was obtained (2.58×10^{-16} mol/count) at 280 nm using a standard solution. After the HPLC analysis, the solution was concentrated and an infrared spectrum was obtained; 2020w, 2000s, 1995s, 1972m, 1940w. Three of these extracts were combined and concentrated to obtain 1 $^{31}P\{^1H\}$ NMR spectrum which was identical with that of starting complex **2** [13]. The quantitative analysis of both the unused catalyst and the used catalyst were compared via HPLC. The unused catalyst had values that ranged between values of 2.2–2.4 wt% loading and the used catalyst had values that ranged from 2.1–2.3 wt%.

5.3. Spent Cab-o-sil control experiment

After the catalyst was extracted from the Cab-o-sil (*vide supra*) the Cab-o-sil was dried under a flow of pure H_2 (30 ml/min) and heated to 40°C for 1.5 h. The flow of carrier gas (H_2) was then routed through the substrate saturator, adjusted to flow rate of 4 ml/min and the system was allowed to come to equilibrium (2 h). Aliquots were drawn at 25°C and 40°C without any discernible isomerization or hydrogenation products.

5.4. Effect of temperature cycling using $Ru_3(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2$ *(2)*

The same reaction conditions and sampling were used in this experiment as described in the general method. Aliquots were obtained initially at 25°C and as the catalyst was cycled twice to 140°C. The elliptical IR heater ensured that heat transfer was rapid < 5 min. At each temperature, the system was allowed to equilibrate for one hour before aliquots were taken. Three samplings were taken for each temperature. Each temperature was maintained for 2 1/2 h. The data in Table 5 reflect the average of these samplings.

5.5. Low pressure homogeneous hydrogenation of 1-octane using $Ru_3(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2$ *(2)*

1-Octene (1.08 g, 9.56 mmol) was added to cluster **2** (16.5 mg, 0.0156 mmol) in toluene (15 ml). The reaction vessel was pressurized with 2 atm of H_2 and heated to 115°C and stirred for 17 h. Analysis by gas chromatography gave the following product distribution; octane (10.3%), *trans*-2-octene (2.5%), *cis*-2-octene (2.3%) and octene (84.7%). The crude reaction mixture was concentrated and chromatographed using alumina. Complex **2** was eluted by using a 2% ethyl acetate/hexane (v/v) solution (14.9 mg, 90%).

5.6. Effect of Lewis acid upon homogeneous hydrogenation of 1-octene catalyzed by $Ru_3(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2$ *(2)*

Complex **2** (16.5 mg, 0.0156 mmol) and 1-octene (1.08 g., 9.56 mmol) in toluene (15 ml) was added to $Et_2O:BF_3$ (1.94 mg, 0.0156 mmol). The reaction vessel was pressurized with 2 atm of H_2 and heated to 115°C and stirred for 17 h. Analysis by gas chromatography afforded octane (14.6%), *trans*-2-octene (4.5%), *cis*-2-octene (3.6%), and 1-octene (78.3%). The catalyst was recovered (13.4 mg, 82%) using the same method as above (*vide supra*).

5.7. High pressure homogeneous hydrogenation of 1-octene using $Ru_3(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2$ *(2)*

A 30 ml Parr bomb with a glass sleeve was charged with **2** (5.0 mg, 0.00474 mmol), 1-octene 10.7 g, 6.37 mmol), and toluene (10.0 ml). The reaction vessel was pressurized to 54 atm of H_2 and heated to 120°C and stirred for 2 h. Analysis by gas chromatography revealed 100% conversion of 1-octene into octane. The catalyst was recovered (2.0 mg, 40%) using the same method as above (*vide supra*).

Acknowledgments

We gratefully acknowledge the financial support of Alcon Laboratories and the Robert A. Welch Foundation.

References

1 For the preceding paper in this series see: E.P. Kyba, M.C. Kerby, R.P. Kashyap, J.A. Mountzouris and R.E. Davis, *J. Am. Chem. Soc., 112* (1990) 905.

2 (a) P.A. Shapley, *Annual Survey of Ruthenium and Osmium for the Year 1986, J. Organomet. Chem., 351* (1988) 145; (b) T. Koudo, S. Yoshii, Y. Tsuji and Y. Watanabe, *J. Mol. Catal., 50* (1989) 31; (c) L.C. Freriks, C.P. deJong-Versloot, A.G.T.G. Kortbeek and J.P. Vandenberg, *J. Chem. Soc., Chem. Commun.*, (1986) 253; (d) T. Venäläinen, T.A. Pakkanen, T.T. Pakkanen and E. Ilskola, *J. Organomet. Chem., 314* (1986) C49; (e) J.A. Smiejy, J.E. Gozum and W.L. Gladfelter, *Organometallics, 5* (1986) 2154; (f) M.J. Sailor, C.P. Brock and P.F. Shriver, *J. Am. Chem. Soc., 109* (1987) 6015.

3 S. Gao and L.D. Schmidt, *J. Catal., 115* (1989) 356.

4 (a) P. Moggi, G. Predier, G. Albanesi and P. Stavros, *Appl. Catal., 53* (1989) L1; (b) A.P. Walker, T. Rayment and R.M. Lambert, *J. Catal., 117* (1989) 102.

5 B.J. Tatarchuk, Y. Kuo and R. Cocco, *J. Catal., 112* (1988) 250.

6 S. Uchiyama and B.C. Gates, *J. Catal., 110* (1988) 388.

7 C.S. Navasimhan, V.M. Deshpande and K. Ramnorayan, *Appl. Catal., 48* (1989) L1.

8 (a) J.G. Goodwin, Jr., S. Goa, D.O. Erdal and F.H. Rogan, *Appl. Catal., 24* (1986) 199; (b) J. Robertson and G. Webb, *Proc. Roy. Soc., 341* (1974) 383.

9 (a) H.H. Lamb and B.C. Gates, *J. Am. Chem. Soc., 108* (1986) 81; (b) R. Pierantozzi, E.G. Valagene, A.F. Nordquist and P.N. Dyer, *J. Mol. Catal., 21* (1983) 189.

10 V.D. Alexieu, N. Binsted, J. Evans, G.N. Greaves and R.J. Price, *J. Chem. Soc., Chem. Commun.*, (1987) 395.

11 (a) R.G. Finke, G. Gaughan, C. Pierpoint and M.E. Cass, *J. Am. Chem. Soc., 103* (1981) 1394; (b) A.J. Carty, *Adv. Chem. Ser., 196* (1982) 163; (c) P. Braunstein, D. Mott, O. Fars, M. Louer, D. Grandjean, J. Fisher and A.J. Mitschler, *J. Organomet. Chem., 213* (1981) 79; (d) H.C. Foley, W.D. Finch, C.G. Pierpoint and G.L. Goeffroy, *Organometallics, 1* (1982) 1379; (e) W.C. Fultz, A.L. Rheingold, P.E. Kreter and D.W. Meek, Inorg. Chem., 22 (1983) 860; (f) A.D. Harley, G. Guskey and G.L. Geoffroy, *Organometallics, 2* (1983) 53; (g) J.M. Ritchey, A.J. Zozulin, D.A. Wrobleski, R.R. Ryan, H.J. Wasserman, D.C. Moody and R.T. Paine, *J. Am. Chem. Soc., 107* (1985) 501; (h) G.N. Mott, R. Grandby, S.A. MacLaughlin, N.J. Taylor and A.J. Carty, *Organometallics, 2* (1983) 189.

12 (a) E.P. Kyba, M.C. Kerby and S.P. Rines, *Organometallics, 5* (1986) 1189; (b) E.P. Kyba, J.D. Mather, K.L. Hassett, J.S. McKennis and R.E. Davis, *J. Am. Chem. Soc., 106* (1984) 5371; (c) E.P. Kyba, M.C. Kerby, R.P. Kashyap, J.A. Mountzouris and R.E. Davis, *Organometallics 8* (1989) 852.

13 (a) C. Clubb, PhD Dissertation, University of Texas at Austin, 1986; (b) M.D. Soucek, PhD Dissertation, University of Texas at Austin, August 1990.

14 (a) B.J. Tatarchuk and Y. Kuo, *J. Catal., 112* (1988) 229; (b) L.

d'Ornelas, H. Theolier, A. Choplin and J.M. Basset, in Y. Yermakav and V. Likholobou (eds.), *Homogeneous and Heterogeneous Catalysis: Proceedings of the Fifth International Symposium on Relations between Homogeneous and Heterogeneous Catalysis*, VNU Science Press, Utrecht, Netherlands, 1986.

15 H. Knözinger and B.C. Gates, in B.C. Gates, L. Guczi and H. Knözinger (eds.), *Metal Clusters in Catalysis*, Elsevier, Amsterdam, 1986, p. 531.

16 (a) C.U. Pittman, Jr., G.M. Wilemon, W.D. Wilson and R.C. Ryan, *Angew. Chem., Int. Ed. Engl., 19* (1980) 478; (b) C.U. Pittman, H. Hilal, M.-J. Don and M.G. Richmond, in W.E. Pascoe (ed.), *Catalysis of Organic Reactions*, Marcel Dekker: New York, 1992, Chapter 27; (c) C.U. Pittman, M.G. Richmond, G.M. Wilemon and M. Absi-Halabi, in J.R. Kosak (ed.), *Catalysis of Organic Reactions*, Marcel Dekker, New York, 1984, Chapter 5.

17 (a) G. Lavigne, N. Lugan and J.-J. Bonnet, *Organometallics, 1* (1982) 1040; (b) N. Lugan, J.-J. Bonnet and J.A. Ibers, *J. Am. Chem. Soc., 107* (1985) 4484; (c) C. Bergounhou, P. Fompeyrine, G. Commenges and J.-J. Bonnet, *J. Mol. Catal., 48* (1988) 285.

18 M.J.D. Low, and J.A. Susumano, *J. Can. Chem., 47* (1969) 3906.