

## Catalytic Activity of Polynuclear Platinum Carbonyl Anions in Homogeneous Hydrogenation Reactions

By Sumit Bhaduri \* and Krishna R. Sharma, Alchemie Research Centre Private Limited, CAFI Site, P.O. Box 155, Thane-Belapur Road, Thane 400 601, Maharashtra, India

The homogeneous hydrogenation of benzaldehyde, heptanal, cyclohexanone, cyclohexene, acetonitrile, and benzonitrile has been studied using  $[\text{NBu}^n_4]_2[\{\text{Pt}_3(\text{CO})_6\}_n]$  (1) as the catalyst over a range of temperature (40–80 °C) and pressure (20–64 lbf in<sup>-2</sup>). Infrared spectroscopic studies suggest the formation of a common intermediate in reactions carried out at  $\geq 60$  °C. Benzaldehyde is the most readily hydrogenated; the nature of the products depends on the pressure of hydrogen used and is selective to either benzyl alcohol or a mixture of benzene and methanol. Kinetic studies on the rate of benzyl alcohol formation indicate a first-order dependence of the rate on the concentration of (1). While the rate shows a Michaelis–Menten type of dependence on the PhCHO concentration, it seems to be independent of H<sub>2</sub> pressure in the range 20–25 lbf in<sup>-2</sup>. Under these conditions, a value of 63.81 kJ mol<sup>-1</sup> for the activation energy is obtained from the Arrhenius plot. A tentative mechanism for PhCHO hydrogenation is discussed.

HOMOGENEOUS catalysis by cluster complexes has attracted considerable attention in the last few years.<sup>1</sup> It has been proposed that such reactions could give a valuable insight into the catalytic reactions involving metal surfaces.<sup>2</sup> The presence of more than one metal atom in a cluster molecule also gives rise to the possibility of catalytic activities in reactions, where multicentre interactions might be important. Examples of the use of clusters as catalytic precursors in the Water Gas shift reaction,<sup>3</sup> selective formation of ethane<sup>4</sup> or ethylene glycol from synthesis gas,<sup>5</sup> hydroformylation with water as a source of hydrogen,<sup>6</sup> and oxidation of hydrocarbons<sup>7</sup> have been reported in the last 10 years. The catalytic activity of  $[\text{Ru}_4\text{H}_4(\text{CO})_{12}]$  and its phosphine derivatives in various hydrogenation and isomerisation reactions as well as the application of a rhodium cluster carbonyl anion for the hydrogenation of nitrobenzene to aniline have also been recently reported.<sup>8–10</sup>

Elegant syntheses of platinum cluster carbonyl anions of general formula  $[\{\text{Pt}_3(\text{CO})_6\}_n]^{2-}$  ( $n = \approx 10, 6, 5, 4, 3, 2$ , or 1) were reported by Longoni and Chini<sup>11</sup> in 1976. The molecular structures of the dianions ( $n = 5, 4, 3$ , or 2) have also been unequivocally established by single-crystal X-ray techniques.<sup>11,12</sup>

We decided to study the catalytic activities of some of these complexes in the homogeneous hydrogenation of a number of unsaturated organic compounds. Metallic platinum in the dispersed state is known to be an efficient catalyst for such reactions. The studies reported here could, therefore, be considered as an attempt to validate the hypothesis that clusters, to a first approximation, may be used as models for surfaces.

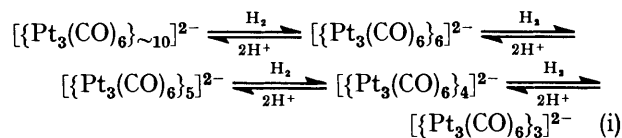
### RESULTS AND DISCUSSION

*Semiquantitative Studies on the Hydrogenation of Model Alkenes, Ketones, Nitriles, and Aldehydes.*—Two potential problems are encountered in the study of cluster-catalysed homogeneous reactions. First, it is difficult to demonstrate experimentally that the catalytically active intermediate(s) is in fact a polynuclear rather than a mononuclear species. Secondly, under

drastic conditions or with fragile clusters, the possibility of decomposition to the metal exists. Catalysis could then occur by finely divided metal particles rather than by the parent molecular cluster. In this work we have used i.r. spectroscopy and kinetic studies to eliminate any uncertainty with regard to both these aspects (see later). The standard technique of illuminating the solution with a bright light source to check that deposition of metal has not taken place has also been used for each system described. Furthermore, filtration of the solutions through Kieselguhr layers during the catalytic runs does not alter the observed activities.

Most of the catalytic runs were carried out with a hydrogen pressure in the range 20–50 lbf in<sup>-2</sup>† and at a temperature of 40–80 °C. The unsaturated organic compound was used as a solvent in several cases, e.g. PhCHO, (CH<sub>3</sub>)<sub>2</sub>CO, CH<sub>3</sub>CN, and PhCN hydrogenation. In other cases, for reasons of lack of solubility, tetrahydrofuran (thf) was used as the solvent. Because of the comparatively low boiling point of thf, diglyme was used as the solvent for kinetic studies involving PhCHO (see later). In most of the catalytic runs, the compound  $[\text{NBu}^n_4]_2[\{\text{Pt}_3(\text{CO})_6\}_5]$  (1) was added as the catalytic precursor.

According to Longoni and Chini,<sup>11</sup> the platinum cluster carbonyl anions activate hydrogen and react with acids as shown in the reaction sequence (i). Several



physicochemical factors, such as pH measurements, the formation of hydrogen on treatment with free acids, characteristic and sequential colour, and i.r. spectroscopic changes on exposure to hydrogen support the above equilibria. Trace quantities of water were found to affect the forward reactions favourably, probably by

† Throughout this paper: 1 lbf in<sup>-2</sup>  $\approx 7.09 \times 10^3$  Pa; 1 Torr = (101 325/760) Pa.

solvating the protons. Longoni and Chini<sup>11</sup> also reported unsuccessful attempts to detect hydride intermediates, if any, that might be involved in these reactions.

Since all the catalytic experiments discussed here involve thoroughly dried solvents and reagents, stepwise reduction of (1) to  $[\{Pt_3(CO)_6\}_3]^{2-}$  has been found to be primarily dependent on the  $H_2$  pressure and reaction temperature. At moderate temperatures and pressures ( $\leq 40^\circ C$ ,  $\leq 20$  lbf in<sup>-2</sup>), conversion of (1) into  $[\{Pt_3(CO)_6\}_3]^{2-}$ , as judged by the colour and i.r. spectroscopic changes, is rather slow ( $t_{\frac{1}{2}} \geq 12$  h). This conversion could be speeded up by increasing either the temperature ( $\geq 60^\circ C$ ) or pressure ( $\geq 34$  lbf in<sup>-2</sup>). The persistence of the violet-red colour of  $[\{Pt_3(CO)_6\}_3]^{2-}$  and i.r. spectroscopic studies show that *only* an increase in the hydrogen pressure at moderate temperatures ( $\leq 40^\circ C$ ) causes the trimeric species not to undergo any further changes. However, with an increase in temperature and under an atmosphere of hydrogen,  $[\{Pt_3(CO)_6\}_3]^{2-}$  changes into (2), a single complex or a mixture of complexes of as yet uncharacterised red-brown carbonyl species with characteristic i.r. bands at 2 024, 1 990, and 1 815 cm<sup>-1</sup> (Figure 1).

The rate of conversion of  $[\{Pt_3(CO)_6\}_3]^{2-}$  into (2) shows a marked dependence on temperature. Thus, at  $80^\circ C$  and 20 lbf in<sup>-2</sup> of  $H_2$ , complete conversion is achieved in *ca.* 3–4 h, whereas at  $60^\circ C$  under the same pressure the time taken is about 10 h. This conversion does not appear to be solvent dependent since virtually the same i.r. spectrum attributable to (2) was obtained in PhCHO, thf, or PhCN (see Table).

For all the model unsaturated organic compounds, the time for a typical catalytic run was *ca.* 12 h. The i.r. spectra recorded at the end of this period were similar to that of (2), except in cases where the reaction temperature was  $\leq 40^\circ C$ . Due to the low boiling points of some of the reactants and expected products, the reaction temperatures in certain cases were deliberately kept low. Thus, acetone and acetonitrile hydrogenation reactions are carried out at  $40^\circ C$  under a hydrogen pressure of

54 lbf in<sup>-2</sup> (see Table). Under these conditions, conversion of (1) into  $[\{Pt_3(CO)_6\}_3]^{2-}$  is complete within 1 h and there is no observable evidence for the formation of (2) at any stage of the reactions.

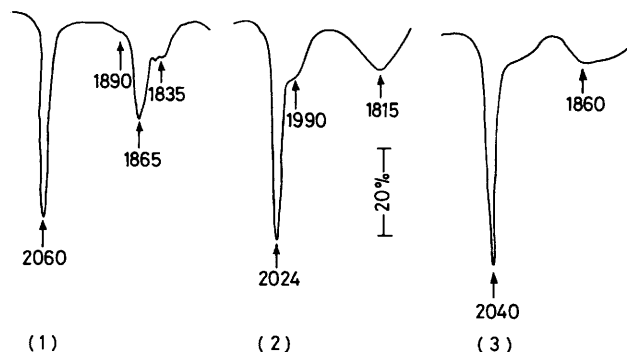


FIGURE 1 Infrared spectra of (1) (150 mg), (2), and (3) in PhCHO (10 cm<sup>2</sup>). Wavenumbers in cm<sup>-1</sup>.

The Table lists turnover numbers, reaction conditions, and other details for various catalytic runs. It can be seen that, apart from benzaldehyde, where the catalytic activity is relatively high, the turnover numbers are rather low. Although total conversion into aniline is observed for nitrobenzene, decomposition of the cluster to finely divided metal takes place. In all other cases illumination with a bright light source shows that deposition of metal does not occur. Furthermore, the total intensity of the carbonyl i.r. bands remains more or less unaltered throughout the course of all the reactions. Had the cluster broken down to finely divided metal, some loss in the intensity of the carbonyl bands would have been expected.

On the basis of the i.r. spectra, it appears that the same species, *i.e.* (2), is involved in the catalytic hydrogenation reactions where the operating temperature is above  $60^\circ C$ . In addition, instead of (1), both  $[\{Pt_3(CO)_6\}_4]^{2-}$  and  $[\{Pt_3(CO)_6\}_3]^{2-}$  salts could be added as catalysts to give more or less the same quantitative results. The role of (1), or for that matter  $[\{Pt_3(CO)_6\}_4]^{2-}$

#### Details of homogeneous catalysis by (1)

Reactant	Product	Reaction conditions			Turnover number (h) <sup>-1</sup>	I.r. bands (cm <sup>-1</sup> ) at the end of the reaction
		θ, °C	Pressure/lbf in <sup>-2</sup>	Solvent		
Benzaldehyde	Benzyl alcohol	80	20	None	18.3 <sup>a</sup> (1.4) <sup>b</sup>	2 024s, 1 990br, m, 1 815br, m
Benzaldehyde	Benzyl alcohol	80	34	None	23.0 <sup>b</sup> (0.9) <sup>a</sup>	As above
Benzaldehyde	Benzene + methanol	80	64	None	23.5 <sup>b</sup> (1.03) <sup>a</sup>	As above
Benzaldehyde	Benzyl alcohol	80	20	Diglyme	18.7 <sup>a</sup> (1.6) <sup>b</sup>	As above <sup>c</sup>
Benzaldehyde	Benzene + methanol	80	20	Diglyme	18.7 <sup>a</sup> (1.6) <sup>b</sup>	As above <sup>c</sup>
Heptanal	Heptanol	60	44	thf	0.3	As above <sup>c</sup>
Cyclohexanone	Cyclohexanol	60	44	thf	0.4	As above <sup>c</sup>
Benzonitrile	Benzylamine	80	44	None	3.8	As above <sup>c</sup>
Acetone	No reaction	40	44	None		
Acetonitrile	Ethylamine	40	44	None	2.6	2 032s, 1 856br, m
Cyclohexene	Cyclohexane	60	44	thf	0.2	As above
Nitrobenzene	Aniline <sup>d</sup>	80	44	None	Complete conversion	

<sup>a</sup> Turnover number based on PhCH<sub>2</sub>OH, defined as mmol of product/(mmol of catalyst × time). <sup>b</sup> Turnover number based on benzene and methanol. <sup>c</sup> Because of the change in the solvent, the i.r. band positions change at the most by  $\pm 5$  cm<sup>-1</sup>. However, the essential pattern remains the same. <sup>d</sup> Decomposition to metal takes place.

or  $[\{\text{Pt}_3(\text{CO})_6\}_3]^{2-}$ , is therefore to generate the catalytically active intermediate (2). The kinetic studies reported for the hydrogenation of PhCHO (see later) are repeatable starting with the tetramer or the trimer. One of the factors responsible for the low turnover numbers for cyclohexanone, heptanal, and cyclohexene is certainly the comparatively low (60 °C) operating temperature. As has already been mentioned, at this temperature, complete conversion of (1) into (2) requires approximately 10 h. Hydrogenation with (2) as the catalyst therefore takes place in only *ca.* 2 h, while in the case of PhCHO the length of this period is *ca.* 9 h.

All attempts to characterize (2), by  $^1\text{H}$  n.m.r. spectroscopy, microanalysis, or by obtaining a single crystal suitable for X-ray diffraction work, have so far been unsuccessful. On the basis of the i.r. data the complex does not appear to be related to the  $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$  tetra-anion reported by Washecheck *et al.*<sup>13</sup> in 1979. Species (2) is only stable in solution for any length of time ( $\geq 5$  min) if a positive hydrogen pressure is maintained; otherwise precipitation of metal takes place. This seems to suggest the presence of labile metal-hydrogen bonds. The appearance of a broad carbonyl band at  $1815\text{ cm}^{-1}$  indicates a bridging carbonyl group, *i.e.* the involvement of at least two metal atoms in the molecular framework of (2).

As was mentioned earlier, for reactions at low operating temperatures ( $\leq 40\text{ }^\circ\text{C}$ ) there is no evidence for the formation of (2). However, quantitative conversion of (1) into  $[\{\text{Pt}_3(\text{CO})_6\}_3]^{2-}$  takes place and the trimeric species remains unchanged throughout the course of the reaction. The slight catalytic activity seen in the case of MeCN and in the first 3–4 h of PhCHO hydrogenation (see later) must therefore be attributed to the hypothetical hydridic species involved in the conversion of (1) into  $[\{\text{Pt}_3(\text{CO})_6\}_3]^{2-}$ . Interestingly,  $[\{\text{Pt}_3(\text{CO})_6\}_4]^{2-}$  was found to be catalytically active for hydroformylation reactions by Longoni and Chini,<sup>11</sup> and this was interpreted as being indicative of the involvement of hydridic species.

The formation of benzene and methanol from benzaldehyde under a comparatively high  $\text{H}_2$  pressure ( $\geq 34\text{ lbf in}^{-2}$ ) is rather intriguing. It must be assumed that PhCHO is first converted into PhCH<sub>2</sub>OH, hydrogenolysis of which leads to the formation of PhH and MeOH. It should be noted that other hydrogenolysis products, such as toluene and water, which necessitate the cleavage of carbon-oxygen rather than carbon-carbon bonds, are not formed even in trace quantities. The authenticity of this observation has been checked by carrying out separate hydrogenolysis experiments with PhCH<sub>2</sub>OH as the reactant. In all the high-pressure PhCHO hydrogenation experiments, almost exclusive (*ca.* 94%) conversion of PhCH<sub>2</sub>OH into benzene and methanol has been observed. At a relatively low hydrogen pressure ( $\leq 20\text{ lbf in}^{-2}$ ), however, PhCH<sub>2</sub>OH is the major product and little PhH and MeOH are formed.

The possibility of (2) being a mixture of cluster carbonyl species has already been mentioned. Further-

more, because of the broadness of the i.r. bands, formation of a new species under  $\text{H}_2$  pressures  $\geq 34\text{ lbf in}^{-2}$ , accompanied by fine changes in the i.r. spectrum, would not be observable. In other words, it is impossible to say on the basis of the i.r. spectra whether or not the observed frequencies reflect the presence of at least two different intermediates. The other alternative is that the rate of conversion of PhCH<sub>2</sub>OH into PhH and MeOH essentially depends on the applied  $\text{H}_2$  pressure, but is catalysed by the same intermediate (2).

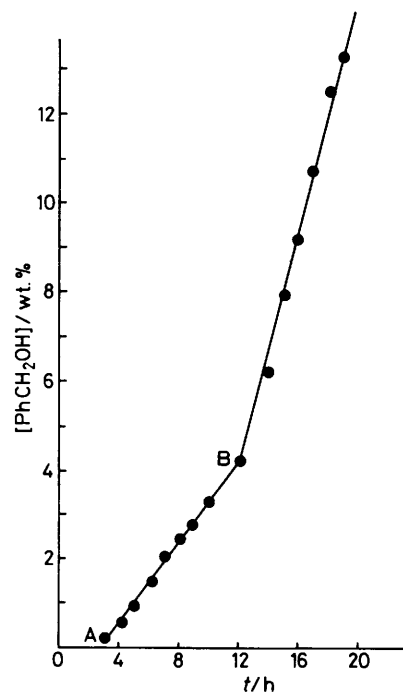


FIGURE 2 Yield of PhCH<sub>2</sub>OH with respect to time. Reaction carried out at 80 °C, 20 lbf in<sup>-2</sup> of H<sub>2</sub> in neat PhCHO (10 cm<sup>3</sup>) and (1) (150 mg) as the catalytic precursor

**Kinetic Studies on the Hydrogenation of PhCHO.**—At a hydrogen pressure  $\leq 20\text{ lbf in}^{-2}$ , 95% of benzaldehyde is converted into benzyl alcohol. Under these conditions, kinetic studies to determine the dependence of the rate of PhCH<sub>2</sub>OH formation on the concentration of PhCHO, the concentration of (1),  $\text{H}_2$  pressure, and temperature have been performed. The compound PhCHO itself has been used as a solvent in the experiments involving variation in temperature, concentration of (1), or  $\text{H}_2$  pressure. Due to the relatively low boiling point of thf it could not be used as a solvent. In order to determine the effect of a variation in PhCHO concentration, therefore, diglyme was used as a solvent.

The hydrogenation of PhCHO, monitored by quantitative product analyses for 24 h, under a hydrogen pressure of 20 lbf in<sup>-2</sup> and at 80 °C (Figure 2), reveals the following points. For the first 3–4 h, the time necessary for complete conversion of (1) into (2), little catalytic activity is observed. The hypothetical hydridic intermediates involved in the conversion of (1) into  $[\{\text{Pt}_3(\text{CO})_6\}_4]^{2-}$  and then to  $[\{\text{Pt}_3(\text{CO})_6\}_3]^{2-}$  might be the active

species at this stage. Conversion of the trimeric species into (2) might involve similar hydridic intermediates which could also contribute to the observed activity. However, as can be seen from the i.r. spectra in Figure 1, the end of this period corresponds to the complete conversion of (1) into (2). Steady conversion of PhCHO into PhCH<sub>2</sub>OH then continues for 8–10 h (curve AB in Figure 2), after which a change in mechanism is observed. This is accompanied by the conversion of (2) into (3), some other single cluster carbonyl species, or a mixture thereof, having the carbonyl band positions shown in Figure 1. The i.r. spectrum of (3) (Figure 1) is that of a sample removed after 20 h of reaction. The conversion of (2) into (3) is a gradual process which only becomes noticeable around point B of Figure 2. For experimental convenience as well as better reproducibility the kinetic studies have been confined to the *initial* rate in the AB region of Figure 2.

Variation of the concentration of (1) in neat PhCHO at 80 °C and 20 lbf in<sup>-2</sup> of H<sub>2</sub> shows the rate to be directly proportional to it (Figure 3). Since, under the reaction

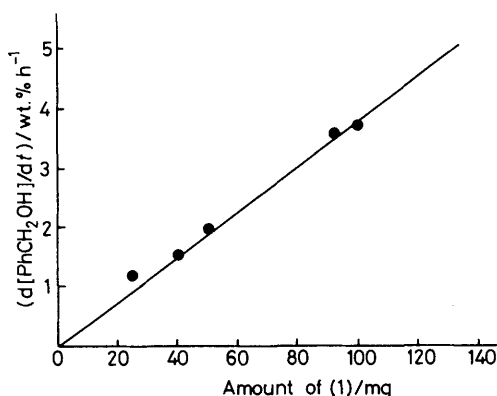


FIGURE 3 Variation of the rate of PhCH<sub>2</sub>OH formation with the concentration of (1). All reactions carried out in neat PhCHO at 80 °C with 20 lbf in<sup>-2</sup> H<sub>2</sub>

conditions, (1) is quantitatively converted into (2), it could be said that the rate is directly proportional to the concentration of (2). Had the rate-determining step been preceded by the establishment of a rapid equilibrium between (1) and a mononuclear species, this simple relationship would not have been expected. Although not conclusive, the first-order dependence of the rate on the concentration of (1), therefore, suggests no involvement of mononuclear species.

Under the same experimental conditions, variation in the concentration of PhCHO in diglyme as solvent manifests Michaelis-Menten type kinetics. This is shown in Figure 4 where rate is plotted against PhCHO concentration. As can be seen from Figure 5, a plot of the inverse of the rate against the inverse of PhCHO concentration gives a straight line. This suggests the formation of an activated complex between the catalytically active intermediate (2) and PhCHO.

Since at higher pressure, PhCH<sub>2</sub>OH is converted into PhH and MeOH (see above), it has not been possible to

determine the order with respect to H<sub>2</sub> pressure. However, a minor variation in H<sub>2</sub> pressure (< 6 lbf in<sup>-2</sup>) has no observable effect on the rate of PhCH<sub>2</sub>OH formation. The variation in the rate with respect to temperature yields a reasonably good Arrhenius plot (Figure 6). The energy of activation is found to be 63.81 kJ mol<sup>-1</sup>.

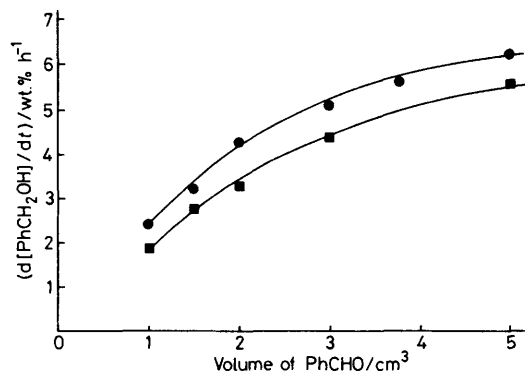


FIGURE 4 Variation of the rate of PhCH<sub>2</sub>OH formation with the concentration of PhCHO: amount of (1) = 20 (■), 30 mg (●). All reactions carried out in diglyme at 80 °C with 20 lbf in<sup>-2</sup> H<sub>2</sub>

Based on the kinetic evidence, a tentative mechanism as shown in the Scheme is proposed. Species (2) is assumed to be a polynuclear hydridic complex, and is formed in step (a) from (1) through successive reduction steps. This is followed by the establishment of a rapid equilibrium step (b), between (2), PhCHO, and the

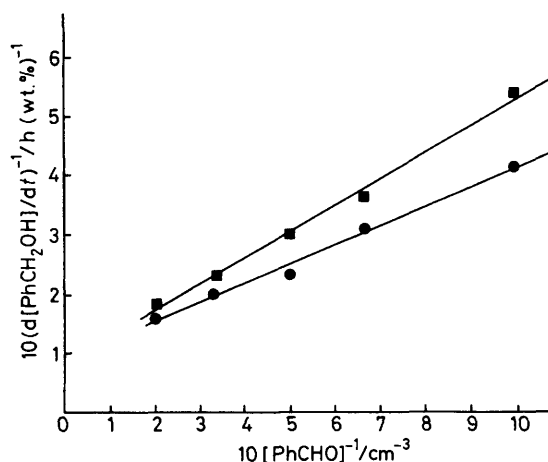


FIGURE 5 Variation of the inverse of rate of PhCH<sub>2</sub>OH formation with the inverse of concentration of PhCHO: amount of (1) = 20 (■), 30 mg (●). All reactions carried out in diglyme at 80 °C with 20 lbf in<sup>-2</sup> H<sub>2</sub>

activated complex, schematically represented as either (4a) or (4b). Since a well characterized complex with the type of bonding shown for (4b) has already been isolated in the reaction of PhCH<sub>2</sub>OH and [Os<sub>3</sub>(CO)<sub>12</sub>], formulation (4b) for the activated complex seems more than likely.<sup>14</sup> In step (c), slow transfer of the other hydride to the alkoxo-group leads to the elimination of PhCH<sub>2</sub>OH and the generation of an unsaturated species

(5) which, in step (d), rapidly reacts with  $H_2$  to complete the catalytic cycle.

It is interesting to note that the above mentioned alkoxo-compound  $[Os_3H(CO)_{10}(OCH_2Ph)]$ , formed from

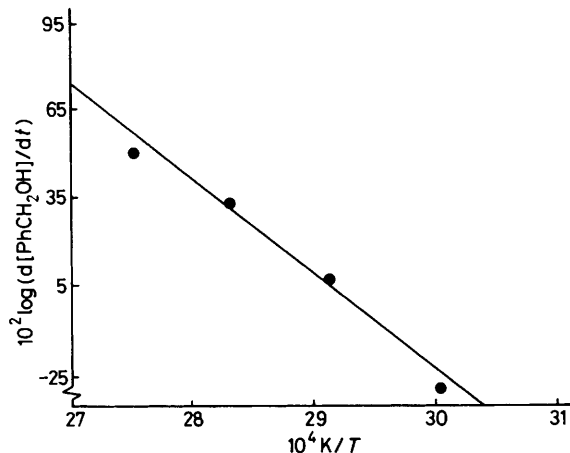
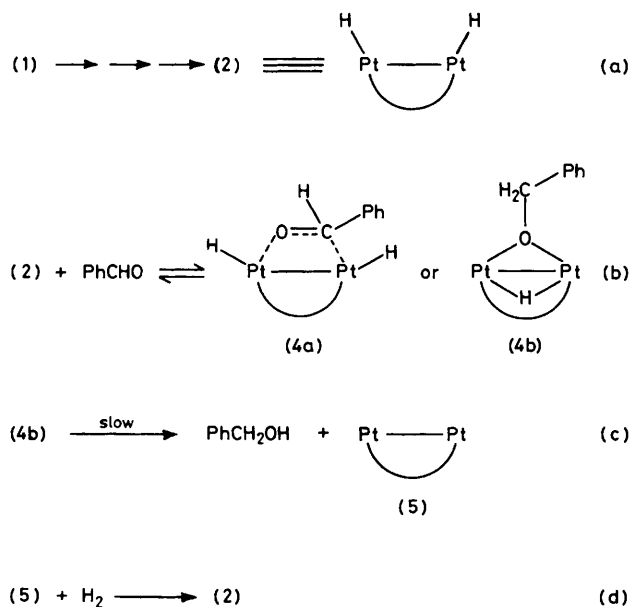


FIGURE 6 Variation of the logarithm of the rate of  $PhCH_2OH$  formation with the inverse of temperature. All reactions carried out in neat  $PhCHO$  ( $10\text{ cm}^3$ ) with (1) (150 mg) as the catalyst and an  $H_2$  pressure of  $20\text{ lbf in}^{-2}$

$[Os_3(CO)_{12}]$  and  $PhCH_2OH$ , gives  $PhH$  and  $PhCHO$  when heated in a sealed tube.<sup>14</sup> The formation of benzene is assumed to take place *via* the *ortho*-metallated  $[Os_3H_2(CO)_9(OCH_2C_6H_4)]$  and the benzyne compound  $[Os_3H_2(CO)_9(C_6H_4)]$ . Conversion of the *ortho*-metallated



SCHEME

species into the benzyne compound is accompanied by the elimination of  $CO$  and  $H_2$ . As has already been mentioned, at  $H_2$  pressures  $\geq 34\text{ lbf in}^{-2}$ , selective formation of benzene and methanol takes place. It is reasonable to assume that the same intermediate, (4b), under comparatively high  $H_2$  pressures is converted into

(5) and a mixture of  $PhH$  and  $MeOH$ . In this case, however, the possibility of formation of a benzyne-type intermediate through the elimination of  $CO$  and  $H_2$  is obviously ruled out. A similar reaction involving ready cleavage of  $C-C$  bonds in  $\alpha$ -hydroxyalkynes, *e.g.*  $PhC\equiv C-CMePhOH$ , in the presence of  $[Ru_3(CO)_{12}]$  and  $[Os_3(CO)_{12}]$  has been recently reported by Deeming and co-workers.<sup>15</sup>

#### EXPERIMENTAL

The platinum cluster carbonyls were prepared according to previously reported procedures.<sup>10</sup> Gas-liquid chromatographic (g.l.c.) analysis was performed with a Pye-Unicam 204 instrument. The reproducibility of each conversion was within  $\pm 2\%$ . Conversion data obtained from two separate experiments were averaged to obtain mean values. Infrared spectra were recorded on a Perkin-Elmer 377 grating spectrophotometer. All solvents and organic compounds were thoroughly dried and distilled under nitrogen before use. Ultrapure and freshly distilled benzaldehyde was used for each experiment since the presence of trace quantities of benzoic acid gave rise to irreproducible results. The air sensitivity of the cluster carbonyls required thorough degassing of all solvents and reagents. The catalytic precursor,  $[NBu_4]_2[Pt_3(CO)_6]_2$ , was not usually stored for more than 2 d, even under an atmosphere of ultrapure argon or under vacuum ( $10^{-3}$  Torr). Prolonged storage of the complex under vacuum led to the formation of pyrophoric, very finely divided platinum metal. The effect of counter ions, other than  $[NBu_4]^+$ , on the catalytic activities, if any, was not studied since the  $[NBu_4]^+$  salt was found to be more stable.

Experiments involving hydrogen pressures  $\geq 34\text{ lbf in}^{-2}$  were carried out in a low-pressure Parr hydrogenation apparatus. Double-jacketted pressure bottles were used for these experiments and a constant temperature was maintained by a flow of water through the outer jacket.

*Kinetic Experiments.*—These experiments were carried out in a double-jacketted vessel with a flat bottom, maintained at a constant temperature by a flow of water through the outer jacket. Thoroughly degassed  $PhCHO$ , or a mixture of  $PhCHO$  and diglyme, was placed in the reaction vessel, and a pressure of  $20\text{ lbf in}^{-2}$  of hydrogen was maintained through a manifold connected directly to a hydrogen gas cylinder. Use of the manifold enabled us to carry out three kinetic runs simultaneously. A solution of  $[NBu_4]_2[Pt_3(CO)_6]_2$  of known concentration in  $PhCHO$ , or  $PhCHO$  and diglyme, was injected through a serum cap into the reaction mixture. This mixture was then vigorously stirred with a magnetic stirrer. Samples were withdrawn at suitable time intervals (0.5 or 1 h) and analysed by i.r. spectroscopy and g.l.c. with chlorobenzene as the internal standard.

We thank Mr. N. Y. Sapre, Mr. P. Y. Shrotri, and Mr. M. Chakraborty for experimental assistance.

[1/1006 Received, 22nd June, 1981]

#### REFERENCES

- A. L. Robinson, *Science*, 1976, **194**, 1150, 1261; E. L. Muetterties, K. G. Caulton, M. G. Thomas, and B. A. Sosinsky, *Proc. Natl. Acad. Sci. USA*, 1976, **73**, 4274; E. L. Muetterties, *Science*, 1977, **196**, 839.
- E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, 1979, **79**, 91.

- <sup>3</sup> C. Ungermaun, V. Landis, S. A. Moya, H. Cohen, H. Walker, R. G. Pearson, R. G. Rinker, and P. C. Ford, *J. Am. Chem. Soc.*, 1979, **101**, 5922.
- <sup>4</sup> G. C. Demitras and E. L. Muetterties, *J. Am. Chem. Soc.*, 1977, **99**, 2796.
- <sup>5</sup> U.S.P., 3,878,290/1975; 3,878,292/1975.
- <sup>6</sup> R. M. Laine, *J. Am. Chem. Soc.*, 1978, **100**, 6451; H. Kang, C. H. Mauldin, T. Cole, W. Slegeir, K. Cann, and R. Pettit, *ibid.*, 1979, **101**, 8323.
- <sup>7</sup> D. M. Roundhill, M. K. Dickson, N. S. Dixit, and B. P. Sudha-Dixit, *J. Am. Chem. Soc.*, 1980, **102**, 5538.
- <sup>8</sup> G. A. Vaglio and M. Valle, *Inorg. Chim. Acta*, 1978, **30**, 161; P. M. Lausarot, G. A. Vaglio, and M. Valle, *ibid.*, 1977, **25**, L107.
- <sup>9</sup> P. Frediani, U. Matteoli, M. Bianchi, F. Piaceuti, and G. Manchi, *J. Organomet. Chem.*, 1978, **150**, 273; C. Bolteghi, S. Gladiali, M. Bianchi, U. Matteoli, P. Frediani, P. G. Vergamini, and E. Benedetti, *ibid.*, 1977, **140**, 221.
- <sup>10</sup> R. C. Ryan, G. M. Wilemon, M. P. Dalsanto, and C. U. Pittman, *J. Mol. Catal.*, 1979, **5**, 319.
- <sup>11</sup> G. Longoni and P. Chini, *J. Am. Chem. Soc.*, 1976, **98**, 7225.
- <sup>12</sup> J. C. Calabrese, L. F. Dahl, P. Chini, G. Longoni, and S. Mertinengo, *J. Am. Chem. Soc.*, 1974, **96**, 2614.
- <sup>13</sup> D. M. Washecheck, E. J. Wucherer, L. F. Dahl, A. Ceriotti, G. Longoni, M. Manassero, M. Sansoni, and P. Chini, *J. Am. Chem. Soc.*, 1979, **101**, 6112.
- <sup>14</sup> K. A. Azam and A. J. Deeming, *J. Chem. Soc., Chem. Commun.*, 1976, 852.
- <sup>15</sup> S. Aime, L. Milone, and A. J. Deeming, *J. Chem. Soc., Chem. Commun.*, 1980, 1168.