Polymer-supported Complexes. Part 4.† Decarbonylation of Polystyrene-anchored Dicarbonyl Rhodium(I) Complexes and Applications as Catalysts in Cyclohexene Hydrogenation

Sumit Bhaduri * and Hanif Khwaja
Alchemie Research Centre Private Limited, CAFI Site, P.O.Box 155, Thane-Belapur Road, Thane 400 601, Maharashtra, India

---

Comparative decarbonylation studies have been carried out on polymer-supported $[Rh(CO)_2L]$ (L = a polymer resin functionalised with pentane-2,4-dionate or ethyldithiocarbamate) and $[RhCl(CO)_2L]$ (L = a polymer resin functionalised with ethylamine or diphenylphosphine) complexes under various conditions. The complexes respond differently to thermal or photochemical treatments as well as in their reactions with NO and hydrogen. The amine and dithiocarbamato-derivatives undergo reversible decarbonylation and evidence for involvement of an intermediate for the amine derivatives is supplied by i.r. spectroscopy. The catalytic activities of these complexes are primarily determined by the ease with which loss of carbon monoxide takes place, and also whether the rhodium–polymer bond remains intact or not under hydrogenation conditions.

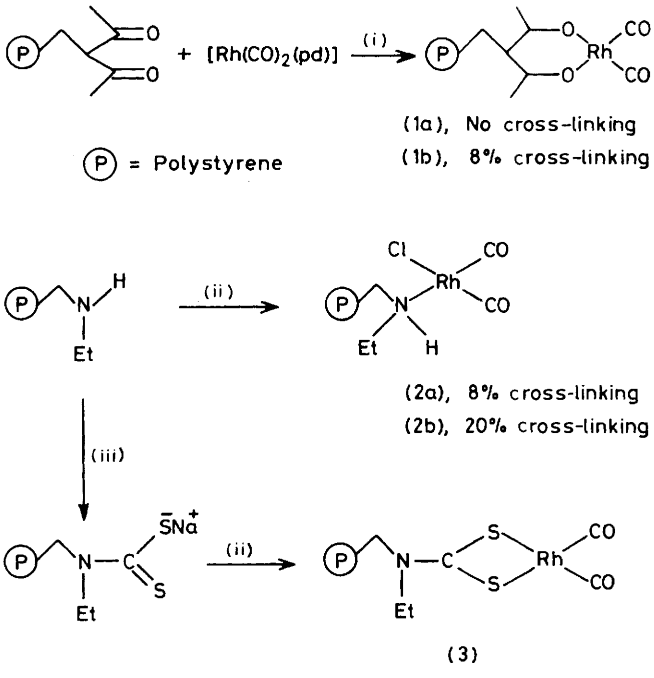
Examples of polymer attachment of transition-metal complexes, leading to the stabilisation of unsaturated mononuclear reaction centres, are known.[1-3] One of the ways of generating co-ordinative unsaturation is to anchor a metal complex with an easily dissociated ligand and then to supply the required thermal or photochemical energy for its ejection. Carbonyl complexes with characteristic i.r. absorptions are ideal for this purpose. Loss of the carbonyl band indicates removal of the CO ligand while its reappearance under an atmosphere of CO suggests that the molecular identity of the anchored complex is unchanged. In other words, *reversible* decarbonylation reactions could be considered as manifestations of the stabilities of polymer-anchored unsaturated metal centres.

One of the important factors for stabilisation is that the covalent links between the polymer and the metal ions should be sufficiently strong to remain intact even after unsaturation is created by removal of the CO ligands. A comparative study on the reversible decarbonylation reactions of various dicarbonyl rhodium(I) complexes, anchored to the polymer through different ligands, would therefore provide information about the capabilities of these ligands for stabilizing unsaturated Rh^I centres. However, thermal or photochemical stability of the polymer–metal bond does not necessarily mean stability with respect to specific chemical reactions. It is possible that under the conditions of a catalytic reaction, be it a hydrogenation or an oxidation, the polymer–metal bond will be cleaved and loss of metal ions or metal aggregate formation would take place. Indeed loss of metal ions has been observed in the case of oxidation reactions involving Bu^tO_2H and polymer-supported $[VO(pd)_2]$ (Hpd = pentane-2,4-dione) or molybdenum(V) dithiocarbamato-complexes as catalysts.[4,5] Use of polymer-supported $[Rh(CO)_2(pd)]$ or $[Rh(CO)_2(cp)]$ (Hcp = cyclopentadiene) in hydrogenation reactions also led to the formation of metal crystallites through polymer–metal bond cleavage.[6,7] In this paper, we describe studies relating to reversible decarbonylation of various dicarbonyl rhodium(I) species, and the stabilities of the polymer–metal bonds under the conditions of catalytic hydrogenation of cyclohexene.

Results and Discussion

(*a*) *Preparation and Characterisation*.—In Schemes 1 and 2, the synthetic methods employed to prepare the polymer-supported complexes (1)—(4) are shown. Supported complexes similar to (2) have been mentioned briefly but not studied in detail.[8] The synthesis and characterisation of the polymer support for (2) and (3) has been described in the preceding paper, while we have already reported some of the results with (1).[6]

Treatment of the dithiocarbamato-functionalised resin with $[Rh_2Cl_2(CO)_4]$ led to the formation of orange-red beads with i.r.-active carbonyl bands at 2 075 and 1 990 cm^{-1}. Its formulation as (3) rather than (2) or (3a) as shown below is based on

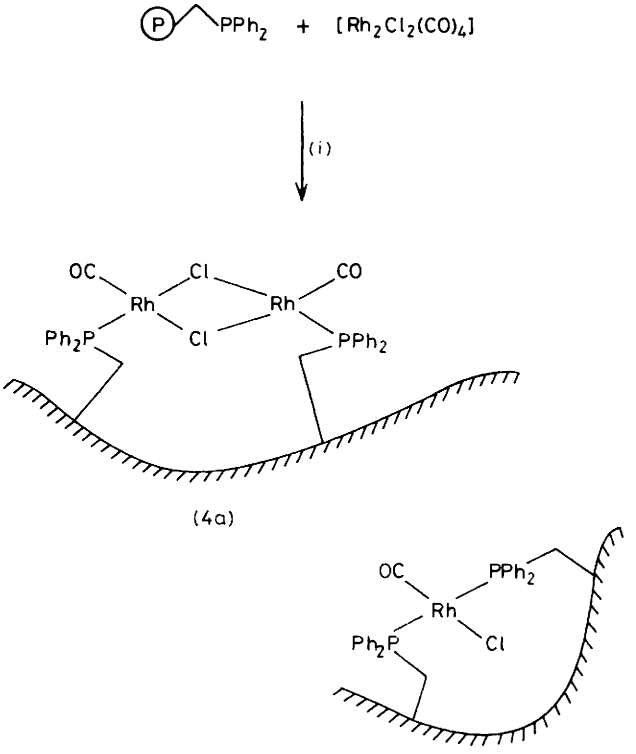


Scheme 1. (i) 80 °C, 24 h, benzene; (ii) 25 °C, 0.5 h, CH_2Cl_2, $[Rh_2Cl_2(CO)_4]$; (iii) 60 °C, 24 h, NaOH, CS_2, thf, EtOH

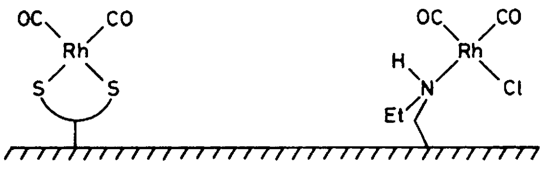
---

† Part 3 is ref. 5.

Non-S.I. unit employed: mmHg ≈ 13.6 × 9.8 Pa.

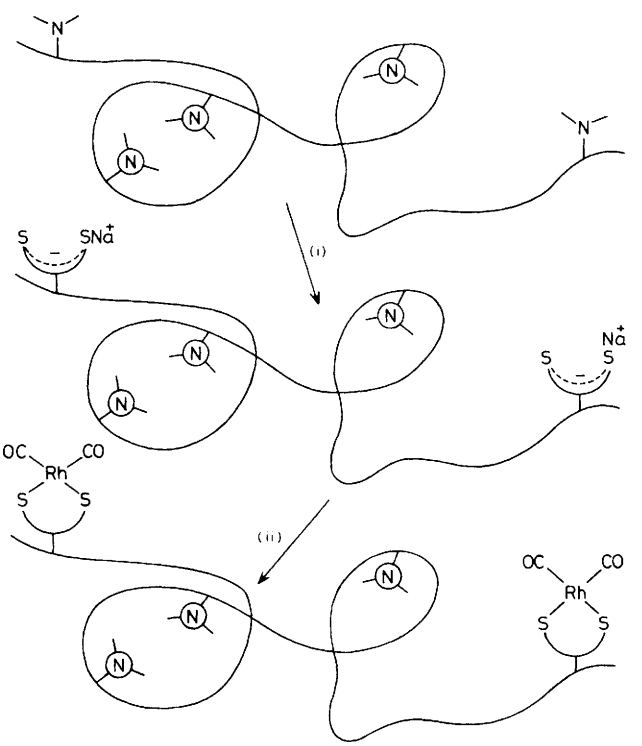


Scheme 2. (i) 25 °C, 0.5 h, CH_2Cl_2



(3a)

the following observations. The free complex $[Rh(CO)_2(S_2CNEt_2)]$ is prepared by the reaction of $[Rh_2Cl_2(CO)_4]$ with $Na[S_2CNEt_2]$ and in dichloromethane has i.r. bands at 2 062 and 2 000 cm^{-1}.[9] The aminated beads, on treatment with $[Rh_2Cl_2(CO)_4]$, led to the formation of (2) with i.r. bands at 2 082 and 2 004 cm^{-1}. The chemical properties of (2) and (3) are very different: on u.v. irradiation or on exposure to an atmosphere of hydrogen the i.r. carbonyl bands of (3) disappeared completely, while no change was observed with (2). Furthermore *reversible* decarbonylation with NO could be effected on (2) but not on (3) (see later). The presence of free amine groups [5] in the dithiocarbamato-functionalised polymer would obviously suggest a formulation such as (3a) rather than (3). The fact that under u.v. irradiation or on treatment with H_2 *complete* disappearance of the ν(CO) bands is observed, and that a residual absorption due to the $[RhCl(CO)_2]$ moiety anchored through $^-$NHEt groups is not seen, rules out such a structure. The reason for this exclusive reaction between dithiocarbamato-groups and $[Rh_2Cl_2(CO)_4]$ seems to be the non-accessibility of the $^-$NHEt groups that do not react with CS_2 and NaOH. This point, *i.e.* non-uniform steric restriction arising out of the mobility of the polymer chain which makes some of the functional groups non-accessible to reactants in the solution, is emphasised diagramatically in Scheme 3.



Scheme 3. (i) CS_2, NaOH; (ii) $[Rh_2Cl_2(CO)_4]$. For clarity the substituents on N atoms are not shown; encircled N denotes non-accessible amine groups

Complex (4) is a literature reported complex and is thought to be a mixture of (4a) and (4b).[10] Table 1 summarises the i.r. band positions, degree of cross-linking, and metal incorporation for complexes (1)—(4). Polymer-supported $[Rh(CO)_2(cp)]$ is very similar to the complexes described in this paper; some relevant data on this complex are therefore included in Table 1.[7,11]

(*b*) *Decarbonylation Reactions.*—With the exception of (4) all the polymer-supported complexes could be decarbonylated in a number of ways. By heating powdered (1), (2), or (3) under vacuum or in a solvent under nitrogen, fully decarbonylated materials as indicated by complete disappearance of the carbonyl bands could be obtained. For complexes (1) and (2), by controlling the duration of heating and temperature, i.r. evidence for the formation of partially decarbonylated intermediates was found (see later). No such intermediate species is observed during the decarbonylation of (3). For (4) even partial loss of CO groups could not be effected by heat treatment.

Although decarbonylation of (1) and (3) could also be brought about by u.v. irradiation, there was no evidence for CO loss by (2) and (4) under these conditions. Decarbonylation along with metal crystallite formation are observed when (1) and (3) react with hydrogen or NO. Hydrogen does not react with (2), the carbonyl bands remain unchanged both in terms of positions and intensities. Table 2 summarizes all the details on the various decarbonylation reactions.

Thermal decarbonylation of (1a) and (1b) monitored by i.r. spectroscopy suggests the formation of partially decarbonylated ' pd '-bridged intermediates (5) and (6) followed by Rh–pd bond cleavage.[6] Recently on the basis of i.r. spectroscopy, formation of oxo-bridged rhodium(I) carbonyl

Table 1. Physicochemical characteristics of polymer-supported dicarbonyl rhodium(I) complexes

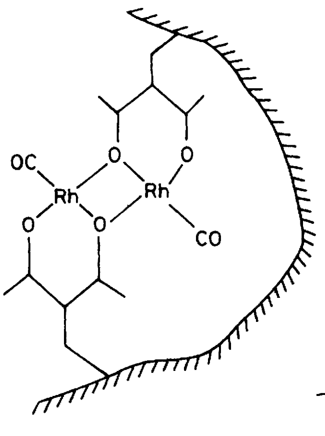
Complex	Degree of cross-linking (%)	Metal incorporation (%)	I.r. bands (cm^{-1})
(1a)	0	1.0	2 080s, 2 010s, 1 700m, 1 580w
(1b)	8	0.6	2 080s, 2 010s, 1 700m, 1 580w
(2a) [a]	8	7.5	2 082s, 2 004s
(2b)	20	3.5	2 082s, 2 004s
(3) [b]	8	4.5	2 075s, 1 990s
(4)	8	5.3	2 060m, 1 970s
Polymer-supported $[Rh(CO)_2(cp)]$ [c]	20	2.9	2 040s, 1 980s

[a] N, 2.6%. [b] N, 3.1; S, 4.2%. [c] From refs. 7 and 11.

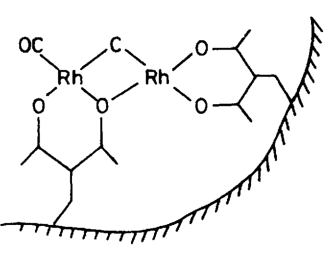
Table 2. Summary of decarbonylation experiments [a]

	Mode of decarbonylation					
Complex	Thermal	Photochemical	Reaction with H_2	Reaction with NO		I.r. bands (cm^{-1}) of the intermediates
(1b)	Yes ($\leqslant 10\%$ rev.)	Yes ($\leqslant 10\%$ rev.)	Yes	Yes (irr.)	(A)	2 087,[b] 2 036[b]
					(B)	2 110[b]
(1a)	Yes (irr.)	Yes (irr.)	Yes	Yes (irr.)	(A)	2 087,[b] 2 036[b]
					(B)	2 110[b]
(2a)	Yes (totally rev.)	No	No	Yes (totally rev.)		1 940[c]
						1 380[d]
(2b)	Yes ($\leqslant 80\%$ rev.)	No	No	Yes (totally rev.)		Barely noticeable[c]
						1 380[d]
(3)	Yes (totally rev.)	Yes (totally rev.)	Yes	Yes (irr.)		
(4)	No	No	No	Yes (essentially irr.)		

[a] rev. = Reversible, irr. = irreversible; A and B represent two different intermediates. [b] Thermal and photochemical decarbonylation. [c] Thermal decarbonylation. [d] Decarbonylation with NO.



(5)



(6)

species from $[Rh_6(CO)_{16}]$, supported on inorganic oxide surfaces, has been shown to take place.[12,13] These intermediates are reported to have i.r. absorptions at 2 093 and 2 038 cm^{-1}, frequencies close to those attributed to (5) (2 087 and 2 036 cm^{-1}). Species (6) is thought to result from Boudouard's reaction involving two co-ordinated CO groups and has one single carbonyl band at 2 110 cm^{-1} indicating the oxidation state of rhodium to be +3. The presence of entrapped CO_2 as shown by a band at 2 340 cm^{-1} further supports this view.

The decarbonylation reactions are totally irreversible for (1a) and are reversible only to a small extent ($\leqslant 10\%$) for (1b). This is considered to be due to the homolytic cleavage of polymer–metal bonds which leads to the formation of metal aggregates. The increased rigidity of the polymer matrix in (1b) prevents formation of metal aggregates to a small extent by keeping a few of the decarbonylated rhodium centres away from each other.

As shown in Figure 1, by carrying out the thermal decarbonylation of (2a) at 65 °C the i.r. spectrum shows a new band at 1 940 cm^{-1}, evidence for an intermediate. Decarbonylation of $[Rh_6(CO)_{16}]$, anchored in amine modified silica, also led to the formation of a partially decarbonylated species, characterised by a new band at 1 943 cm^{-1}. It has been proposed that initially formed dicarbonyl rhodium(I) units are converted into monocarbonyl species through the loss of carbon monoxide.[14] However, in this case, the exact co-ordination environments around the rhodium(I) centres are not known and are difficult to estimate, for both the di- and the mono-carbonyl complexes. Two alternative formulations (7) and (8) could be proposed for the intermediate involved in the decarbonylation of (2a). Since three-co-ordinate isolable complexes like (8) are not known, it is difficult to make any reasonable estimate about the expected i.r. frequencies of the carbonyl bands. Formulation (8), however, can be ruled out in view of the following facts. The 8% cross-linked polymer does have sufficient mobility to act as a bidentate chelate. Several reactions of the ' pd ' functionalised 8% cross-linked polystyrene are clear indications of such mobility.[6] Excess amine is known to give $[RhCl(CO)_2R_2]$ (R = amine) type complexes on reaction with $[Rh_2Cl_2(CO)_4]$.[15] Under decarbonylation conditions it is reasonable to expect the formation of the polymer-supported analogue of $[RhCl(CO)R_2]$. The new carbonyl band at 1 940 cm^{-1} is barely noticeable in the decarbonylation of (2b), the polymer-supported complex with 20% cross-linked polystyrene. For a formulation such as (7) a weak band caused by the severely restricted mobility of the polymer chain is to be expected.

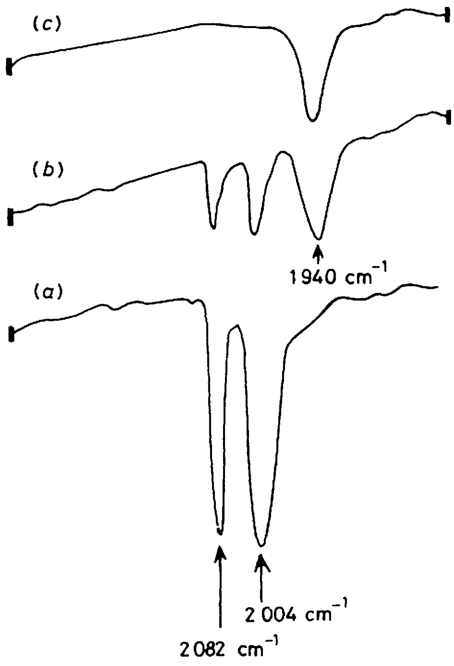
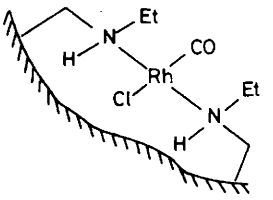
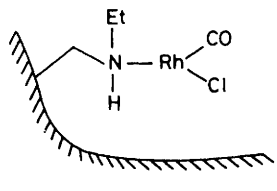


Figure 1. Controlled decarbonylation of (2a) carried out at 65 °C in thf under N_2 and monitored by i.r. spectroscopy: (*a*), (*b*), and (*c*) are spectra taken at t = 0, 36, and 60 h respectively



(7)



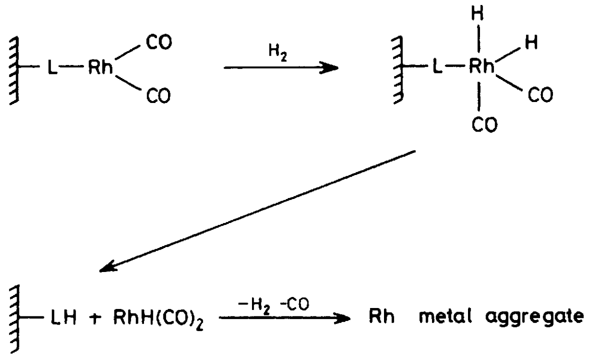
(8)

Had (8) been the correct formulation, variation in cross-linking should not have had any effect on the intensity of the new band. A *trans* rather than *cis* configuration is proposed for (7) since $[RhCl(CO)L_2]$ (L = donor ligand) complexes are known to have *trans* configurations.

Prolonged heating (72 h) at 65 °C or for a shorter duration (12 h) at 109 °C led to complete decarbonylation of (2a) and (2b). Both (2a) or (2b) could be regenerated from the decarbonylated materials by exposing them to a CO atmosphere at ambient or higher pressures. Regeneration was quantitative and more facile with (2a) than with (2b). This is thought to result from the restricted diffusion of CO through the 20% cross-linked polymer matrix.

Complete thermal decarbonylation followed by quantitative regeneration was also observed for (3). In this case, however, there was no evidence for the formation of any intermediate species. As has already been mentioned, (3) can be fully decarbonylated by u.v. irradiation with a mercury lamp. Here again no intermediates are observed. Complex (4) is resistant towards the loss of CO; the i.r. bands, attributable to a mixture of (4a) and (4b), do not show any loss of intensity even when compound (4) is heated at 120 °C under vacuum (10^{-3} mm Hg) for 24 h.

Complexes (1) and (3) react with hydrogen to give decarbonylated metal aggregates dispersed in the polymer matrix.



Scheme 4. L = cp$^-$, pentane-2,4-dionate, or ethyldithiocarbamate

This is inferred from the loss of the carbonyl i.r. bands after reaction and the colour, grey-black with a metallic gleam, of the resultant materials. Formation of metal has also been observed in the case of polymer-supported $[Rh(CO)_2(cp)]$ as a hydrogenation catalyst.[7] It is interesting to note that polymer–metal bond cleavage with hydrogen is encountered only with ligands which are anions due to loss of a proton, *i.e.* Brønstead bases. Under hydrogenation conditions, addition of hydrogen to the supported complex as depicted in Scheme 4 would lead to polymer–metal bond cleavage followed by the formation of metal aggregates. As expected, (2) and (4) both containing neutral ligands have metal–polymer linkages that are totally inert to treatment with hydrogen.

Decarbonylation of species (1)—(4) could be effected by treatment with NO in solution or in the solid state. With the exception of (2) irreversible decarbonylation and absence of any new well characterised i.r. band, attributable to a nitrosyl or nitrosyl derived group, were observed in each case. Reaction of powdered (2) with NO, with or without a solvent, gave a material with a sharp i.r. band at 1 380 cm^{-1} indicating the presence of nitro-groups. Interestingly (2) could be quantitatively regenerated from the decarbonylated material by reacting it with CO.

Reaction of dicarbonyl rhodium(I) species with NO is known to lead to the formation of nitro-derivatives together with the formation of CO_2 and N_2O.[16] The reverse reaction, *i.e.* formation of the dicarbonyl derivative with the elimination of CO_2 and N_2O in the reaction of the nitro-derivative with CO, is also known. It is important to note that the ability of (2) to react with NO and CO in a reversible manner makes it a potential candidate for a catalyst for the conversion of CO plus NO to CO_2 and N_2O.[17]

(*c*) *Catalytic Reactions.*—It has already been mentioned that the reactions of (1) and (3) with hydrogen lead to decarbonylation and the formation of metal aggregates. Hydrogenation of cyclohexene, the reaction studied in this work, with (1) or (3) as the catalyst is therefore catalysed by dispersed rhodium metal in the polymer matrix. However, depending on the mode of prior activation noticeable differences in the catalytic activity of (1) are observed.[6] Complex (3) is a poor catalyst, with or without activation, none or very little cyclohexane is formed in 6 h at 65 °C. The absence of noticeable catalytic activity in spite of the formation of metal aggregates may well be due to the inhibitory effect of the sulphur ligands.

The rate of hydrogenation of cyclohexene with (2a), (7), and totally decarbonylated (2a) has been studied. As expected and shown in Figure 2 maximum rate is observed with the totally decarbonylated material. It should be noted, however, that the results shown in Figure 2 are for the first 6 h of reaction. Had the reactions been continued for a

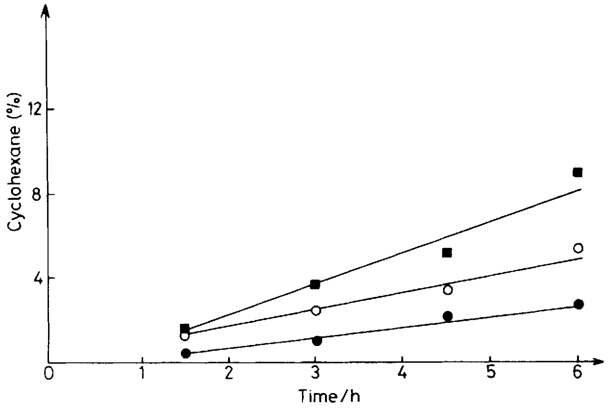


Figure 2. Hydrogenation of cyclohexene at 65 °C and atmospheric pressure of hydrogen catalysed by complex (2a) (●), complex (7) (○), and totally decarbonylated (2a) (■)

sufficiently long time ($\geqslant$72 h), the rates of hydrogenation with all the species would have eventually become the same. This has been confirmed by separate experiments. The initial rate of hydrogenation is a reflection of the degree of co-ordinative unsaturation around the metal centres.

In partially decarbonylated (2a), *i.e.* (7), although some of the rhodium centres are four-co-ordinate, one of the metal–amine linkages could be easily broken for activation of hydrogen. This explains the higher rate of hydrogenation with (7) rather than with (2a). In the case of hydrogenation with totally decarbonylated material, (2a) could be regenerated even after 72 h of reaction by exposing the catalyst to an atmosphere of carbon monoxide. Although not shown in Figure 2, (4) has been found to be a much poorer catalyst compared to (2a). This again fits in well with the observation that (4) is resistant towards CO loss, *i.e.* creation of co-ordinative unsaturation.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 377 grating spectrophotometer. Gas-chromatographic (g.c.) analyses were performed with a Pye Unicam 204 instrument. Divinylbenzene cross-linked polystyrene beads (8%) of fine mesh were kindly supplied by Industrial and Agricultural Engineering Co. (Bombay) Ltd. Soluble polystyrene and 20% cross-linked polystyrene were purchased from the Aldrich Chemical Co. (U.K.) Ltd. and Strem Chemicals (U.S.A.). Complexes (1), (4), dithiocarbamate-, and amine-functionalised polymers were prepared according to reported methods.[5,6,10] Unless otherwise specified, all reactions were carried out under nitrogen in dry distilled solvents. Rhodium estimations were carried out by atomic absorption spectroscopy using the standard addition method to avoid matrix interference.

Preparation of (2).—Aminated beads (1.0 g) were swollen in CH_2Cl_2 (50 cm^3) for 2 h at room temperature. The complex $[Rh_2Cl_2(CO)_4]$ (0.25 g, 0.642 mmol) was added to the mixture and stirred for 0.5 h. The orange-brown beads of (2) were filtered off, washed with CH_2Cl_2, hexane, and dried under vacuum.

Preparation of (3).—Dithiocarbamate-functionalised beads (1) (1.0 g) were swollen in CH_2Cl_2 (50 cm^3) for 2 h at room temperature. The complex $[Rh_2Cl_2(CO)_4]$ (0.25 g, 0.642 mmol) was added to the mixture and stirred for 0.5 h. The orange-red beads of (3) were filtered, washed off with dichloromethane, hexane, and dried under vacuum.

Thermal Decarbonylation of (2).—Beads of (2) (1.5 g) in a finely powdered state were heated at 100 °C under vacuum (10^{-3} mmHg). The i.r. spectra of the material were recorded periodically as a KBr disc. Decarbonylation was also effected by heating a preformed KBr disc of (2) at 100 °C under vacuum (10^{-3} mmHg) or by heating powdered (2) at 65 °C in thf (thf = tetrahydrofuran) under nitrogen. The time given for the decarbonylation experiments depended on the extent of decarbonylation desired. At 100 °C, 16 h was enough to give complete decarbonylation while at 65 °C, in thf, under nitrogen the time required was 72 h. Thermal decarbonylation experiments with (1) and (3) were carried out in a similar fashion.

Photochemical Decarbonylation of (1).—A KBr disc of powdered (1) was irradiated with ultraviolet radiation from a mercury lamp. The i.r. spectra were periodically recorded. Total decarbonylation was achieved in *ca.* 0.5 h. A decarbonylation experiment with (3) was carried out in a similar fashion.

Catalytic Experiments.—Powdered beads of (2a) (0.15 g) were placed in thf (20 cm^3) and cyclohexene (1 cm^3) at 65 °C. The solution was stirred magnetically under an atmosphere of hydrogen (760 mmHg) and small portions (0.1 cm^3) of the solution were periodically removed using a syringe for gas-chromatographic studies with chlorobenzene as the internal standard. The catalytic runs with (3), (7), totally decarbonylated (2a), and (4) were carried out similarly.

References

1 R. H. Grubbs, C. Gibbons, L. C. Kroll, W. O. Bonds, jun., and C. H. Brubaker, jun., *J. Am. Chem. Soc.*, 1973, **95**, 2373.
2 P. Perkins and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1979, **101**, 3895.
3 G. Gubitosa, M. Boldt, and H. H. Brintzinger, *J. Am. Chem. Soc.*, 1977, **99**, 5174.
4 S. Bhaduri, A. Ghosh, and H. I. Khwaja, *J. Chem. Soc., Dalton Trans.*, 1981, 447.
5 S. Bhaduri and H. Khwaja, preceding paper.
6 S. Bhaduri, H. I. Khwaja, and V. G. Khanwalkar, *J. Chem. Soc., Dalton Trans.*, 1982, 445.
7 B. H. Chang, R. H. Grubbs, and C. H. Brubaker, jun., *J. Organomet. Chem.*, 1979, **172**, 81.
8 W. O. Haag and D. D. Whitehurst, Proc. 5th Int. Cong. Catal., 1972, North Holland, Amsterdam, 1973, vol. 1, p. 465.
9 F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, 1964, **3**, 1398.
10 G. Strathdes and R. Given, *Can. J. Chem.*, 1974, **52**, 3000.
11 H. S. Tung and C. H. Brubaker, jun., *J. Organomet. Chem.*, 1981, **216**, 129.
12 A. K. Smith, F. Hugnes, A. Theolier, J. M. Basset, R. Ugo. G. M. Zanderighi, J. L. Bilhou, V. Bilhou-Bougnol, and W. F. Graydon, *Inorg. Chem.*, 1979, **18**, 2104.
13 J. L. Bilhou, V. Bilhou-Bougnol, W. F. Graydon, J. M. Basset, A. K. Smith, G. M. Zanderighi, and R. Ugo, *J. Organomet. Chem.*, 1978, **153**, 73.
14 H. Knozinger, E. W. Thornton, and M. Wolf, *J. Chem. Soc., Faraday Trans. 1*, 1979, 1888.
15 D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1965, 1900.
16 S. Bhaduri, B. F. G. Johnson, C. J. Savory, J. A. Segal, and R. H. Walter, *J. Chem. Soc., Chem. Commun.*, 1974, 809.
17 J. A. McCleverty, *Chem. Rev.*, 1979, **1**, 53.

Received 2nd April 1982; *Paper* 2/562