Polymer-supported Complexes. Part 2.† Polystyrene-anchored Pentane-2,4-dionato-complexes of Transition Metals: Synthesis, Reactions, and Catalytic Properties

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Soluble and divinylbenzene cross-linked (8%) polystyrene functionalized with ' pd ' groups (Hpd = pentane-2,4-dione) interact with $M(pd)_n$ (M = Fe, n = 3; M = Co, n = 2; M = Cu, n = 2; M = Zr, n = 4), $[VO(pd)_2]$, $[Rh(CO)_2(pd)]$, $TiCl_4$, $[Ni(en)_2]Cl_2$ (en = $H_2NCH_2CH_2NH_2$), and $FeCl_3$ to give polymer-anchored metal complexes. Thermal decarbonylation of polymer-anchored $[Rh(CO)_2(pd)]$, monitored by i.r. spectroscopy, suggests formation of a partially decarbonylated pd-bridged intermediate followed by Rh–pd bond cleavage. Hydrogenation of cyclohexene at 109 °C and atmospheric pressure of cyclohexene is catalysed by polymer-supported $[Fe(pd)_3]$ and $[Rh(CO)_2(pd)]$. Formation of metal crystallites on the polymer seems to be responsible for the observed catalytic activities.

ANCHORING of catalytically active transition-metal complexes to a polymer support has recently attracted considerable attention.[1] In certain cases polymer attachment has been shown to lead to stabilization of co-ordinatively unsaturated mononuclear reaction centres.[2] Two factors are considered to be of importance for such stabilization. First, the polymer matrix should be rigid so that non-adjacent metal centres are unable to approach each other. Secondly, the covalent link between the polymer and the metal centres must be sufficiently strong to remain intact during the course of the reaction. In this paper, we describe the interaction of polystyrene resin, cross-linked or soluble, functionalized with pentane-2,4-dionate groups, with various transition-metal ions and complexes. We also, describe thermal decarbonylation of polymer-supported $[Rh(CO)_2(pd)]$ (Hpd = pentane-2,4-dione) where the i.r. signals of organic and inorganic carbonyl groups could be successfully used to study surface reactions involving metal–ligand and metal–polmer bond cleavage. Catalytic properties of polymer-supported $[VO(pd)_2]$ in reactions involving t-butyl hydroperoxide and the behaviour of the functionalized resin as a polydentate ligand have been reported recently.[3a,3b]

RESULTS AND DISCUSSION

(*a*) *Preparation and Characterization.*—The functionalized resin, (1a), can be obtained by treating chloromethylated, divinylbenzene cross-linked (8%), macroporous polystyrene beads with Hpd and a catalytic amount of sodium ethoxide in a swelling solvent such as tetrahydrofuran (thf).[3a] The i.r. spectrum of the resultant beads shows a broad band of medium intensity at 1 700 cm^{-1}, attributable to the carbonyl-stretching frequency of the pd group. Chloromethylation followed by base-catalysed reaction with Hpd can also be performed on linear polystyrene to give a soluble, functionalized derivative (1b). The i.r. spectrum of (1b) is similar to that of (1a), except that the band at 1 700 cm^{-1} is more intense due to a higher degree of functionalization. The degree of functionalization, calculated on the basis of analytical data, is *ca.* 13 and 22% for (1a) and (1b) respectively. As reported by other research workers active in the area of polymer-supported reactions,[4a] a high degree ($\approx$51%) of chloromethylation is obtained. A significant amount of free chloromethylated groups appears to be present after the base-catalysed reaction with Hpd.

As shown in Schemes 1—3, (1a) and (1b) undergo two different types of reactions. Reactions (i) and (iii) are essentially ligand-exchange reactions between the functionalized polymer and $[M(pd)_n]$ complexes, whereas (v)—(vii) require mobility of the polymer chain so that it can act as a polydentate ligand. The formation of (2a)—(2e) and (3a), (3b) are best represented by equations (1) and (2). Each product shows an i.r. band at

$$[M(pd)_n] + (1a) \longrightarrow (2a)\text{—}(2e) + Hpd \quad (1)$$

$$[Rh(CO)_2(pd)] + (1a),(1b) \longrightarrow (3a),(3b) + Hpd \quad (2)$$

ca. 1 580 cm^{-1} which can be assigned to the ketonic stretch of the co-ordinated pd groups. The band at 1 700 cm^{-1} diminishes in intensity only moderately, indicating that the degree of metal loading is not high. Accordingly, quantitative metal analyses also show that the metal content usually lies between 0.3 and 1.0% (see Table). The low metal loading is probably a reflection of the non-accessibility of the functional group due to steric restrictions.

The polymer-supported dicarbonyl rhodium complexes (3a) and (3b) are also conveniently synthesized through ligand-exchange reactions.[5a] The metal content for (3b) is comparatively high in accordance with the high degree of functionalization of the parent polymer (1b). Whilst the free complex $[Rh(CO)_2(pd)]$ has i.r. bands for the inorganic carbonyl groups at 2 070 and 2 005 cm^{-1}, both (3a) and (3b) have corresponding bands at 2 080 and 2 010 cm^{-1}.

As has been pointed out by several workers, analytical data for the characterization of polymer-supported complexes should be used with caution, and mainly as a

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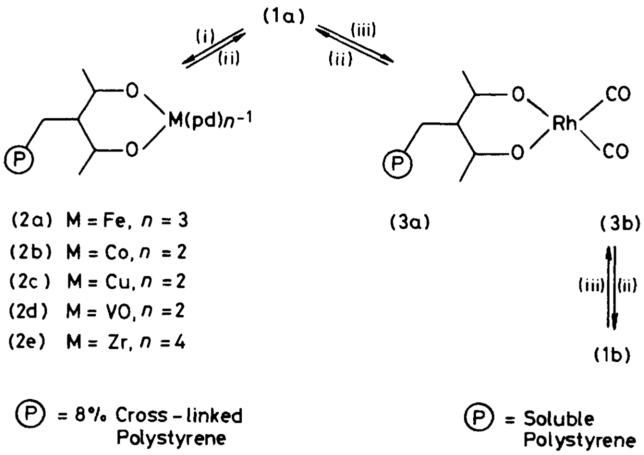
† For Part 1 see ref. 3(*a*).

qualitative rather than a quantitative guide.[4a,4b] It could therefore be argued that the reaction between [Fe(pd)$_3$] and (1a) actually leads to the formation of a species like (7) (see Scheme 3) rather than (2a), where two pd groups bound to the metal are not connected to the polymer. Thus alternative formulations involving total chelation by the polymer support for species (2a)—(2e) could well satisfy the experimental analytical data.



SCHEME 1 (i) M(pd)$_n$; (ii) dilute acid; (iii) [Rh(CO)$_2$(pd)]

Indirect evidence for the formulations of (2a)—(2e) comes from their reactions with mineral acids [reaction (ii), Scheme 1]. In all these reactions resin (1a) is regenerated, presumably according to equation (3).

$$(2a)\text{—}(2e) + n\text{HX} \longrightarrow (1a) + (n-1)\text{Hpd} + \text{MX}_n \quad (3)$$

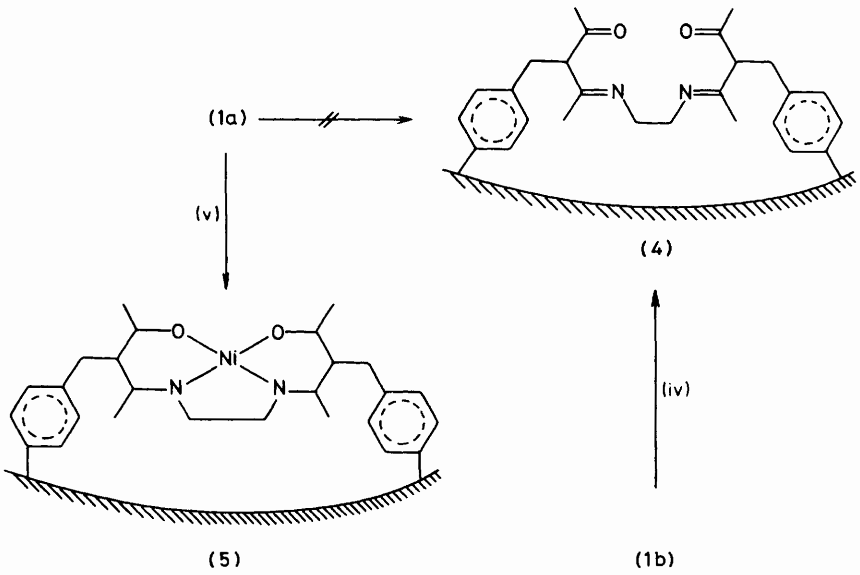
Although the regeneration of (1a) from species (2a)—(2e) by acid treatment is a facile reaction, it only proceeds with difficulty for (7), and more drastic conditions have to be employed. The difference in reactivities is best explained in terms of the encapsulated nature of (7) as opposed to the open environments around the metal atoms in (2a)—(2e).

The reaction of ethylenediamine (en) with Hpd to give the quadridentate Schiff-base ligand *NN'*-ethylenebis(acetylacetoneimine) is well known.[6] Attempts to effect such reactions involving the pd groups of (1a) and (1b) give interesting results. While (4) could be obtained by treating (1b) with en, even under drastic conditions a similar approach fails with (1a). From the analytical data it is found that *ca.* 7% of the pd groups of (1b) react with en. For (1a), its lowered mobility prevents the close approach of non-adjacent pd groups, and consequently the Schiff-base condensation reaction cannot take place. However, the known[6] template synthesis reaction with [Ni(en)$_2$]Cl$_2$ could be performed on (1a) to give (5). Formation of (5) indicates that this species must have enough thermodynamic or kinetic stability to extract the required mobility from the polymer back-bone. Treatment of (5) with H$_2$S or CN$^-$ does not remove the nickel(II) ion from the polymer matrix to give a cross-linked analogue of (4).

The compound TiCl$_4$ is known to undergo reaction with Hpd to give [Ti(pd)$_2$Cl$_2$].[7] Here again, such a reaction involving the pd groups of (1a) would require that the strain imposed on the polymer back-bone is compensated by the stability of the final product. Treatment of (1a) with TiCl$_4$ in dichloromethane leads to the formation of (6), characterized on the basis of i.r. and analytical data. The free complex [Ti(pd)$_2$Cl$_2$] in the presence of moisture changes to a μ-oxo-species.[8] The colour and i.r. spectrum of (6) do not change on leaving in air for 2—3 d. This may be taken as an indication of the enhanced stability of the polymer-supported species towards hydrolysis; the limited mobility of the polymer back-bone is perhaps responsible, since formation of a μ-oxo-bridge would require close approach of the two Ti centres. A similar reaction is observed when (1a) is treated with FeCl$_3$ in a swelling solvent such as tetrahydrofuran.[5b] As mentioned already, based on its resistance towards reaction with mineral acid to reproduce (1a), the reaction product is best formulated as (7). It is more than probable that a mixture of iron(III) centres in three different environments is present. These are metal ions linked to the polymer back-bone through one, two, or three pd groups respectively, with solvent molecules satisfying the six-co-ordination around the metal centres in the first two cases. However, the predominant species must be (7), since reaction (vi) was successfully carried out in a solvent such as toluene to give the same metal content, and it is unlikely that extensive co-ordination by toluene could take place.

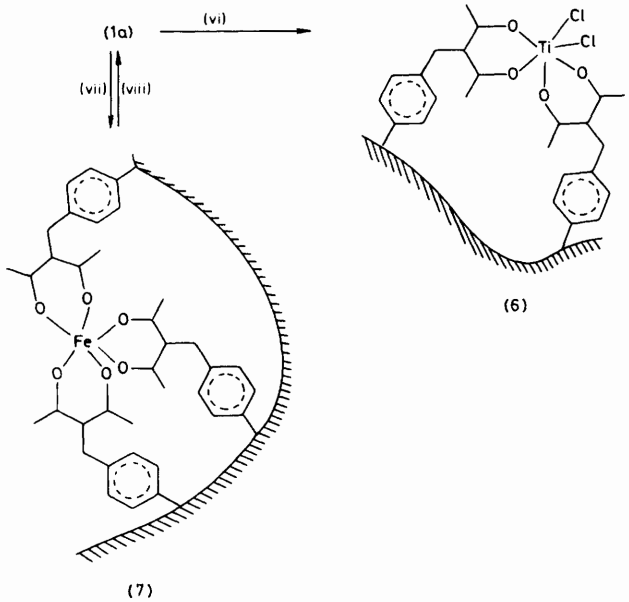
Complex	Colour	Analysis (%) C	H	Metal	Characteristic i.r. bands (cm^{-1})
(1a)	Off-white	80.8	7.5		1 700
(1b)	Off-white	70.9	7.1		1 700
(2a)	Dark red	80.3	7.3	0.6	1 700, 1 580
(2b)	Pink	80.6	7.0	0.3	1 700, 1 580
(2c)	Light blue	80.4	7.3	0.3	1 700, 1 570
(2d)	Blue-black	80.6	7.2	0.4	1 700, 1 570
(2e)	Pale yellow	80.1	7.3	0.4	1 700, 1 580
(3a)	Light yellowish brown	80.1	7.2	0.6	2 080, 2 010, 1 700, 1 580
(3b) [a]	Light yellow	79.0	7.3	1.0	2 080, 2 010, 1 700, 1 580
(4) [b]	Off-white	79.5	7.6		1 515
(5) [c]	Reddish brown	80.4	7.5		1 560
(6)	Orange-red	80.6	7.2	0.4	1 700, 1 570
(7)	Orange-yellow	80.5	7.3	0.2	1 700, 1 570

[a] $\delta(CH_3)$ 2.12 p.p.m., in CDCl$_3$; δCH not observed. [b] N = 1.3%. [c] N = 0.2%.



SCHEME 2 (iv) en; (v) $[Ni(en)_2(py)Cl_2]$

(*b*) *Thermal Decarbonylation of* (3a) *and* (3b).—Polymer anchoring of $[Rh(CO)_2(pd)]$ on phosphinated polystyrene through the loss of one carbonyl group has been reported.[9] However, for studying the stabilization (if any) of co-ordinatively unsaturated mononuclear metal centres, species (3a) and (3b) would obviously be the more useful since three i.r.-active carbonyl ligands, one organic and two inorganic, could be used as a probe. As shown in Figures 1 and 2, the reactions that actually take place on thermal or photochemical treatment of (1a) or (1b) are conveniently monitored by following the changes in the i.r.-active inorganic or organic carbonyl bands with respect to time. Compounds (3a) or (3b) in the powdered form or as KBr discs are heated at 120 °C under vacuum or argon, and the i.r. spectra are recorded at suitable time intervals. The changes observed are independent not only of the physical state of the polymer, *i.e.* powder or KBr disc, but also of the atmosphere under which it is heated, *i.e.* vacuum or argon. The higher thermal conductivity and the ability of the KBr disc to trap at least partially the liberated gas (see later) is preferred. Ultra-violet irradiation with a mercury lamp on (3a) or (3b) gives rise to similar spectral changes, but the rate of CO loss is much faster in this case. The free complex $[Rh(CO)_2(pd)]$, either in a KBr matrix or in solution, when heated or irradiated, does not show any of these spectral



SCHEME 3 (vi) $TiCl_4$; (vii) $FeCl_3$; (viii) concentrated acid

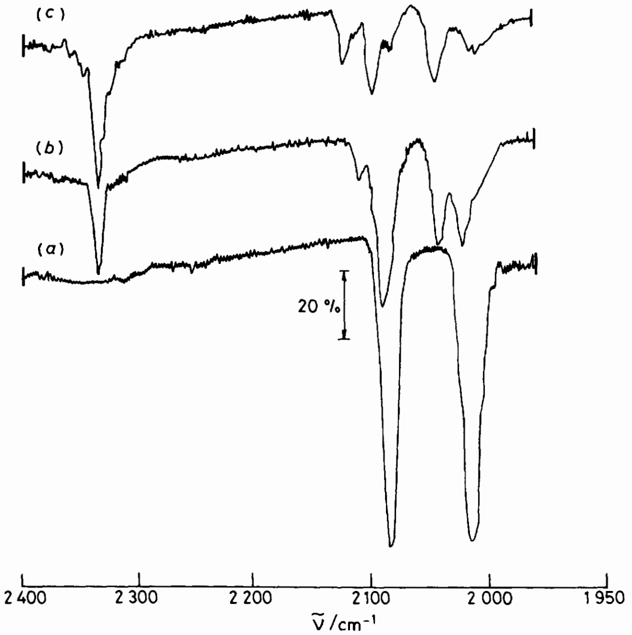


FIGURE 1 Thermal decarbonylation of (3b) monitored by i.r. spectroscopy (transmittance scale indicated). Time intervals for (*a*), (*b*), and (*c*) are $t = 0$, 1, and 2 h respectively

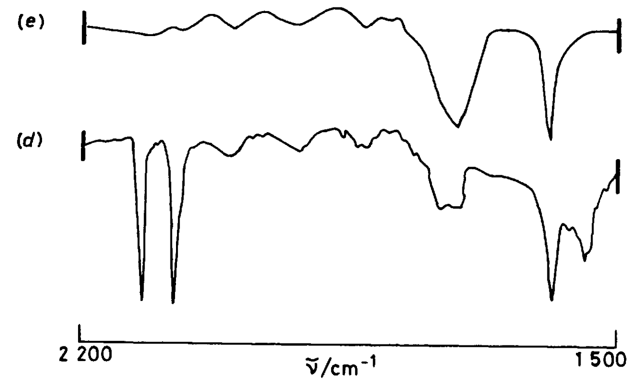


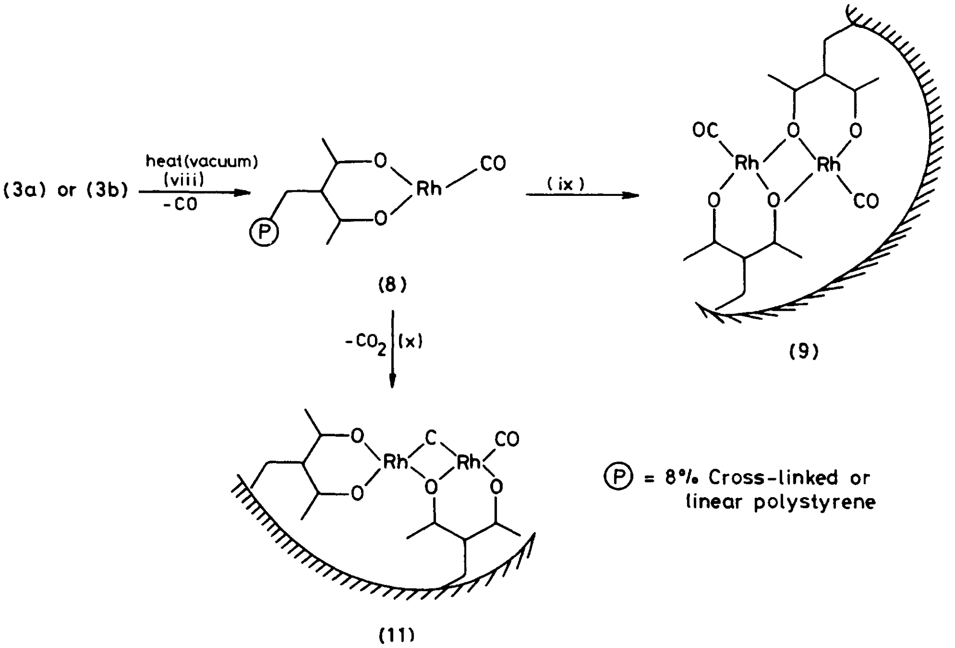
FIGURE 2 Thermal decarbonylation of (3b) monitored by i.r. spectroscopy. Time intervals for (*d*) and (*e*) are $t = 0$ and 3 h respectively

changes. Rapid and complete removal of the i.r. bands for the inorganic carbonyl and the co-ordinated keto-group takes place along with rapid formation of metal.

The i.r. data shown in Figures 1 and 2 are best explained in terms of the reactions shown in Schemes 4 and 5. Loss of one carbonyl ligand in step (viii) produces the hypothetical monocarbonyl species (8) which, in step (ix), undergoes dimerization on the polymer surface to give (9). Although we are unable to provide direct spectroscopic evidence for the formation of (8), decarbonylation of $Rh(CO)_2$ groups on ligand-modified silica has been shown to lead to the formation of Rh(CO) groups.[10] Also, generation of (9), for which spectroscopic evidence is available (see later), is best explained through the formation of (8) where co-ordinative unsaturation around the metal centre would favour dimerization. The direct evidence for decarbonylation comes from the fact that the total intensity of all the inorganic carbonyl bands in spectrum (*b*) is about half of that of spectrum (*a*).

Recently, on the basis of i.r. spectroscopy, formation of oxo-bridged rhodium(I) carbonyl species from $[Rh_6(CO)_{16}]$, on supported inorganic oxide surfaces, has been shown to take place.[11,12] These intermediates are reported to have i.r. absorptions at 2 093 and 2 038 cm^{-1}. The appearance of the new bands at 2 087 and 2 036 cm^{-1} in our studies can therefore be reasonably attributed to the formation of (9). Dimer formation through pd bridges on the polymer surface undoubtedly causes significant distortion from the ideal C_{2h} symmetry and two i.r. bands are observed; in spectrum (*b*), superimposition of the band at 2 087 cm^{-1} on the original at 2 080 cm^{-1} causes its broadening and a slower decrease in intensity than that of the band at 2 010 cm^{-1}. The relative intensities of the bands at 2 087, 2 036, and 2 010 cm^{-1} would suggest that about half the rhodium(I) centres have the ligand environment as shown in (9), whilst the other half retain the original one as in (3b). However, after heating for 2 h [spectrum (*c*)] the concentration of (9) is obviously higher than that of (3b) and further decarbonylation is evident from the loss of intensity of all the bands. Absence of any new bands between 1 700 and 1 900 cm^{-1} indicates that no carbonyl-bridged species are present.

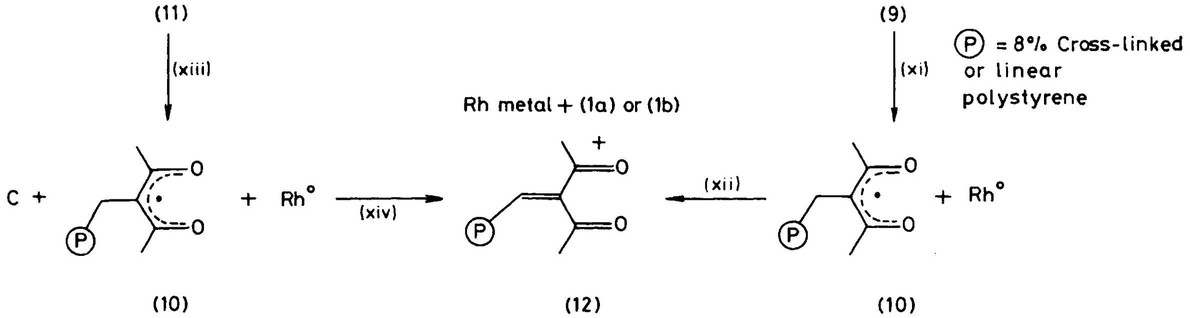
It is important to note that, for the formation of (9), mobility of the polymer back-bone is required. This facilitates bridge formation through non-adjacent pd groups. In accordance with this, the bands at 2 087 and 2 036 cm^{-1} attributable to (9) are always much more intense and more well-defined with (3b) than with (3a),



SCHEME 4

i.e. as expected, formation of (9) takes place more readily on the surface of linear polystyrene than on that of the cross-linked polymer.

The bands at 2 340 and 2 110 cm^{-1} definitely correspond to CO_2 trapped inside the KBr disc and some rhodium(III) carbonyl species respectively. The reduced back bonding from Rh^{III} would shift the carbonyl stretch over 2 100 cm^{-1}. By heating powdered (3a) or (3b) in a sealed tube under vacuum, evolution of CO_2 could be confirmed from the i.r. spectrum of the evolved gases. Since the vacuum under which the heating is carried out is of the order of 10^{-3} mmHg,* oxidation of CO with adsorbed oxygen is unlikely. The reaction between (3b) and (8) in step (x) of Scheme 4, to give CO_2 and a hypothetical carbide species (11), could be considered as a possibility. The formal oxidation state of rhodium in (11) is three, and therefore, is expected to have an i.r. band over 2 100 cm^{-1}.[13] Similar reactions are known with polynuclear metal carbonyls where under suitable conditions they are transformed to carbide species along with the evolution of CO_2.[14]



SCHEME 5

After heating for 3 h, almost complete disappearance of the bands due to inorganic carbonyl groups and co-ordinated keto-groups is observed [Figure 2, spectra (d), (e)]. The explanations for these observations are: further decarbonylation of (9) and (11) along with Rh–pd bond cleavage [steps (xi) and (xiii), Scheme 5]. The radical species (10) must undergo transformations to give back the original organic carbonyl band at 1 700 cm^{-1}.

Since no other reactant is present, (1a) or (1b) can only be formed from (10) by inter- or intra-molecular rearrangement pathways. Species (12) having α and β unsaturated keto-groups would be expected to show an i.r. absorption below 1 700 cm^{-1}. Due to the broadness of the original band of (1a) or (1b) at 1 700 cm^{-1} no well defined new band is observed, but a slight broadening towards lower frequency does indeed occur.

Finally, it must be mentioned that the decarbonylation reactions are totally irreversible for (3b) and reversible only to a very small extent ($<10\%$) for (3a). Recently, reversible decarbonylation of 20% cross-linked polystyrene-supported $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ has been reported.[15] The rigidity of the polymer matrix due to high cross-linking presumably prevents formation of metal aggregates by keeping decarbonylated cobalt centres away from each other.[16] The small extent of reversible decarbonylation observed with (3a) as opposed to (3b) can similarly be explained.

(*c*) *Catalytic Reactions.*—The catalytic activities of all the species shown in Schemes 1—3 have been tested for the hydrogenation of olefins in solution. Only (2a), (3a), and (3b) can act as catalysts under moderate conditions, but in all these cases formation of metal crystallites on the polymer appear to take place. Characteristic induction times and an irreversible loss of the i.r. bands for the co-ordinated CO and pd are observed. A solution of $[Rh(CO)_2(pd)]$, when exposed to hydrogen at atmospheric pressure, does undergo slow decomposition and finely divided metal powder separates out. This compound is also known to react with CO and H_2 under pressure, to give various rhodium carbonyl clusters.[17] The reaction presumably proceeds through protonation of the pd ligand, followed by aggregation and carbonylation of $Rh(CO)_2$ units which are stabilized under the CO pressure.

Under an atmosphere of hydrogen a gradual disappearance of the i.r. bands for the CO and co-ordinated keto-groups, along with a change in colour of the beads from yellow-brown to grey, are observed. A somewhat similar system, cross-linked polystyrene-supported $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$, has been reported to catalyse olefin hydrogenation reactions.[18] Metal formation has been observed in these cases also.

Data derived from hydrogenation of cyclohexene, 4-methylcyclohexene, and 2-methylbut-2-ene with (3a) as a catalyst are shown in Figure 3. The compound $[Rh(CO)_2(pd)]$ in solution and under the same conditions is inactive as a catalyst for all these reactions. It should be pointed out that pretreatment of (3a) under different conditions seems to have an effect on its catalytic activity. On a ligand-modified silica surface, very small crystallites of more or less uniform size have been shown to be formed from $Rh(CO)_2$ groups through decarbonylation and hydrogenation.[19] It is possible that pretreatment of (3a) under different conditions gives rise to metal crystallites of different sizes, thereby influencing the observed catalytic activity.

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

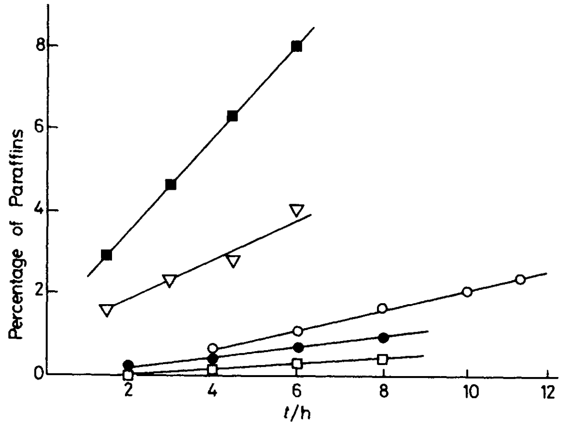

FIGURE 3 Hydrogenation of olefins catalysed by (3a) at 109 °C and atmospheric pressure of hydrogen. ○, No prior activation; (●), activation by heating under H_2 for 12 h; □, activation by heating under Ar for 12 h; ▽, 4-methylcyclohexene, and (■), 2-methylbut-2-ene with activation by heating under H_2 for 6 h

EXPERIMENTAL

Infrared and n.m.r. spectra were taken on a Perkin-Elmer 377 grating spectrophotometer and XL 100 instruments respectively. Metal contents were usually determined by treating the metal-containing polymer with *aqua regia* for 6 h at 100 °C, and then estimating the metal concentration in the diluted, filtered solution, using an IL 751 atomic absorption spectrophotometer. Gas chromatographic analyses were performed with a Pye Unicam 204 instrument. A Carlo–Erba 1106 instrument was used for microanalyses. The Cl percentages not shown in the Table were calculated by indirect methods. Divinylbenzene cross-linked polystyrene beads (8%) of fine mesh were kindly supplied by Industrial and Agricultural Engineering Company (Bombay) Ltd. Soluble polystyrene pellets of density 1.047 (glass transition temp. = 100 °C, m.p. = 237.5 °C) were purchased from the Aldrich Chemical Company (U.K.) Ltd. Unless otherwise specified, all reactions were carried out under nitrogen in dry distilled solvents. Chloromethylation was carried out according to a reported procedure.[4a]

Preparation of Cross-linked Polystyrene-supported [Rh(CO)$_2$(pd)] (3a).—Chloromethylated 8% cross-linked polystyrene beads (5 g) were heated for 24 h at 65 °C with pentane-2,4-dione (2.5 g) and sodium ethoxide (0.2 g) in thf (50 cm^3). The beads were then filtered off, washed with thf, and dried under vacuum. These functionalized beads (2.5 g) were heated at 80 °C for 24 h with [Rh(CO)$_2$(pd)] in benzene. The filtered beads (3a) were extracted with benzene in a Soxhlet apparatus for another 12 h and then filtered off and dried. All the other polymer-supported complexes (2a)—(2e) were prepared in a similar manner.

Preparation of Soluble Polystyrene-supported [Rh(CO)$_2$(pd)] (3b).—A solution of chloromethylated soluble polystyrene (5 g) in thf (100 cm^3) was heated at 65 °C with pentane-2,4-dione (4 g) and sodium ethoxide (0.4 g) for 24 h. The polymer was precipitated by the addition of methanol, cut into small pieces, and redissolved in benzene (100 cm^3). It was reprecipitated and dried after heating the benzene solution at 80 °C with [Rh(CO)$_2$(pd)] (1.0 g) for 24 h.

Reaction of (1b) *with Ethylenediamine.*—A solution of pd-functionalized soluble polystyrene (5 g) in thf (100 cm^3) was heated with ethylenediamine (2.5 g) for 24 h at 65 °C. The resultant polymer (4) was precipitated by adding methanol, washed with methanol and hexane, and then dried.

Reaction of (1a) *with* [Ni(en)$_2$]Cl$_2$.—Beads of (1a) (2.0 g) were first swollen in toluene for 2 h and then refluxed with [Ni(en)$_2$]Cl$_2$ (2.5 g) in methanol (80 cm^3) in the presence of seven or eight drops of pyridine for 24 h. The brown-red beads were filtered off under nitrogen, washed thoroughly with dichloromethane, dried, and stored under vacuum.

Reaction of (1a) *with* FeCl$_3$.—Beads of (1a) (3.0 g) were refluxed with FeCl$_3$ (3.0 g) in a mixture of toluene (100 cm^3) and methanol (25 cm^3) for 6 h. The brown beads were filtered off, washed with water and methanol, and finally dried in an oven at *ca.* 100 °C.

Catalytic Experiments.—Beads of (1a) (1.5 g) were placed in toluene (20 cm^3) and cyclohexene (1 cm^3) at 109 °C. The solution was stirred magnetically under an atmosphere of hydrogen (760 mm Hg), and small portions (0.1 cm^3) of the solution were periodically removed by syringe for gas chromatographic analysis with chlorobenzene as the internal standard. The catalytic runs with other olefins were carried out similarly.

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