Anion Exchange Resin Supported Cluster Carbonyl Anions as Catalysts †

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Anion exchange resin IRA 401 has been shown to be an effective support material for anchoring of anionic carbonyl clusters. Cluster mobility on the polymer surface has been clearly observed by u.v.–visible, i.r., and photoelectron spectroscopic techniques. A polymer-supported species derived from a rhodium and platinum mixed-metal cluster shows positive activity for ring hydrogenation reactions which is absent in derivatives obtained from homonuclear clusters of either metal.

Much of the current interest in evaluating carbonyl clusters supported on inorganic and organic polymers as catalysts originates from the view that anchored carbonyl clusters, under suitable conditions, could be the ideal precursors for bare metal clusters, or very small metal particles of unique catalytic properties.[1,2] Some of the catalytic reactions with supported clusters reported in the literature, such as dehydrocyclisation and skeletal isomerisation of n-hexane [2d] and the Fischer–Tropsch synthesis with a high selectivity to propylene,[2k] lend support to such a view. Since the surface hydroxyl groups of inorganic oxides like silica and alumina react with carbonyl clusters, in most cases the supported species on such support materials are different from the parent clusters and are difficult to characterise.[2] One approach to avoid this problem is to use an organic or inorganic support with a pendant ligand group capable of effecting a CO substitution reaction.[3] This limits the number of clusters that could be anchored in this way since the analogous substitution reactions for the free clusters and ligands in solution would have to be established first. Although there are a few examples of use of ion exchange resins in cluster catalysed reactions,[4,5] to our knowledge the viability of this as a general method for anchoring *anionic* carbonyl clusters remains unexplored. This method is especially attractive since there exists a large number of fully characterised anionic clusters, isolable in most cases as the tetra-alkylammonium salts.

The work described in this paper has been undertaken to provide answers to the following questions. (*i*) How general and effective is the method of supporting clusters with anion exchange resins? (*ii*) Once supported, how mobile are the cluster molecules; to what extent does polymer anchoring prevent the free movements of the anchored molecules? It is important to know this, since the loss of the original molecular identity and the formation of metal aggregates on the polymer surface, often inferred from decarbonylation studies,[6] must be primarily an effect of such mobility. (*iii*) For a model reaction, could all supported clusters be used as precursors for conventional heterogeneous catalysts; more importantly, could a catalyst whose activity is indicative of an alloy type of material be generated from a mixed-metal cluster?

Results and Discussion

Synthesis, Characterisation, and Mobility/Decarbonylation of the Polymer-supported Clusters.—Amberlite anion exchange resin IRA 401 has been used as the support material to synthesise the polymer-supported derivatives of the following typical anionic clusters: $[Pt_{15}(CO)_{30}]^{2-}$, $[Rh_5Pt(CO)_{15}]^-$, $[Rh_{12}(CO)_{30}]^{2-}$, $[Fe_3H(CO)_{11}]^-$, and $[Ru_4H_{4-n}(CO)_{12}]^{n-}$ (n = 1 or 2), designated as (1), (2), (3), (4), and (5) respectively.

The syntheses reported for (1)—(3) involve reaction of $Na_2[PtCl_6]$, a mixture of $Na_2[PtCl_6]$ and $RhCl_3$, and $[Rh_2(CO)_4Cl_2]$ respectively with CO in methanol and in the presence of appropriate amounts of base.[7–9] The ruthenium clusters are synthesised by treating $[Ru_4H_4(CO)_{12}]$ with excess base in ethanol.[10] The anion exchange reactions have been effected in methanol at ambient temperatures under inert atmosphere with perfectly dry IRA 401 in chloride form. The amounts of metal incorporation have been determined by atomic absorption or spectrophotometric analysis and found to be 1—2% for all the polymer-supported derivatives. Complexes (1), (4), and (5) have i.r. spectra identical to those of the original clusters but (2) and (3) do not (Figures 1 and 2). Compound (5) is formulated as a mixture of polymer-supported $[Ru_4H_3(CO)_{12}]^-$ and $[Ru_4H_2(CO)_{12}]^{2-}$ since its i.r. spectrum matches well with reported spectra for the free anions, and is thought to be a result of the use of excess of base.[10]

$[Pt_{15}(CO)_{30}]^{2-}$ is one of the few carbonyl clusters for which *X*-ray photoemission studies have been reported.[11] It is therefore of interest to compare the photoelectron spectroscopic data of (1) with those of the free complex. As shown in Figure 3, using two pairs of spin–orbit split peaks a reasonable fit is obtained for the rather weak and broad platinum $4f$ photoelectron signal of (1). The lower energy signal is about eight times as strong as the other and the platinum $4f_{\frac{7}{2}}$ binding energies are 72.6 and 74.8 eV respectively. The binding energy of the former signal is consistent with the value of 72.8 eV reported by Apai *et al.*[11] for the free complex. The second component is assigned to a Pt^{IV} impurity which most likely originates from small quantities of unreacted $Na_2[PtCl_6]$, the starting material for the synthesis of $[Pt_{15}(CO)_{30}]^{2-}$. The platinum carbonyl cluster anions of the general formula $[\{Pt_3(CO)_6\}_n]^{2-}$ (n = 3—6) have been found to possess characteristic u.v.–visible spectra.[12] As shown in Figure 4 the u.v.–visible spectra of (1) and of $[NBu^n_4]_2[Pt_{15}(CO)_{30}]$ are also similar.

Among the other polymer-supported derivatives, cluster (2) was also examined by photoelectron spectroscopy because of its interesting catalytic properties (see later). The atomic ratio of platinum to rhodium at the surface (upper 50 Å) was found to be 1.6 as opposed to 0.2, the value expected for the free complex. Presumably the bulk of the rhodium remains deeply embedded in the support giving rise to a high platinum to rhodium atomic ratio on the surface. Platinum $4f_{\frac{7}{2}}$ and rhodium $3d_{\frac{5}{2}}$ binding energies (71.1 and 307.3 eV respectively) indicate that both the metals are probably in the zero oxidation state.

$[Pt_{15}(CO)_{30}]^{2-}$ in solution undergoes reaction with hydrogen,

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† *Non-S.I. units employed*: eV = 1.60×10^{-19} J, lbf in^{-2} = 6.89×10^3 Pa, mmHg = 133 Pa.

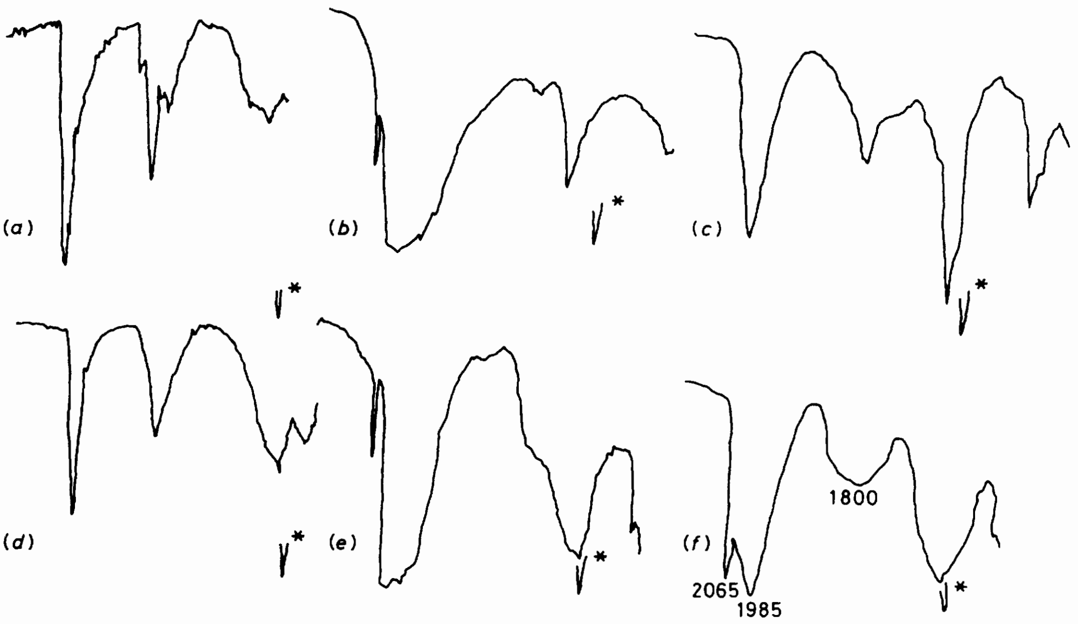

Figure 1. I.r. spectra (KBr discs) of the clusters (*a*) $[NBu^n_4]_2[Pt_{15}(CO)_{30}]$, (*b*) $[NHEt_3][Fe_3H(CO)_{11}]$, and (*c*) $[NEt_4][Rh_5Pt(CO)_{15}]$ and the corresponding polymer-supported derivatives, (*d*), (*e*), and (*f*) respectively. Peaks due to polystyrene (1 600 cm^{-1}) are marked with an asterisk. I.r. data [8] for $[Rh_5Pt(CO)_{15}]^-$ in thf (spectrum not shown): 2 082vw, 2 038s, 2 011m, 1 991ms, and 1 800ms cm^{-1}

Table. Turnover numbers and spectroscopic data for hydrogenation reactions using the polymer-supported clusters as catalysts

Parent cluster	Polymer-supported derivative	I.r. [a] (cm^{-1}) and photoelectron [b] (eV) data	Catalytic activity: turnover number [c] (h^{-1}) for reactions (A)	(B)	(C)	(D)	(E)	(F)
$[Pt_{15}(CO)_{30}]^{2-}$	(1)	2 050s, 1 860m [72.6] [h]	122,[d] 49 [e] 675 [i]	114	87 [j] 78 [j] 12 [k]	161	6	0 [g]
$[Pt_{15}(CO)_{30}]^{2-}$	(1) [l]	[71.7],[h,l] [72.0] [h,m]						
$[Pt_{15}(CO)_{30}]^{2-}$	(1) [n]	2 020s,[l] 1 830m,[l] [71.7],[h,l] 2 030s [m] [72.0] [h,m]						
$[Rh_5Pt(CO)_{15}]^-$	(2)	2 065s, 1 985vs 1 800m, br [71.1],[q] [307.3] [r]	85	4		346	4	45,[g] 12,[o] 4 [p]
$[Rh_{12}(CO)_{30}]^{2-}$	(3)	2 065s, 2 045s 1 985vs, 1 770m, br	0.02	0	0	0.01	0	
$[Fe_3H(CO)_{11}]^-$	(4)	2 065w, sp, 1 990vs, br, 1 965s, br, 1 720w (sh)	0	0		0.02	0	
$[Ru_4H_{4-n}(CO)_{12}]^{n-}$ (n = 1 or 2)	(5)	2 070w, sp, 2 035vs, 2 020vs, 1 995vs, 1 950s, br, 1 890m (sh), 1 750 (sh)	0	0.01	0	0	0	

[a] s = strong, vs = very strong, m = medium, w = weak, br = broad, sp = sharp, sh = shoulder. [b] Values are given in square brackets. [c] Unless otherwise stated, the catalytic reactions were carried out with polymer-supported derivatives without any prior activation. For (3) and (4) no observable increase in catalytic activity is found with decarbonylated materials. Turnover number = (mmol of product)/(mmol of cluster × time in hours). Ring hydrogenation reactions were carried out at 200 lbf in^{-2} of hydrogen at 70 °C. Other hydrogenation reactions were carried out in tetrahydrofuran (thf) at 60 °C under 20 lbf in^{-2} of hydrogen. Key to reactions: (A) cyclohexene to cyclohexane; (B) butanal to butanol; (C) benzaldehyde to benzyl alcohol; (D) nitrobenzene to aniline; (E) acetonitrile to ethylamine; (F) see appropriate footnotes. [d] Catalysis by (1). [e] Catalysis by (1) decarbonylated with H_2. [f] 60 lbf in^{-2}. [g] Benzene to cyclohexane. [h] Platinum $4f_{7/2}$. [i] Catalysis by (1) decarbonylated thermally. [j] 35 lbf in^{-2} H_2. [k] 20 lbf in^{-2} H_2. [l] Thermally decarbonylated. [m] Decarbonylated with H_2. [n] Recarbonylated after decarbonylation. [o] Toluene to methylcyclohexane. [p] Phenol to cyclohexanol. [q] Platinum $4f_{7/2}$ of (2). [r] Rhodium $3d_{5/2}$ of (2).

$$4[NBu^n_4]_2[Pt_{15}(CO)_{30}] + H_2 \longrightarrow 4[NBu^n_4]_2[Pt_{12}(CO)_{24}] + 2H^+ + [Pt_{12}(CO)_{24}]^{2-} \qquad (i)$$

$$3[NBu^n_4]_2[Pt_{12}(CO)_{24}] + H_2 \longrightarrow 3[NBu^n_4]_2[Pt_9(CO)_{18}] + 2H^+ + [Pt_9(CO)_{18}]^{2-} \qquad (ii)$$

equations (i) and (ii), which can be monitored by i.r. or more effectively by u.v.-visible spectroscopy.[7-12] Had these reactions where changes in nuclearity are involved taken place on the polymer surface, the mobility of the anchored molecules could be determined. Thus (1), when reacted with hydrogen (20 lbf in^{-2}, 3 h, tetrahydrofuran, 60 °C), shows characteristic

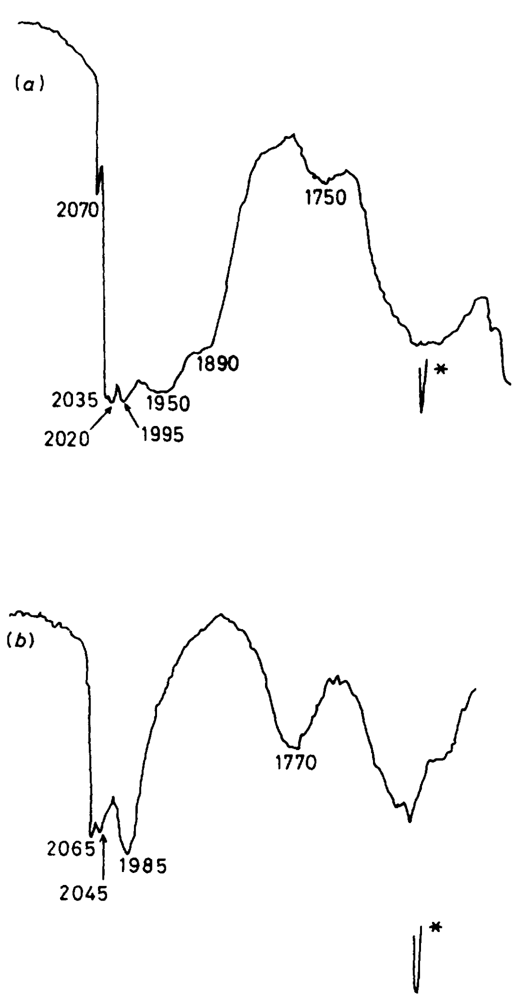

Figure 2. I.r. spectra (KBr discs) of the polymer-supported clusters (*a*) $[Ru_4H_{4-n}(CO)_{12}]^{n-}$ (5; n = 1 or 2) and (*b*) $[Rh_{12}(CO)_{30}]^{2-}$ (3). Peaks due to polystyrene (1 600 cm^{-1}) are marked with an asterisk. I.r. data [10] for $[Ru_4H_3(CO)_{12}]^-$: 2 067vw, 2 037s, 2 031 (sh), 2 017s, 1 998vs, 1 975m, 1 948w, and 1 930w cm^{-1}. I.r. data [10] for $[Ru_4H_2(CO)_{12}]^{2-}$: 2 027w, 1 985w, 1 950s, 1 940s, 1 899m, 1 881m, 1 809vw, 1 763m, and 1 753m (sh) cm^{-1}. I.r. data [9] for $[Rh_{12}(CO)_{30}]^{2-}$: 2 070w, 2 053s, 2 040s, 2 007, 1 807w, and 1 771s cm^{-1}

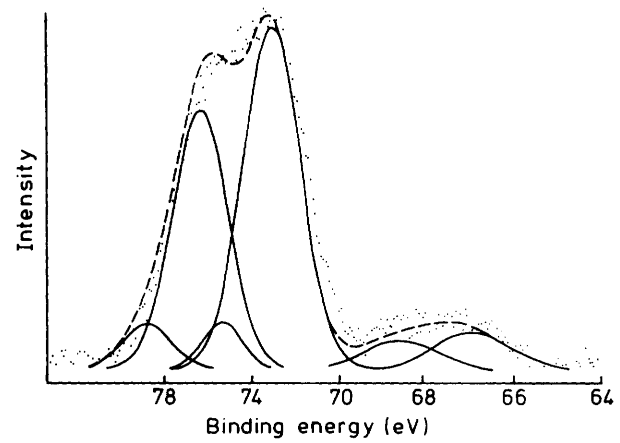

Figure 3. *X*-Ray photoelectron spectrum of (1). The experimental is dashed

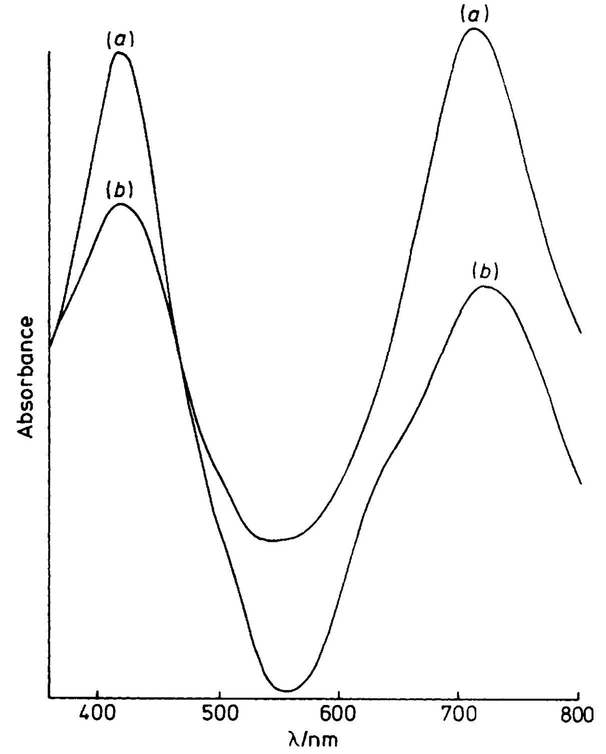

Figure 4. U.v.-visible spectra of (*a*) $[NBu^n_4]_2[Pt_{15}(CO)_{30}]$ in acetonitrile and (*b*) polymer-supported cluster (1) as a Nujol mull

changes in the u.v.-visible spectra suggesting the step-wise occurrence of reactions (i) and (ii) (Figure 5). This indicates considerable mobility of the cluster molecules on the polymer surface. Prolonged (>48 h) treatment with hydrogen leads to complete decarbonylation of (1) as is evident from the total loss of i.r. carbonyl bands. Decarbonylation could also be effected by heating (65 °C, 10^{-3} mmHg) powdered (1). Under atmospheric pressure of CO, the decarbonylated materials could be recarbonylated in both cases. However, on the basis of i.r. and photoelectron data the resultant species are considered to be different from (1) (see Table). The inability of (1) to undergo *reversible* decarbonylation is expected in the light of the observed mobility of $[Pt_{15}(CO)_{30}]^{2-}$ ions on the polymer surface.

Under the conditions mentioned above, none of the other polymer-supported derivatives can be decarbonylated by treatment with hydrogen. Compounds (3) and (4) could be decarbonylated thermally but do not undergo recarbonylation ($\leqslant$100 lbf in^{-2} of CO). Compounds (2) and (5) are resistant towards CO loss by thermal treatment. Heating (2) but not (5) at higher temperatures ($\geqslant$120 °C) does reduce the intensities of the carbonyl bands but under these conditions, reactions involving the NR_4^+ groups present in the polymer are possible. This is so since the specified thermal stability of the anion-exchange resin is $\leqslant$75 °C.

Catalytic Activities of the Polymer-supported Clusters.— All the polymer-supported derivatives have been tested as catalysts for the hydrogenation of a few typical functional groups. Direct metal estimations before and after the catalytic runs clearly established that leaching of supported materials does not take place. As can be seen from the Table, (1) and (2) are reasonably active catalysts while (3), (4), and (5) show little, if any, activity at all. $[NBu^n_4]_2[Pt_{15}(CO)_{30}]$ has been used as the homogeneous catalyst precursor for the hydrogenation

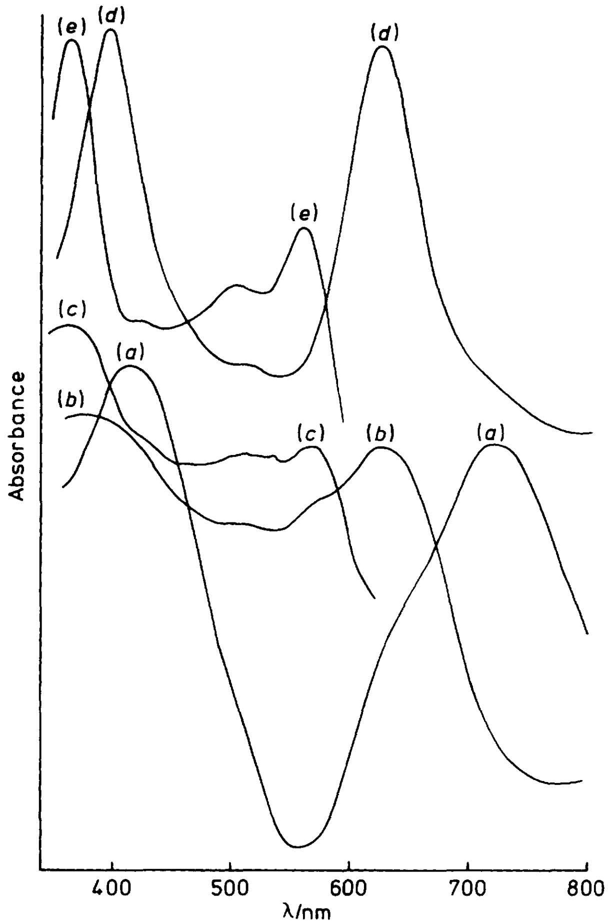

Figure 5. U.v.-visible (Nujol mull) spectral changes when the polymer-supported cluster (1) is reacted with hydrogen (20 lbf in^{-2}, 60 °C, thf solvent): (*a*) initial spectrum of (1); (*b*) spectrum after 1.5 h; (*c*) spectrum after 3 h; (*d*) spectrum of $[Pt_{12}(CO)_{24}]^{2-}$ in MeCN; (*e*) spectrum of $[Pt_9(CO)_{18}]^{2-}$ in MeCN

of benzaldehyde;[13] the pressure of hydrogen has been found to have a remarkable effect on the nature of the products, benzyl alcohol or benzene and methanol. In contrast, when (1) is used as the catalyst the only product formed is benzyl alcohol irrespective of the hydrogen pressure. This indicates formation of *different* catalytic intermediates in the homogeneous and the resin-supported reactions. With increased pressures a pronounced increase in the turnover numbers is seen (see Table).

Compound (1), thermally decarbonylated (1), and (1) decarbonylated by reaction with hydrogen exhibit differences in cyclohexene hydrogenation activities. Decarbonylation and the associated mobility of the $[Pt_{15}(CO)_{30}]^{2-}$ ions are expected to lead to the formation of highly dispersed metal crystallites and therefore to high catalytic activity. This is the case for the thermally decarbonylated (1), but surprisingly prior decarbonylation of (1) with hydrogen results in a lowering of activity. A possible explanation could be that the metal crystallites which form differ in size and shape depending on the mode of decarbonylation. The fact that decarbonylation with hydrogen goes through the intermediate formations of $[Pt_{12}(CO)_{24}]^{2-}$ and $[Pt_9(CO)_{18}]^{2-}$, while thermal decarbonylation does not involve such intermediate species, support this hypothesis.

Among the polymer-supported derivatives, (2) is the only one which shows catalytic activity with respect to aromatic ring hydrogenation reactions. It should be noted here that neither (1) nor (3), clusters containing *only* platinum or rhodium atoms, show any activity for aromatic-ring hydrogenation whereas (2), a heteronuclear cluster of platinum and rhodium, does. Interestingly, with (2) as the catalyst ring hydrogenation is observed with phenol, anisole, and toluene but not with aniline or nitrobenzene. With the latter only aniline and no cyclohexylamine is obtained. After repeated use of (2) for benzene hydrogenation (four runs), although the photoelectron spectrum of (2) remains virtually unchanged, there is an observable loss in the CO band intensity in the i.r. spectrum. However, treatment of the used catalyst with CO at atmospheric pressure gives a species having an i.r. spectrum identical with that of freshly prepared (2).

As mentioned earlier, the work described here was undertaken to provide full or partial answers to three specific questions. In conclusion, it could therefore be said first, that the anchoring of anionic clusters on anion exchangers may be considered as a general method for the preparation of supported derivatives. However, with certain clusters the anchored derivatives, (2) in this case, may be very different from the parent cluster. Secondly, spectroscopic monitoring of the decarbonylation of (1) with hydrogen gives clear evidence for the mobility of the anchored species on the polymer surface. Thirdly, decarbonylation leading to the formation of metal crystallites does not necessarily mean positive catalytic activity. An example is the lack of activities with decarbonylated (3) and (4). Finally (2), the polymer-supported derivative of the heteronuclear cluster, which is admittedly different from the parent cluster, does indeed exhibit unique catalytic properties.

Experimental

In solution the complex anions $[Pt_{15}(CO)_{30}]^{2-}$, $[Rh_5Pt(CO)_{15}]^-$, $[Rh_{12}(CO)_{30}]^{2-}$, $[Fe_3H(CO)_{11}]^-$, and $[Ru_4H_{4-n}(CO)_{12}]^{n-}$ (n = 1 or 2) with sodium as the counter ion were synthesised according to previously reported procedures.[7-10] The anion exchange resin IRA 401 was purchased from Aldrich Chemical Company (U.K.) and used in the chloride form. Gas-liquid chromatographic analysis was performed with a Pye-Unicam 204 instrument. I.r. spectra were recorded on a Perkin-Elmer 377 grating spectrophotometer. Atomic absorption measurements were carried out on a IL 751 spectrophotometer. U.v.-visible spectra were recorded on a Pye-Unicam SP8 100 spectrometer. The photoelectron spectroscopic analyses were carried out by Dr. R. A. Marbrow of the New Science Group of I.C.I. All solvents and organic compounds were thoroughly dried and distilled under nitrogen before use. The air sensitivity of most of the cluster anions required thorough degassing of all solvents and reagents.

Synthesis of Polymer-supported $[Pt_{15}(CO)_{30}]^{2-}$, (1).—The cluster $Na_2[Pt_{15}(CO)_{30}]$ (0.11 g, 0.029 mmol) was generated[7] from $Na_2[PtCl_6]\cdot 6H_2O$ (0.25 g, 0.44 mmol) by reductive carbonylation in methanol (25 cm^3) containing sodium acetate trihydrate (0.48 g, 3.52 mmol). The anion exchange resin (1.5 g) pre-washed with dilute HCl (1 mol dm^{-3}), deionised water, ethanol, and dichloromethane and then dried thoroughly under vacuum (10^{-3} mmHg) at 60 °C for 24 h, was added to the methanol solution. The mixture was stirred for 2 h; the resin was filtered off, washed repeatedly with methanol, and dried under vacuum. All the other polymer-supported derivatives were synthesised by similar procedures.

Catalytic 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. The appropriate thoroughly degassed organic compound (cyclohexene, butanal, *etc.*), the polymer-supported cluster, and tetrahydrofuran were placed in the reaction vessel and a pressure of 20 lbf in^{-2} of hydrogen was maintained through a manifold connected directly to a hydrogen gas cylinder. The mixture was vigorously stirred with a magnetic stirrer and the sample analysed at the end of a fixed time period.

Experiments involving hydrogen pressures $\geqslant 20$ lbf in^{-2} were carried out in a small (100 cm^3) Parr pressure reactor.

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