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Attachment of Tetranuclear Iridium Carbonyl Clusters onto Functionalized Silica Supports

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Well defined and characterized metal clusters have found increasing interest as catalysts in recent years. Several attempts have been described to attach molecular carbonyl cluster compounds onto chemically functionalized supports, namely polymers or silica. $Rh_6(CO)_{16}$ has been claimed to probably maintain its structural integrity when bound onto phosphinated polystyrene matrices [1–4], while polymer-bound analogues of $[Ir_4(CO)_{11}(PPh_3)]$ and $[Ir_4(CO)_{10}(PPh_3)_2]$ [5] and of $[Fe_2Pt(CO)_8(PPh_3)_2]$, $[RuPt_2(CO)_5(PPh_3)_3]$, $[HAuOs_3(CO)_{10}(PPh_3)]$ [6] have successfully been synthesized. Similar attachment of $[Os_3(CO)_{11}(PPh_3)]$, $[H_2Os_3(CO)_9(PPh_3)]$ and $[HAuOs_3(CO)_{10}(PPh_3)]$ analogues onto phosphinated silica supports has been described [6, 7]. We wish to report here the synthesis and characterization by i.r. spectroscopy of analogues of $[Ir_4(CO)_{12-x}(PPh_3)_x]$ (X = 1, 2, and 3) attached onto phosphinated silica supports.

The support material was the same as used previously [8] and contained 0.3 pendent $-(CH_2)_3P(C_6H_5)_2$ surface ligands per nm^2. The attached species were identified by comparison of their i.r. carbonyl stretching spectra with those of analogous molecular compounds. A Perkin-Elmer model 580 B spectrometer was used, the spectra slit being typically 3.3 cm^{-1} at 2100 cm^{-1}.

An attempt to attach the tetrairidium cluster onto the pendent propyl diphenylphosphine ligands by ligand exchange of $Ir_4(CO)_{12}$ from chlorobenzene solution at 373 K was unsuccessful, this probably being due to the extremely slow substitution of the first phosphine ligand as shown by Karel and Norton [9]. We have therefore prepared silica-attached tetranuclear iridium clusters using a modification of Stuntz and Shapley's synthesis [10] of mono- and disubstituted phosphorus derivatives of $Ir_4(CO)_{12}$, which had proved successful for the attachment of the analogous clusters onto polymers [5]. $Ir(CO)_2$(*p*-toluidine)Cl in 2-methoxyethanol–water was reduced by zinc in the presence of phosphinated silica at 363 K under 5 atm of CO for 90 min. The carbonyl i.r. spectrum of the resulting silica attached tetranuclear iridium cluster is compared with its mono-substituted analogue $[Ir_4(CO)_{11}(PPh_3)]$ in Fig. 1, spectra 1 and 2. On the basis of this comparison, the attached species can clearly by identified as a mono-substituted tetranuclear iridium cluster. Some minor differences between the two spectra are due to an incomplete compensation of the silica background. Remarkably, only mono-substituted species are formed during the direct synthesis although the ligand density on the silica surface would allow for di-substituted clusters to be formed. However, steric restrictions might be more severe on the surface than in solution.

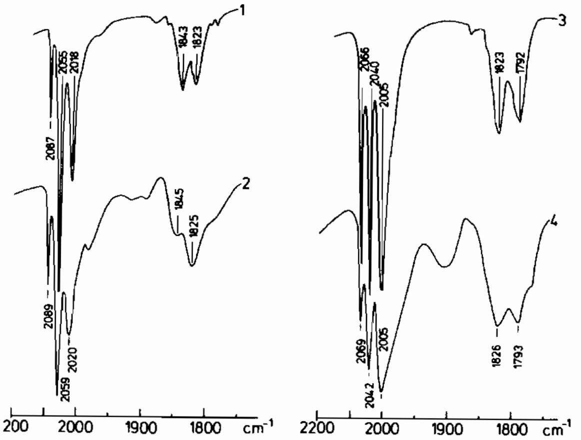

Fig. 1. I.r. spectra of tetranuclear iridium cluster compounds: (1) $[Ir_4(CO)_{11}(PPh_3)]$ in CH_2Cl_2; (2) $[Ir_4(CO)_{11}(PPh_2(CH_2)_3-]$ silica attached; (3) $[Ir_4(CO)_{10}(PPh_3)_2]$ in CH_2Cl_2; (4) $[Ir_4(CO)_{10}(PPh_3)(PPh_2(CH_2)_3-)]$ silica attached.

In contrast, the phosphinated polymers gave exclusively mono-substituted tetrairidium clusters only when the P concentration was low, while mixtures of mono- and disubstituted clusters were formed on polymers having higher P concentrations [5].

Di- and tri-substituted attached tetranuclear iridium clusters were obtained by ligand exchange reactions, which become possible because of the acceleration of subsequent substitutions by phosphine substitution on one metal atom in $Ir_4(CO)_{12}$ [9]. The di- and tri-substituted clusters have been prepared by contacting chlorobenzene solutions containing $[Ir_4(CO)_{11}(PPh_3)]$ or $[Ir_4(CO)_{10}(PPh_3)_2]$ (these clusters were prepared according to Stuntz and Shapley's synthesis [10]), respectively, with sus-

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pended phosphinated silica particles at 358 K for 30 or 5 min, respectively under N_2 atmospheres. Attempts to attach $[Ir_4(CO)_{11}(PPh_3)]$ by ligand exchange under 1 atm of CO were unsuccessful.

The resulting attached species are identified by their carbonyl i.r. spectra as the di- (*cf.* Fig. 1, spectra 3 and 4) and tri-substituted tetranuclear iridium clusters, respectively. The bands of the disubstituted species are broadened as compared to those of $[Ir_4(CO)_{10}(PPh_3)_2]$. The material obtained by ligand exchange of $[Ir_4(CO)_{10}(PPh_3)_2]$ gave rise to i.r. bands at 2047(s), 1997(vs), and 1792(s) cm^{-1}, which compare well with those reported for $[Ir_4(CO)_9(PPh_3)_3]$ (2042(ms), 2015(sh), 1982(vs), 1962(sh), 1772(s, br) cm^{-1}) [11]. The attached clusters can therefore be identified as $[Ir_4(CO)_{10}(PPh_3)(PPh_2(CH_2)_3\text{–})]$ and $[Ir_4(CO)_9(PPh_3)_2(PPh_2(CH_2)_3\text{–})]$ which indicates that the attachment occurred via a single CO-surface ligand exchange in each case.

A preliminary study was also carried out regarding the thermal stability of the attached iridium clusters in CO and in CO free environments, which showed that the cluster integrity is maintained at temperatures below approximately 350 K. The mono- and di-substituted clusters are partially being substituted by pendent surface ligands to form $[Ir_4(CO)_{10}(PPh_2(CH_2)_3\text{–})_2]$ and $[Ir_4(CO)_9(PPh_3)(PPh_2(CH_2)_3\text{–})_2]$, respectively, when the corresponding materials are treated *in vacuo* at 340 K. These processes are slowly reversed on admission of 1 atm of CO at 340 K. A complete detachment of the cluster by formation of $Ir_4(CO)_{12}$ could, however, not be observed. The tri-substituted attached cluster could analogously be slowly carbonylated at 340 K in 1 atm of CO, this process again being reversible on evacuation. Admission of H_2 (0.4 atm) or C_2H_4 (0.65 atm) at 340 K gave rise to significant changes in the carbonyl stretching region of all samples, which, however, were completely reversed on evacuation and exposure to CO. This suggests the probable retention of the cluster integrity also in H_2 and ethylene atmospheres, and the possible use of these attached tetranuclear iridium clusters as catalysts for gas phase hydrogenation reactions.

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