

Polymer-bound Tetranuclear Iridium Carbonyl Catalyst

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Summary An iridium cluster has been attached to a solid and identified by i.r. spectroscopy as $[\text{Ir}_4(\text{CO})_{11}\text{Ph}_2\text{P}(\text{polymer})]$ [where the polymer is poly(styrene-divinylbenzene)]; the solid is an active catalyst for ethylene hydrogenation at 303 K and 1 atm.

ONE of the central problems in catalysis is the preparation and characterization of unique, well-defined metal clusters attached to solids. Several workers have prepared catalysts by combining metal cluster compounds with supports,¹ but none has fully determined the structure of an attached

cluster. We report here the synthesis and characterization by i.r. spectroscopy of the polymer-bound analogues of $[\text{Ir}_4(\text{CO})_{11}(\text{PPh}_3)]$ and $[\text{Ir}_4(\text{CO})_{10}(\text{PPh}_3)_2]$.

The iridium clusters were attached to two forms of 2%-cross-linked polystyrene. The first polymer support was synthesized from the monomers styrene, divinylbenzene, and *p*-bromostyrene, giving 11 μm thick membranes optimally suited to transmission i.r. spectroscopy.^{2,3} The other support was chloromethylated poly(styrene-divinylbenzene) beads (Merrifield Polymer, Fluka, 200–400 mesh). In both polymers, the halogens were replaced by PPh_2 groups by reaction with LiPPh_2 .⁴

The polymer-attached tetranuclear iridium clusters were prepared using a modification of Stuntz and Shapley's synthesis⁵ of mono- and di-substituted phosphorus derivatives of dodecacarbonyltetrairidium. Complex $[\text{Ir}(\text{CO})_2(p\text{-toluidine})\text{Cl}]$ in benzene-tetrahydrofuran-water was reduced by zinc in the presence of phosphinated polystyrene. The reaction mixture was maintained at 363 K under 4 atm of CO for 30–60 min. The resulting polymer-bound clusters were identified by comparison of their i.r. spectra with those of the analogous molecular species (Table and Figure). Synthesis with the phosphinated polymer mem-

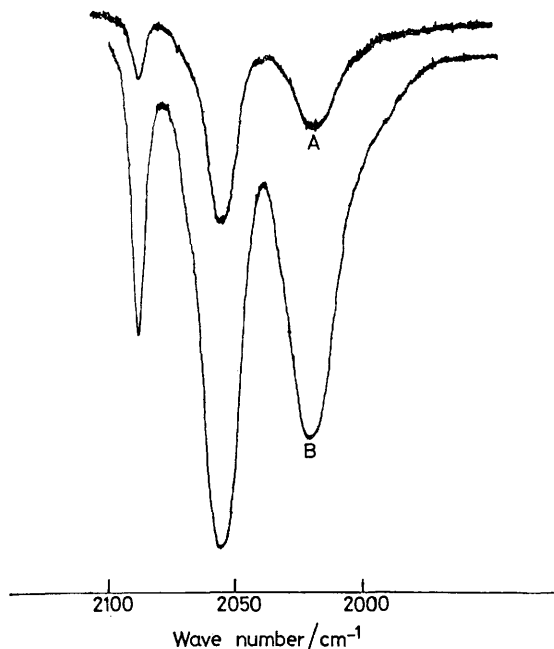


FIGURE. Terminal carbonyl i.r. spectra of (A) an 11 μm thick membrane of $[\text{Ir}_4(\text{CO})_{11}\text{Ph}_2\text{PC}_6\text{H}_4\text{-}p\text{-(polymer)}]$ at 303 K and (B) $[\text{Ir}_4(\text{CO})_{11}(\text{PPh}_3)]$ in CH_2Cl_2 at 303 K.

brane having a low concentration of P (0.69 wt %) yielded only the mono-substituted tetrairidium carbonyl, whereas the polymer beads with a higher P content (1.28 wt %) gave a mixture of the mono- and di-substituted clusters (Table).

¹ J. P. Collman, L. S. Hegedus, M. P. Cooke, J. R. Norton, G. Dolcetti, and D. N. Marquardt, *J. Amer. Chem. Soc.*, 1972, **94**, 1789; G. C. Smith, T. P. Chojnacki, S. R. Dasgupta, K. Iwatate, and K. L. Watters, *Inorg. Chem.*, 1975, **14**, 1419; K. Iwatate, S. R. Dasgupta, R. L. Schneider, G. C. Smith, and K. L. Watters, *Inorg. Chim. Acta*, 1975, **15**, 191; M. Ichikawa, *J.C.S. Chem. Comm.*, 1976, 26.

² G. Zundel, 'Hydration and Intermolecular Interaction. Infrared Investigations with Polyelectrolyte Membranes,' Academic Press, New York, 1969.

³ R. Thornton, Ph.D. Thesis, University of Delaware, Newark, 1973.

⁴ C. Tamborski, F. E. Ford, W. L. Lehn, G. J. Moore, and E. J. Soloski, *J. Org. Chem.*, 1962, **27**, 619.

⁵ G. F. Stuntz and J. R. Shapley, *Inorg. Chem.*, 1976, **15**, 1994.

The membrane containing mono-substituted tetrairidium clusters was tested as an ethylene hydrogenation catalyst in a flow reactor which was also an i.r. cell.³ The rate of the catalytic reaction at 1 atm and 303 K was roughly 10^{-3} mol per g iridium per second, and the activity declined to about one-fourth of the original value in 13 h of continuous operation. The i.r. spectrum of the functioning catalyst at 303 K was almost indistinguishable from the spectrum of the originally prepared catalyst, but at 368 K, the intensities of the terminal CO bands decreased by *ca.* 10% when

TABLE

Characterization of polymer-bound tetrairidium clusters and molecular analogues

Sample	Solvent or phase	$\nu_{\text{CO}}/\text{cm}^{-1}$
$[\text{Ir}_4(\text{CO})_{11}(\text{PPh}_3)]$	CH_2Cl_2	2088m, 2056vs, 2020s, 1887vw, 1847m, 1825m
$[\text{Ir}_4(\text{CO})_{10}(\text{PPh}_3)_2]$	CH_2Cl_2	2067m, 2041s, 2006s, 1827mb, 1795mb
Membrane ^a	—	2087m, 2055vs, 2017s, 1848m
Beads ^b	KBr	2090, 2054, 2016; 2068, 2044, 2006

^a $[\text{Ir}_4(\text{CO})_{11}\text{Ph}_2\text{PC}_6\text{H}_4\text{-}p\text{-(polymer)}]$; analysis: 0.69 wt % P, 0.38 wt % Ir. The second bridging carbonyl band was obscured by an absorption indicative of the polymer backbone. ^b $[\text{Ir}_4(\text{CO})_{11}\text{Ph}_2\text{PCH}_2\text{C}_6\text{H}_4\text{-}p\text{-(polymer)}]$ and $[\text{Ir}_4(\text{CO})_{10}(\text{Ph}_2\text{PCH}_2\text{C}_6\text{H}_4\text{-}p)_2\text{-(polymer)}]$; analysis: 1.28 wt % P, 11.1 wt % Ir. The overlap between the four bridging CO bands with each other and polymer bands prevented assignment of frequencies.

flowing helium was replaced by flowing hydrogen plus ethylene. As the temperature of the membrane in helium was raised to 393 K, the carbonyl bands merged into a broad band suggestive of CO bonded to aggregated metal species; under flow of hydrogen plus ethylene, the band disappeared. These results suggest that the tetrairidium cluster carbonyl functioned as a catalyst having a small fraction of the carbonyl ligands replaced by reactant ligands. The presumed presence of aggregated metal at 393 K, however, leaves open the possibility that aggregated metal species were responsible for the catalysis.

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