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Preliminary communication

MULTIDENTATE LIGAND STABILISED METAL CARBONYL CLUSTER COMPLEXES; REACTIONS WITH PHOSPHINES AND IMMOBILISATION ON SILICA OR ORGANIC POLYMERS

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Summary

The tridentate-phosphine stabilised cluster complexes $M_4(CO)_9[HC(PPh_2)_3]$ (M = Rh, Ir) react with monodentate phosphines, L, to give $M_4(CO)_8(L)[HC(PPh_2)_3]$ ($L = PPh_3$, $Ph_2PCH_2CH_2Si(OEt)_3$) in which the monodentate phosphine is coordinated to the apical metal atom. A similar reaction of $Ru_3(CO)_{10}(dppm)$ (dppm = bisdiphenylphosphinomethane) with L gives $Ru_3(CO)_9(L)(dppm)$. Immobilisation of these complexes, to give unique supported clusters, has been achieved either by treating $M_4(CO)_9[HC(PPh_2)_3]$ and $Ru_3(CO)_{10}(dppm)$ with phosphinated silica or phosphinated polystyrene-divinylbenzene or by treating $M_4(CO)_8(L)[HC(PPh_2)_3]$ and $Ru_3(CO)_9(L)(dppm)$ ($L = Ph_2PCH_2CH_2Si(OEt)_3$) with silica.

The stabilisation of transition metal cluster complexes by the use of multidentate ligands is receiving a great deal of attention at the present time [1—8]. The aim is to prevent metal cluster fragmentation occurring during the course of catalytic reactions. There is also considerable interest in the immobilisation of cluster complexes to provide either supported molecular metal clusters or highly dispersed metal particles which could provide highly selective heterogeneous catalysts [8].

As part of our investigations into multidentate ligand stabilised metal carbonyl clusters [3,4], we have found that such clusters undergo selective reactions with further phosphine ligands, and this has provided a route to immobilised clusters in which only one species is present on the support.

The tetranuclear, tridentate phosphine stabilised complexes $M_4(CO)_9[HC(PPh_2)_3]$ (M = Rh, Ir) undergo selective substitution by monodentate phosphines at the apical metal atom to give the complexes $M_4(CO)_8(L)[HC(PPh_2)_3]$ ($L = PPh_3$, $Ph_2PCH_2CH_2Si(OEt)_3$). Similarly, reaction of monodentate phosphines with

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TABLE 1

INFRARED AND ^{31}P NMR DATA

Complex	ν(CO) (cm^{-1})^a	$\delta(^{31}P\{^1H\})^b$
$Ir_4(CO)_8[HC(PPh_2)_3](PPh_3)$	2026m, 1989s, 1953w, 1942w, 1919vw	−15.4m (PPh_3); −47.0m ($(Ph_2P)_3CH$)
$Ir_4(CO)_8[HC(PPh_2)_3][Ph_2PCH_2CH_2Si(OEt)_3]$	2022m, 1987s, 1951w, 1941w, 1917vw	−17.0br m (PPh_2CH_2); −47.7br m ($(Ph_2P)_3CH$)
$Ir_4(CO)_8[HC(PPh_2)_3](Ph_2PCH_2CH_2SiOSi\equiv)$	2029m, 1994s, 1960sh, 1948sh, 1919sh	
$Ir_4(CO)_8[HC(PPh_2)_3](Ph_2PCH_2$-polymer)	2026m, 1990s, 1959sh, 1944sh, 1918sh	
$Rh_4(CO)_8[HC(PPh_2)_3](PPh_3)$	2020s, 1992sh, 1985vs, 1848sh, 1827m, 1784s, 1761sh	15.1m ($(Ph_2P)_3CH$); 25.0m (PPh_3)
$Rh_4(CO)_8[HC(PPh_2)_3][Ph_2PCH_2CH_2Si(OEt)_3]$	2020s, 1990sh, 1982vs, 1846sh, 1826m, 1783s	13.4m ($(Ph_2P)_3CH$); 23.9m (PPh_2CH_2)
$Rh_4(CO)_8[HC(PPh_2)_3](Ph_2PCH_2CH_2SiOSi\equiv)$	2022s, 1998sh, 1988vs, 1847sh, 1835w, 1802m, 1780sh	
$Rh_4(CO)_8[HC(PPh_2)_3](Ph_2PCH_2$-polymer)	2016s, 1987sh, 1978vs, 1848sh, 1830m, 1796s, 1778s	
$Ru_3(CO)_9(dppm)(PPh_3)$	2052w, 1992s, 1975s, 1942m	36.59 (PPh_3)(t, J(P—P) 9.3); 15.47 (dppm)(d)
$Ru_3(CO)_9(dppm)[Ph_2PCH_2CH_2Si(OEt)_3]$	2051w, 1990s, 1974s, 1940m	37.38 (PPh_2CH_2)-(t, J(P—P) 8.5); 18.30 (dppm)(d)
$Ru_3(CO)_9(dppm)(Ph_2PCH_2CH_2SiOSi\equiv)$	2053w, 1992s, 1975s, 1947sh	
$Ru_3(CO)_9(dppm)(Ph_2PCH_2$-polymer)	2051w, 1989s, 1973s, 1940sh	

^{a}Soluble complexes as CH_2Cl_2 solutions; supported complexes as Nujol mulls. ^{b}Chemical shifts with respect to 85% H_3PO_4 as external reference; $CDCl_3$ solutions; d = doublet, t = triplet, m = multiplet; coupling constants in Hz.

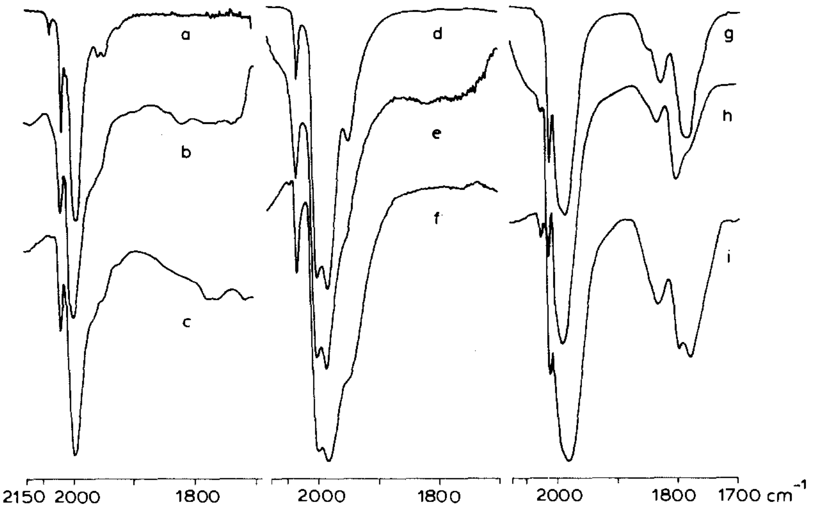

Fig. 1. IR spectra of homogeneous and supported complexes. (a) $Ir_4(CO)_8[HC(PPh_2)_3](PPh_3)$; (b) $Ir_4(CO)_8[HC(PPh_2)_3](Ph_2PCH_2CH_2SiOSi\equiv)$; (c) $Ir_4(CO)_8[HC(PPh_2)_3](Ph_2PCH_2$-polymer); (d) $Ru_3(CO)_9(dppm)(PPh_3)$; (e) $Ru_3(CO)_9(dppm)(Ph_2PCH_2CH_2SiOSi\equiv)$; (f) $Ru_3(CO)_9(dppm)Ph_2PCH_2$-polymer); (g) $Rh_4(CO)_8[HC(PPh_2)_3](PPh_3)$; (h) $Rh_4(CO)_8[HC(PPh_2)_3](Ph_2PCH_2CH_2SiOSi\equiv)$; (i) $Rh_4(CO)_8[HC(PPh_2)_3](Ph_2PCH_2$-polymer).

$Ru_3(CO)_{10}(dppm)$ selectively gives $Ru_3(CO)_9(L)(dppm)$. Infrared and ^{31}P NMR spectroscopic data for these complexes are given in Table 1, and Fig. 1. Remarkably, the iridium complexes still do not contain bridging CO ligands [9]. A similar reaction between $Co_4(CO)_9[HC(PPh_2)_3]$ and PMe_3 has recently been reported [2].

Since these reactions take place cleanly and quantitatively to give only one product, we have carried out analogous reactions with phosphinated silica and phosphinated polystyrene-divinylbenzene copolymer in order to obtain supported clusters in which there is only one cluster species present on the support. Thus, for example, reaction of $Ir_4(CO)_9[HC(PPh_2)_3]$ with phosphinated silica (non-porous silica, surface area 400 m^2 g^{-1}, containing 0.52% P in the form of $\equiv SiOSiCH_2CH_2PPh_2$ [10]) proceeds smoothly in refluxing toluene followed by soxhlet extraction to give $Ir_4(CO)_8[HC(PPh_2)_3][Ph_2PCH_2CH_2SiOSi\equiv]$ (Fig. 2).

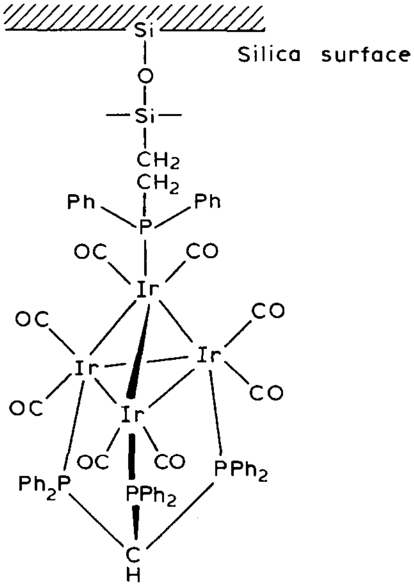

Fig. 2. Proposed structure of $Ir_4(CO)_8[HC(PPh_2)_3](Ph_2PCH_2CH_2SiOSi\equiv)$.

Similar reactions have been carried out between the phosphinated silica and $Rh_4(CO)_9[HC(PPh_2)_3]$ or $Ru_3(CO)_{10}(dppm)$ to give $Rh_4(CO)_8[HC(PPh_2)_3]$-$(Ph_2PCH_2CH_2SiOSi\equiv)$ and $Ru_3(CO)_9(dppm)(Ph_2PCH_2CH_2SiOSi\equiv)$, respectively. The infrared spectra of these supported cluster complexes, obtained as Nujol mulls, are virtually identical to their homogeneous analogues (Fig. 1). Using a phosphinated polystyrene-divinylbenzene copolymer (2% cross-linking, 2.87% P in the form of polymer-CH_2PPh_2 [11]), the analogous Ir, Rh and Ru clusters have been supported on an organic polymer (Table 1 and Fig. 1).

The silica-supported clusters, $M_4(CO)_8[HC(PPh_2)_3](Ph_2PCH_2CH_2SiOSi\equiv)$ and $Ru_3(CO)_9(dppm)(Ph_2PCH_2CH_2SiOSi\equiv)$, have also been obtained by treating the homogeneous complexes, $M_4(CO)_8[HC(PPh_2)_3][Ph_2PCH_2CH_2Si(OEt)_3]$ and $Ru_3(CO)_9(dppm)[Ph_2PCH_2CH_2Si(OEt)_3]$ with silica (non-porous silica, surface area 400 m^2 g^{-1}, pre-treated at 380°C under vacuum to remove physisorbed water). This route leads to the identical silica-supported clusters as those obtained above using phosphinated-silica.

We are currently investigating the stability and catalytic activity of these supported clusters.

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References

1 J.J. de Boer, J.A. van Doorn and C. Masters, J. Chem. Soc., Chem. Commun., (1978) 1005.
2 A.A. Bahsoun, J.A. Osborn, C. Voelker, J.J. Bonnet and G. Lavigne, Organometallics, 1 (1982) 1114.
3 D.F. Foster, B.S. Nicholls and A.K. Smith, J. Organomet. Chem., 236 (1982) 395.
4 D.F. Foster, B.S. Nicholls and A.K. Smith, J. Organomet. Chem., 244 (1983) 159.
5 G. Lavigne, N. Lugan and J.J. Bonnet, Nouv. J. Chim., 5 (1981) 423.
6 F. Iwasaki, M.J. Mays, P.R. Raithby, P.L. Taylor and P.J. Wheatley, J. Organometal. Chem., 213 (1981) 185.
7 R.C. Ryan, C.U. Pittman and J.P. O'Connor, J. Am. Chem. Soc., 99 (1977) 1986.
8 J. Evans, Chem. Soc. Rev., 10 (1981) 159, and ref. therein.
9 A recent determination of the crystal structure of $Ir_4(CO)_9[HC(PPh_2)_3]$ by X-ray diffraction methods, (J.A. Clucas, M.M. Harding, B.S. Nicholls and A.K. Smith, unpublished work) confirms that all CO ligands are terminal in this complex.
10 K.G. Allum, R.D. Hancock, I.V. Howell, S. McKenzie, R.C. Pitkethly and P.J. Robinson, J. Organomet. Chem., 87 (1975) 203.
11 K.G. Allum, R.D. Hancock, I.V. Howell, R.C. Pitkethly and P.J. Robinson, J. Organomet. Chem., 87 (1975) 187.