Generalised Cluster Anchoring to Oxide Supports

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Summary Anchored clusters of the types $(\mu\text{-H})M_3(CO)_{10}\{\mu\text{-S}(CH_2)_3(OXIDE)\}$ and $Co_3(CO)_9(\mu_3\text{-C-OXIDE})$ [OXIDE = $SiR_{3-x}(oxide)_x$, oxide = SiO_2, $\gamma\text{-}Al_2O_3$, TiO_2, ZnO, MgO, SnO_2] have been prepared and characterised by ir spectroscopy

LIGAND anchoring of carbonyl cluster complexes to inorganic oxides allows controlled syntheses of a particular species on the support surface but it has been restricted to silica gel [1] The catalytic activity of pyrolysed rhodium clusters is support-dependent[2] and this provides the impetus for preparing characterisable species on a variety of oxides We have used bridging ligands to reduce the problem of cluster breakdown [3]

$(\mu\text{-H})M_3(CO)_{10}\{\mu\text{-S}[CH_2]_3Si(OMe)_3\}$
(1) M = Ru
(2) M = Os

$(\mu\text{-H})Ru_3(CO)_{10}\{\mu\text{-S}[CH_2]_3(OXIDE)\}$
(3)

$HRu_3(CO)_{10}(SPr^n)$
(4)

$(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-S}[CH_2]_3(OXIDE)\}$
(5)

OXIDE = $SiR_{3-x}(oxide)_x$

The ruthenium and osmium complexes (**1**) and (**2**) were prepared by a method similar to that of Lewis *et al* [4] Complex (**1**) was adsorbed on all six oxides used (SiO_2, $\gamma\text{-}Al_2O_3$, TiO_2 SnO_2, ZnO, and MgO) from hexane solution at room temperature The pale yellow solids all exhibited i r ν_{CO} patterns appropriate to the formulation (**3**) [TiO_2 2103m, 2080w, 2065vs, 2054s 2023vs, 2006m, and 1994w cm^{-1}, *cf* (**1**) in C_6H_{12} 2105m 2093w, 2065vs, 2056s, 2025s, 2012m, 2007m, 1996w, and 1966vw cm^{-1}] Blank experiments using the complex (**4**) indicated that the silyl group was important in complex–oxide binding but doubt remains that the methoxide groups have been substituted by surface oxygens under such mild conditions

To avoid this problem $HS[CH_2]_3(OXIDE)$ materials were prepared by refluxing an oxide suspension in a xylene solution of $HS[CH_2]_3Si(OMe)_3$ followed by prolonged Soxhlet extraction with Et_2O (SnO_2 darkened during this treatment) The reaction of excess of $Ru_3(CO)_{12}$ with these functionalised oxides in refluxing benzene for 15 min afforded solids which primarily contained (**3**) Two extra i r bands at *ca* 2084 and *ca* 2036 cm^{-1} were also observed and these were reduced in intensity when the functionalised oxide was treated with Me_3SiCl prior to reaction with $Ru_3(CO)_{12}$, suggesting some surface involvement The supported clusters (**3**) were thermally less stable than (**4**) decomposing after *ca* 2 h at 50 °C *in vacuo* to give two broad ν_{CO} bands *e g* ZnO 2055mbr and 1975wbr cm^{-1} This two-band pattern is also eventually formed in the reaction of $Ru_3(CO)_{12}$ with the oxide itself in refluxing benzene *e g* ZnO, 2055mbr and 1970wbr cm^{-1} † Some oxides also give an intermediate species with a more

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† The frequencies of these patterns are dependent upon the oxide and also upon whether it has been treated with $HS[CH_2]_3Si(OMe)_3$, Me_3SiCl, or $NH(SiMe_3)_2$ The higher frequency band is generally more intense so unless the C–Ru–C angle is less than 90°, which is very unlikely, these spectra cannot be attributed to vibrationally isolated $Ru(CO)_2$ or C_{3v} $Ru(CO)_3$ units

complex i.r. pattern. Initially γ-Al$_2$O$_3$ also exhibits absorptions similar in intensity pattern to those of (**3**) but with significantly different frequencies (2104vw, 2064m, 2056m, 2038m, and 2025m; also 1990mbr and 1950wbr cm^{-1}) which probably result from a similar molecular geometry and may be attributed to (μ-H)Ru$_3$(CO)$_{10}$(μ-O-oxide). Pretreatment of MgO with NH(SiMe$_3$)$_2$ leads to a complex ν_{CO} pattern in the reaction with Ru$_3$(CO)$_{12}$ (2040m, 2010m, 1993w, 1982w, 1968w, 1935w, 1925w, 1817w, and 1788w cm^{-1}) indicative of a cluster anion. Unlike the Fe$_3$(CO)$_{12}$/MgO system,[5] there is no evidence for the [HM$_3$(CO)$_{11}$]$^-$ anion[6] under these conditions. In spite of these complex reactions between Ru$_3$(CO)$_{12}$ and the oxides the anchored materials (**3**) could still be synthesised.

Room temperature interaction of complex (**2**) with the six oxides yielded complex (**5**) which withstood Soxhlet extraction with Et$_2$O and MeOH (6 h each). Complex (**5**) could also be synthesised by the reaction of HS[CH$_2$]$_3$-(OXIDE) with Os$_3$(CO)$_{12}$ in refluxing toluene for 6 h. The i.r. spectra of these materials are unaltered after *ca.* 4 months. Again Os$_3$(CO)$_{12}$ reacts at the thiol part of the molecule even when treatment with the oxide under similar conditions afforded metal carbonyl containing solids (except for SnO$_2$). γ-Al$_2$O$_3$, TiO$_2$, and MgO species exhibited two broad ν_{CO} bands but SiO$_2$[7] and ZnO gave more complex i.r. spectra indicative of (μ-H)Os$_3$(CO)$_{10}$(μ-O-oxide). Interestingly pretreatment of TiO$_2$ with Me$_3$SiCl also allowed this type of species to be observed.

Finally stirring oxide suspensions in a CH$_2$Cl$_2$ solution of Co$_3$(CO)$_9$(μ_3CSiCl$_3$)[8] (2107w, 2058vs, and 2041m cm^{-1}) and subsequent Soxhlet extraction with MeOH yielded Co$_3$-(CO)$_9$(μ_3-C-OXIDE) (*e.g.* Al$_2$O$_3$: 2105w, 2056vs, and 2041 cm^{-1}); these also have long shelf-lives.

These results demonstrate that in spite of complex interactions between the oxides and the carbonyl clusters, ligand anchored materials can be synthesised. They also show the value of employing bridging ligands which unlike diarylalkylphosphines[9] are known to form single monosubstituted cluster complexes when treated with the metal carbonyls.[4]

We thank Degussa and INCO Europe for Chemicals and the S.R.C. for support (B.P.G.).

(*Received*, 28*th May* 1980; *Com.* 567.)

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