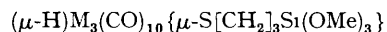


Generalised Cluster Anchoring to Oxide Supports

By JOHN EVANS* and BENJAMIN P GRACEY

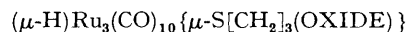
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Summary Anchored clusters of the types $(\mu\text{-H})\text{M}_3(\text{CO})_{10}\{\mu\text{-S}(\text{CH}_2)_3(\text{OXIDE})\}$ and $\text{Co}_3(\text{CO})_9(\mu_3\text{-C-OXIDE})$ [OXIDE = $\text{SiR}_{3-x}(\text{oxide})_x$, oxide = SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, TiO_2 , ZnO , MgO , SnO_2] have been prepared and characterised by ir spectroscopy

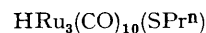


(1) M = Ru

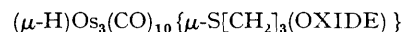
(2) M = Os



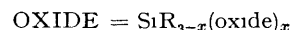
(3)



(4)



(5)



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 gel¹ The catalytic activity of pyrolysed rhodium clusters is support-dependent² 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 breakdown³

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 , $\gamma\text{-Al}_2\text{O}_3$, TiO_2 , SnO_2 , ZnO , and MgO) from hexane solution at room temperature The pale yellow solids all exhibited ir 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 $\text{HS}[\text{CH}_2]_3(\text{OXIDE})$ materials were prepared by refluxing an oxide suspension in a xylene solution of $\text{HS}[\text{CH}_2]_3\text{Si}(\text{OMe})_3$ followed by prolonged

Soxhlet extraction with Et_2O (SnO_2 darkened during this treatment) The reaction of excess of $\text{Ru}_3(\text{CO})_{12}$ with these functionalised oxides in refluxing benzene for 15 min afforded solids which primarily contained (3) Two extra ir 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 $\text{Ru}_3(\text{CO})_{12}$, 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 $\text{Ru}_3(\text{CO})_{12}$ 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

† The frequencies of these patterns are dependent upon the oxide and also upon whether it has been treated with $\text{HS}[\text{CH}_2]_3\text{Si}(\text{OMe})_3$, Me_3SiCl , or $\text{NH}(\text{SiMe}_3)_2$ 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 $\text{Ru}(\text{CO})_2$ or C_{3v} $\text{Ru}(\text{CO})_3$ units

complex i.r. pattern. Initially γ -Al₂O₃ 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 $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-O-oxide})$. Pretreatment of MgO with NH(SiMe₃)₂ leads to a complex ν_{CO} pattern in the reaction with Ru₃(CO)₁₂ (2040m, 2010m, 1993w, 1982w, 1968w, 1935w, 1925w, 1817w, and 1788w cm⁻¹) indicative of a cluster anion. Unlike the Fe₃(CO)₁₂/MgO system,⁵ there is no evidence for the [HM₃(CO)₁₁]⁻ anion⁶ under these conditions. In spite of these complex reactions between Ru₃(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 Et₂O and MeOH (6 h each). Complex (5) could also be synthesised by the reaction of HS[CH₂]₃-(OXIDE) with Os₃(CO)₁₂ in refluxing toluene for 6 h. The i.r. spectra of these materials are unaltered after ca. 4 months. Again Os₃(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 SnO₂). γ -Al₂O₃, TiO₂, and MgO species exhibited two broad ν_{CO} bands but SiO₂⁷ and ZnO gave more complex i.r. spectra indicative of $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-O-oxide})$. Interestingly pretreatment of TiO₂ with Me₃SiCl also allowed this type of species to be observed.

Finally stirring oxide suspensions in a CH₂Cl₂ solution of Co₃(CO)₉(μ_3 CSiCl₃)⁸ (2107w, 2058vs, and 2041m cm⁻¹) and subsequent Soxhlet extraction with MeOH yielded Co₃-(CO)₉(μ_3 -C-OXIDE) (e.g. Al₂O₃: 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 diarylalkylphosphines⁹ are known to form single mono-substituted cluster complexes when treated with the metal carbonyls.⁴

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¹ S. C. Brown and J. Evans, *J. Chem. Soc., Chem Commun.*, 1978, 1063; R. Pierantozzi, K. J. McQuade, B. C. Gates, M. Wolf, H. Knözinger, and W. Ruhmann, *J. Am. Chem. Soc.*, 1979, **101**, 5436.

² M. Ichikawa, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2268, 2273.

³ H. Knözinger, E. W. Thornton, and M. Wolf, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 1888.

⁴ G. R. Crooks, B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc. (A)*, 1969, 797.

⁵ F. Hugues, A. K. Smith, Y. Ben Taarit, J. M. Basset, D. Commereuc, and Y. Chauvin, *J. Chem. Soc., Chem. Commun.*, 1980, 68.

⁶ B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. Süß, *J. Chem. Soc., Dalton Trans.*, 1979, 1356.

⁷ R. Ugo, R. Psaro, G. M. Zanderighi, J. M. Basset, A. Theolier, and A. K. Smith, *Fundam. Res. Homogeneous Catal.*, 1979, **3**, 579.

⁸ D. Seyferth, C. N. Rudie, and M. O. Nestle, *J. Organomet. Chem.*, 1979, **178**, 227.

⁹ A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. (A)*, 1970, 897.