Standardised Tethering of Ru_3—Ru_6 Clusters to High Surface Area Oxides

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The complexes $Ru_3(CO)_{11}L$, $H_4Ru_4(CO)_{11}L$, $Ru_5C(CO)_{14}L$, and $Ru_6C(CO)_{16}L$ [L = $PPh_2CH_2CH_2Si(OEt)_3$] have been isolated and used to tether Ru_{3-6} units to oxide surfaces (SiO_2, Al_2O_3, and TiO_2) in a standard manner.

Particle-size effects on the catalytic activity of materials derived from oxide-supported metal carbonyl clusters have been suggested.[1] However, testing this suggestion has not been possible since the designed tethering of clusters of differing nuclearity by a standard link has not been reported. By combining radical anion catalysed substitution reactions[2] with purification of complexes of the anchoring ligand $PPh_2CH_2CH_2Si(OEt)_3$ (**1**) by flash chromatography[3] we have developed molecularity-specific routes to supported ruthenium clusters.

$PPh_2CH_2CH_2Si(OEt)_3$
(**1**)

$Ru_3(CO)_{11}\{PPh_2CH_2CH_2Si(OEt)_3\}$
(**2**)

$H_4Ru_4(CO)_{11}\{PPh_2CH_2CH_2Si(OEt)_3\}$
(**3**)

$Ru_5C(CO)_{14}\{PPh_2CH_2CH_2Si(OEt)_3\}$
(**4**)

$Ru_6C(CO)_{16}\{PPh_2CH_2CH_2Si(OEt)_3\}$
(**5**)

$Ru_3(CO)_{11}\{PPh_2CH_2CH_2Si(OEt)_3\}$ (**2**) and $H_4Ru_4(CO)_{11}$-$\{PPh_2CH_2CH_2Si(OEt)_3\}$ (**3**) were prepared by the Na–Ph_2CO catalysed substitution of stoicheiometric mixtures of (**1**) with $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ respectively in solution in tetrahydrofuran (thf). $Ru_5C(CO)_{14}\{PPh_2CH_2CH_2Si(OEt)_3\}$ (**4**) and $Ru_6C(CO)_{16}\{PPh_2CH_2CH_2Si(OEt)_3\}$ (**5**) were obtained by controlled substitution in solution by (**1**) into $Ru_5C(CO)_{15}$ (at −40 °C) and $Ru_6C(CO)_{17}$ (at 0 °C) respectively in methylene dichloride. All four complexes were purified by flash chromatography on Nagel Silica Gel 60 using light petroleum (b.p. 40—60 °C)–methylene dichloride solvent mixtures with the column pressurised by nitrogen (*ca.* 10 lb in^{-2})†. We have found this technique to have wide applicability in cluster chemistry. The ^1H n.m.r. spectra of complexes (**2**)—(**5**) contained the expected ligand resonances: *e.g.* (**2**) in $CDCl_3$, δ 7.45 (m, 10H, Ph), 3.77 [q, J(HH) 7 Hz, 6H, O–CH_2–], 2.54 (m, 2H, P–CH_2–), 1.10 [t, J(HH) 7 Hz, 9H, O–CH_2–CH_3], and 0.48 (m, 2H, Si–CH_2). Satisfactory elemental analyses and ^{31}P n.m.r.

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† *E.g.* for complex (**2**): a slurry on silica gel was formed by removing the thf under reduced pressure and added to the top of a light petroleum–silica column. After elution of $Ru_3(CO)_{12}$, increasingly polar CH_2Cl_2–light petroleum solvent mixtures were used. Complex (**2**) can be separated with 20—30% CH_2Cl_2 with the disubstituted derivative requiring a 40% CH_2Cl_2 level.

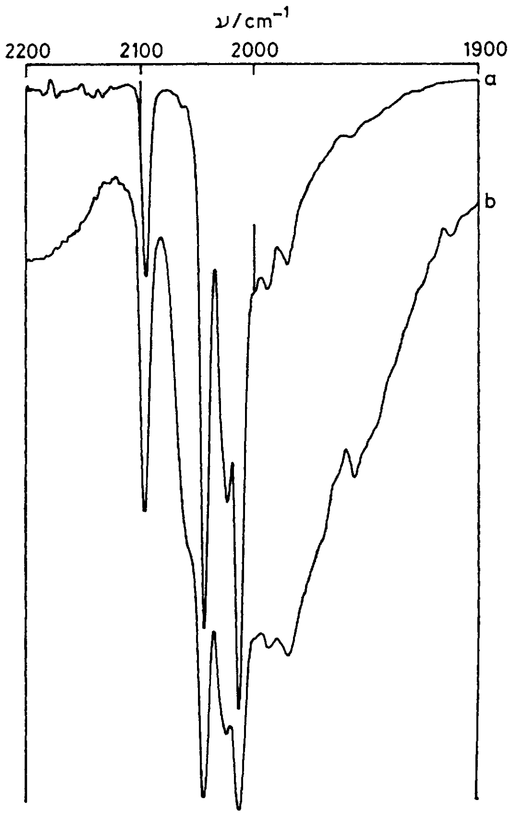

Figure 1. I.r. spectra (2200—1900 cm^{-1}) of (**2**): (a) in cyclohexane, and (b) on alumina.

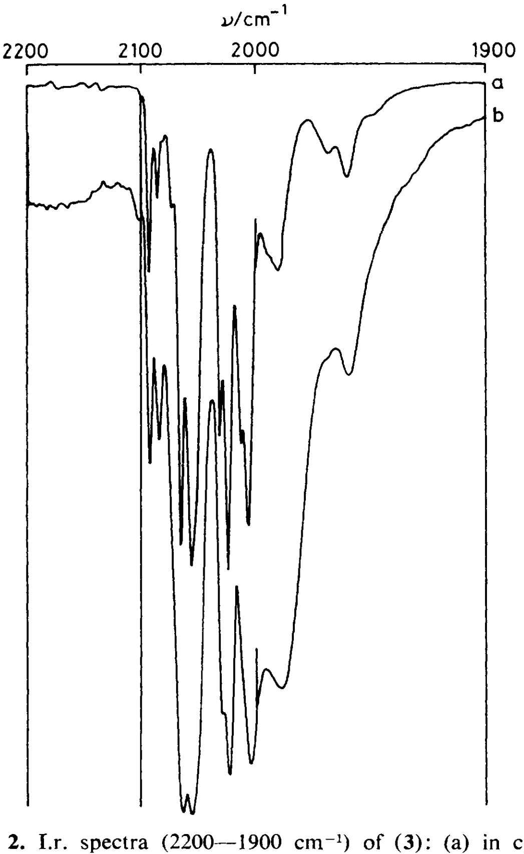

Figure 2. I.r. spectra (2200—1900 cm^{-1}) of (**3**): (a) in cyclohexane, and (b) on alumina.

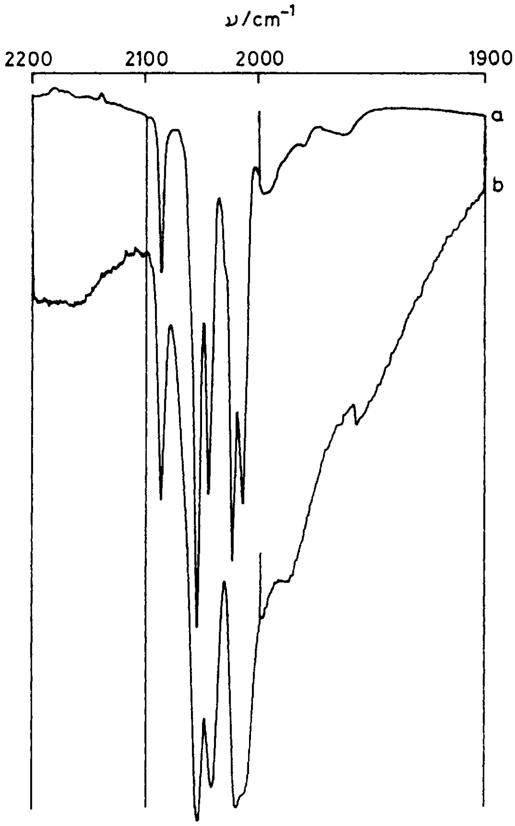

Figure 3. I.r. spectra (2200—1900 cm^{-1}) of (**4**): (a) in cyclohexane, and (b) on alumina.

spectra were also obtained for these derivatives and the formulation of (**2**) was confirmed by a mass spectrum obtained by fast xenon atom bombardment of a solution in dipentylphenol. This included a group of peaks centred at 990 a.m.u. due to $(M + \mathrm{H})^+$ as the highest masses present.

Complexes (**2**)—(**5**) were interacted with silica (Aerosil), alumina (aluminium oxide C), and titania (P25) in cyclohexane or CH_2Cl_2 at room temperature for 4 days. These reactions were carried out under a carbon monoxide atmosphere to prevent decomposition. The oxides obtained exhibited the colours of the initial complexes and close agreement was found between the band maxima of their electronic spectra obtained by diffuse reflectance with those of the appropriate precursor complex in cyclohexane solution.[‡] Further strong evidence for the integrity of the supported clusters was obtained from their i.r. carbonyl fingerprints. Spectra for the $Ru_3(CO)_{11}L$, $H_4Ru_4(CO)_{11}L$, and $Ru_5C(CO)_{14}L$ species [L = $PPh_2CH_2CH_2Si(OEt)_3$] in cyclohexane solution and on alumina (as a Nujol mull) are shown in Figures 1—3. The spectra of $Ru_6C(CO)_{16}L$ on the oxides were similar to those obtained by the reaction of $Ru_6C(CO)_{17}$ with phosphinated silica.[4] Probable molecular structures for the supported complexes are shown in Figure 4; these have been established by *X*-ray diffraction studies on the close analogues $Ru_3(CO)_{11}$-

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[‡] Electronic spectra (λ_{max}), (**2**) in cyclohexane: 420, 300sh, 250sh, and 208 nm; on silica: 424, 376, 288sh, 244sh, and 208 nm; (**3**) in cyclohexane: 370, 300 w, sh, 240sh, and 210 nm; on silica: 364, 248, and 216 nm; (**4**) in cyclohexane: 530, 400 w, sh, 340sh, 270w, sh, and 208 nm; on silica: 530, 396sh, 336sh, and 220 nm; (**5**) in cyclohexane: 520w, sh, 420, 310sh, and 210 nm; on silica: 520w, 420, 308sh, and 210 nm.

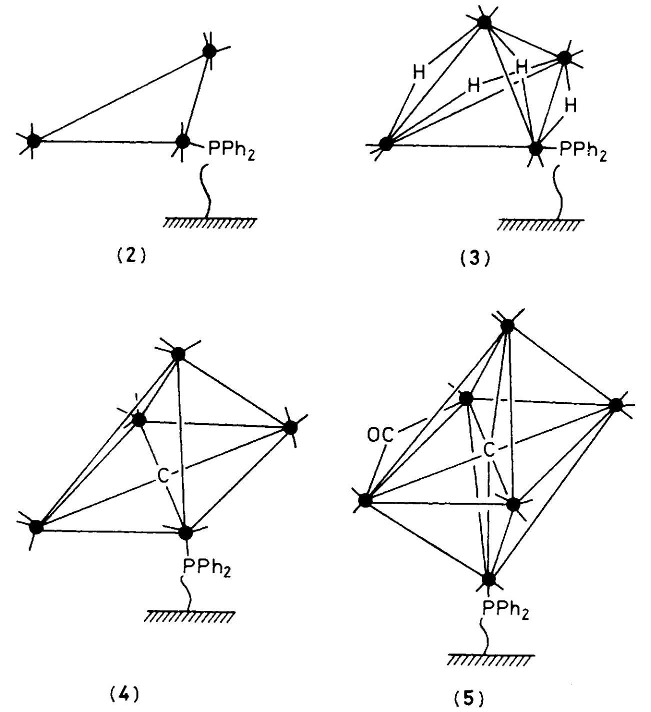

Figure 4. Probable structures of the supported Ru_3—Ru_6 cluster units.

(PPh_3),[5] $H_4Ru_4(CO)_{11}\{P(OMe)_3\}$,[6] $Ru_5C(CO)_{14}(PPh_3)$,[7] and $Ru_6C(CO)_{16}(PPh_2Et)$.[4]

Previous reports of tethering metal carbonyl clusters to oxide supports by means of an anchoring ligand have been isolated to particular systems for which specific syntheses had been devised, *e.g.* $Os_3(CO)_{11}(PPh_2R)$,[8] $HAuOs_3(CO)_{10}(PPh_2R)$,[9] $Ru_6C(CO)_{16}(PPh_2R)$,[4] and $Ru_3(CO)_9(PPh_2R)_3$.[10] This report shows that procedures can be developed to synthesise series of anchored complexes of different nuclearities with standardised metal–support links. Anchoring of preformed complexes like **(2)**—**(5)** by hydrolysis of the silyl group in the phosphine ligand **(1)** has been demonstrated by ^{31}P n.m.r. spectroscopy to yield more specific materials than by complexing the metals on to functionalised oxides.[11] We are now investigating the chemistry of this series of materials to probe for particle-size effects.

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