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Tethering of a Phosphinidene Stabilised Cluster to Oxide Supports

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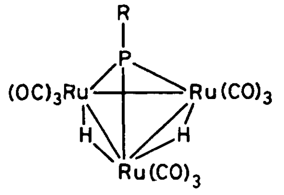
The complex $(\mu\text{-H})_2Ru_3(CO)_9\{\mu_3\text{-PCH}_2CH_2Si(OEt)_3\}$ (**1a**) has been supported on SiO_2, Al_2O_3, TiO_2, MgO, and ZnO; the phosphinidene ligand stabilises the cluster under catalytic conditions.

Interest in tethering transition metal carbonyl clusters to inorganic oxide supports *via* capping ligands has arisen following evidence that clusters containing capping or bridging ligands possessed greater stability under catalytic conditions than their terminally substituted counterparts.[1] We report here the preparation of the phosphinidene capped cluster $H_2Ru_3(CO)_9\{\mu_3\text{-PCH}_2CH_2Si(OEt)_3\}$ (**1a**) *via* a novel route which overcomes many of the problems in this area of chemistry. The cluster has been characterised by comparison with its close structural analogue $H_2Ru_3(CO)_9(PPh)$ (**1b**).[2] The catalytic activity of (**1a**) tethered to alumina, towards pentene isomerisation has been compared with that of the homogeneous analogue (**1b**). This work represents the first occasion in which a cluster has been tethered to an inorganic oxide support *via* a μ_3 capping phosphinidene ligand; it demonstrates the retention of catalytic activity on progression from a homogeneous to a heterogeneous species and unusual stability under catalytic conditions.

The preparative route is shown in Scheme 1. The ligand $HP(Ph)\{CH_2CH_2Si(OEt)_3\}$(**2a**)[3] was prepared by the photochemical addition of H_2PPh to $CH_2{=}CHSi(OEt)_3$.[4] Radical anion catalysis was used in step i to improve the yields of the various phosphine and phosphido derivatives (**3**), (**4**), and (**5**) compared to thermal routes.[5] Terminal, rather than bridging substitution is only found in the case of R = Ph in step i forming $Ru_3(CO)_{11}(PPh_2H)$ (**3b**). A mixture of (**4**) and (**5**) can be separated from unreacted $Ru_3(CO)_{12}$ and any multiply substituted clusters by flash chromatography. On heating (**3b**) at 50 °C in heptane solution, a mixture of the phenyl phosphido derivatives (**4b**) and (**5b**) is rapidly formed.† The interconversion reported for (**4b**) and (**5b**)[6] is paralleled by (**4a**) and (**5a**) [R = $CH_2CH_2Si(OEt)_3$]. The conversion of $(\mu\text{-H})Ru_3(CO)_9(\mu\text{-PPh}_2)$ (**5b**) into $(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-PPh})$ (**1b**), has been previously demonstrated[6] and when mixtures of (**4a**) and (**5a**)



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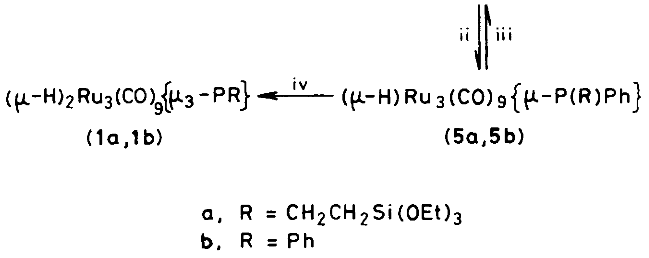

Scheme 1. i, Na, Ph_2CO, tetrahydrofuran, 20 min; ii, 50 °C, heptane, N_2 flow; iii, 50 °C, CO (1 atm); iv, H_2, heptane, 70 °C, 2 h.

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† Selected spectroscopic data for (**4a**), (**5a**), and (**3b**) (i.r. measured in cyclohexane, ^1H n.m.r. in C_6D_6): (**4a**) i.r., ν(CO) 2098m, 2053s, 2047s, 2019vs, 2000w, 1994m, and 1988w cm^{-1}; ^1H n.m.r.: δ 7.7 (m,2H,Ph), 7.02(m,3H,Ph), 3.66(q,6H,CH_3CH_2O), 1.96(m,2H, CH_2CH_2P), 1.07(t,9H,CH_3CH_2O), 0.72(m,2H,$SiCH_2CH_2$), and −16.50[d,1H,μ-*H*,*J*(PH) 28 Hz]. (**5a**) i.r., ν(CO) 2081m, 2053s, 2028s, 2012m, 2003w, 1991w, and 1984w cm^{-1}; ^1H n.m.r.: δ ligand as for (**4a**), −16.36[d,1H,μ-*H*,*J*(PH) 23 Hz]. (**3b**) i.r., ν(CO) 2097m, 2045s, 2030s, 2014vs, 1996w, and 1985w cm^{-1}; ^1H n.m.r.: δ 7.35 (m,4H,Ph), 6.95(m,6H,Ph), and 6.45[d,1H,PPh_2H,*J*(PH) 365 Hz].

Table 1

	Homogeneous[a]		Heterogeneous[b]	
Pentene isomer	Conversion	Turnovers	Conversion	Turnovers
trans 2-ene	*trans* 2-ene → 1-ene	0.5 ± 0.1	*trans* 2-ene → 1-ene	0.9 ± 0.2
	trans 2-ene → *cis* 2-ene	3.3 ± 0.2	*trans* 2-ene → *cis* 2-ene	1.57 ± 0.2
cis 2-ene	*cis* 2-ene → *trans* 2-ene	9.0 ± 0.5	*cis* 2-ene → *trans* 2-ene	4.5 ± 0.4
	cis 2-ene → 1-ene	1.1 ± 0.1	*cis* 2-ene → 1-ene	0.8 ± 0.1
1-ene	1-ene → *trans* 2-ene	17.0 ± 0.6	1-ene → *trans* 2-ene	9.0 ± 0.3
	1-ene → *cis* 2-ene	6.3 ± 0.5	1-ene → *cis* 2-ene	4.6 ± 0.4

[a] 4 mg of (**1b**) and 16 μl of pentene in 2 ml of CH_2Cl_2, 24 h at 80 °C. [b] 85.1 mg of (**1a**) on Al_2O_3 [catalyst loading 4.47% by weight (1.41% Ru)] *i.e.* 4 mg of (**1a**) and 16 μl of pentene in 2 ml of CH_2Cl_2, 24 h at 80 °C. Blank runs on alumina showed no detectable conversion under these conditions.

are interacted with hydrogen the P–Ph bond is cleaved, allowing $(\mu\text{-H})_2Ru_3(CO)_9\{\mu_3\text{-PCH}_2CH_2Si(OEt)_3\}$ (**1a**) to be formed in good yield [62% from $Ru_3(CO)_{12}$].‡ Again flash chromatography was employed to remove any decomposition or condensation products.[7] In all cases the carbonyl i.r. absorptions for the silylalkyl derivatives match closely with their phenyl analogues.[2,6]

Complex (**1a**) was allowed to interact with suspensions of the oxides SiO_2, Al_2O_3, TiO_2, MgO, and ZnO by stirring in CH_2Cl_2 solution for several days. After filtration, washing with acetone and drying, the oxides exhibited a range of colour, from cream (MgO, SiO_2) through to pale yellow (Al_2O_3). Close agreement was found between the oxides' electronic spectra (diffuse reflectance) and that of a CH_2Cl_2 solution of (**1a**).§ Further, the i.r. carbonyl fingerprints of oxide tethered versions of (**1a**) (Nujol mull) were found to match closely with those of cyclohexane and, particularly, CH_2Cl_2 solutions of (**1a**) and (**1b**) (Figure 1).

Most of the detailed differences between solution and oxide supported i.r. spectra appear due to the polarities of these environments and are minimised using the more polar organic solvent.

Catalysis experiments were performed using a 25-fold excess of the required pentene, with the complexes in CH_2Cl_2 solution or suspension (for the homogeneous and heterogeneous systems, respectively) in sealed tubes. After 24 h the ratios of the various pentenes present were determined by g.l.c. When tethered to alumina (**1a**) is found to possess *ca.* 60% of the activity of the homogeneous species (**1b**) (Table 1). Following the catalysis run, the only species present on the alumina detectable by i.r. spectroscopy is the original cluster (**1a**) (Figure 1). However, it is apparent that some cluster decomposition occurs as the alumina becomes beige in colour. Further catalysis runs on these previously used samples show less overall activity (approximately one third of that shown in the initial experiment). Again, complex (**1a**) is the only species detectable by i.r. spectroscopy, but the colour of the oxide darkens further. Thus, it is clear that either (**1a**), or some short-lived breakdown product is the active species.

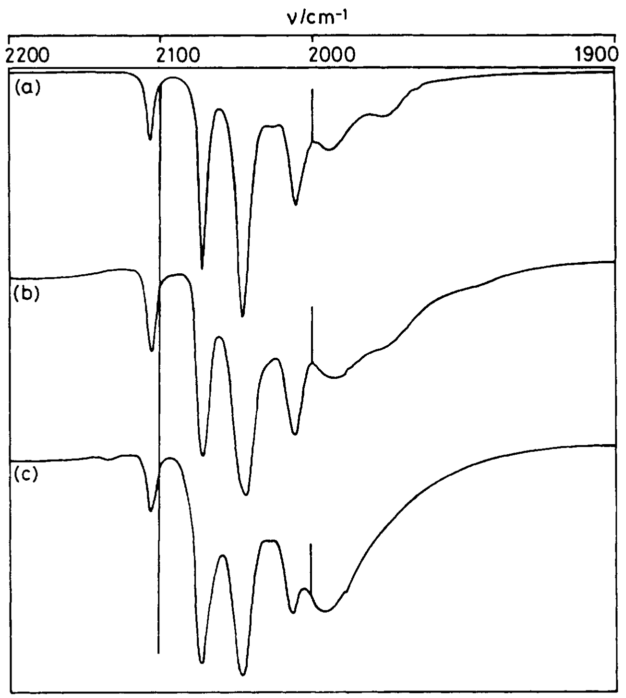

Figure 1. I.r. spectra in the ν(CO) region of (a) (**1a**) in CH_2Cl_2, (b) (**1a**) on Al_2O_3 (4.5mg/100mg), and (c) sample (b) after two catalysis runs.

Pyrolysis of clusters containing mixed aryl–alkyl phosphines shows that the aryl group is lost preferentially.[8] Pyrolysis or hydrogenolysis of clusters containing the ligand $HP(Ph)\{CH_2CH_2Si(OEt)_3\}$ thus allows the specific preparation of phosphinidene capped ruthenium carbonyl clusters, avoiding the synthesis of the primary phosphine $H_2P[CH_2]_2Si(OEt)_3$. Such clusters clearly hold considerable promise. Complex (**1a**) is far more stable than either of the two tri-ruthenium clusters previously tethered. Samples of the terminally substituted cluster $Ru_3(CO)_{11}\{PPh_2[CH_2]_2Si(OEt)_3\}$[9] on silica and alumina were no longer usable after *ca.* 2 weeks at −10 °C, although greater stability under a CO atmosphere was noted. Samples of the bridging species $H_2Ru_3(CO)_{10}\{S[CH_2]_3Si(OMe)_3\}$[10] were found to discolour on heating to 50 °C *in vacuo*. In addition

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‡ Selected spectroscopic data for (**1a**) (i.r. measured in cyclohexane, ^1H and ^{13}C n.m.r. in $CDCl_3$, ^{31}P n.m.r. in CH_2Cl_2 shift relative to H_3PO_4): (**1a**) i.r., ν(CO) 2105m, 2073s, 2047vs, 2028w, 2015s, 1997m, and 1983m cm^{-1}; n.m.r.: ^1H, δ 3.9(q,6H,OCH_2), 3.1(m, 2H,PCH_2), 1.25(t,9H,CH_3), 1.1(m,2H,CH_2Si), and −19.26[d,2H, μ-*H*,*J*(PH) 15 Hz]; $\{^1H\}^{13}C$, δ 14.25[d,*J*(PC) 22 Hz,*C*H$_2$Si], 18.32(s,*C*H$_3$), 25.43[d,*J*(PC) 55 Hz,P*C*H$_2$], 58.91(s,O*C*H$_2$), and 191.1 p.p.m. (br.,*C*O); $\{^1H\}^{31}P$, δ 324.38 p.p.m.

§ Electronic spectra of (**1a**): in CH_2Cl_2, 393, 287, and 230 nm; on SiO_2, 393, 320, 287, and 230 nm; on Al_2O_3, 404, 290, and 238 nm; on ZnO, 416, 332, 300, and 230 nm.

to this stabilisation the phosphinidene tethered cluster shows some catalytic activity which is retainable on tethering. Accordingly, attempts to obtain higher nuclearity clusters containing capping phosphinidene ligands are currently being made.

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