Anchoring of Cobalt, Ruthenium, and Osmium Carbonyls to Oxides by Pendant Thiol and Phosphine Ligands

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Thermal and photochemical anchoring of $[Ru_4H_4(CO)_{12}]$ to phosphinated SiO_2 and Al_2O_3 afforded a mixture of mono- and di-substitution products. The species $Os_3H(CO)_{10}[S(CH_2)_3Si(OMe)_{3-x}(O{-}M'O_n)_x]$ can be formed either by interacting $[Os_3H(CO)_{10}\{S(CH_2)_3Si(OMe)_3\}]$ with an oxide ($M'O_n = SiO_2, Al_2O_3, TiO_2, SnO_2, ZnO$, or MgO) or by reacting $[Os_3(CO)_{12}]$ with $HS(CH_2)_3Si(OMe)_{3-x}(O{-}M'O_n)_x$. Similar procedures carried out on the ruthenium analogue were less satisfactory due to its lower stability in contact with the oxides. Under similar conditions to those employed to react $[M_3(CO)_{12}]$ with $HS(CH_2)_3Si(OMe)_{3-x}(O{-}M'O_n)_x$, the carbonyl binds to the unfunctionalised oxide as $M_3H(CO)_{10}(O{-}M'O_n)$ and/or oxidised metal carbonyl species. Surface protection by $SiMe_3Cl$ or $NH(SiMe_3)_2$ is incomplete. The compound $[Co_3(CO)_9(CSiCl_3)]$ reacts with the same six oxides (as powders) under mild conditions to afford the stable $Co_3(CO)_9[CSiCl_{3-x}(O{-}M'O_n)_x]$.

METAL carbonyl cluster complexes offer new routes to supported metal catalysts.[1] Ideally, the preformed skeletons would be maintained on the support to afford a material with a single metal particle size. Direct interaction of carbonyl clusters with high-surface-area oxides can give rise to chemisorbed derivatives, as observed for $[Os_3(CO)_{12}]$ on silica and alumina.[2] But in this, and other situations, *e.g.* $[Rh_4(CO)_{12}]$ on alumina,[3] the clusters do not retain their original nuclearity. Attempts to stabilise osmium,[4] rhodium,[5,6] iridium,[7] and mixed-metal[8] clusters on silica using a pendant alkyldiphenylphosphine have been reported. However, vacuum treatment or hydrogenation conditions can still cause the clusters to lose their integrity.[6,9-11] In this work we aimed to generalise the ligand-anchoring procedure to other oxides, and also to stabilise clusters further by means of bridging ligands. A preliminary account has been published by the authors[12] and another report of anchoring triosmium clusters to silica *via* a pendant thiol is also in the literature.[13]

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 580B spectrometer with a model 3500 Data Station, electronic spectra on a Pye Unicam SP700, mass spectra on an AEI MS12, and ^1H n.m.r. spectra on a Varian Associates XL100. Metal analyses were by neutron activation.

Silica (Aerosil 200 and 380), alumina (Aluminium OXIDC), and titania (Titanoxid P25) were supplied by Degussa. The alumina and titania areas were 100 ± 15 and 50 ± 15 $m^2\ g^{-1}$ respectively. The tin(IV) oxide (high purity) and magnesia (chromatographic grade) were purchased from Aldrich and BDH respectively. Most oxides were dried by heating to 120 °C *in vacuo* for 48 h; ZnO was dried similarly at 50 °C. The following complexes were prepared by published procedures: $[Ru_4H_4(CO)_{12}]$,[14] $[Ru_4H_4(CO)_{11}(PPh_3)]$,[15] $[Ru_4H_4(CO)_{10}(PPh_3)_2]$,[16] $[Ru_4H_4(CO)_9(PPh_3)_3]$,[16] $[Co_3(CO)_9(CSiX_3)]$ (X = Cl, OH, or Et),[17] and $[M_3H(CO)_{10}(SPr^n)]$ (M = Ru or Os).[18]

All reactions were carried out under nitrogen, unless otherwise stated.

Preparation of Ligand-functionalised Oxides.—The phosphinated species $PPh_2CH_2CH_2Si(OEt)_{3-x}(O{-}M'O_n)_x$ ($M'O_n = SiO_2$ or Al_2O_3) were prepared from $PPh_2CH_2CH_2Si(OEt)_3$ according to the procedure described for silica.[19]

$HS(CH_2)_3Si(OMe)_{3-x}(O{-}M'O_n)_x$ ($M'O_n = SiO_2, Al_2O_3, SnO_2, MgO, ZnO$, *or* TiO_2). In a typical reaction, a suspension of the oxide (5 g) was refluxed in a xylene (50 cm^3) solution of $HS(CH_2)_3Si(OMe)_3$ (0.6 g) for 6 h and then stirred at room temperature for 15 h. The solid was filtered off, extracted with Et_2O for 4 h in a Soxhlet apparatus, and dried *in vacuo* for 16 h.

Silylation of the Oxides.—(*a*) *By* $SiMe_3Cl$. A suspension of the oxide (0.2 g) in a benzene (5 cm^3) solution of $SiMe_3Cl$ (0.04 g) was stirred for 16 h at 30 °C, filtered, the product washed with CH_2Cl_2 (three times), and dried *in vacuo.*

(*b*) *By* $NH(SiMe_3)_2$. The amine (1 cm^3) was added to a slurry of the oxide (1 g) in CCl_4 and shaken overnight. The solid was recovered by filtration, washed, and dried *in vacuo.*

Preparation of $[Ru_3H(CO)_{10}\{S(CH_2)_3Si(OMe)_3\}]$.—The compounds $[Ru_3(CO)_{12}]$ (0.294 g) and $HS(CH_2)_3Si(OMe)_3$ (0.0903 g) were refluxed in dry benzene (30 cm) for 15 min, during which time the solution colour changed from orange to yellow. The reaction mixture was allowed to cool, filtered, and the solvent removed from the filtrate. The residue was extracted with hexane and dried *in vacuo* to afford the *product* as an orange oil (0.146 g, 40%). The product is slightly air and heat sensitive and was frozen at 0 °C. I.r. (hexane): 2 106w, 2 093vw, 2 064s, 2 056s, 2 025vs, 2 012m, 2 007m, 1 994w, and 1 966w cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 3.5 (s, 9 H, OCH_3), 2.5 (t, 2 H, SCH_2), 2—0.5 (m, 4 H, $SiCH_2CH_2CH_2S$), and −15.4 (s, 1 H, RuH).

Preparation of $[Os_3H(CO)_{10}\{S(CH_2)_3Si(OMe)_3\}]$.—The compounds $[Os_3(CO)_{12}]$ (0.054 g) and $HS(CH_2)_3Si(OMe)_3$ (1.1 equivalents) were refluxed in toluene (60 cm^3) for 6 h, allowed to cool, and the mixture was filtered. The solvent was removed and the residue extracted with hexane (10 cm^3) and dried *in vacuo* to afford the *product* as a yellow crystalline solid (0.046 mg, 75%). I.r. (hexane): 2 108m, 2 067s, 2 058s, 2 024s, 2 018s, 2 005w, 1 998s, 1 989s, 1 983w (sh), and 1 955w br cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 3.5 (s, 9 H, OCH_3), 2.5 (t, 2 H, $-SCH_2CH_2$), 2—0.5 (m, 4 H, CH_2CH_2Si), and −16.9 (s, 1 H, OsH).

Reaction of $[Ru_4H_4(CO)_{12}]$ *with* $PPh_2CH_2CH_2Si(OEt)_{3-x}(O{-}M'O_n)_x$.—*Thermal method.* A suspension of $PPh_2CH_2CH_2Si(OEt)_{3-x}(O{-}SiO_2)_x$ was refluxed in a solution of $[Ru_4H_4(CO)_{12}]$ (1P : 2Ru_4) in light petroleum (b.p. 40—60 °C) for 4 h. The orange-brown solid was filtered off and dried *in vacuo.* I.r. (Nujol): 2 092vw, 2 084vs (sh), 2 054br s, 2 028s, 2 015s, and 1 997vs cm^{-1}.

Photochemical method. A slurry of $PPh_2CH_2CH_2Si$-

$(OEt)_{3-x}(O{-}M'O_n)_x$ was stirred in a *n-pentane* solution of $[Ru_4H_4(CO)_{12}]$ (1P : $2Ru_4$) and irradiated with a 125-W mercury lamp with a Pyrex filter. The reaction was monitored by removing aliquots of the solid and recording i.r. spectra of Nujol mulls. Irradiation for 35 min was required to afford relatively strong ν_{CO} absorptions. I.r. (Nujol): $M'O_n = SiO_2$ 2 092w, 2 083w, 2 062 (sh), 2 049br vs, 2 024s, 2 003m, and 1 990br m; Al_2O_3 2 092w, 2 082w, 2 049br vs, 2 026s, 2 002m, and 1 987br cm^{-1}.

Reaction of $[Ru_3H(CO)_{10}\{S(CH_2)_3Si(OMe)_3\}]$ *with Oxides.*—A suspension of the oxide (0.2 g) was stirred in a hexane (40 cm^3) solution of $[Ru_3H(CO)_{10}\{S(CH_2)_3Si(OMe)_3\}]$ (0.01 g) for 2 h. The pale yellow powders were collected by filtration, washed with CH_2Cl_2 (3 × 30 cm^3), and dried *in vacuo.* I.r. (Nujol): oxide = SiO_2 2 106w, 2 083w, 2 065w, 2 055w, and 2 026s; Al_2O_3 2 105w, 2 082vw, 2 066s, 2 056s, 2 023vs, and 2 009 (sh); TiO_2 2 103m, 2 080w, 2 065vs, 2 054s, 2 023vs, 2 006m, and 1 994w; ZnO 2 105w, 2 067vs, 2 055s, 2 036w, 2 022s, and 1 993w; SnO_2 2 104m, 2 080w, 2 064vs, 2 054s, 2 022s, 2 006m, and 1 993 (sh); MgO 2 106w, 2 080w, 2 060 (sh), 2 051s, 2 040s, and 2 000m cm^{-1}.

After some weeks at room temperature, these samples became cream with new i.r. spectra (recorded after 12 weeks). I.r. (Nujol): $[Ru_3H(CO)_{10}\{S(CH_2)_3Si(OMe)_3\}]$ (decomp.) 2 111w, 2 026br m, and 1 970br m; oxide = SiO_2 2 120br w, 2 030br m, and 1 995br m; Al_2O_3 2 100br w, 2 040br s, and 1 985br s; TiO_2 2 070br m and 2 000br w; ZnO 2 055br m and 1 975br w; SnO_2 2 035br m and 1 985br s cm^{-1}.

Interaction of $[Ru_3H(CO)_{10}(SPr^n)]$ *with Oxides.*—This was carried out as above. I.r. (hexane): $[Ru_3H(CO)_{10}(SPr^n)]$ 2 105m, 2 082vw, 2 065vs, 2 058s, 2 042w, 2 026s, 2 014w, 2 008m, and 1 996m; oxide = SiO_2 2 104w, 2 064w, 2 055w, and 2 024m; Al_2O_3 2 028m and 1 980br m; TiO_2 2 060br vw, 1 995vw (sh), and 1 950vw (sh); ZnO 2 030br w and 1 975br w; SnO_2 no ν_{CO} peaks observed; MgO 2 040br m and 1 968br m cm^{-1}.

Reaction of $[Ru_3(CO)_{12}]$ *with* $HS(CH_2)_3Si(OMe)_{3-x}(O{-}M'O_n)_x$.—A suspension of the oxide (0.1 g) was refluxed in a benzene solution (30 cm^3) of excess of $[Ru_3(CO)_{12}]$ (0.05 g) and allowed to cool. The bright yellow solids were collected by filtration, washed with CH_2Cl_2 (2 × 25 cm^3) and MeOH (2 × 25 cm^3), and dried *in vacuo.* I.r. (Nujol): $M'O_n = SiO_2$ 2 104w, 2 090 (sh), 2 078 (sh), 2 064vs, 2 054s, 2 038m, 2 023s, and 2 008; Al_2O_3 2 108w, 2 094w, 2 084m, 2 067s, 2 056vs, 2 026s, 2 010s, and 2 000br s; TiO_2 2 104w, 2 091lw, 2 081lw, 2 064vs, 2 053vs, 2 023vs, and 2 006vs; ZnO 2 104w, 2 082m, 2 063vs, 2 054s, 2 036s, 2 021vs, 2 006vs, and 1 999br s; SnO_2 2 104w, 2 064w, 2 053w, 2 020w, and 2 000m; MgO 2 104w, 2 094vw, 2 082w, 2 063m, 2 052s, 2 038?, 2 024m, and 2 000br s cm^{-1}.

The preparations were repeated on a sample of the thiolated oxides which had been treated with $SiMe_3Cl$. Analyses: Aerosil 380 2.55% Ru, 0.07% Os; Al_2O_3 1.08% Ru, 0.04% Os. I.r. (Nujol): $M'O_n = SiO_2$ 2 105w, 2 092w, 2 080vw, 2 064vs, 2 056s, 2 038m, 2 023vs, and 2 007s; Al_2O_3 2 105w, 2 092w, 2 081w, 2 064s, 2 052s, 2 038m, 2 023s, 2 008vs, 1 998br vs, and 1 945m; TiO_2 2 104m, 2 091w, 2 080w, 2 064vs, 2 053s, 2 038w, 2 022s, 2 006vs, and 1 999br s; ZnO 2 102w, 2 080w, 2 064m, 2 054s, 2 023m, 2 008m, and 1 998br m; SnO_2 2 104vw, 2 090vw, 2 080w, 2 062w, 2 052w, and 2 000br s; MgO 2 104w, 2 063m, 2 055m, 2 023m, and 2 000br w cm^{-1}.

Reaction of $[Ru_3(CO)_{12}]$ *with Oxides* $(M'O_n)$.—This was carried out under the same conditions as for the reaction with thiolated oxides. Analyses: Aerosil 380 0.21% Ru, 0.02% Os; Al_2O_3 1.51% Ru, 0.04% Os. I.r. (Nujol): SiO_2 2 060s, 2 032m, and 2 011w; Al_2O_3 2 104vw, 2 080w, 2 064m, 2 056m, 2 038m, 2 025m, 1 990br m, and 1 950br w; TiO_2 2 066br s and 1 998br m; ZnO 2 055br m and 1 970br m; SnO_2 2 061br w and 1 987br w; MgO 2 082w, 2 042br m, 1 984vs, and 1 966br vs cm^{-1}. After 1 week: 2 046br m and 1 965br m cm^{-1}.

These reactions were repeated on oxides silylated using (*a*) $SiMe_3Cl$ and (*b*) $NH(SiMe_3)_2$. I.r. (Nujol): SiO_2 (*a*) and (*b*) no ν_{CO}; Al_2O_3 (*a*) 2 070br s and 1 996br m, (*b*) 2 068br vw and 1 985br w; TiO_2 (*a*) 2 064br vw and 1 994br m, (*b*) 2 057br m and 1 985br w; ZnO (*a*) 2 065br s and 1 997br m, (*b*) 2 050br m and 1 967br w; SnO_2 (*a*) 2 065br w and 1 993br w, (*b*) 2 060br w, 2 030br w, and 1 975br w; MgO (*a*) 2 070br w and 2 000br vw, (*b*) 2 040br m, 2 010m, 1 993br w, 1 982br w, 1 968br w, 1 935br w, 1 925br w, 1 817br w, and 1 788br w cm^{-1}.

Reaction of $[Os_3H(CO)_{10}\{S(CH_2)_3Si(OMe)_3\}]$ *with Oxides* $(M'O_n)$.—This was carried out as described for the ruthenium analogue excepting that the solids were extracted with Et_2O (6 h) and MeOH (6 h) in a Soxhlet apparatus. In all cases this caused some leaching, but pale yellow solids were obtained. Osmium analyses: Aerosil 380, 0.36; Al_2O_3, 2.94; TiO_2, 3.17; MgO, 1.00; ZnO, 1.33%. I.r. (Nujol): oxide = SiO_2 2 109m, 2 069s, 2 058s, and 2 024vs; Al_2O_3 2 109m, 2 067s, 2 057s, 2 023vs, 1 997br m, and 1 986br m; TiO_2 2 107m, 2 067s, 2 056s, 2 023vs, 1 998br m, and 1 988br m; ZnO 2 108w, 2 067s, 2 057s, 2 022vs, 1 997br m, and 1 988br m; SnO_2 2 107w, 2 066s, 2 056m, 2 021s, 1 997br w, and 1 985br w; MgO 2 108m, 2 067s, 2 056s, 2 022vs, and 1 998br m cm^{-1}.

Reaction of $[Os_3(CO)_{12}]$ *with* $HS(CH_2)_3Si(OMe)_{3-x}(O{-}M'O_n)_x$.—A suspension of the thiolated oxide (0.5 g) was refluxed in a toluene solution (40 cm^3) of $[Os_3(CO)_{12}]$ (0.025 g) for 6 h and allowed to cool. The mixture was filtered and the solid residue extracted with Et_2O (5 h) in a Soxhlet apparatus. No leaching occurred, and the *products* were obtained as yellow solids. Osmium analyses: Aerosil 200, 2.01; Al_2O_3, 2.24; TiO_2, 1.96; MgO, 0.95; ZnO, 1.95%. I.r. (Nujol): $M'O_n = SiO_2$ 2 108m, 2 068s, 2 057s, 2 020s, 1 999br s, and 1 980br; Al_2O_3 2 109m, 2 067s, 2 057s, 2 024s, 1 995br, and 1 988br; TiO_2 2 109m, 2 067s, 2 057s, 2 024s, 1 995br, and 1 988br; ZnO 2 108m, 2 067s, 2 057s, 2 022s, 1 997br, and 1 986br; SnO_2 2 108m, 2 067s, 2 057s, 2 022s, 1 997br and 1 986br; MgO 2 110m, 2 067s, 2 057s, 2 024s, and 1 992br s cm^{-1}.

This procedure was repeated on samples of thiolated oxides treated with $SiMe_3Cl$. Osmium analyses: Aerosil 200, 2.32; Aerosil 380, 2.74; Al_2O_3, 1.79; TiO_2, 2.13; MgO, 0.78; ZnO, 0.25%. I.r. (Nujol): SiO_2 2 108m, 2 067s, 2 059m, 2 023vs, 1 997br m, 1 987br m, and 1 980 (sh); Al_2O_3 2 109m, 2 067s, 2 058s, 2 023s, 1 995br m, and 1 987br m; TiO_2 2 109m, 2 067vs, 2 058s, 2 024s, 1 995br m, and 1 987br m; ZnO 2 110w, 2 067s, 2 059m, 2 024s, 1 997br m, and 1 987br m; SnO_2 2 108m, 2 066s, 2 056s, 2 021s, 1 997br m, and 1 988br m; MgO 2 109m, 2 066s, 2 058s, 2 022s, 1 995br m, and 1 988br m cm^{-1}.

Reaction of $[Os_3(CO)_{12}]$ *with Oxides* $(M'O_n)$.—This was carried out as described for the reaction between $[Os_3(CO)_{12}]$ and the thiolated oxides. Osmium analyses: Aerosil 380, 1.00; Al_2O_3, 2.26; TiO_2, 0.93; MgO, 1.70; ZnO, 1.90%. I.r. (Nujol): SiO_2 2 115w, 2 078s, 2 064m, 2 024vs, 2 014 (sh), and 1 985br m; Al_2O_3 2 021br s and 1 947br m; TiO_2 2 030br m and 1 947br w; ZnO 2 108w, 2 067m, 2 059w

2 045 (sh), 2 020s, 2 018 (sh), 2 000br s, 1 990w, and 1 985w; SnO_2 no ν_{CO} observed; MgO 2 015br m and 1 930br w cm^{-1}.

A similar procedure was carried out on oxides treated with $SiMe_3Cl$. I.r. (Nujol): SiO_2 2 124br w, 2 114w, 2 078m, 2 065m, 2 026s, 2 014 (sh), 1 999w, and 1 987br w; Al_2O_3 2 106vw, 2 060br m, 2 034br s, 1 950br m, and 1 925br w; TiO_2 2 104w, 2 065m, 2 056w, and 2 026s; ZnO 2 025br m, 1 980br w, and 1 970br w cm^{-1}; MgO no ν_{CO} observed.

Repeating the reaction of $[Os_3(CO)_{12}]$ with oxides in refluxing toluene for 5 h, with no Soxhlet extraction, afforded different i.r. spectra for Al_2O_3, TiO_2, MgO, and ZnO. I.r. (Nujol): Al_2O_3 2 102w, 2 083 (sh), 2 061s, 2 048s, 2 015vs, 2 001 (sh), 1 941m br, and 1 919m br; TiO_2 2 117m, 2 102w, 2 062w, 2 048w, 2 015vs, and 1 940w br; ZnO 2 102w, 2 085w, 2 060s, 2 047s, 2 016vs, 2 001s (sh), 1 978m (sh), and 1 929br m; MgO 2 102w, 2 059m, 2 045s, 2 033w, 2 015vs, 1 998m (sh), 1 967br m (sh), and 1 929m br cm^{-1}.

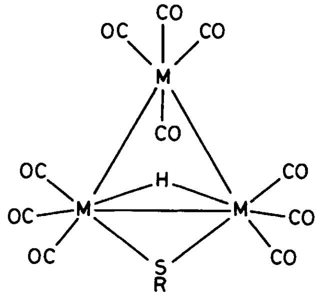
Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ *with* $SiPh_3(OH)$.—A solution of $[Os_3(CO)_{10}(MeCN)_2]$ in dry benzene was prepared by gradual addition of NMe_3O in CH_3CN to $[Os_3(CO)_{12}]$ (0.066 g) and MeCN (5 cm^3) in benzene (50 cm^3). On successive additions, $[Os_3(CO)_{11}(MeCN)]$ [i.r. 2 105w, 2 053s, 2 041s, 2 021m, 2 000vs, 1 984 (sh), and 1 981m cm^{-1}] and subsequently $[Os_3(CO)_{10}(MeCN)_2]$ [i.r. 2 078s, 2 052m, 2 022br, 1 993 (sh), 1 984s, and 1 964m cm^{-1}] were formed. Triphenylsilanol (2 equivalents) was added to the reaction mixture which was then left overnight. The solvent was removed and the residue chromatographed on 20 × 20 cm silica t.l.c. plates with hexane as solvent. Two bands were obtained which afforded $[Os_3H(CO)_{10}(OH)]$ [20] and $[Os_3H(CO)_{10}(OSiPh_3)]$ (7).[21] I.r. (hexane) for (7): 2 112w, 2 100vw, 2 072s, 2 063s, 2 044w, 2 027s, 2 022 (sh), 2 001s, 1 997 (sh), 1 990m, 1 985m, and 1 958w cm^{-1}. ^1H N.m.r.: δ 7.40 (m, 15 H) and -12.59 (s, 1 H).

Reaction of $[Co_3(CO)_9(CSiCl_3)]$ *with Oxides* $(M'O_n)$.—A suspension of the oxide (100 mg) was refluxed in a solution of $[Co_3(CO)_9(CSiCl_3)]$ (0.005 g) under CO in CH_2Cl_2 (25 cm^3) for 15 min. The solids were collected by filtration, extracted with Et_2O (2 h) under CO in a Soxhlet apparatus, and dried *in vacuo* for 16 h to afford purple powders. I.r. (Nujol): SiO_2 2 109w, 2 060m, and 2 043; Al_2O_3 2 105w, 2 056vs, and 2 041s; TiO_2 2 106w, 2 056s, and 2 040vs; ZnO 2 105w, 2 054s, and 2 044s; SnO_2 2 104w, 2 054s, and 2 040s; MgO 2 106vw, 2 056s, and 2 038m cm^{-1}.

RESULTS AND DISCUSSION

$[Ru_4H_4(CO)_{12}]$ *and Phosphinated Oxides*.—The compound $[Ru_4H_4(CO)_{12}]$ (1) was reacted with $PPh_2CH_2CH_2Si(OEt)_{3-x}(O\text{–}SiO_2)_x$ under analogous conditions to those reported to give a monosubstituted product with PPh_3.[22] However, comparing the ν_{CO} bands in the i.r. spectrum of the product with those of $[Ru_4H_4(CO)_{12-x}(PPh_3)_x]$ (x = 1, 2, or 3) [16] in hexane suggests a mixture of substitution products. The weak absorptions at 2 092 and 2 083 cm^{-1} correlate with bands observed for the mono- and di-substituted products respectively. There are many coincidences between the absorptions of the different substitution products, but the presence of the strong broad absorption at 1 990 cm^{-1} indicates there is probably also an appreciable concentration of the tri-substituted product. It is interesting that control of thermal substitution could be effected on phosphinated polystyrene–divinylbenzene co-polymers by altering the polymer structure.[23] Photochemically induced anchoring was attempted on phosphinated silica and alumina, under conditions reported to afford $[Ru_4H_4(CO)_{11}(PPh_3)]$ even in an excess of PPh_3.[15] A substantially longer irradiation time was required to give reasonably strong ν_{CO} bands than to cause monosubstitution in solution (35 rather than 7 min). The spectra initially differed from those obtained by the thermal reaction, with the bands at 2 092 and 2 083 cm^{-1} being markedly more intense. All bands could be assigned assuming a mixture of mono- and di-substituted products. On standing for several weeks, the spectra of these two materials were converted into those obtained from the thermal reaction. Whilst anchoring of the tetraruthenium cluster had been achieved on silica and alumina, the lack of product specificity was undesirable.

Anchoring of $[M_3(CO)_{12}]$ *(M = Ru or Os) on Thiolated Oxides*.—Thiolate ligands were employed to anchor triruthenium and triosmium clusters since single products are formed from the reactions of $[M_3(CO)_{12}]$ and RSH.[18] Secondly, the presence of the bridging groups would be anticipated to stabilise the clusters more than a terminal ligand. Thus $[M_3H(CO)_{10}\{S(CH_2)_3Si(OMe)_3\}]$, M = Ru (2) and Os (3), were synthesised under the same conditions as required to form $[M_3H(CO)_{10}(SPr^n)]$, M = Ru (4) and Os (5), without any problems of separating several complexes each having the silyl group.



M	R
(2) Ru	$(CH_2)_3Si(OMe)_3$
(3) Os	$(CH_2)_3Si(OMe)_3$
(4) Ru	Pr^n
(5) Os	Pr^n

Two anchoring procedures were attempted. First, (2) and (3) were allowed to bind to the oxides at room temperature. The materials containing the more robust osmium complex were subsequently extracted with refluxing Et_2O, causing some loss of (3) (identified by its i.r. spectrum) from the oxides. From the intensities of the recorded i.r. spectra it is evident that anchoring, *via* nucleophilic substitution at the $Si(OMe)_3$ by surface hydroxyl groups, had occurred to a much smaller extent on silica than on alumina or titania. In spite of the larger surface area of Aerosil 380, the osmium loading was only one tenth of that on Al_2O_3 and TiO_2. In all cases, the carbonyl absorptions agreed very closely with those of the two isolable analogues (3) and (5). Spectra obtained on alumina are shown in Figure 1. The second method was to interact $[Os_3(CO)_{12}]$ with $HS(CH_2)_3Si(OMe)_{3-x}(O-M'O_n)_x$ in refluxing toluene. Again this afforded satisfactory results and the loading on silica gel was increased. Using samples of the functionalised oxides which had been treated with $SiMe_3Cl$ caused slight improvements in spectral quality, *viz.* smaller line-widths in some cases and resolution of the weaker bands between 2 000 and 1 970 cm^{-1}. Little change in metal uptake was noted, apart from zinc oxide. All these materials have long shelf-lives. Further confirmation of the identity of $Os_3H(CO)_{10}[S(CH_2)_3Si(OMe)_{3-x}(O-SiO_2)_x]$ was obtained by diffuse reflectance u.v.-visible measurements, which showed bands at ≈30 000 and 25 270 cm^{-1}. These can be correlated with two lower energy bands in the solution (cyclohexane) spectrum of $[Os_3H(CO)_{10}(SPr^n)]$ (45 600, 39 500, 30 700, and 25 500 cm^{-1}).

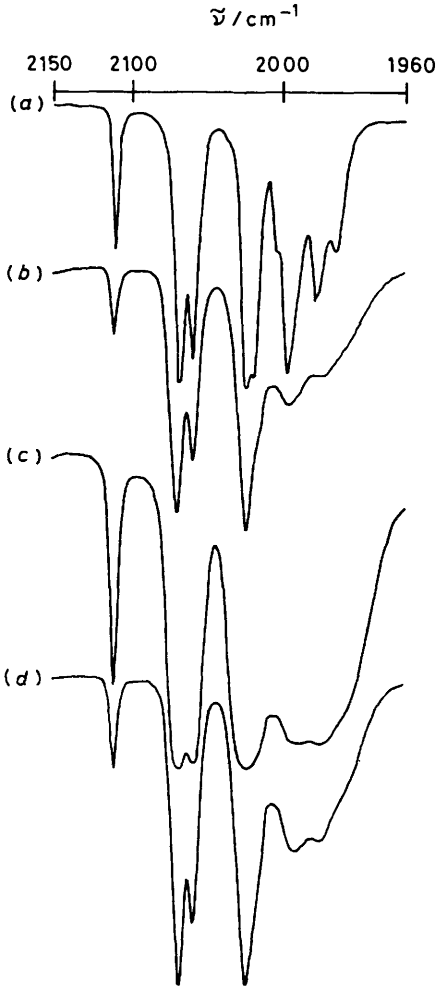


FIGURE 1 I.r. spectra (2 150—1 960 cm^{-1}) of (*a*) (3) in hexane, (*b*) (3) on Al_2O_3, (*c*) the product of $[Os_3(CO)_{12}]$ and $HS(CH_2)_3Si(OMe)_{3-x}(O-Al_2O_3)_x$, and (*d*) the product of $[Os_3(CO)_{12}]$ and thiolated alumina previously treated with $SiMe_3Cl$

Similar experiments were carried out on the ruthenium analogues. Interaction of (2) with the oxides at room temperature again afforded solids which exhibited ν_{CO} spectra similar to those of (2) itself,* as illustrated for alumina in Figure 2. However, these materials are less stable than their osmium analogues and the extraction procedure was not employed, so doubt remains as to whether substitution at the silicon atom by surface hydroxyls had been achieved. Interaction of $[Ru_3H(CO)_{10}(SPr^n)]$ (4) with oxides under similar conditions did demonstrate the importance of the $-Si(OMe)_3$ grouping in the chemisorption of the cluster. I.r. spectra obtained on these solids were very weak and were recorded on a 10- or 20-fold transmittance expansion, indicating only slight uptake of (4). The ν_{CO} bands which were observed for the species derived from (4) were oxide dependent. Interacting $[Ru_3(CO)_{12}]$ with the thiolated oxides afforded $Ru_3H(CO)_{10}[S(CH_2)_3Si(OMe)_{3-x}(O-M'O_n)_x]$ species. On silica ($M'O_n$), this appeared to be specific, but on Al_2O_3 (Figure 2), TiO_2, ZnO, and MgO an additional broad ν_{CO} absorption near 2 000 cm^{-1} was also apparent. The i.r. spectrum obtained on thiolated SnO_2 was of very poor quality, arising from the darkening and increased

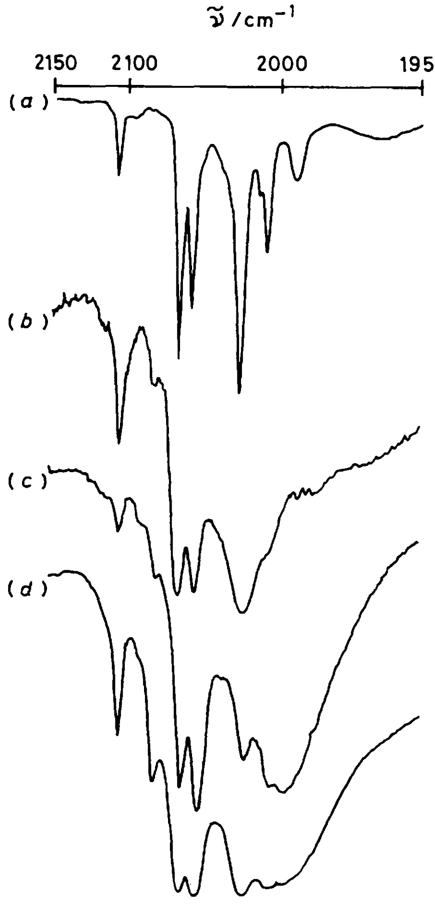


FIGURE 2 I.r. spectra (2 150—1 954 cm^{-1}) of (*a*) (2) in hexane, (*b*) (2) on Al_2O_3, (*c*) the product of $[Ru_3(CO)_{12}]$ and $HS(CH_2)_3Si(OMe)_{3-x}(O-Al_2O_3)_x$, and (*d*) the product of $[Ru_3(CO)_{12}]$ and thiolated alumina previously treated with $SiMe_3Cl$

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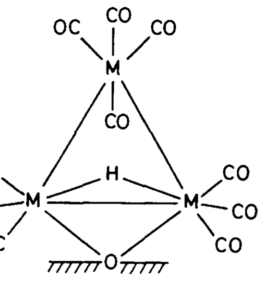
* The loading on silica was again small, but could be increased by raising the temperature to 40 °C under a stabilising CO atmosphere.

opacity of the oxide during the reaction with $HS(CH_2)_3$-$Si(OMe)_3$. Use of a $SiMe_3Cl$-treated ligand–oxide caused only small improvements in the specificity of the anchoring reaction, but did prolong the lifetime of the trinuclear complex (by a factor of 2). Shelf-lives, before total decomposition as monitored by the carbonyl absorptions at 2 105 and 2 066 cm^{-1}, were of the order of weeks at −20 °C. Both (2) and (4) were more stable than the anchored complexes and among the latter, stability on alumina and silica was greater than on titania and ZnO.

Interaction of $[M_3(CO)_{12}]$ *with Oxides.*—Reactions between metal carbonyls and functionalised oxides involve competition between the pendant ligands and the oxide surface itself. Blank reactions were carried out by interacting the trinuclear clusters with the oxides under the same conditions as used for the thiolated oxides. Interaction of $[Os_3(CO)_{12}]$ with oxides ($M'O_n$) has been reported under different conditions and been shown to form $Os_3H(CO)_{10}(O-M'O_n)$ (6) species on SiO_2,[2,24-26] Al_2O_3,[2,25,26] ZnO,[26] and TiO_2;[26] evidence for (6) includes i.r. comparisons with $[Os_3H(CO)_{10}(OSiPh_3)]$,[2,24-26] extended *X*-ray absorption fine structure (EXAFS),[2,24] electronic absorption,[27] and low-frequency Raman spectra.[27] Under more vigorous conditions $Os^{II}(CO)_2$ and $Os^{II}(CO)_3$ centres are thought to be generated.[2,24-26] The blank reaction between $[Os_3(CO)_{12}]$ and unfunctionalised silica yielded a material which exhibited carbonyl i.r. absorptions qualitatively similar to those observed on the thiolated oxide (Figure 3). However, the frequencies for the product with unfunctionalised silica are higher and the two species can be differentiated. Under these conditions (6) had been formed with high specificity. It is interesting that, in spite of this reaction between $[Os_3(CO)_{12}]$ and the surface of silica gel, the pendant thiol of the functionalised oxide selectively binds the cluster. Only on SiO_2 and TiO_2 were the metal loadings reduced on the unfunctionalised oxide. Under these conditions, the species (6) was also observed on ZnO and on this oxide, Al_2O_3, TiO_2, and MgO, spectra attributable to oxidised carbonyl-containing species were observed. Under slightly milder conditions of 5 h in refluxing toluene and no subsequent Soxhlet extraction, (6) was evident on TiO_2 and MgO and predominant on Al_2O_3 and ZnO (Figure 4). Unlike the situation on the functionalised oxides where there is negligible transmission of any oxide electronic effects through the anchoring ligand to the cluster carbonyl ligands, the frequencies of the carbonyl vibrations of (6) are oxide dependent [silica > (7) > alumina > ZnO] (Figure 4). So apparently silica is a more electron-withdrawing ligand than alumina or ZnO. The species (6) was also observed on an $SiMe_3Cl$-treated titania after the longer reflux time (6 h) and subsequent extraction. In all cases, the use of the silylating agent markedly reduced the metal uptake, but for Al_2O_3, SiO_2, ZnO, and TiO_2 protection was incomplete.



(6)

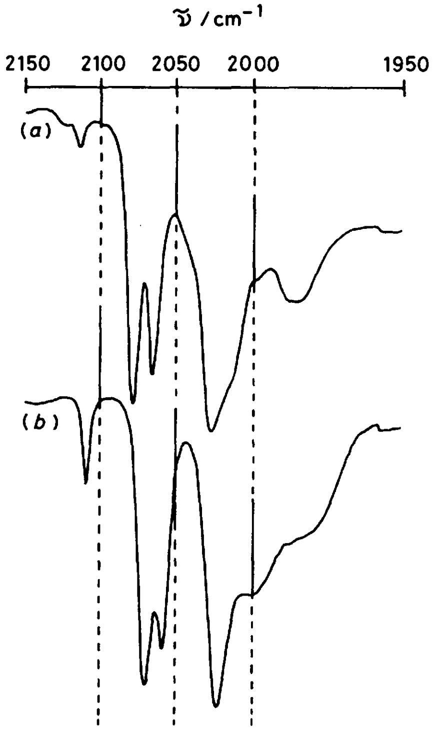


FIGURE 3 I.r. spectra (2 150—1 950 cm^{-1}) of (*a*) (6) on silica and (*b*) $Os_3H(CO)_{10}[S(CH_2)_3Si(OMe)_{3-x}(O-SiO_2)_x]$

Interaction of $[Ru_3(CO)_{12}]$ with silica in refluxing benzene (15 min) afforded a material which exhibited the same i.r. spectrum as obtained by Robertson and Webb [28] on a sample prepared by depositing $[Ru_3(CO)_{12}]$ from CH_2Cl_2 onto silica at room temperature. It is very similar to that of $[Ru_3(CO)_{12}]$ in solution and may be due to a chemisorbed dispersion of the cluster on silica gel. Bands attributable to a species (6) were observed on alumina [Figure 4(*e*)]. While the ruthenium * uptake was markedly reduced on the unthiolated silica, a slight increase was observed on alumina. On alumina and the remaining oxides, broad carbonyl absorptions were observed due to decomposed clusters; this has been monitored in detail on alumina.[29] However, the frequencies of these broad absorptions do not correlate with the broader absorptions near 2 000 cm^{-1} evident in the reaction of $[Ru_3(CO)_{12}]$ with most thiolated oxides or with those of the decomposed $[Ru_3H(CO)_{10}\{S(CH_2)_3Si$-

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* A low level of osmium was detected in the ruthenium samples.

$(OMe)_3\}]$–oxide materials. Evidently, on the functionalised oxides these uncharacterised metal carbonyl fragments are bound to one or more sulphur atoms. Attempts to protect the oxide surface by two silylating agents, $SiMe_3Cl$ and $NH(SiMe_3)_2$, were partially successful. Both reagents essentially prevented the uptake of $[Ru_3(CO)_{12}]$ by silica and greatly reduced the uptake on the other oxides. The former agent, $SiMe_3Cl$, was more effective. Magnesia, treated with $NH(SiMe_3)_2$, afforded a very complex carbonyl i.r. pattern when reacted with $[Ru_3(CO)_{12}]$ which included ν_{CO} bands at 1 817 and 1 788 cm^{-1}; this is probably from an unknown cluster anion or anions.

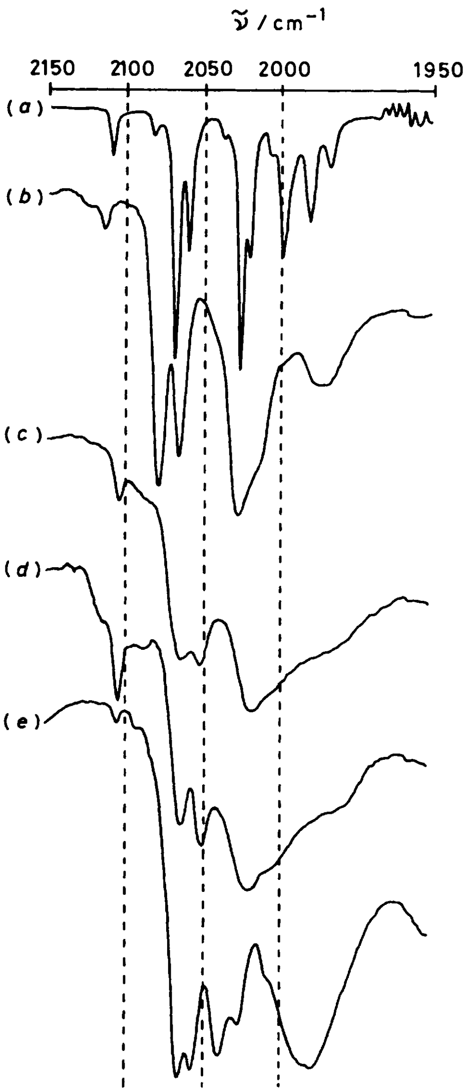
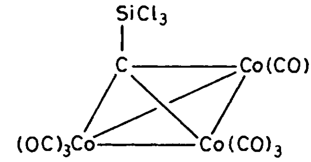


FIGURE 4 I.r. spectra (2 150—1 950 cm^{-1}) of (a) (7) in hexane, (b) (6) from $[Os_3(CO)_{12}]$ and silica, (c) (6) from $[Os_3(CO)_{12}]$ and alumina, (d) (6) from $[Os_3(CO)_{12}]$ and zinc oxide, and (e) (6) from $[Ru_3(CO)_{12}]$ and alumina

Interaction of $[Co_3(CO)_9(CSiCl_3)]$ (8) *with Oxides.*—Binding of (8) to the six oxides studied could be effected at moderate temperatures. The uptake from CH_2Cl_2 solution onto alumina was rapid at room temperature, but mild heating was required to drive the reaction to completion for the other oxides. The purple solids are all air stable and exhibit ν_{CO} i.r. patterns which are very similar to those of $[Co_3(CO)_9(CSiCl_3)]$ [17] (2 107w, 2 058vs, and 2 041m cm^{-1}) and $[Co_3(CO)_9\{CSi(OH)_3\}]$ [17] (2 107w, 2 059vs, and 2 042m cm^{-1}) in CH_2Cl_2 solution. The compound $[Co_3(CO)_9(CSiEt_3)]$, with more electron-donating silyl substituents, has absorptions at rather lower frequencies (2 101m, 2 052vs, 2 039s, 2 019m, and 2 004vw cm^{-1}).



(8)

Conclusions.—It is apparent that the ligand-anchoring procedures, principally developed on silica gel, can be applied to other oxides of various acidities. In spite of fairly complex reactions between oxide surfaces and these metal carbonyl clusters studied, the pendant thiol ligands nevertheless specifically bind the carbonyls. No electronic effects are apparently transmitted from the oxides through the pendant ligands to the carbonyl ligands, as any oxide-dependent reactivity stems from the surface environment and is not intrinsic to the cluster. However, trinuclear species of the type $M_3H(CO)_{10}(O–M'O_n)$ (M = Ru or Os) do show oxide ($M'O_n$) derived electronic effects and may have intrinsic reactivity differences. Complexes of the type $Ru_3H(CO)_{10}[S(CH_2)_3Si(OMe)_{3-x}(O–M'O_n)_x]$ are less stable than the isolable analogues *e.g.* $[Ru_3H(CO)_{10}(SPr^n)]$, and decompose to carbonyl fragments in which the metal is bound to sulphur. The anchored osmium species, however, are stable and are the subject of a reactivity and catalytic study which will be reported elsewhere.

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