*Journal of Organometallic Chemistry*, 295 (1985) 99–108
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# THE REACTIONS OF FREE AND SURFACE ANCHORED PHOSPHINES WITH MULTIDENTATE LIGAND STABILISED METAL CARBONYL CLUSTER COMPLEXES

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(Received May 28th, 1985)

## Summary

The trinuclear, bidentate-phosphine stabilised cluster complexes, $M_3(CO)_{10}(dppm)$ [M = Ru, Os; dppm = bis(diphenylphosphino)methane] undergo selective substitution by monodentate phosphines, L, to give $M_3(CO)_9(dppm)L$ [L = $PPh_3$, $Ph_2PCH_2CH_2Si(OEt)_3$] in which the monodentate phosphine coordinates to the uncomplexed metal atom. Similarly, the tetranuclear, tridentate-phosphine stabilised cluster complexes, $M_4(CO)_9[HC(PPh_2)_3]$ (M = Co, Rh, Ir) undergo selective substitution by L at the apical metal atom to give $M_4(CO)_8[HC(PPh_2)_3]L$. Immobilisation of these species to give unique supported clusters has been achieved either by treating $M_3(CO)_{10}(dppm)$ and $M_4(CO)_9[HC(PPh_2)_3]$ with phosphinated silica or phosphinated polystyrene-divinylbenzene, or by treating $M_3(CO)_9(dppm)L$ and $M_4(CO)_8[HC(PPh_2)_3]L$ [L = $Ph_2PCH_2CH_2Si(OEt)_3$] with silica.

## Introduction

The use of multidentate ligands to stabilise transition metal cluster complexes by preventing cluster fragmentation during the course of catalytic reactions, is currently receiving a great deal of attention [1–10]. There is also considerable interest in the immobilisation of cluster complexes to provide either supported molecular metal clusters or highly dispersed metal particles which may lead to selective heterogeneous catalysts [7]. Although little attention has yet been paid to the immobilisation of cluster complexes by pendant multidentate ligands [11–13], such systems may be expected to stabilise the supported cluster as well as preventing leaching from the support surface.

The reaction of multidentate ligand stabilised cluster complexes with monodentate phosphines has been reported for the cobalt complex $Co_4(CO)_9\{HC(PPh_2)_3\}$ [2,14] which undergoes substitution reactions with phosphine ligands at the apical Co atom. We now report in full the results of our studies on the reactions of

0022-328X/85/$03.30

stabilised clusters of the type $M_3(CO)_{10}(dppm)$ and $M_4(CO)_9\{HC(PPh_2)_3\}$ with both free and surface anchored monodentate phosphines. A preliminary account of part of this work has been published [15].

## Experimental

Infra-red spectra were recorded as Nujol mulls between NaCl plates or as dichloromethane solutions in matched 0.5 mm NaCl solution cells on a Perkin–Elmer 681 spectrometer with a model 3500 Data Station. NMR spectra were recorded at ambient temperature on a JEOL FX-90Q spectrometer (City of London Polytechnic) or a Bruker WM250 multinuclear spectrometer (University of Liverpool) operating in the Fourier-transform mode with proton-noise decoupling ($^{31}P$). Chemical shifts are relative to $SiMe_4$ ($^1H$) or 85% $H_3PO_4$ ($^{31}P$), with downfield chemical shifts as positive. Microanalyses were carried out by Elemental Micro-Analysis Ltd., (Devon).

Polymer beads (Amberlite XAD-2, polystyrene-divinylbenzene copolymer containing 2% crosslinking), purchased from BDH, were functionalised by chloromethylation [16] followed by reaction with $LiPPh_2$ [17] (2.87% P in the form of polymer-$CH_2PPh_2$). Silica (non-porous, surface area 400 $m^2$ $g^{-1}$), purchased from Lancaster Synthesis Ltd., was dried by heating to 380°C in vacuo for 48 h prior to functionalisation with $Ph_2PCH_2CH_2Si(OEt)_3$ [18] on refluxing in toluene [19] (0.52% P in the form of $Ph_2PCH_2CH_2SiOSi\equiv$). The complexes $M_3(CO)_{10}(dppm)$ (M = Ru [20] and Os [21]) and $M_4(CO)_9\{HC(PPh_2)_3\}$ (M = Co, Rh and Ir [2]) were prepared by published procedures.

All reactions were carried out under nitrogen or carbon monoxide atmospheres using dry, degassed solvents and standard Schlenk-line techniques.

### *A. Preparation of molecular species*

#### *Preparation of $Ru_3(CO)_9(dppm)(PPh_3)$*

A mixture of $Ru_3(CO)_{10}(dppm)$ (0.131 g, 0.135 mmol) and $PPh_3$ (0.0364 g, 0.139 mmol) in THF (30 ml) was heated under reflux with stirring for 2 h. The resulting deep red solution was distilled to dryness in vacuo, and the residue recrystallised from $CH_2Cl_2$/petroleum ether (60/80°C) by slow evaporation, yielding deep red flakes of the product (0.121 g, 74%). $^{31}P$ NMR ($CDCl_3$) 36.6(t, $PPh_3$), 15.5(d, $^3J(PP)$ 9.3 Hz, dppm); Found: C, 52.90; H, 3.47; P, 7.78. $C_{52}H_{37}O_9P_3Ru_3$ calcd.: C, 51.95; H, 3.10; P, 7.73%.

#### *Preparation of $Ru_3(CO)_9(dppm)\{Ph_2PCH_2CH_2Si(OEt)_3\}$*

As above, using $Ru_3(CO)_{10}(dppm)$ (0.311 g, 0.321 mmol) and $Ph_2PCH_2CH_2Si(OEt)_3$ (0.121 g, 0.321 mmol). Precipitation with heptane gave a red powder of the product (0.214 g, 50%). $^{31}P$ NMR ($CDCl_3$) 36.8(t, $Ph_2PCH_2$), 18.3(d, $^3J(PP)$ 8.5 Hz, dppm); $^1H$ NMR ($CDCl_3$) 0.53(m, $SiCH_2$, 2H), 1.15(t, $^3J(HH)$ 7.0 Hz, $CH_3$, 9H), 2.45(m, $PCH_2$, 2H), 3.71(qr, $^3J(HH)$ 7.0 Hz, $OCH_2$, 6H), 4.17(t, $^2J(PH)$ 10.1 Hz, dppm, 2H) and 7.2–7.5(m, Ph, 30H).

#### *Preparation of $Os_3(CO)_9(dppm)(PPh_3)$*

A mixture of $Os_3(CO)_{10}(dppm)$ (0.203 g, 0.162 mmol) and $PPh_3$ (0.0450 g, 0.172 mmol) in toluene (50 ml) was heated under reflux with stirring for 4 h. The resulting orange solution was distilled to dryness in vacuo, and the residue recrystallised from cold acetone/ethanol, yielding small yellow rectangular crystals of the product (0.175 g, 63%). $^{31}$P NMR ($C_6D_5CD_3$, −50°C) (ABX type spectrum) −0.1(d, $^{3}J_{AX}$ 2.4 Hz, $PPh_3$), −25.0(d of d, $^{2}J_{AB}$ 54.7 Hz, $^{3}J_{AX}$ 2.4 Hz, dppm), −29.4 (d, $^{2}J_{AB}$ 54.7 Hz, dppm; (+90°C) −0.9 (s, br, $PPh_3$), −29.1 (s, br, dppm); Found: C, 44.49; H, 2.96; P, 6.36. $C_{52}H_{37}O_9Os_3P_3$ calcd.: C, 42.86; H, 2.56; P, 6.38%.

### *Preparation of* $Os_3(CO)_9(dppm)\{Ph_2PCH_2CH_2Si(OEt)_3\}$

As above, using $Os_3(CO)_{10}(dppm)$ (0.331 g, 0.268 mmol) and $Ph_2PCH_2CH_2Si(OEt)_3$ (0.110 g, 0.292 mmol). Distillation to dryness, in vacuo, of the reaction solution and precipitation from $CH_2Cl_2$/heptane gave a yellow/orange powder of the product (0.260 g, 61%). $^{31}$P NMR ($C_6D_5CD_3$, −90°C) (ABX type spectrum) −1.8 (d, $^{3}J_{AX}$ 3.2 Hz, $PPh_3$), −24.0 (d of d, $^{2}J_{AB}$ 55.2, $^{3}J_{AX}$ 3.2 Hz, dppm), −28.3 (d, $^{2}J_{AB}$ 55.2 Hz, dppm); (+90°C) −3.9 (s, br, $PPh_3$), −29.1 (s, br, dppm); $^{1}$H NMR ($CDCl_3$) 0.44 (m, $SiCH_2$, 2H), 1.12(t, $^{3}J$(HH) 7.0 Hz, $CH_3$, 9H), 2.63 (m, $PCH_2$, 2H), 3.68 (qr, $^{3}J$(HH) 7.0 Hz, $OCH_2$, 6H), 4.90 (t, $^{2}J$(PH) 10.4 Hz, dppm, 2H) and 7.2–7.5 (m, Ph, 30H).

### *Preparation of* $Co_4(CO)_8\{HC(PPh_2)_3\}(PPh_3)$

A mixture of $Co_4(CO)_9\{HC(PPh_2)_3\}$ (0.213 g, 0.202 mmol) and $PPh_3$ (0.0646 g, 0.246 mmol) in THF (40 ml) was heated under reflux with stirring for 3 h, at which

TABLE 1

INFRARED DATA

| Complex | $\nu$(CO) (cm$^{-1}$) [a] |
|---|---|
| $Ru_3(CO)_9(dppm)(PPh_3)$ | 2052w,1992s,1975s,1942m |
| $Ru_3(CO)_9(dppm)\{Ph_2PCH_2CH_2Si(OEt)_3\}$ | 2051w,1990s,1974s,1940m |
| $Ru_3(CO)_9(dppm)(Ph_2PCH_2CH_2SiOSi{\equiv})$ | 2053w,1992s,1975s,1947sh |
| $Ru_3(CO)_9(dppm)(Ph_2PCH_2$-polymer) | 2051w,1989s,1973s,1940sh |
| $Ru_3(CO)_8(dppm)_2$ | 2039m,1979sh,1962vs,1939sh,1897w,1886w |
| $Os_3(CO)_9(dppm)(PPh_3)$ | 2061m/w,1998s,1977vs,1960sh,1934m |
| $Os_3(CO)_9(dppm)(\eta^1$-dppm) | 2060m/w,2000sh,1995s,1975vs,1957sh,1929m |
| $Os_3(CO)_9(dppm)\{Ph_2PCH_2CH_2Si(OEt)_3\}$ | 2061m/w,1996s,1975vs,1956sh,1931m |
| $Os_3(CO)_9(dppm)(Ph_2PCH_2CH_2SiOSi{\equiv})$ | 2061m/w,1997s,1976vs,1960sh,1935m |
| $Os_3(CO)_9(dppm)(Ph_2PCH_2$-polymer) | 2061m/w,1994s,1975vs,1960sh,1924m |
| $Co_4(CO)_8\{HC(PPh_2)_3\}(PMe_3)$ [b] | 2010s,1970vs,1950sh,1760m,1740m |
| $Co_4(CO)_8\{HC(PPh_2)_3\}(PPh_3)$ | 2004m,1969vs,1797w,1772m,1745sh |
| $Co_4(CO)_8\{HC(PPh_2)_3\}(Ph_2PCH_2CH_2Si\ (OEt)_3\}$ | 2011m,1972vs,1801w,1769m,1754sh |
| $Co_4(CO)_8\{HC(PPh_2)_3\}(Ph_2PCH_2CH_2SiOSi{\equiv})$ | 2013m,1977vs,1806m,1779m,1748sh |
| $Co_4(CO)_8\{HC(PPh_2)_3\}(Ph_2PCH_2$-polymer) | 2007m,1969vs,1802w,1775m,1754sh |
| $Rh_4(CO)_8\{HC(PPh_2)_3\}(PPh_3)$ | 2020s,1992sh,1985vs,1848sh,1827m,1784s,1761sh |
| $Rh_4(CO)_8\{HC(PPh_2)_3\}\{Ph_2PCH_2CH_2Si\ (OEt)_3\}$ | 2020s,1990sh,1982vs,1846sh,1826m,1783s, |
| $Rh_4(CO)_8\{HC(PPh_2)_3\}(Ph_2PCH_2CH_2SiOSi{\equiv})$ | 2022s,1998sh,1988vs,1847sh,1835w,1802m,1780sh |
| $Rh_4(CO)_8\{HC(PPh_2)_3\}(Ph_2PCH_2$-polymer) | 2016s,1987sh,1978vs,1848sh,1830m,1796s,1778s |
| $Ir_4(CO)_8\{HC(PPh_2)_3\}(PPh_3)$ | 2026m,1989s,1953w,1942w,1919vw |
| $Ir_4(CO)_8\{HC(PPh_2)_3\}(Ph_2PCH_2CH_2Si(OEt)_3\}$ | 2022m,1987s,1951w,1941w,1917vw |
| $Ir_4(CO)_8\{HC(PPh_2)_3\}(Ph_2PCH_2CH_2SiOSi{\equiv})$ | 2029m,1994s,1960sh,1948sh,1919sh |
| $Ir_4(CO)_8\{HC(PPh_2)_3\}(Ph_2PCH_2$-polymer) | 2026m,1990s,1959sh,1944sh,1918sh. |

[a] Soluble complexes as $CH_2Cl_2$ solutions; supported complexes as Nujol mulls. [b] Reference 2.

time the infra-red bands of the starting material had disappeared. The dark green solution was then reduced in volume and heptane added to precipitate the crude product. Attempted recrystallisation from $CH_2Cl_2$/heptane led to reformation of the starting cluster $Co_4(CO)_9\{HC(PPh_2)_3\}$, so the pure product could not be obtained. However its IR spectrum (Table 1) is similar to that of $Co_4(CO)_8\{HC(PPh_2)_3\}(PMe_3)$ [2].

*Preparation of* $Co_4(CO)_8\{HC(PPh_2)_3\}\{Ph_2PCH_2CH_2Si(OEt)_3\}$

As above, using $Co_4(CO)_9\{HC(PPh_2)_3\}$ (0.104 g, 0.0985 mmol) and $Ph_2PCH_2CH_2Si(OEt)_3$ (0.114 g, 0.303 mmol). A green powder of the product was obtained by precipitation with heptane (0.083 g, 60%). $^{31}P$ NMR $(CDCl)_3$ 40.4 (s, br, $HC(PPh_2)_3$), 26.0 (s, $Ph_2PCH_2$); $^{1}H$ NMR ($CDCl_3$) 0.61 (m, $SiCH_2$, 2H), 1.19 (t, $^{3}J$(HH) 7.0 Hz, $CH_3$, 9H), 2.51 (m, $PCH_2$, 2H), 3.76 (qr, $^{3}J$(HH) 7.0 Hz, $OCH_2$, 6H), 5.86 (qr, $^{2}J$(PH) 8.7 Hz, $HC(PPh_2)_3$, 1H) and 7.4–7.9 (m, Ph, 40H).

*Preparation of* $Rh_4(CO)_8\{HC(PPh_2)_3\}(PPh_3)$

A solution of $PPh_3$ (0.0200 g, 0.0839 mmol) in $CH_2Cl_2$ (10 ml) was added dropwise with stirring to a $CH_2Cl_2$ (10 ml) solution of $Rh_4(CO)_9\{HC(PPh_2)_3\}$ (0.0940 g, 0.0763 mmol) over 15 min. After stirring for a further 3 h, the product was crystallised by the addition of petroleum ether and slow evaporation, yielding small flaky brown crystals (0.101g, 90%). $^{31}P$ NMR ($CDCl_3$) 25.4 (d of qr, $^{1}J$(RhP) 131, $^{3}J$(PP) 65 Hz, $PPh_3$), 15.0 [d of d of m, $^{1}J$(RhP) 107, $^{3}J$(PP) 65 Hz, $HC(PPh_2)_3$]; Found: C, 51.93; H, 3.51; P, 8.94. $C_{63}H_{46}O_8P_4Rh_4$ calcd.: C, 51.60; H, 3.61; P, 8.45%.

*Preparation of* $Rh_4(CO)_8\{HC(PPh_2)_3\}\{Ph_2PCH_2CH_2Si(OEt)_3\}$

As above using $Rh_4(CO)_9\{HC(PPh_2)_3\}$ (0.0981 g, 0.0796 mmol) and $Ph_2PCH_2CH_2Si(OEt)_3$ (0.0372 g, 0.0988 mmol) in THF solvent. Addition of heptane and distillation in vacuo of the THF yielded a red/brown powder of the product (0.108 g, 86%). $^{31}P$ NMR ($CDCl_3$) 23.9 (d of qr, $^{1}J$(RhP) 138, $^{3}J$(PP) 69 Hz, $Ph_2PCH_2$), 13.3 [d of d of m, $^{1}J$(RhP) 113, $^{3}J$(PP) 69 Hz, $HC(PPh_2)_3$]; $^{1}H$ NMR ($CDCl_3$) 0.69 (m, $SiCH_2$, 2H), 1.21 (t, $^{3}J$(HH) 7.0 Hz, $CH_3$, 9H), 1.88 (m, $PCH_2$, 2H), 2.71 (qr, $^{2}J$(PH) 8.1 Hz, CH, 1H), 3.78 (qr, $^{3}J$(HH) 7.0 Hz, $OCH_2$, 6H) and 6.8–7.8(m, Ph, 40H).

*Preparation of* $Ir_4(CO)_8\{HC(PPh_2)_3\}(PPh_3)$

A mixture of $Ir_4(CO)_9\{HC(PPh_2)_3\}$ (0.150 g, 0.0944 mmol) and $PPh_3$ (0.0261 g, 0.0995 mmol) in toluene (50 ml) was heated under reflux, with stirring, for 8 h. The resulting, still yellow, solution was distilled to dryness in vacuo, and the residue recrystallised from $CH_2Cl_2$/heptane by slow evaporation, yielding bright yellow crystals of the product (0.045 g, 30%). $^{31}P$ NMR ($CDCl_3$) −47.0 (m, $HC(PPh_2)_3$), −15.4 (m, $PPh_3$); Found: C, 42.09; H, 2.91. $C_{63}H_{46}Ir_4O_8P_4$ calcd.: C, 41.49; H, 2.54%.

*Preparation of* $Ir_4(CO)_8\{HC(PPh_2)_3\}\{Ph_2PCH_2CH_2Si(OEt)_3\}$

As above, using $Ir_4(CO)_9\{HC(PPh_2)_3\}$ (0.0805 g, 0.0507 mmol) and $Ph_2PCH_2CH_2Si(OEt)_3$(0.0279 g, 0.0741 mmol). Precipitation from $CH_2Cl_2$/heptane gave a yellow powder of the product (0.065 g, 60%). $^{31}P$ NMR ($CDCl_3$) −47.7 (m,

$HC(PPh_2)_3$) −17.0 (m, $Ph_2PCH_2$); $^1H$ NMR ($CDCl_3$) 0.80 (m, $SiCH_2$, 2H), 1.17 (t, $^3J(HH)$ 7.0 Hz, $CH_3$, 9H), 1.56 (m, $PCH_2$, 2H), 3.74(qr, $^3J(HH)$ 7.0 Hz, $OCH_2$, 6H), 6.8–7.8(m, Ph, 40H) and 11.34 (qr, $^2J(PH)$ 6.1 Hz, CH, 1H).

## *B. Preparation of immobilised analogues*

### *Preparation of silica-supported clusters*

*(a) By substitution.* A suspension of phosphinated silica (1 g) was heated under reflux with a stirred solution of $Ru_3(CO)_{10}(dppm)$ (0.031 g) in THF (50 ml) for 3 h. The resulting orange solid was filtered off and soxhlet extracted with $CH_2Cl_2$ for 3 h prior to drying in vacuo. Found: Ru, 0.68; P, 0.63%; calcd.: Ru, 0.68: P, 0.64%. The following were prepared in a similar way: $Os_3(CO)_{10}(dppm)$ (0.093 g), toluene for 2.5 h, bright yellow. Found: Os, 1.53; P, 0.75; calcd.: Os, 1.53; P, 0.77%. $Co_4(CO)_9\{HC(PPh_2)_3\}$ (0.042 g) THF for 2 h, green. Found: Co, 0.64; P, 0.90; calcd.: Co, 0.64; P, 0.86%. $Ir_4(CO)_9\{HC(PPh_2)_3\}$ (0.034 g), toluene for 5 h, yellow. Found: Ir, 1.32; P, 0.70; calcd.: Ir, 1.32; P, 0.69%. $Rh_4(CO)_9\{HC(PPh_2)_3\}$ (0.090 g), toluene for 4 h at room temperature, brown. Found: Rh, 1.41; P, 0.84; calcd.: Rh, 1.41; P, 0.83%.

*(b) By hydrolysis.* A suspension of silica (1 g) was heated under reflux a stirred solution of $Os_3(CO)_9(dppm)\{Ph_2PCH_2CH_2Si(OEt)_3\}$ (0.053 g) in benzene (20 ml) for 3 h, then treated as in (a) above. Found: Os, 0.52; P, 0.085; calcd.: Os, 0.52; P, 0.10%. The following were prepared similarly: $Ir_4(CO)_8\{HC(PPh_2)_3\}\{Ph_2PCH_2CH_2Si(OEt)_3\}$ (0.056 g), toluene for 5 h. Found: Ir, 1.8; P, 0.12%; calcd.: Ir 1.8; P, 0.29%. $Co_4(CO)_8\{HC(PPh_2)_3\}\{Ph_2PCH_2CH_2\text{-}Si(OEt)_3\}$ (0.051 g), toluene, 2 h at 50–60°C. Found: Co, 0.29; P, 0.32; calcd.: Co, 0.29; P, 0.15%. $Ru_3(CO)_9(dppm)\{Ph_2PCH_2CH_2Si(OEt)_3\}$ (0.077 g), toluene for 18 h at room temperature under a CO atmosphere. Found: Ru, 0.10; P, $<0.05$; calcd.: Ru, 0.10; P, 0.03%. $Rh_4(CO)_8\{HC(PPh_2)_3\}\{Ph_2PCH_2\text{-}CH_2Si(OEt)_3\}$ (0.069 g), toluene for 24 h at room temperature under a CO atomosphere.

All the oxides were paler in colour than those formed in the substitution reactions.

### *Preparation of polymer-supported clusters*

A suspension of phosphinated polymer (1 g) was heated under reflux with stirring, in a solution of $Ru_3(CO)_{10}(dppm)$ (0.090 g) in THF (30 ml) for 2 h, then treated as in (a) above. Found: Ru, 2.7; P, 2.87; calcd.: Ru, 2.7; P, 3.19%. $Os_3(CO)_{10}(dppm)$ (0.053 g), toluene for 2.5 h. Found: Os, 1.00; P, 2.99; calcd.: Os, 1.00; P, 2.93%. $Co_4(CO)_9\{HC(PPh_2)_3\}$ (0.055 g), THF for 2 h. Found: Co, 0.37; P, 2.80; calcd.: Co, 0.37; P, 2.98%. $Ir_4(CO)_9\{HC(PPh_2)_3\}$ (0.054 g), toluene for 9 h. Found: Ir, 0.40; P, 3.01; calcd.: Ir, 0.40; P, 2.90%. $Rh_4(CO)_9\{HC(PPh_2)_3\}$ (0.10 g), THF for 20 h at room temperature. Found: Rh, 1.41; P, 2.82; calcd.: Rh, 1.41; P, 3.08%.

The polymer beads had similar colours to their phosphinated silica analogues.

### *Reaction of $Ru_3(CO)_9(dppm)(Ph_2PCH_2\text{-polymer})$ with dppm*

Orange/red beads of $Ru_3(CO)_9(dppm)(Ph_2PCH_2\text{-polymer})$ were treated with excess dppm in refluxing THF. The solvent gradually changed from colourless to orange over several hours. Filtration gave pale coloured beads, and the solution was shown to contain $Ru_3(CO)_8(dppm)_2$ by comparison of its infra-red spectrum with that of a known sample.

## Results and Discussion

The reaction of $M_3(CO)_{10}(dppm)$ (Ru, Os) with equimolar amounts of monodentate phosphines, L, proceeds smoothly in refluxing THF and toluene, respectively, leading to the clean formation of the trisubstituted derivatives $M_3(CO)_9(dppm)(L)$ [$L = Ph_3P$, $Ph_2PCH_2CH_2Si(OEt)_3$]. The infra-red spectra (Fig. 1) indicate the expected all-terminal carbonyl ligand structure, and a comparison with the spectrum of $Os_3(CO)_9(dppm)(\eta^1\text{-dppm})$ (Table 1), whose structure has been determined by X-ray crystallography [22] indicates that the phosphine substitutes into an equatorial position. The $^{31}P$ NMR spectra of $Ru_3(CO)_9(dppm)(L)$ (see Experimental) indicate that equatorial substitution occurs at the uncomplexed metal atom, since both P atoms of the dppm ligand are equivalent. This equivalence is caused by a fluxional process which involves the $PPh_3$ ligand rapidly exchanging between the two available equatorial sites on the Ru atom. This fluxional process has been frozen out for the osmium complexes at −50°C (see Experimental), when the two phosphine groups of the dppm ligand are no longer equivalent, and indeed, only become equivalent on the NMR time-scale at +90°C. We are currently investigating the mechanism of this fluxional process by $^{31}P$ and $^{13}C$ NMR spectroscopy using the

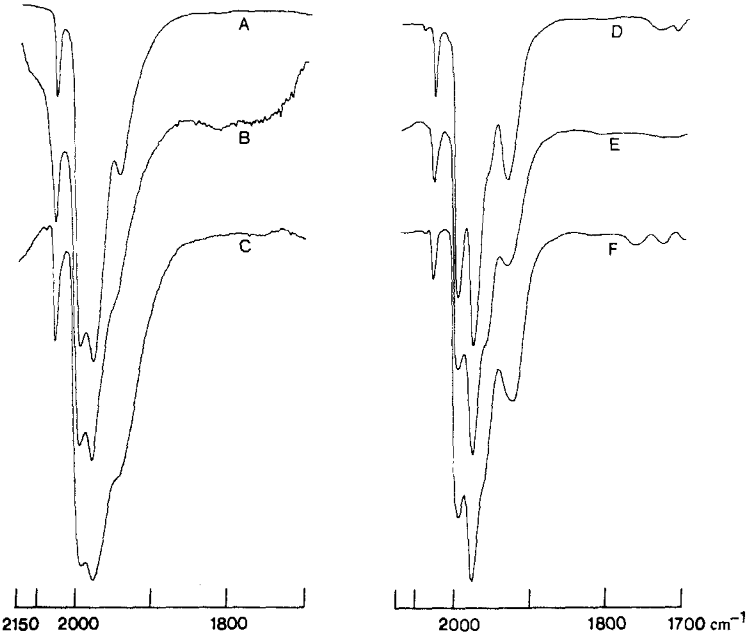

Fig. 1. IR spectra of homogeneous and supported ruthenium and osmium complexes. (a) $Ru_3(CO)_9(dppm)(PPh_3)$; (b) $Ru_3(CO)_9(dppm)(Ph_2PCH_2CH_2SiOSi\equiv)$; (c) $Ru_3(CO)_9(dppm)(Ph_2PCH_2\text{-polymer})$; (d) $Os_3(CO)_9(dppm)(PPh_3)$; (e) $Os_3(CO)_9(dppm)(Ph_2PCH_2CH_2SiOSi\equiv)$; (f) $Os_3(CO)_9(dppm)(Ph_2PCH_2\text{-polymer})$.

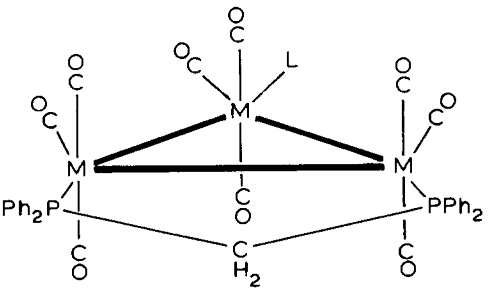

Fig. 2. Proposed structure for the clusters $M_3(CO)_9(dppm)(L)$ (M = Ru, Os) (L = $Ph_3P$, $Ph_2PCH_2CH_2Si(OEt)_3$, $Ph_2PCH_2CH_2SiOSi\equiv$, $Ph_2PCH_2$-polymer).

spin saturation transfer technique, but it is expected that a mechanism similar to that observed for the analogous complex $Os_3(CO)_9\{P(OMe)_3\}(PPh_3)_2$ [23] is operating. The spectroscopic data therefore show that the complexes $M_3(CO)_9(dppm)(L)$ have the structure shown in Fig. 2.

Similar reactions of $M_4(CO)_9\{HC(PPh_2)_3\}$ with equimolar amounts of monodentate phosphines in refluxing hydrocarbon (M = Co, Ir) or at room temperature in $CH_2Cl_2$ (M = Rh), lead to selective substitution at the apical metal atom to give the complexes $M_4(CO)_8\{HC(PPh_2)_3\}(L)$. Spectroscopic data (Experimental and Fig. 3) again show the complexes to have symmetrical structures related to that of their parent cluster [2] (Fig. 4). The carbonyl structure of the tetrasubstituted iridium

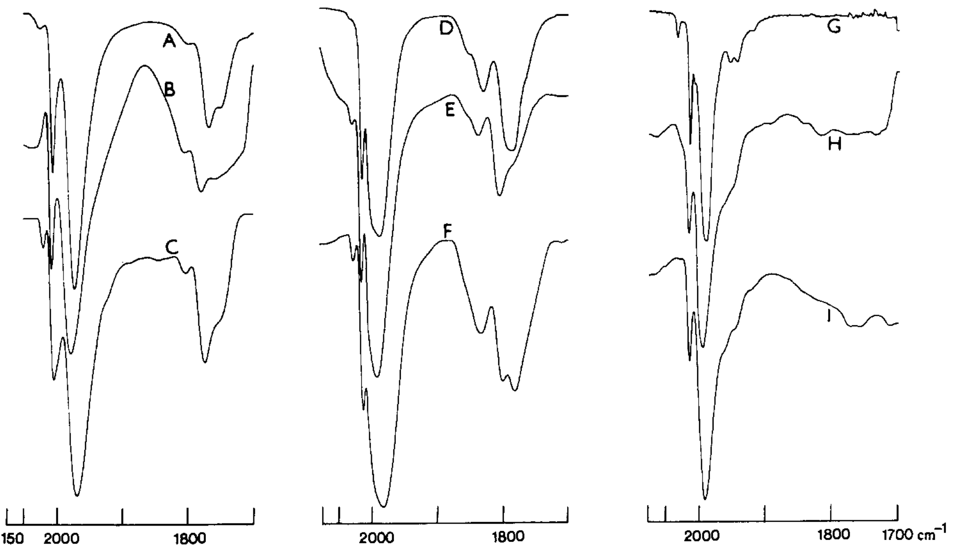

Fig. 3. IR spectra of homogeneous and supported cobalt, rhodium and iridium complexes. (a) $Co_4(CO)_8\{HC(PPh_2)_3\}\{Ph_2PCH_2CH_2Si(OEt)_3\}$; (b) $Co_4(CO)_8\{HC(PPh_2)_3\}(Ph_2PCH_2CH_2SiOSi\equiv)$; (c) $Co_4(CO)_8\{HC(PPh_2)_3\}(Ph_2PCH_2$-polymer); (d) $Rh_4(CO)_8\{HC(PPh_2)_3\}(PPh_3)$; (e) $Rh_4(CO)_8\{HC(PPh_2)_3\}(Ph_2PCH_2CH_2SiOSi\equiv)$; (f) $Rh_4(CO)_8\{HC(PPh_2)_3\}(Ph_2PCH_2$-polymer); (g) $Ir_4(CO)_8\{HC(PPh_2)_3\}(PPh_3)$; (h) $Ir_4(CO)_8\{HC(PPh_2)_3\}(Ph_2PCH_2CH_2SiOSi\equiv)$; (i) $Ir_4(CO)_8\{HC(PPh_2)_3\}(Ph_2PCH_2$-polymer).

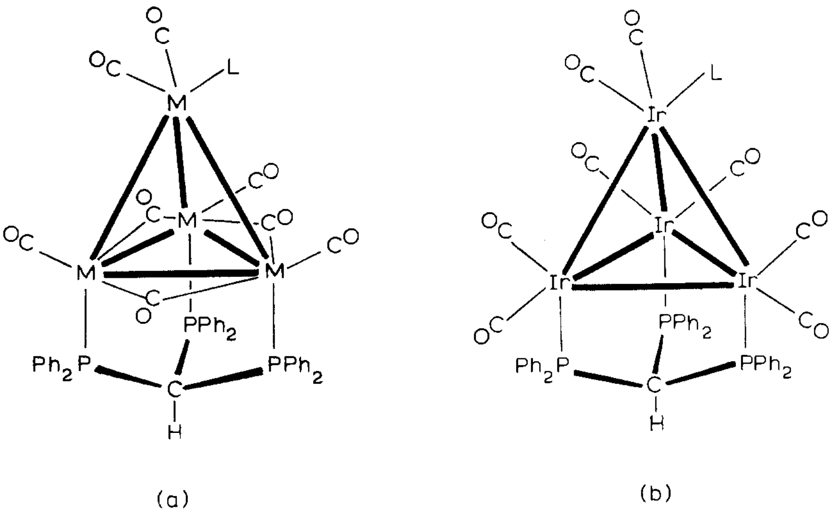

Fig. 4. (a) Proposed structures for the clusters $M_4(CO)_8\{HC(PPh_2)_3\}(L)$ (M = Co, Rh), and (b) $Ir_4(CO)_8\{HC(PPh_2)_3\}(L)$ ($L = Ph_3P$, $Ph_2PCH_2CH_2Si(OEt)_3$, $Ph_2PCH_2CH_2SiOSi\equiv$, $Ph_2PCH_2$-polymer).

complexes remains all-terminal, as found in the parent cluster [23]. This remarkable feature suggests the absence of bridging carbonyls to be caused by the presence of the capping ligand [24]. The cobalt derivative $Co_4(CO)_8\{HC(PPh_2)_3\}(PPh_3)$ is unstable in solution with respect to loss of $PPh_3$, giving almost quantitative reformation of the starting cluster. This ruled out full characterisation, although the infra-red spectrum of a freshly prepared sample is identical with that reported for $Co_4(CO)_8\{HC(PPh_2)_3\}(PMe_3)$ [2].

Since these reactions take place cleanly and quantitatively to give one product, we carried out analogous reactions with phosphinated silica ($Ph_2PCH_2CH_2SiOSi\equiv$) and phosphinated polystyrene-divinylbenzene copolymer ($Ph_2PCH_2$-polymer) in order to obtain supported clusters in which there is only one cluster species present on the support. Thus, the clusters $M_3(CO)_{10}(dppm)$ and $M_4(CO)_9\{HC(PPh_2)_3\}$ react smoothly with the phosphinated supports, under the same reaction conditions employed in the preparation of their molecular analogues, to give $M_3(CO)_9(dppm)(L)$ and $M_4(CO)_8\{HC(PPh_2)_3\}(L)$ ($L = Ph_2PCH_2CH_2SiOSi\equiv$, $Ph_2PCH_2$-polymer). The silica-supported clusters have also been obtained by treating the homogeneous complexes, $M_3(CO)_9(dppm)\{Ph_2PCH_2CH_2Si(OEt)_3\}$ and $M_4(CO)_8\{HC(PPh_2)_3\}$-$\{Ph_2PCH_2CH_2Si(OEt)_3\}$ with silica.

The infra-red spectra of all the supported clusters are virtually identical to those of their molecular analogues (Table 1, Figs. 1 and 3). The cleanest method of immobilisation appears to be that induced by substitution with phosphinated supports. Immobilisation in this way not only gives higher metal loadings (Table 2), but also excellent agreement between found and calculated values for the phosphorus contents (see Experimental), suggesting little or no decomposition of the reactant cluster. Presumably, high surface coverage by long chain phosphine groups protects the cluster from active surface groups during the substitution reactions. In contrast, immobilisation by hydrolysis can produce significant decomposition of the cluster. For example, attachment of the rhodium cluster $Rh_4(CO)_8\{HC$-

TABLE 2

METAL LOADINGS OF IMMOBILISED CLUSTERS

| Metal | Loadings (mmol cluster per g support) | | |
|---|---|---|---|
| | Hydrolysis with $SiO_2$ | Substitution with $Ph_2PCH_2CH_2SiOSi\equiv$ | Substitution with $Ph_2PCH_2$-polymer |
| Ruthenium | 0.0033 | 0.022 | 0.089 |
| Osmium | 0.0091 | 0.027 | 0.018 |
| Cobalt | 0.012 | 0.027 | 0.016 |
| Rhodium | – | 0.034 | 0.034 |
| Iridium | 0.023 | 0.017 | 0.0053 |

$(PPh_2)_3\}\{Ph_2PCH_2CH_2Si(OEt)_3\}$ in this way, even at room temperature, produces a pale coloured support exhibiting a weak infra-red spectrum similar to that of its molecular analogue but with several impurity bands. Such decomposition reactions are well known to occur during the immobilisation of $Rh_4(CO)_{12}$ by pendant phosphines onto silica [25,26].

Thus, the method of using highly substituted clusters has proved to be a selective route to the immobilisation of single species on insoluble supports. However, since anchorage depends on single metal–phosphine bonds, which in the case of tetranuclear clusters are easily broken in the presence of CO or other ligands, leaching of the complex from the support is a problem. The supported ruthenium cluster, for example, may be removed from the support by reaction with dppm according to the following equation:

$$Ru_3(CO)_9(dppm)(Ph_2P\text{-support}) + dppm \xrightarrow{THF} Ru_3(CO)_8(dppm)_2 + Ph_2P\text{-support}$$

## Acknowledgements

We thank the SERC for studentships (DFF and BSN) and Johnson-Matthey plc for generous loans of ruthenium trichloride and rhodium trichloride. We also thank Dr. W. McFarlane (City of London Polytechnic) for providing $^1H$ and $^{31}P$ NMR spectra through the SERC low-field NMR service.

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