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REACTIONS OF METAL CARBONYL CLUSTER COMPLEXES WITH MULTIDENTATE PHOSPHINE LIGANDS; REACTIONS WITH METHYLTRIS(DIALKYLPHOSPHINO)SILANES

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Summary

The tridentate phosphine-substituted cluster complexes, $Ru_3(CO)_9[CH_3Si(PR_2)_3]$ (R = Et, Pr), $Rh_6(CO)_{13}[CH_3Si(PBu_2)_3]$ and $M_4(CO)_9[CH_3Si(PR_2)_3]$ (M = Co, R = Et, Pr, Bu; M = Rh, Ir, R = Et) have been prepared. Spectroscopic characterisation shows that in all cases the ligand caps a triangular face of the metal atom framework.

Introduction

Compounds of the type $CH_3Si(PR_2)_3$ were first reported in 1970 [1], but their potential use as tridentate phosphine ligands has received very little attention. The dibutylphosphine derivative, $CH_3Si(PBu_2)_3$, reacts with $Ru_3(CO)_{12}$ to give $Ru_3(CO)_9[CH_3Si(PBu_2)_3]$, in which the ligand caps the triangular array of Ru atoms and makes the cluster more resistant to dissociation than $Ru_3(CO)_{12}$ under Fischer–Tropsch catalytic reactions conditions [2]. This is the only report, to our knowledge, of the use of tris(dialkylphosphino)silanes as multidentate ligands in metal cluster complexes.

As part of our investigation into the reactions of transition metal cluster complexes with multidentate phosphine ligands, we have studied the reactions of $Ru_3(CO)_{12}$, $Rh_6(CO)_{16}$ and $M_4(CO)_{12}$ (M = Co, Rh, Ir) with $CH_3Si(PR_2)_3$ (R = Et, Pr, Bu), and here we report the results of these studies.

Experimental

IR spectra were recorded in 0.5 mm NaCl cells on a Perkin–Elmer 681 spectrophotometer. NMR spectra were recorded on a Bruker WM250 or a Jeol FX-90Q instrument. Microanalyses were carried out by Elemental Micro-Analysis Ltd. (Devon).

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All reactions were carried out under nitrogen or argon atmosphere using dry, degassed solvents. $Ru_3(CO)_{12}$ [3], $Rh_6(CO)_{16}$ [4], $Co_4(CO)_{12}$ [5], $Rh_4(CO)_{12}$ [6], $Ir_4(CO)_{12}$ [7], and $CH_3Si(PR_2)_3$ [1], were prepared by previously published methods.

Preparation of $Ru_3(CO)_9[CH_3Si(PEt_2)_3]$

$Ru_3(CO)_{12}$ (320 mg, 0.50 mmol) in tetrahydrofuran (50 cm^3) was heated under reflux with $CH_3Si(PEt_2)_3$ (171 mg, 0.55 mmol) for 3 h. The solvent was removed under reduced pressure to give a deep red residue. Repeated washing with a dichloromethane/petroleum ether mixture eventually yielded a yellow solid which was recrystallised from methanol/acetone to give yellow crystals of the product (63 mg, 14%). (Found: C, 30.52; H, 3.83; P, 10.56. $C_{22}H_{33}O_9P_3Ru_3Si$ calcd.: C, 30.54; H, 3.85; P, 10.74%).

$Ru_3(CO)_9[CH_3Si(PPr_2)_2]$ was prepared in the same manner from $Ru_3(CO)_{12}$ and $CH_3Si(PPr_2)_3$ (Yield 7%). (Found: C, 35.42; H, 4.73; P, 9.73. $C_{28}H_{45}O_9P_3Ru_3Si$ calcd.: C, 35.40; H, 4.79; P, 9.78%).

Preparation of $Rh_6(CO)_{13}[CH_3Si(PBu_2)_3]$

A mixture of $Rh_6(CO)_{16}$ (326 mg, 0.306 mmol) and $CH_3Si(PBu_2)_3$ (139 mg, 0.290 mmol) in toluene (50 cm^3) was stirred at room temperature for 24 h. The resulting red solution was filtered and evaporated to dryness under reduced pressure to give a red solid which was recrystallised from dichloromethane/petroleum ether giving red crystals of the product (22 mg, 5%).

Preparation of $Co_4(CO)_9[CH_3Si(PEt_2)_3]$

$CH_3Si(PEt_2)_3$ (250 mg, 0.81 mmol) in hexane (30 cm^3) was added dropwise over 1 h to a well-stirred solution of $Co_4(CO)_{12}$ (460 mg, 0.80 mmol) in hexane (50 cm^3). Stirring was continued for a further 15 h; then the black precipitate was filtered, washed with hexane, and recrystallised from dichloromethane/hexane to give large deep maroon crystals of the product (204 mg, 31%). (Found: C, 32.64; H, 4.17; P, 11.41. $C_{22}H_{33}O_9P_3Co_4Si$ calcd.: C, 32.00; H, 4.03; P, 11.25%).

$Co_4(CO)_{12}$ reacted with $CH_3Si(PPr_2)_3$ and $CH_3Si(PBu_2)_3$ under the same conditions to give $Co_4(CO)_9[CH_3Si(PPr_2)_3]$ (55%) (Found: C, 38.00; H, 5.13; P, 10.52. $C_{28}H_{45}O_9P_3Co_4Si$ calcd.: C, 38.11; H, 5.14; P, 10.53%) and $Co_4(CO)_9[CH_3Si(PBu_2)_3]$ (50%) (Found: C, 42.21; H, 5.99; P, 9.47. $C_{34}H_{57}O_9P_3Co_4Si$ calcd.: C, 42.25; H, 5.94; P, 9.61%), respectively.

Preparation of $Rh_4(CO)_9[CH_3Si(PEt_2)_3]$

$CH_3Si(PEt_2)_3$ (106 mg, 0.34 mmol) in hexane (20 cm^3) was added dropwise over 1 h to a stirred solution of $Rh_4(CO)_{12}$ (228 mg, 0.30 mmol) in hexane (50 cm^3). The mixture was stirred for 15 h at room temperature to give a deep red precipitate which was filtered, washed with hexane, and recrystallised from dichloromethane/hexane to give deep red needles of the product (150 mg, 51%). (Found: C, 25.9; H, 3.54; P, 10.1. $C_{22}H_{33}O_9P_3Rh_4Si$ calcd.: C, 27.1; H, 3.42; P, 9.5%). The product decomposes rapidly in air, and some decomposition also occurs under nitrogen, so that an analytically pure sample could not be obtained.

Preparation of $Ir_4(CO)_9[CH_3Si(PEt_2)_3]$

$Ir_4(CO)_{12}$ (295 mg, 0.27 mmol) and $CH_3Si(PEt_2)_3$ (90 mg, 0.29 mmol) were added to tetrahydrofuran (50 cm^3). $Me_3NO \cdot 2H_2O$ (32 mg, 0.29 mmol) in methanol (5 cm^3) was added dropwise to the stirred mixture. The reaction mixture gradually deepens to an orange colour during this addition. The resulting solution was stirred at room temperature for 15 h, after which time a small amount of unreacted $Ir_4(CO)_{12}$ was removed by filtration. The remaining solution was evaporated to dryness under reduced pressure to leave a red solid. Column chromatography on Florisil, eluting with 5/1 petroleum ether/dichloromethane, gave a yellow band of the product which was recrystallised from dichloromethane/hexane (18 mg, 5%). The complex is rather unstable in air and nitrogen, so that satisfactory microanalyses were not obtained. However, characterisation by spectroscopic methods was possible.

Results and discussion

$CH_3Si(PR_2)_3$ (R = Et, Pr) reacts with $Ru_3(CO)_{12}$ in refluxing tetrahydrofuran to form the yellow complexes $Ru_3(CO)_9[CH_3Si(PR_2)_3]$. These complexes have very similar infrared spectra (Table 1) to that of the previously reported $Ru_3(CO)_9[CH_3Si(PBu_2)_3]$ [2]. ^1H and ^{31}P NMR spectroscopic data for these complexes are also given in Table 1 (together with the previously unreported data for $Ru_3(CO)_9[CH_3Si(PBu_2)_3]$ and the free ligands), and are completely consistent with a structure in which each of the phosphine groups in the ligand coordinate to a different Ru atom in the cluster, thus capping the triangular array of Ru atoms.

$Rh_6(CO)_{16}$ reacts with $CH_3Si(PBu_2)_3$ to give a very low yield of $Rh_6(CO)_{13}[CH_3Si(PBu_2)_3]$. The infrared spectrum of this complex (Table 1) shows the presence of terminal and bridging CO ligands. Interestingly, the spectrum is similar to that of $Rh_6(CO)_{14}(Ph_2PCH_2PPh_2)$ [8], except that the bands are all shifted to lower frequencies, as expected for an increase in the number of coordinated phosphine groups. The ^{31}P NMR spectrum of $Rh_6(CO)_{13}[CH_3Si(PBu_2)_3]$, at room temperature, shows all the phosphorus atoms to be equivalent and coordinated to rhodium. A very low yield of this reaction has precluded any further studies of this complex, so that while it seems likely that the tridentate phosphine ligand caps one of the triangular faces of the Rh_6 octahedron, the distribution of the carbonyl ligands has not been determined.

The reaction of $Co_4(CO)_{12}$ with $CH_3Si(PR_2)_3$ (R = Et, Pr, Bu) in hexane at room temperature leads to the formation of $Co_4(CO)_9[CH_3Si(PR_2)_3]$. Spectroscopic data for these complexes (Table 1) indicate that the structures are analogous to those proposed [9] for $M_4(CO)_9[HC(PPh_2)_3]$ (M = Co, Rh) in which the tridentate ligand caps a carbonyl-bridged triangular face of the metal tetrahedron. A similar reaction between $Rh_4(CO)_{12}$ and $CH_3Si(PEt_2)_3$ leads to the corresponding rhodium complex, $Rh_4(CO)_9[CH_3Si(PEt_2)_3]$.

$Ir_4(CO)_{12}$ reacts directly with $CH_3Si(PEt_2)_3$ to give a low yield of $Ir_4(CO)_9[CH_3Si(PEt_2)_3]$;. a slightly higher yield is obtained by carrying out the reaction in tetrahydrofuran in the presence of an equimolar quantity of trimethylamine oxide. The infrared spectrum of $Ir_4(CO)_9[CH_3Si(PEt_2)_3]$ (Table 1) indicates the presence of bridging carbonyl ligands (bands at 1861vw, 1821m, 1791m, cm^{-1}), in contrast to the analogous complex $Ir_4(CO)_9[HC(PPh_2)_3]$ in which only terminal carbonyl ligands are present [9,10]. Thus, we propose the same structure for $Ir_4(CO)_9[CH_3Si(PEt_2)_3]$ as that proposed for the analogous Co and Rh complexes.

TABLE I

INFRARED AND NMR DATA

Compound	ν(CO)(cm^{-1})[a]	δ ^{31}P{^{1}H}[b] (ppm)	δ ^{1}H[c] (ppm)
$CH_3Si(PEt_2)_3$		-76.3(J(P–Si) 31)	0.93q, CH_3(J(P–H) 3.3) 2.5m, 1.3m, Et
$CH_3Si(PPr_2)_3$		-90.4	0.87q, CH_3(J(P–H) 3.2)
$CH_3Si(PBu_2)_3$		-89.0	0.88q, CH_3(J(P–H) 3.2)
$Ru_3(CO)_9[CH_3Si(PEt_2)_3]$	2040s, 1992s, 1948w,sh, 1928s, 1832vw,sh, 1794s	-26.8(J(P–Si) 23)	0.66q, CH_3(J(P–H) 2.4) 2.1m, 1.4m, Et
$Ru_3(CO)_9[CH_3Si(PPr_2)_3]$	2040vs, 1992s, 1946sh, 1926s, 1835vw, 1792s	-33.5	0.56q, CH_3(J(P–H) 2.4)
$Ru_3(CO)_9[CH_3Si(PBu_2)_3]$[d]	2041vs, 1992s, 1945sh, 1926s, 1836vw, 1792s	-33.7	0.55q, CH_3(J(P–H) 2.5)
$Co_4(CO)_9[CH_3Si(PEt_2)_3]$	2039s, 1988s, 1960m, 1820vw, 1777s	-1.5	0.50br, CH_3
$Co_4(CO)_9[CH_3Si(PPr_2)_3]$	2035s, 1987s, 1958m, 1818vw, 1775s	-7.7	0.40br, CH_3
$Co_4(CO)_9[CH_3Si(PBu_2)_3]$	2037s, 1987vs, 1958m, 1818vw, 1776s	-7.25	0.40br, CH_3
$Rh_4(CO)_9[CH_3Si(PEt_2)_3]$	2069w,sh, 2042m, 1993s, 1846vw, 1802m	-30.3 d of m (^1J(P–Rh) 106)	0.45q, CH_3(J(P–H) 2.9)
$Rh_6(CO)_{13}[CH_3Si(PBu_2)_3]$	2069s, 2035vs, 2008m, 1981w, 1783w, 1760m, 1733s	-28.1 d of m (^1J(P–Rh) 110)	0.68q, CH_3(J(P–H) 3.0)
$Ir_4(CO)_9[CH_3Si(PEt_2)_3]$	2062m, 2036s, 1999s, 1816vw, 1821m, 1791m	-45.3	0.84q, CH_3(J(P–H) 6.7)

[a] CH_2Cl_2 used as solvent. [b] δ (relative to H_3PO_4); CD_2Cl_2 solution. All resonances are singlets except where coupling to Si is resolved. [c] δ (relative to TMS); CD_2Cl_2 solution. All coupling constants given in Hz. d = doublet; q = quartet, m = multiplet; br = broad resonance. The resonances of the alkyl groups (Et, Pr, Bu) attached to phosphorus all occur as complex multiplets in the range 2.5–1.3 δ. [d] Infrared data is in agreement with published data (ref. [2]).

The difference between the structures of $Ir_4(CO)_9[HC(PPh_2)_3]$ and $Ir_4(CO)_9[CH_3Si(PEt_2)_3]$ may reflect the greater basicity of $CH_3Si(PEt_2)_3$ compared to $HC(PPh_2)_3$.

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10 A recent review [11] on ^{31}P NMR chemical shifts of chelating phosphine complexes suggested on the basis of ^{31}P NMR data that in the complex $Ir_4(CO)_9[HC(PPh_2)_3]$, the tridentate ligand is chelated to a single iridium atom. However, we have recently carried out a single crystal X-ray analysis of the complex $Ir_4(CO)_8(Ph_2PCH_2PPh_2)_2$ [12]. This has shown that the ligand bridges two iridium atoms, although in this complex the ^{31}P NMR chemical shifts also suggest the ligand is chelating to a single iridium atom [8]. Thus, we assume that these complexes do not obey the ΔR rule developed by Garrou [11].
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Note added in proof. $Rh_4(CO)_9[CH_3Si(PPr_2)_3]$ ($R = Pr$, Bu) have also been synthesised, and are characterised by the following spectroscopic data:

$Rh_4(CO)_9[CH_3Si(P^nPr_2)_3]$: $\nu(CO)(CH_2Cl_2$ soln.) 2040s, 1992vs, 1972sh, 1847vw, 1801s; $^{31}P\{^1H\}$ NMR ($CDCl_3$) -37.2 d of m (^1J(P–Rh) 103 Hz); ^1H NMR ($CDCl_3$) 0.32 q, CH_3 (J(P–H) 3.0 Hz).

$Rh_4(CO)_9[CH_3Si(P^nBu_2)_3]$: $\nu(CO)(CH_2Cl_2$ soln.) 2039s, 1992vs, 1972sh, 1847vw, 1800s; $^{31}P\{^1H\}$ NMR ($CDCl_3$) -36.2 d of m (^1J (P–Rh) 102 Hz); ^1H NMR ($CDCl_3$) 0.33 q, CH_3 (J(P–H) 2.8 Hz).