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Syntheses of ruthenium-containing heterometallic complexes by use of tridentate phosphine ligands

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Abstract

Treatment of [RuCl(dppee)(η-C_5H_5)] [dppee = 1,1-bis(diphenylphosphino)ethene] with $HPPh_2$ gives the addition product [RuCl{$(PPh_2)_2CHCH_2PPh_2$} (C_5H_5)], **1**. The uncoordinated phosphine group of complex **1** reacts with [IrCl$(CO)_2$(*p*-toluidine)] to give the heterobimetallic complex [RuCl(C_5H_5){$(PPh_2)_2CHCH_2PPh_2$}IrCl$(CO)_2$], **2**. Complex **1** reacts with [Fe$(CO)_5$] to yield [RuCl(C_5H_5){$(PPh_2)_2CHCH_2PPh_2$}Fe$(CO)_4$], **3**, and with [Mo$(CO)_6$] to give the heterometallic complex [RuCl(C_5H_5){$(PPh_2)_2CHCH_2PPh_2$}Mo$(CO)_5$], **4**. Complex **1** also reacts with [$RuCl_2$(*p*-cymene)$]_2$, [$Ru_3(CO)_{12}$] and [$Ru_3(CO)_{10}$(dppee)] to give the homometallic complexes [RuCl(C_5H_5){$(PPh_2)_2CHCH_2PPh_2$}$RuCl_2$(*p*-cymene)], **5**, [RuCl(C_5H_5){$(PPh_2)_2CHCH_2PPh_2$}$Ru_3(CO)_{11}$], **6**, and [RuCl(C_5H_5){$(PPh_2)_2CHCH_2PPh_2$}$Ru_3(CO)_9$(dppee)], **7**, respectively.

Keywords: Ruthenium; Iron; Iridium; Molybdenum; Heterometallic complexes; Tridentate phosphines

1. Introduction

We have previously reported the ring-opening reaction of [RuCl(dppee)(η-C_5H_5)] with [RhCl$(CO)_2]_2$ which leads to formation of the heterobimetallic complex [(C_5H_5)Ru(μ-CO$)_2${μ-$PPh_2C(=CH_2)PPh_2$}$RhCl_2$] [1]. It has been reported that the dppee ligand readily undergoes a Michael-type addition reaction with $HPPh_2$ to give the tridentate phosphine ligand $(PPh_2)_2CHCH_2PPh_2$. This addition reaction occurs both on the uncomplexed dppee [2] and, more readily, on complexed dppee [3]. We have now employed this reaction to synthesise [RuCl{$(PPh_2)_2CHCH_2PPh_2$}(C_5H_5)] **1**, and made use of the dangling phosphine created in this way to synthesise heterometallic complexes. We report below the results of the treatment of complex **1** with [IrCl$(CO)_2$(*p*-toluidine)], [Fe$(CO)_5$], [Mo$(CO)_6$], [$RuCl_2$(*p*-cymene)$]_2$, [$Ru_3(CO)_{12}$] and [$Ru_3(CO)_{10}$(dppee)].

2. Results and discussion

The complex [RuCl(dppee)(C_5H_5)] is prepared in high yield by treatment of [RuCl$(PPh_3)_2$(C_5H_5)] with dppee [1]. The complex [RuCl{$(PPh_2)_2CHCH_2PPh_2$}(C_5H_5)], **1**, is formed in quantitative yield by the base (KO^{t}Bu) catalysed addition of diphenylphosphine to [RuCl(dppee)(C_5H_5)] solution in tetrahydrofuran. The ^{31}P NMR spectrum of **1** (Table 1) consists of a doublet at δ 36.8 ppm [^3J(PP) = 9.8 Hz] as a result of the two coordinated phosphorus atoms and a triplet at δ −22.0 because of the uncoordinated phosphorus atom.

The presence of a "dangling" phosphine in complex **1** provides an opportunity for further reactions with different metal centres, and reactions of this type reported here are summarised in Scheme 1. Thus, complex **1** reacts with [IrCl$(CO)_2$(*p*-toluidine)] at 50°C to give the heterometallic complex [RuCl(C_5H_5){$(PPh_2)_2CHCH_2PPh_2$}IrCl$(CO)_2$], **2**, in good yield. On coordination to Ir, the ^{31}P NMR signal of the dangling phosphine moves from δ −22.0 to δ 17.2, and the PP coupling constant is reduced to 3.7 Hz (see Table 1). The IR spectrum of **2** shows two ν(CO) bands (2015,

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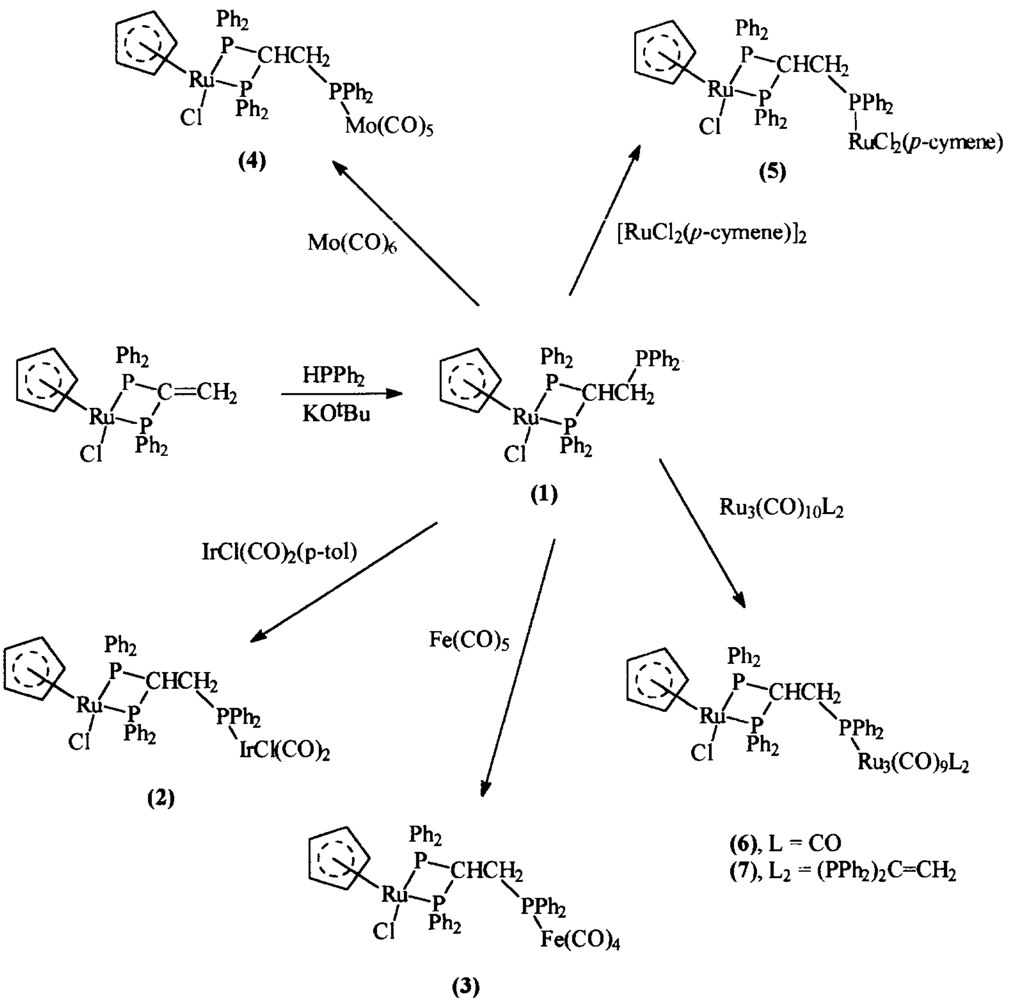
Table 1
Spectroscopic data

Compound	^{31}P NMR [a]	IR (cm^{-1}) [b]
(1)	36.8 [d, J(PP) 9.8, P_A], −22.0 [t, P_x]	
(2)	43.5 [d, J(PP) 3.7, P_A], 17.2 [t, P_X]	2015s, 1965s
(3)	66.8 [t, J(PP) 4.9, P_X], 42.4 [d, P_A]	2070m, 2020s, 1990vs, 1940m
(4)	41.1 [d, J(PP) 4.9, P_A], 32.3 [t, P_X]	2072m, 1980s, 1940vs
(5)	39.9 [d, J(PP) 4.9, P_A], 21.7 [t, P_X]	
(6)	41.6 [d, J(PP) 4.9, P_A], 31.5 [t, P_X]	2100w, 2060s, 2050sh, 2025s, 2010s, 1988sh, 1950sh
(7)	41.1 [d, J(PP) 3.7, P_A], 32.7 [m, P_X, dppee]	2080w, 2050w, 2000sh, 1990s, 1972s, 1940sh, 1925sh

[a] In THF/C_6D_6; coupling constants in Hz; P_A refers to two equivalent P atoms bound to Ru, P_X refers to the unique P atom
[b] ν(CO), in CH_2Cl_2

1965 cm^{-1}), indicating the expected *cis* arrangement of the CO ligands at the square-planar Ir atom.

Complex (**1**) also reacts with $Fe(CO)_5$ to give [RuCl(C_5H_5){$(PPh_2)_2CHCH_2PPh_2$}$Fe(CO)_4$] **3**, and with $Mo(CO)_6$ on irradiation to give [RuCl(C_5H_5){$(PPh_2)_2CHCH_2PPh_2$}$Mo(CO)_5$] **4**. The ruthenium–iron complex **3** was identified from its IR spectrum, which shows ν(CO) bands typical of a $Fe(CO)_4$ moiety [4] (Table 1). The ^{31}P NMR spectrum of **3** shows a triplet at δ 66.8 because of the phosphorus atom coordinated to $Fe(CO)_4$, similar to that previously reported for the di-iron complex [$Fe_2(CO)_7${$(PPh_2)_3CH$}] which also contains a $Fe(CO)_4P$ fragment [5]. The complex **4** is also characterised by IR and NMR spectroscopy (Table 1). Thus, the IR spectrum of **4** in the ν(CO) region is virtually identical to that reported for complexes of the



Scheme 1.

type [Mo(CO)$_5$(PR$_3$)] [6], and the ^{31}P NMR chemical shift of the P atom bound to Mo (δ 32.3) is similar to that reported for [Mo(CO)$_5$(PPh$_3$)].

The reactions of complex **1** with other ruthenium complexes was also investigated. Thus, complex **1** reacts with [RuCl$_2$(*p*-cymene)]$_2$ to form the diruthenium complex [RuCl(C$_5$H$_5$){(PPh$_2$)$_2$CHCH$_2$PPh$_2$}RuCl$_2$(*p*-cymene)], **5**, with [Ru$_3$(CO)$_{12}$] to give [RuCl(C$_5$H$_5$)-{(PPh$_2$)$_2$CHCH$_2$PPh$_2$}Ru$_3$(CO)$_{11}$] **6**, and with [Ru$_3$(CO)$_{10}${(PPh$_2$)$_2$C=CH$_2$}] to give [RuCl(C$_5$H$_5$)-{(PPh$_2$)$_2$CHCH$_2$PPh$_2$}Ru$_3$(CO)$_9${(PPh$_2$)$_2$C=CH$_2$}], **7**. These complexes were characterised by IR and NMR spectroscopy (Table 1). The ruthenium cluster complex **6** has an IR spectrum which is virtually identical in the ν(CO) region to that of [Ru$_3$(CO)$_{11}$L] [7], while the IR spectrum of **7** is very similar to that of the previously reported complexes [Ru$_3$(CO)$_9$(dppm)L] [L=PPh$_3$ or PPh$_2$CH$_2$CH$_2$Si(OEt)$_3$] [8] and [(CO)$_3$Fe{(PPh$_2$)$_2$-CHCH$_2$PPh$_2$}Ru$_3$(CO)$_9${(PPh$_2$)$_2$C=CH$_2$}] [4]. The ^{31}P NMR spectra of **6** and **7** also support their formulation as cluster complexes of triruthenium in which an equatorial carbonyl ligand has been substituted by the dangling phosphine group of complex **1**, although in the case of complex **7** the spectrum is complicated by the overlap of the resonances from the (PPh$_2$)$_2$C=CH$_2$ ligand with that of the unique phosphorus on the (PPh$_2$)$_2$CHCH$_2$PPh$_2$ ligand.

Complex **5** is characterised by its ^{31}P NMR spectrum, which indicates that the expected halide bridge cleavage reaction has occurred on reaction with the dangling phosphine group of complex **1**.

3. Experimental details

All reactions were carried out under nitrogen unless otherwise stated, using dry, degassed solvents and standard Schlenk-line techniques. IR spectra were recorded as dichloromethane solutions in 0.5 mm NaCl cells on a Perkin-Elmer 681 spectrophotometer; NMR spectra were recorded on Jeol FX-60 or Bruker WM250 instruments. Chemical shifts are relative to 85% H$_3$PO$_4$ for ^{31}P NMR spectra. Microanalyses were carried out in the Department of Chemistry, Liverpool University. The compounds (PPh$_2$)C=CH$_2$ [9], (PPh$_2$)$_2$CHCH$_2$PPh$_2$ [2], [IrCl(CO)$_2$(*p*-toluidene)] [10], [RuCl$_2$(*p*-cymene)]$_2$ [11], [Ru$_3$(CO)$_{12}$] [12] and [Ru$_3$(CO)$_{10}${(PPh$_2$)$_2$C=CH$_2$}] [13] were prepared by published procedures.

3.1. Preparation of [RuCl{(PPh$_2$)$_2$C=CH$_2$}(C$_5$H$_5$)]

A solution of [RuCl(PPh$_3$)$_2$(C$_5$H$_5$)] (0.362 g, 0.48 mmol) and (PPh$_2$)$_2$C=CH$_2$ (0.203 g, 0.52 mmol) in benzene (100 cm^3) was refluxed for 5 h. The volume of the solution was reduced to 15 cm^3 by evaporation under vacuum, and hexane (50 cm^3) was added. On standing for 24 h at −20°C the solution gave dark red crystals of [RuCl{(PPh$_2$)$_2$C=CH$_2$}(C$_5$H$_5$)] (0.24 g, 85%). Anal. Found: C, 62.0; H, 4.4. C$_{31}$H$_{27}$ClP$_2$Ru calc.: C, 62.2; H, 4.5%; M$^+$ at *m/z* 598. M$^+$ based on ^{101}Ru and ^{35}Cl, 598.

3.2. Preparation of [RuCl{(PPh$_2$)$_2$CHCH$_2$PPh$_2$}-(C$_5$H$_5$)] 1

A mixture of diphenylphosphine (0.012 g, 0.064 mmol) and [RuCl{(PPh$_2$)$_2$C=CH$_2$}(C$_5$H$_5$)] (0.038 g, 0.064 mmol) in THF (30 cm^3) was stirred at room temperature for 0.5 h in the presence of a catalytic amount of KO^{t}Bu. The resulting pale-yellow solution was evaporated to dryness and the yellow residue was washed with pentane (3 × 10 cm^3 portions) and recrystallised from THF, to give complex **1** as a yellow solid (0.035 g, 70%). Anal. Found: C, 65.1; H, 4.7, C$_{43}$H$_{38}$ClP$_3$Ru calc.: C, 65.9; H, 4.9%.

3.3. Preparation of [RuCl(C$_5$H$_5$){(PPh$_2$)$_2$CHCH$_2$-PPh$_2$}IrCl(CO)$_2$] 2

A mixture of [IrCl(CO)$_2$(*p*-toluidene)] (0.025 g, 0.064 mmol) and complex **1** (0.050 g, 0.064 mmol) in THF (30 cm^3) was stirred at 50°C for 24 h. The resulting solution was evaporated to dryness and the residue was recrystallised from THF/benzene to give complex **2** as a yellow solid (0.049 g, 70%). Anal. Found: C, 50.1; H, 3.2. C$_{45}$H$_{38}$Cl$_2$O$_2$P$_3$IrRu calc.: C, 50.6; H, 3.6%.

3.4. Preparation of [RuCl(C$_5$H$_5$){(PPh$_2$)$_2$CHCH$_2$-PPh$_2$}Fe(CO)$_4$] 3

A mixture of complex **1** (0.050 g, 0.064 mmol) with an equimolar amount of [Fe(CO)$_5$] (0.013 g, 0.064 mmol) in THF (10 cm^3) was stirred at 40°C for 4 h. The resulting red solution was evaporated to dryness, and the residue was recrystallised from THF/benzene to yield small red crystals of complex **3** in 80% yield. Anal. Found: C, 59.0; H, 4.0. C$_{47}$H$_{38}$ClO$_4$P$_3$FeRu calc.: C, 59.3; H, 4.0%.

3.5. Preparation of [RuCl(C$_5$H$_5$){(PPh$_2$)$_2$CHCH$_2$-PPh$_2$}Mo(CO)$_5$] 4

A mixture of [Mo(CO)$_6$] (0.0176 g, 0.067 mmol) and complex **1** (0.052 g, 0.067 mmol) in THF (30 cm^3) was heated at 40°C for 2 h. ^{31}P NMR spectroscopy showed that no reaction had occurred. The mixture was placed in a quartz tube and irradiated with light from a mercury UV lamp for 2 h. Slow evaporation of the solution produced orange crystals of complex **4** (0.039 g, 57%). Anal Found: C, 56.0; H, 3.3. C$_{48}$H$_{38}$ClO$_5$P$_3$MoRu calc.: C, 56.5; H, 3.7%.

3.6. Preparation of $[RuCl(C_5H_5)\{(PPh_2)_2CHCH_2PPh_2\}RuCl_2(p\text{-}cymene)$ 5

A mixture of $[RuCl_2(p\text{-cymene})]_2$ (0.027 g, 0.044 mmol) in $CHCl_3$ (3 cm^3) and complex **1** (0.07 g, 0.089 mmol) in THF (30 cm^3) was heated at 50°C for 2 h. The resulting red-orange solution was evaporated to dryness and the residue recrystallised from THF/benzene, by slow evaporation, to yield orange crystals of complex **5** (0.074 g, 77%). Anal. Found: C, 58.3; H, 4.3. $C_{53}H_{52}Cl_3P_3Ru_2$ calc.: C, 58.4; H, 4.8%.

3.7. Preparation of $[RuCl(C_5H_5)\{(PPh_2)_2CHCH_2PPh_2\}Ru_3(CO)_{11}]$ 6

A mixture of $[Ru_3(CO)_{12}]$ (0.044 g, 0.069 mmol) and complex **1** (0.054 g, 0.069 mmol) in THF (30 cm^3) was stirred at 50°C for 3 h, during which the colour of the solution gradually changed from yellow-orange to red-orange. The solution was evaporated to dryness and the residue recrystallised from THF/benzene to yield red-orange crystals of complex **6** (0.063 g, 65%). Anal. Found: C, 46.1; H, 2.6. $C_{54}H_{38}ClO_{11}P_3Ru_4$ calc.: C, 46.5; H, 2.7%.

3.8. Preparation of $[RuCl(C_5H_5)\{(PPh_2)_2CHCH_2PPh_2\}Ru_3(CO)_9\{(PPh_2)_2C{=}CH_2\}]$ 7

A mixture of $[Ru_3(CO)_{10}\{(PPh_2)_2C{=}CH_2\}]$ (0.051 g, 0.052 mmol) and complex **1** (0.041 g, 0.052 mmol) in THF (30 cm^3) was stirred at 50°C for 2 h. The resulting red-orange solution was evaporated to dryness and the residue recrystallised from THF/benzene to yield deep-orange crystals of complex **7** (0.07 g, 79%). Anal. Found: C, 53.8; H, 4.0. $C_{78}H_{60}ClO_9P_5Ru_4$ calc.: C, 54.0; H, 3.5%.

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