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Syntheses of ruthenium–iridium heterobimetallic complexes using tridentate phosphine ligands

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Abstract

Complexes of the type [Ru(C_5H_5)Cl{(PPh_2)$_2$C=CH_2}] undergo Michael-type addition with a diphenylphosphine and the products can be used for further syntheses of heterobimetallic complexes. The uncoordinated phosphine group of [Ru(C_5H_5)Cl{(PPh_2)$_2$CH$CH_2$$PPh_2$}] (**1**) reacts with $Ir_4(CO)_{12}$ to give mono-, di- and tri-substituted heterobimetallic cluster complexes **2**, **3** and **4**, respectively.

Keywords: Ruthenium complexes; Iridium complexes; Heterobimetallic complexes; Tridentate phosphine complexes

1. Introduction

Heterometallic complexes have attracted considerable interest in recent years in relation to possible design of new bifunctional catalysts. Bimetallic catalysis has become an area of major interest and applies to homogeneous, heterogenised or heterogeneous processes [1]. The use of multidentate phosphine ligands to achieve heterobinuclear synthesis is a popular and convenient route which can lead to stable heterometallic bonds, owing to the presence of the bridging phosphine ligand [2], and also increases the stability of the metal framework. It has been shown that the ligand dppee (dppee = 1,1-bis(diphenylphosphino)ethene), Ph_2PC=CH_2PPh_2, readily undergoes a Michael-type addition reaction with PPh_2H to give the tridentate phosphine ligand (Ph_2P)$_2$CH$CH_2$$PPh_2$ (tppe). This addition reaction occurs both on the uncomplexed dppee [3] and, more readily, on complexed dppee [4,5]. We have made use of this reaction to synthesise 'dangling' phosphine complexes of [Ru(C_5H_5)Cl{(PPh_2)CH$CH_2$$PPh_2$}] (**1**) which provide convenient starting materials for the synthesis of heteronuclear metal complexes.

Particular interest is focused on the preparation of heterobimetallic complexes of [Ru(C_5H_5)Cl{(PPh_2)-CH$CH_2$$PPh_2$}] (**1**) with dodecacarbonyltetrairidium.

2. Results and discussion

The complex [Ru(C_5H_5)Cl(dppee)] is prepared in high yield by a ligand exchange reaction between [Ru(C_5H_5)Cl(PPh_3)$_2$] and dppee as previously reported [6]. The complex [Ru(C_5H_5)Cl{(PPh_2)$_2$CH$CH_2$$PPh_2$}] (**1**) is formed in quantitative yield by the base ($KOBu^t$) catalysed addition of diphenylphosphine to a tetrahydrofuran solution of [Ru(C_5H_5)Cl(dppee)]. The ^{31}P NMR spectrum of **1** consists of a doublet (δ 36.8 ppm) due to the two coordinated phosphorus atoms and a triplet (δ −22.0 ppm) with $^3J(PP) = 9.8$ Hz, due to the uncoordinated phosphorus atom.

The presence of a 'dangling' phosphine in complex **1** provides an opportunity for further reactions with different metal centres. Examples of such complexes are illustrated in Scheme 1.

The syntheses and spectroscopic characterisation of these complexes have already been described together with some of their subsequent thermal rearrangement [7].

Our attentions have been centred on substitution reactions involving loss of carbon monoxide from the tetranuclear metal carbonyl cluster [$Ir_4(CO)_{12}$] by the 'dangling' phosphine ligand of [Ru(C_5H_5)Cl{(PPh_2)$_2$-CH$CH_2$$PPh_2$}] (**1**). The parent cluster carbonyl [$Ir_4(CO)_{12}$] is generally considered to be rather unreactive and has an all-terminal CO ligand structure

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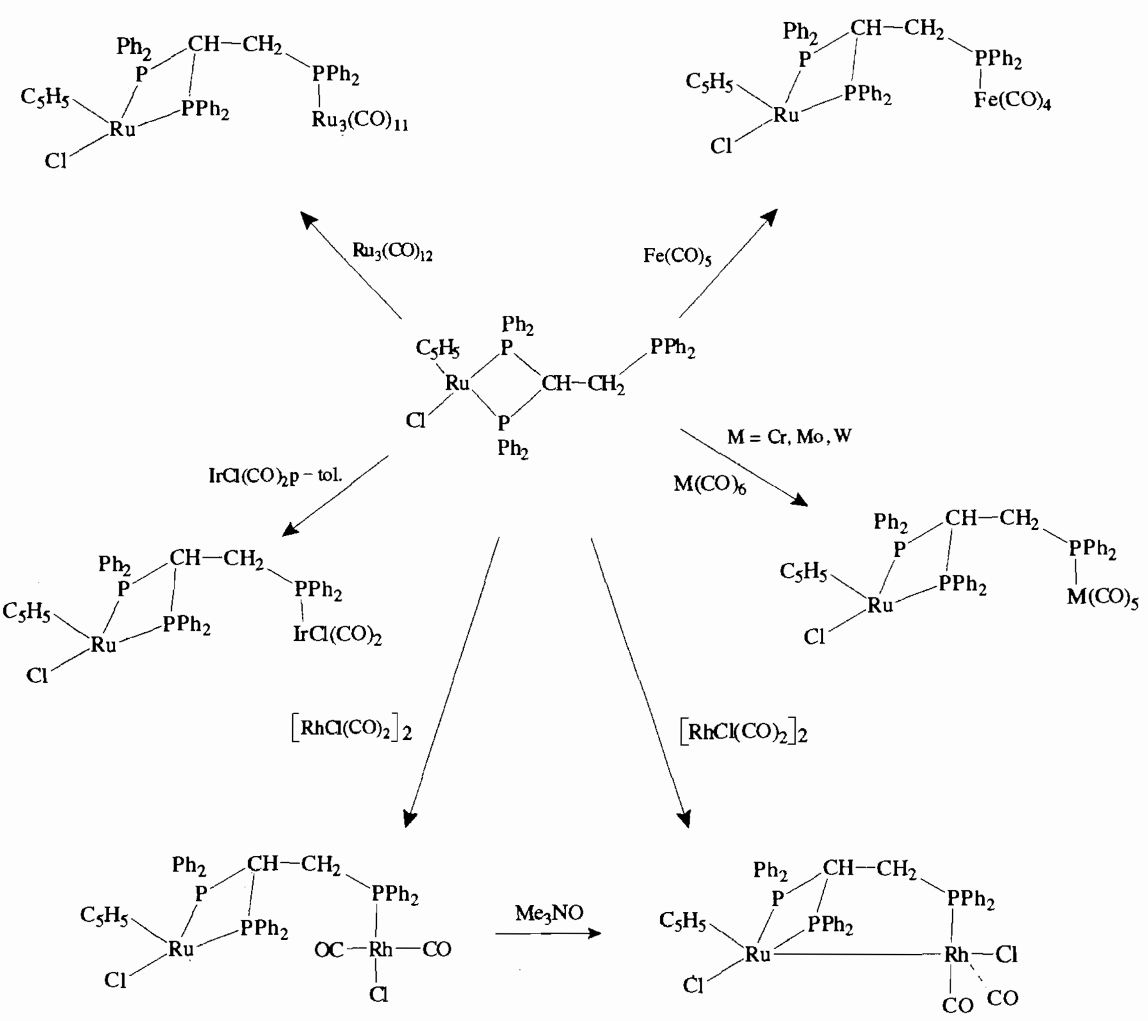


Scheme 1.

[8]. Phosphine substitution to give $[Ir_4(CO)_{12-n}L_n]$ ($n = 1$–4) induces a change to the structure in which three carbonyl groups are edge-bridging around a basal plane. We found that the reaction of complex **1** with equimolar quantities of $[Ir_4(CO)_{12}]$ in tetrahydrofuran and $Me_3NO \cdot 2H_2O$ in methanol gives rise to two products. The heterobimetallic complexes observed are the mono- and tri-substituted products $[Ir_4(CO)_{11}\{tppeRu(C_5H_5)Cl\}]$ (**2**) and $[Ir_4(CO)_9\{tppeRu(C_5H_5)Cl\}_3]$ (**4**). It is expected that the tri-substituted product will be the maximum possible, since the degree of substitution depends on the bulk of the entering ligand as reported by Stuntz and Shapley [9] and Darkesmith and Whyman [10].

In an attempt to observe mono- and di-substituted species $[Ru(C_5H_5)Cl(tppe)]$ was added to $[Ir_4(CO)_{11}Br][NEt_4]$; this allowed the direct synthesis of $[Ir_4(CO)_{11}\{tppeRu(C_5H_5)Cl\}]$ (**2**) and $[Ir_4(CO)_{10}\{tppeRu(C_5H_5)Cl\}_2]$ (**3**). Thus, it is most probable that the mono-substitution by phosphine–ruthenium in $[Ir_4(CO)_{12}]$ accelerates the rate of the reaction for subsequent substitutions to form di- and tri-substituted Ru–Ir₄ complexes, as reported by Karel and Norton [11] and Lieto and co-workers [12]. All attempts to separate the heterobimetallic clusters **2**, **3** and **4** from these reactions by chromatography on a florisil column or silica led to the decomposition of the products. IR spectra of the heterometallic clusters in the carbonyl stretching region show absorption which can be attributed to terminal and bridging carbonyl groups (Table 1), and

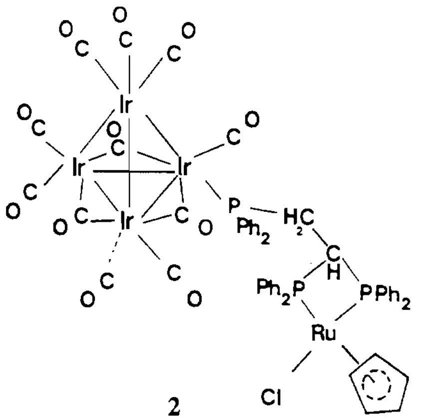
Table 1
IR data of ruthenium–iridium heterometallic complexes

Complexes	$\nu(CO)^a$ (cm^{-1})
$[Ir_4(CO)_{11}\{tppeRu(C_5H_5)Cl\}]$	2088m, 2065m, 2018s, 1840m, 1818m
$[Ir_4(CO)_{10}\{tppeRu(C_5H_5)Cl\}_2]$	2065s, 2030sh, 2000sh, 1975s, 1820m, 1775m(br)
$[Ir_4(CO)_9\{tppeRu(C_5H_5)Cl\}_3]$	2040 ms, 2010–1995vs, 1980s, 1790m(br), 1775m(br)

[a] CH_2Cl_2 solvent.

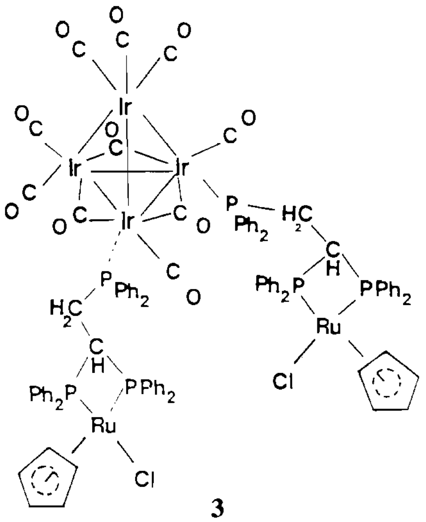
so the structures of the substituted species differ from that of the parent carbonyl. The IR bands were assigned on the basis of a comparison with the spectra reported for $Ir_4(CO)_{12-x}L_x$ when $L = PPh_3$ [13].

The IR spectrum of the mono-substituted species $[Ir_4(CO)_{11}\{tppeRu(C_5H_5)Cl\}]$ (**2**) (Table 1) is virtually identical to those reported by Stuntz and Shapley [13]. It indicates the expected bands for bridging carbonyl ligands and a comparison with the spectrum of $[Ir_4(CO)_{11}(PPh_3)]$ [9] indicates that the phosphine substitutes into a basal axial position. The $^{31}P\{^1H\}$ NMR spectrum of complex **2** clearly shows the presence of three coordinated phosphorus atoms. Accordingly, $[Ir_4(CO)_{11}\{tppeRu(C_5H_5)Cl\}]$ (**2**) shows two sets of resonances. At +41.4 ppm, there is a doublet, corresponding to the two equivalent phosphorus atoms bound to the Ru atom which results from phosphorus–phosphorus coupling of 2.44 Hz. A resonance at −33.7 ppm (a shift of −11.7 ppm from the free ligand structure **1**, −22 ppm), due to the phosphorus atom coordinated to the iridium metal framework, consists of a triplet which results from phosphorus–phosphorus coupling of 2.44 Hz and is assigned to structure **2** with $[Ru(C_5H_5)Cl(tppe)]$ coordinated in a basal axial site. A comparison with the ^{31}P NMR spectrum of $[Ir_4(CO)_{11}(PPh_3)]$, which shows a ^{31}P signal at −13.0 ppm (a shift of 7.0 ppm from free PPh_3) and has a structure with a basal axial PPh_3 ligand [11,12], substantiates our assignment, since axial P ligands appear at higher field than radical P ligands.



2

In the di-substituted species $[Ir_4(CO)_{10}\{tppeRu(C_5H_5)Cl\}_2]$ (**3**), it was found that one ruthenium cyclopentadiene triphosphine complex is in a radical position (P_2) with respect to the bridging carbonyls and one $[Ru(C_5H_5)Cl(tppe)]$ complex (P_1) is axial. The IR spectrum of complex **2** (Table 1) is identical to those reported [9,10,12,14,15] for complexes of the type $Ir_4(CO)_{12}L_2$. It shows bands for bridging carbonyl ligands, and a comparison with $[Ir_4(CO)_{10}(PPh_3)_2]$ [10,14,15] indicates that one phosphine substitutes into a basal axial site and the other one substitutes into a basal radial position. The $^{31}P\{^1H\}$ NMR spectrum of product **3** shows that all the phosphorus atoms are coordinated. It displays four sets of resonances. Configuration **3** has one radial ligand (P_2) and one axial ligand (P_1) of equal intensity (1:1). The resonance at 5.1 ppm is a triplet (*J*(PP) 2.44 Hz) due to the phosphorus atom (P_2) coordinated to the iridium metal framework in a basal radial position. At 44.9 ppm there is a doublet (*J*(PP) 2.44 Hz) corresponding to the two equivalent phosphorus atoms P_3 and P_4 bound to the ruthenium atom. For the second substitution, P_1, there is a triplet (*J*(PP) 2.44 Hz) at −14.5 ppm due to the second iridium atom in a basal axial position. At 45.1 ppm, there is a doublet (*J*(PP) 2.44 Hz) corresponding to the two equivalent phosphorus atoms P_5 and P_6 bound to the ruthenium atom. The two resonances at 5.1 and −14.5 ppm have a 1:1 intensity (with the radial P having a shift of 27.1 ppm from the free ligand). These data suggest that structure **3** is present in solution and that the signal due to the radial phosphorus ruthenium complex appears at lower field than that of the axial phosphorus form $[Ru(C_5H_5)Cl(tppe)]$ coordinated to the iridium atom in the basal plane. There is agreement between these results and those previously reported [13]. There is also no coupling between the axial and radial $[Ru(C_5H_5)Cl(tppe)]$ complexes as reported by Stuntz and Shapley [13].



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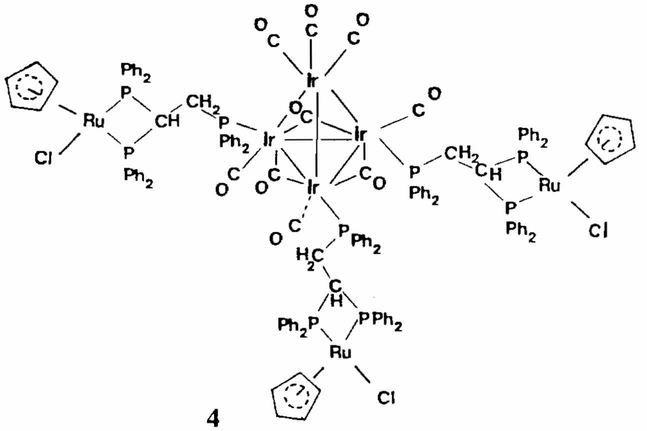
The tri-substituted derivative, $[Ir_4(CO)_9\{tppeRu(C_5H_5)Cl\}_3]$ (**4**) has the usual tetrahedral arrangement of iridium atoms, with three bridging carbonyl ligands around the basal plane. All known compounds of the type $Ir_4(CO)_9L_3$ have the samc structure [14,15], in which two of the ligands are coordinated in basal radial sites and the third ligand in a basal axial site. The IR spectrum of complex **4** (Table 1) is virtually identical to those previously reported for $Ir_4(CO)_9L_3$ [10,15]. However, the ^{31}P NMR spectrum shows resonances at 15.0 (t, *J*(PP) 2.44 Hz) and −13.1 (t, *J*(PP) 2.44 Hz) in a 2:1 ratio, due to the phosphorus atoms coordinated to iridium. There are corresponding resonances at 41.4 (d) and 42.3 (d) ppm due to the phosphorus atoms coordinated to iridium.



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Unfortunately, an adequate interpretation of the data is hindered by the complexity of the IR spectra due to the carbonyl ligands coordinated to the Ru atoms, the carbonyl ligands coordinated to the Ir atoms, and also the presence of more than one product at the same time. In some other systems it has proved possible to isolate the mono- and di-substituted complexes, particularly by use of chromatographic methods [16]. But in this case, chromatography on a florisil column or silica column of the products from the reaction led to the decomposition of the products.

3. Experimental

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 solution in 0.5 mm NaCl cells on a Perkin-Elmer 681 spectrometer. NMR spectra were recorded on JEOL FX-60 or Bruker WM250 instruments. Chemical shifts are relative to 85% H_3PO_4 for the ^{31}P NMR spectrum. Thin layer chromatographic separations were carried out on either 20×20 cm plates or 100×20 coated with Kieselguhr (purchased from Aldrich Chemical Company Inc.) was used for column chromatography. Chromatography on a florisil column was also used. Microanalyses were carried out in the Department of Chemistry, University of Liverpool. The compounds dppee [17], $[Ru(C_5H_5)Cl\{(PPh_2)_2C{=}CH_2\}]$ [6], $[Ru(C_5H_5)Cl\{(PPh_2)_2CHCH_2PPh_2\}]$ (**1**) [7] and $Ir_4(CO)_{12}$ [18] were prepared according to published procedures.

3.1. Preparations

3.1.1 $[Ir_4(CO)_{11}\{tppeRu(C_5H_5)Cl\}]$ (2) and $[Ir_4(CO)_9\{tppeRu(C_5H_5)Cl\}_3]$ (4)

The compound $NMe_3O \cdot 2H_2O$ (0.01 g, 0.089 mmol) in methanol (10 cm^3) was added dropwise over 10 min to a thf suspension (30 cm^3) at 60 °C of $Ir_4(CO)_{12}$ (0.0987 g, 0.089 mmol) and $[Ru(C_5H_5)Cl(tppe)]$ (0.07 g, 0.089 mmol). During the addition period nearly all the cluster dissolved to give an orange solution. IR monitoring confirmed the reaction was complete. After stirring for a further 30 min ^{31}P NMR analysis of the crude reaction mixture indicated the two products **2** and **4** were obtained.

3.1.2. $[Ir_4(CO)_{11}Br][NEt_4]$

Five-fold excess tetraethylammonium bromide (0.1253 g, 0.596 mmol) in thf (10 cm^3) was added to a thf suspension (30 cm^3) of $Ir_4(CO)_{12}$ (0.1318 g, 0.119 mmol). Refluxing the yellow solution under argon for 5 h resulted in the orange solution of $[Ir_4(CO)_{11}Br][NEt_4]$. IR monitoring confirmed the complete reaction had occurred.

3.1.3. $[Ir_4(CO)_{11}\{tppeRu(C_5H_5)Cl\}]$ (2) and $[Ir_4(CO)_{10}\{tppeRu(C_5H_5)Cl\}_2]$ (3)

$[Ru(C_5H_5)Cl(tppe)]$ (0.086 g, 0.119 mmol) in thf (10 cm^3) was added to the orange solution of $[Ir_4(CO)_{11}Br][NEt_4]$ (0.1565 g, 0.119 mmol), with stirring. The colour of the solution gradually changed from orange to reddish orange and then turned very quickly to yellowish brown. The reaction was followed by IR and ^{31}P NMR spectroscopies. Spectroscopic analysis indicated that two products were obtained. The solution was distilled to dryness in vacuo and the residue was divided into two parts. Chromatography on a florisil column of part of the product in CH_2Cl_2 or separation by chromatography on silica led to the decomposition of the product. The second part was recrystallised from thf/C_6H_6 yielding yellow needles of the products (not suitable for X-ray crystallography) and the mixture could not be separated.

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