

SYNTHESIS AND REACTIVITY OF IRON-IRIDIUM HETEROBIMETALLIC COMPLEXES USING TRIDENTATE PHOSPHINE LIGANDS

BY

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تحضير مترابكات ثنائية الفلز من الحديد والإيريديوم
باستخدام مرتبطات الفوسفين ثلاثية المخلب

نجوى نوار

درس تفاعل المترابك $[(CO)_3 Fe \{ (PPh_2)_2 C=CH_2 \}]$ مع ثنائي فينيل الفوسفين وفق تفاعل مايكل للإضافة .

وقد استخدمت المترابكات الناتجة في تحضير مترابكات ثنائية الفلز غير المتجانس . وقد أظهرت الدراسة أن مجموعة الفوسفين غير المرتبطة في المترابك

$[(CO)_3 Fe \{ (PPh_2)_2 CHCH_2 PPh_2 \}]$ تتفاعل مع المترابك $[Ir_2 (CO)_{12}]$ بحيث يتشكل مترابكات أحادية أو ثنائية أو ثلاثية الإحلال الكربوني للمترابكات المعقدة ثنائية الفلز غير المتجانس .

Key Words: Iron, Iridium, Phosphine, Bimetallic complexes.

ABSTRACT

Treatment of $\{Fe (CO)_3 \{ (PPh_2)_2 C=CH_2 \}\}$ with PPh_2H gives the addition product $[Fe (CO)_3 \{ (PPh_2)_2 CHCH_2 PPh_2 \}]$ (1). The uncoordinated phosphine group of complex 1 reacts with $Ir_4 (CO)_{12}$ to give mono-, di- and tri-substituted heterobimetallic cluster complexes.

INTRODUCTION

Substitution reaction of carbonyl ligands in $Ir_4 (CO)_{12}$ by phosphine or phosphite ligands have been fairly extensively studied [1-6]. Although the parent cluster carbonyl $Ir_4 (CO)_{12}$, has an all-terminal CO ligand structure [7], phosphine substitution to give $\{Ir_4 (CO)_{12-n} L_n\}$ ($n = 1-4$) induces a change to a structure in which three carbonyl groups are edge-bridging around a basal plane [8].

As part of our investigation into the preparation of heterometallic complexes of $[Fe (CO)_3 \{ (PPh_2)_2 CHCH_2 PPh_2 \}]$ (1) with transition metal carbonyls [9], we have investigated the reactivity of $[Fe (CO)_3 \{ (PPh_2)_2 CHCH_2 PPh_2 \}]$ towards $Ir_4 (CO)_{12}$ in order to synthesize mixed-metal clusters. In the present work complexes of type $\{Fe (CO)_3 \{ (PPh_2)_2 C=CH_2 \}\}$ undergo Michael type addition with a diphenyl phosphine and the products can be used for further synthesis of heterobimetallic complexes. The uncoordinated

phosphine group of $[Fe (CO)_3 \{ (PPh_2)_2 CHCH_2 PPh_2 \}]$ (1) reacts with $Ir_4 (CO)_{12}$ to give mono-, di- and tri-substituted heterobimetallic cluster complexes.

EXPERIMENTAL

All reactions were carried out under nitrogen unless otherwise stated, using dry, degassed solvents and standard Schlenk-line techniques. Infrared spectra were recorded as dichloromethane solution in 0.5 mm NaCl cells on Perkin Elmer 681 spectrometer, NMR spectra on JEOL FX-60 or Bruker WM250 instruments. Chemical shifts are relative to 85% H_3PO_4 for ^{31}P NMR spectrum. Microanalyses were carried out in the Department of Chemistry, University of Liverpool. The compounds $[(PPh_2)_2 C=CH_2]$, dppee [10], $\{Fe (CO)_3 \{ (PPh_2)_2 C=CH_2 \}\}$ [9], $[Fe (CO) \{ (PPh_3)_2 CHCH_2 PPh_2 \}]$ and $Ir_4 (CO)_{12}$ were prepared according to published procedures [7].

Preparation of Cluster Complexes

 $[\text{Ir}_4(\text{CO})_{12}\text{Br}][\text{NEt}_4]$

5-fold excess tetraethylammonium bromide (0.1253g, 0.596 mmol) in thf (10 cm^3) was added to a thf suspension (30 cm^3) of $\text{Ir}_4(\text{CO})_{12}$ (0.1318g, 0.119 mmol). Refluxing the yellow solution under argon for 5 hours resulted the orange solution of $[\text{Ir}_4(\text{CO})_{11}\text{Br}][\text{NEt}_4]$. Infrared monitoring confirmed reaction completion.

 $[\text{Ir}_4(\text{CO})_{11}\{\text{PPh}_2\text{CH}_2\text{CH}(\text{PPh}_2)_2\text{Fe}(\text{CO})_3\}](2)$ and $[\text{Ir}_4(\text{CO})_{10}\{\text{PPh}_2\text{CH}_2\text{CH}(\text{PPh}_2)_2\text{Fe}(\text{CO})_3\}_2](3)$

$[\text{Fe}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{CH}(\text{PPh}_2)_2\}]$ (0.086g, 0.119 mmol) in thf (10 cm^3) was added to the orange solution of $[\text{Ir}_4(\text{CO})_{11}\text{Br}][\text{NEt}_4]$ (0.1565g, 0.119 mmol), with stirring. The colour of the solution gradually changed from orange to reddish-orange and then turned fast to yellowish-brown. The reaction was followed by infrared and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy which indicated that two products were obtained. The solution was evaporated to dryness in vacuo and the residue was divided to two parts. Chromatography, on a florisil column of part of product in CH_2Cl_2 led to the decomposition of the product. The second part was recrystallised from thf C_6H_6 and gave yellow needles of the complexes (2) and (3).

 $[\text{Ir}_4(\text{CO})_{11}\{\text{PPh}_2\text{CH}_2\text{CH}(\text{PPh}_2)_2\text{Fe}(\text{CO})_3\}](2)$ and $[\text{Ir}_4(\text{CO})_9\{\text{PPh}_2\text{CH}_2\text{CH}(\text{PPh}_2)_2\text{Fe}(\text{CO})_3\}_3](4)$

The compound $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (0.0155g, 0.093 mmol) in methanol (10 cm^3) was added dropwise over 10 min. to a thf suspension (30 cm^3) at 60°C of $\text{Ir}_4(\text{CO})_{12}$ (0.0987g, 0.089 mmol) and $[\text{Fe}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{CH}(\text{PPh}_2)_2\}]$ (0.0498g, 0.093 mmol). During the addition period nearly all the cluster dissolved to give an orange solution. Infrared monitoring confirmed complete reaction after stirring for a further 30 minutes. $^{31}\text{P}\{^1\text{H}\}$ NMR analysis of the crude reaction mixture

indicated the formation of the two products 2 and 4.

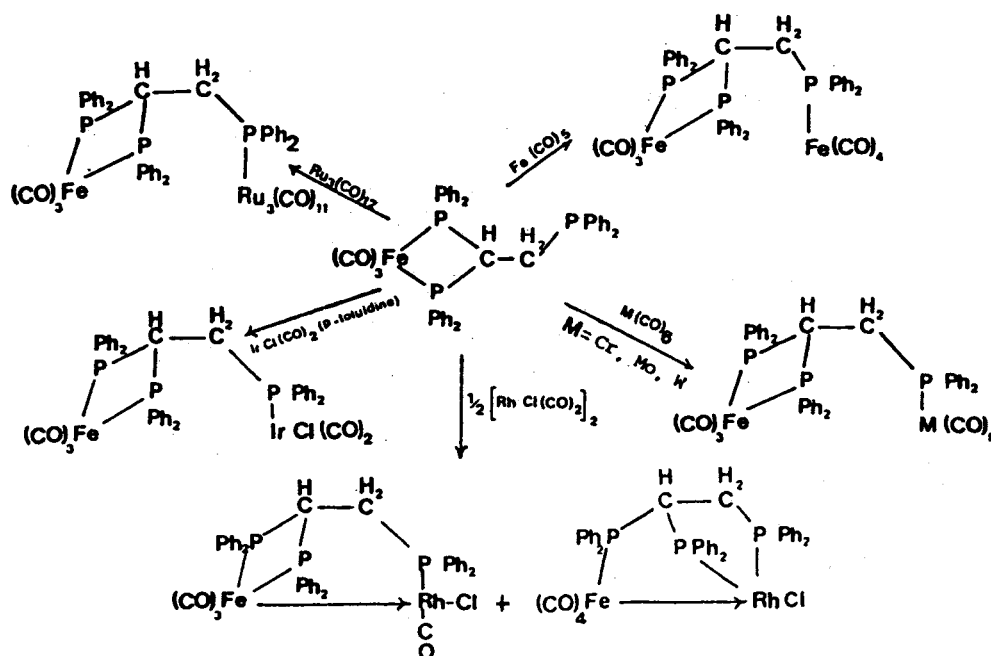
RESULTS AND DISCUSSION

The complex $[\text{Fe}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{CH}(\text{PPh}_2)_2\}]$ (1) is prepared in quantitative yield by the base (t-BuOK) - catalysed addition of diphenylphosphine to a tetrahydrofuran solution of $[\text{Fe}(\text{CO})_3(\text{PPh}_2)_2\text{C}=\text{CH}_2]$ as previously reported [9]. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of (1) consists of a doublet (δ 37.8 ppm) due to the two co-ordinated phosphorus atoms and a triplet (δ -21.9 ppm) with $^3J(\text{PP}) = 11.0\text{ Hz}$, due to the unco-ordinated phosphorus atom.

The presence of a 'dangling' phosphine in complex (1) provide an opportunity for further reactions with different metal centres. Examples of such complexes are illustrated as below. (Scheme 1).

Our attentions have been centred on substitution reactions involving loss of carbon monoxide in tetranuclear metal carbonyl cluster $\text{Ir}_4(\text{CO})_{12}$ by the 'dangling' phosphine ligand from $[\text{Fe}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{CH}(\text{PPh}_2)_2\}]$ (1). Although, $\text{Ir}_4(\text{CO})_{12}$ is generally considered to be rather unreactive, we found that the reaction of $[\text{Fe}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{CH}(\text{PPh}_2)_2\}]$ (1) with equimolar amounts of $\text{Ir}_4(\text{CO})_{12}$ in tetrahydrofuran and $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ in methanol gives rise to two products. The heterobimetallic complexes observed are the mono- and tri-substituted products $[\text{Ir}_4(\text{CO})_{11}\{\text{PPh}_2\text{CH}_2\text{CH}(\text{PPh}_2)_2\text{Fe}(\text{CO})_3\}_3]$ (2) and $[\text{Ir}_4(\text{CO})_9\{\text{PPh}_2\text{CH}_2\text{CH}(\text{PPh}_2)_2\text{Fe}(\text{CO})_3\}_3]$ (4). It is expected that the tri-substituted product would be the only possible, since the degree of substitution depends on the bulk of the entering ligand as reported by Stuntz [11] and Drakesmith and Whyman [9].

In an attempt to observe mono- and di-substituted species, $[\text{Fe}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{CH}(\text{PPh}_2)_2\}]$ (1) was added to $[\text{Ir}_4(\text{CO})_{11}\text{Br}][\text{NEt}_4]$, and this allowed the direct synthesis of $[\text{Ir}_4(\text{CO})_{11}\{\text{PPh}_2\text{CH}_2\text{CH}(\text{PPh}_2)_2\text{Fe}(\text{CO})_3\}](2)$ and $[\text{Ir}_4(\text{CO})_{10}$



Scheme 1

$\{(\text{PPh}_2)_2 \text{CH}_2 \text{CH} (\text{PPh}_2)_2 \text{Fe} (\text{CO})_3\}_2$ (3). Thus, it is most probable that the mono-substitution by phosphine-iron in $\text{Ir}_4 (\text{CO})_{12}$ accelerates the rate of the reaction for subsequent substitutions to form di- and tri-substituted Fe- Ir_4 complexes, as reported by Karel and Norton [6] and Lieto [12]. All attempts to separate the heterometallic clusters, (2, 3 and 4) in these reactions by chromatography, on a florisil column, led to the decomposition of the products. Infrared spectra of the heterometallic clusters in the carbonyl-stretching region show absorptions which can be attributed to terminal and bridging carbonyl groups Table 1, and so the structures of the substituted species differ from that of the parent carbonyl. The proposed structures of these products are shown in Figures 2, 3 and 4. The infrared bands were assigned on the basis of a comparison with the spectra reported for $[\text{Ir}_4 (\text{CO})_{12-n} \text{L}_n]$ where $\text{L} = \text{PPh}_3$.

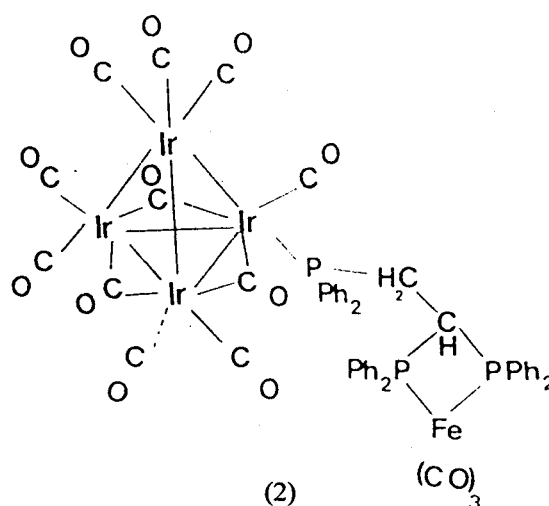
Table 1
Infrared data of iron-iridium bimetallic complexes

Complexes	$\nu (\text{CO}) (\text{cm}^{-1})^a$
$[\text{Ir}_4 (\text{CO})_{11} \{ \text{tppeFe} (\text{CO})_3 \}]$	2084 m, 2062 m, 2018 s, 1980 s (Fe $(\text{CO})_3$), 1910-1900 s, br (Fe $(\text{CO})_3$), 1840 m, 1820.
$[\text{Ir}_4 (\text{CO})_{10} \{ \text{tppeFe} (\text{CO})_3 \}_2]$	2065 s, 2040 s, 2000 vs, 1989 vs (Fe IR), 1910- 1900 s, br (Fe $(\text{CO})_3$), 1820 m, 1789m.
$[\text{Ir}_4 (\text{CO})_9 \{ \text{tppeFe} (\text{CO})_3 \}_3]$	2040 ms, 2015 sh, 1982 vs (fe, Ir), 1962 sh, 1910-1900 s, br (Fe $(\text{CO})_3$), 1772 s, br.

^a $\text{CH}_2 \text{Cl}_2$ Solvent.

The infrared spectrum of the mono-substituted species $[\text{Ir}_4 (\text{CO})_{11} \{ \text{PPh}_2 \text{CH}_2 \text{CH} (\text{PPh}_2)_2 \text{Fe} (\text{CO})_3 \}]$ 2, Table 1, is virtually identical to those reported by Stuntz and Shapley [11] for complexes of the $[\text{Ir}_4 (\text{CO})_{11} \text{L}]$ with the addition of the bands due to the $\text{Fe} (\text{CO})_3$ group. It indicates the expected bands for bridging carbonyl ligands and a comparison with the spectrum of $[\text{Ir}_4 (\text{CO})_{11} (\text{PPh}_3)]$ [11], indicates that the phosphine substitutes into a basal axial position. The $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum of complex (2), has clearly shows the presence of three co-ordinated phosphorus atoms. Accordingly, $[\text{Ir}_4 (\text{CO})_{11} \{ \text{PPh}_2 \text{CH}_2 \text{CH} (\text{PPh}_2)_2 \text{Fe} (\text{CO})_3 \}]$ 2, shown two sets of resonances. At +43.6 ppm, there is a doublet, corresponding to the two equivalent phosphorus atoms bound to the Fe atoms which results from phosphorus-phosphorus coupling of 2.44 Hz. A resonance at -30.4 ppm, (a shift of -9.0 ppm from the free ligand) due to the phosphorus atom co-ordinated to the iridium metal framework, consists of a triplet which results from phosphorus-phosphorus coupling with coupling constant of 2.44 Hz (structure 2) with $[\text{Fe} (\text{CO})_3 \{ (\text{PPh}_2)_2 \text{CHCH}_2 \text{PPh}_2 \}]$ co-ordinated in a basal-axial site. A comparison with the $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum of $[\text{Ir}_4 (\text{CO})_{11} (\text{PPh}_3)]$, 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 [8-13],

substantiates our assignment, since axial P ligands appear at higher field than radial P ligands.



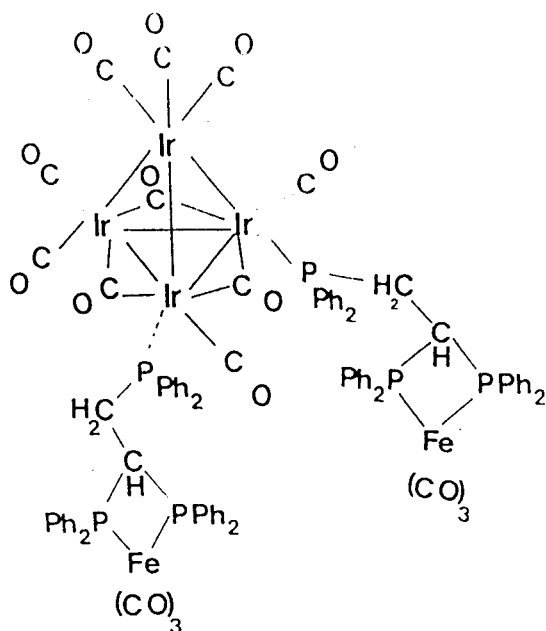
In the di-substituted species $[\text{Ir}_4 (\text{CO})_{10} \{ \text{PPh}_2 \text{CH}_2 \text{CH} (\text{PPh}_2)_2 \text{Fe} (\text{CO})_3 \}_2]$ (3), it was found that one iron carbonyl triphosphine complex is in a radial position (P_2) with respect to the bridging carbonyls and one $[\text{Fe} (\text{CO})_3 \{ (\text{PPh}_2)_2 \text{CHCH}_2 \text{PPh}_2 \}]$ complex (P) is axial. The infrared spectrum of complex (3), (Table 1), is identical to those reported [3, 11, 12, 14, 15] for complexes of the type $[\text{Ir}_4 (\text{CO})_{12} \text{L}_2]$. It shows bands for bridging carbonyl ligands, and a comparison with the $[\text{Ir}_4 (\text{CO})_{10} (\text{PPh}_3)_2]$ [3, 14, 15], indicates that one phosphine substitutes into a basal axial site and the other one substitutes into a basal radial position. The $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum of product (3), shows that all the phosphorus atoms are co-ordinated. 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). A resonance at 14.0 ppm there is a triplet ($J(\text{PP})$ 2.44 Hz) due to the phosphorus atom P_2 , co-ordinated to the iridium metal framework in a basal radial position. At 44.5 ppm there is a doublet ($J(\text{PP})$ 2.44 Hz), corresponding to the two equivalent phosphorus atoms P_3 and P_4 bound to the iron atom. For the second substitution, P_1 , there is a triplet ($J(\text{PP})$ 2.44 Hz) at -13.0 ppm due to the second iridium atom in a basal axial position. At 45.1 ppm, there is a doublet ($J(\text{PP})$ 2.44 Hz) corresponding to the two equivalent phosphorus atoms P_5 and P_6 bound to the iron atom. The two resonance at 14.0 and -13.0 ppm have the intensity (1:1) (with the radial P having a shift of 35.0 ppm from the free ligand). These data suggest that structure (3) is present in solution and that the signal due to the radial phosphorus iron complex appears at lower field than that of the axial phosphorus from $[\text{Fe} (\text{CO})_3 \{ (\text{PPh}_2)_2 \text{CHCH}_2 \text{PPh}_2 \}]$ co-ordinated to the iridium atom in the basal plane. There is agreement between these results and those previously reported [6]. It is also found that there is no coupling between the axial and radial $[\text{Fe} (\text{CO})_3 \{ (\text{PPh}_2)_2 \text{CHCH}_2 \text{PPh}_2 \}]$ complexes as reported by Stuntz and Shapley [11].

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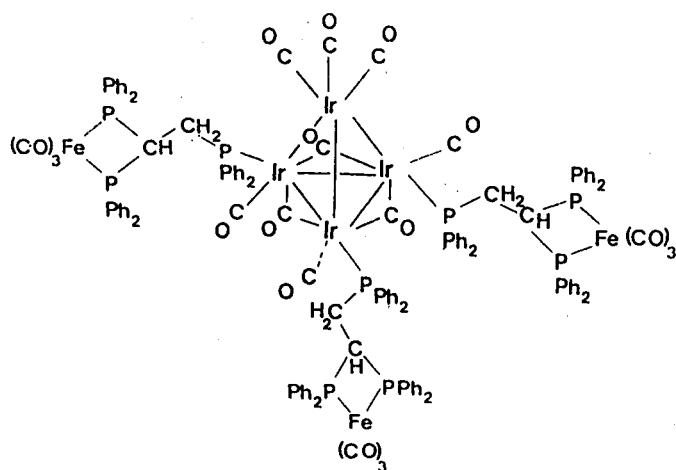
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(3)

The tri-substituted derivative, $[\text{Ir}_4(\text{CO})_9(\text{PPh}_2)_2\text{CH}_2\text{CH}(\text{PPh}_2)_2\text{Fe}(\text{CO})_3]_2$ (4), has the usual tetrahedral arrangement of iridium atoms, with three bridging carbonyl ligands around the basal plane. All known compounds of the type $[\text{Ir}_4(\text{CO})_9\text{L}_3]$ have the same structure [14, 15], in which two of the ligands are co-ordinated in basal radial sites and the third ligand in a basal axial site. The infrared spectrum of complex $[\text{Ir}_4(\text{CO})_9(\text{PPh}_2\text{CH}_2\text{CH}(\text{PPh}_2)_2\text{Fe}(\text{CO})_3)_3]$ (4), Table 1, is virtually identical to those previously reported for $[\text{Ir}_4(\text{CO})_9\text{L}_3]$ [10, 15]. However, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows resonances at -14.0 (t, J (PP) 2.44 Hz) and -58.8 (t, J (PP) 2.44 Hz) in a ratio (1:2) respectively, due to the phosphorus atoms co-ordinated to iridium. There are corresponding resonances at 42.2 ppm (d) and 44.5 ppm (d) due to the phosphorus atoms co-ordinated to iridium. There are corresponding resonances at 42.2 ppm (d) and 44.5 ppm (d) due to the phosphorus atoms co-ordinated to iron atoms.



(4)

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