Journal of Organometallic Chemistry, 309 (1986) C56–C58
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

THE USE OF BIDENTATE PHOSPHINE LIGANDS IN THE SYNTHESIS OF IRON–RHODIUM HETEROBIMETALLIC COMPLEXES.

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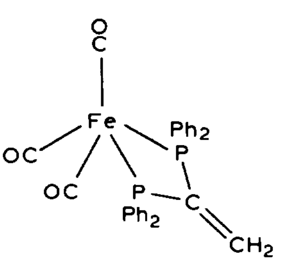
(Received April 18th, 1986)

Summary

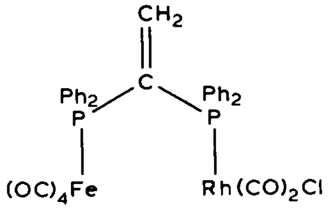
Treatment of Fe(CO)$_3$(dppee) (**1**) (dppee = 1,1-bis(diphenylphosphino)ethene) with [RhCl(CO)$_2$]$_2$ leads to the immediate formation of the known heterobimetallic complex (CO)$_4\overline{\text{Fe}(\mu\text{-dppee})\text{Rh}}$(CO)Cl (**3**) as the major product, together with an unstable, uncharacterised iron–rhodium complex. Complex **3** reacts with Me$_3$NO to give a complex proposed as FeRh(μ-CO)(μ-dppee)(CO)$_3$Cl (**4**). The heterobimetallic complex (CO)$_4$Fe(μ-dppee)Rh(CO)$_2$Cl (**2**), which does not contain an Fe–Rh bond, has been identified as a short-lived intermediate in the reaction of Fe(CO)$_4$(dppee) with [RhCl(CO)$_2$]$_2$.

The use of bidentate phosphine ligands, especially bis(diphenylphosphino)methane, dppm, in the synthesis of heterobimetallic complexes is receiving a great deal of attention [1]. Complexes containing chelating dppm ligands such as *trans*-[OsX$_2$(dppm)$_2$] (X = Cl or Br) [2], [M(dppm)$_2$]Cl$_2$ (M = Pd or Pt) [3], [M(CO)(dppm)$_2$]Cl (M = Rh or Ir) [4], and RuH$_2$(dppm)$_2$ [5] all undergo ring-opening reactions with a variety of metal species to give heterobimetallic complexes containing the M(μ-dppm)$_2$M′ moiety. The reaction of RuH$_2$(dppm)$_2$ with [MCl(COD)]$_2$ (M = Rh, Ir) [6] is the only example to our knowledge of a ring opening reaction leading to a heterobimetallic complex containing a single bridging bidentate phosphine ligand. However, a recent report [7] has shown heterobimetallic complexes of the type (CO)$_4$(μ-PP)RhCl(CO) (μ-PP = μ-dppm or μ-dppee) are formed when Fe(CO)$_4$Fe(η^1-dppm) or Fe(CO)$_4$(η^1-dppee) are treated with [RhCl(CO)$_2$]$_2$. We now report the results of our studies on the related reaction between Fe(CO)$_3$(dppee) and [RhCl(CO)$_2$]$_2$.

Our interest in metal complexes containing the dppee ligand led us to the synthesis and structural characterisation of Fe(CO)$_3$(dppee) (**1**) [8], in which the dppee ligand forms a strained chelate ring to the iron atom. We now find that treatment of a dichloromethane solution of complex **1** with 0.5 mol. equiv. of [RhCl(CO)$_2$]$_2$ leads instantaneously to the formation of the known heterobimetallic



(1)



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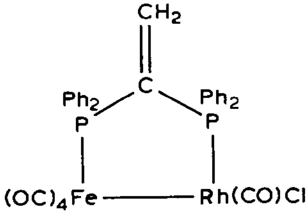

(3)

complex (CO)$_4\overline{\text{Fe}(\mu\text{-dppee})\text{Rh}}$(CO)Cl (**3**) (infrared and NMR spectroscopic data of all complexes are given in Table 1), in greater than 50% yield. ^{31}P NMR evidence was also obtained for a minor heterobimetallic product (δ 75.0 (d, J(PP) 84 Hz), 54.8 ppm (dd, J(PP) 84 Hz, J(PRh) 151 Hz)). This minor product has only a short lifetime in the reaction mixture. A second minor heterobimetallic product of the reaction is obtained after long reaction times (18 h) (δ 63.3 (d, J(PP) 35), 51.2 (dd, J(PP) 35, J(PRh) 165), but as yet this has not been further characterised.

Treatment of complex **3** with 1 equivalent of Me$_3$NO, leads to the slow transformation of **3** into the new dark green complex provisionally characterised as FeRh(μ-CO)(μ-dppee) (CO)$_3$Cl (**4**). The infrared spectrum of this complex (Table 1) shows the presence of a bridging CO ligand, while the ^{31}P NMR spectrum (Table 1) clearly shows the dppee ligand is bridging between the Fe and Rh atoms. We are currently carrying out an X-ray structural determination of complex **4** to determine the precise arrangement of the ligands.

TABLE 1

INFRARED AND ^{31}P NMR DATA

Complex	^{31}P{^{1}H} NMR [a] δ (ppm) (rel. H$_3$PO$_4$)	ν(CO) (cm^{-1}) (CH$_2$Cl$_2$ solution)
(CO)$_4$Fe(μ-dppee)Rh(CO)$_2$Cl (**2**)	63.1 (d, J(PP) 132) 35.6 (dd, J(PP) 132, J(PRh) 114)	
(CO)$_4\overline{\text{Fe}(\mu\text{-dppee})\text{Rh}}$(CO)Cl (**3**)	66.4 (d, J(PP) 130) 50.9 (dd, J(PP) 130, J(PRh) 149)	2062s, 2014s, 1988s 1948m, 1922s
FeRh(μ-CO)(μ-dppee)(CO)$_3$Cl (**4**)	73.5 (d, J(PP) 98) 34.5 (dd, J(PP) 98, J(PRh) 179)	1960s, 1936m, 1918w 1860w

[a] CD$_2$Cl$_2$ solution for complex **2**, C$_6$D$_6$ solution for complexes **3** and **4**. Coupling constants in Hz.

The formation of complex **3** from the reaction of Fe(CO)$_3$(dppee) with [RhCl(CO)$_2$]$_2$ involves the transfer of a CO ligand from Rh to Fe, whereas when complex **3** is formed from Fe(CO)$_4$(η^1-dppee) [7], a CO ligand is lost from [RhCl(CO)$_2$]$_2$. We therefore attempted to observe an intermediate species, (CO)$_4$Fe(μ-dppee)Rh(CO)$_2$Cl (**2**) by treating (CO)$_4$Fe(η^1-dppee) with [RhCl(CO)$_2$]$_2$ at low temperatures and/or under a CO atmosphere. We found that at low temperature (258 K) an unstable heterobimetallic complex is observed, in addition to **3**, which rapidly disappears on warming the reaction mixture to room temperature. This complex remains unchanged if the solution is kept in a sealed tube at 258 K. This new heterobimetallic complex is also observed when the treatment of Fe(CO)$_4$(η^1-dppee) with [RhCl(CO)$_2$]$_2$ is carried out under CO atmosphere. This evidence, together with the spectroscopic data given in Table 1, which clearly show the dppee ligand to bridge between Fe and Rh atoms, leads us to formulate this unstable complex as (CO)$_4$Fe(μ-dppee)Rh(CO)$_2$Cl (**2**), which does not contain an Fe–Rh bond. Clearly, CO ligand loss from the Rh atom in complex **2** occurs extremely rapidly to give complex **3** where the CO is replaced by an Fe → Rh donor bond. The dppm analogues of complexes **2**, **3** and **4** have also been prepared.

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