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# REACTIONS OF METAL CARBONYL DERIVATIVES

## XIV*. BRIDGED PHOSPHIDO DERIVATIVES OF IRON AND RUTHENIUM

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## SUMMARY

The tertiary phosphines $P(C_6H_5)_2R$ $[R = M(\pi\text{-}C_5H_5)(CO)_2$ $(M = Fe$ or $Ru)]$ readily effect the displacement of the chloro group in $[M'(\pi\text{-}C_5H_5)(CO)_2Cl]$ $(M' = Fe$ or Ru) to give bridged cationic species of the type $[MM'(\pi\text{-}C_5H_5)_2(CO)_4P(C_6H_5)_2]^+$. Treatment of $[Fe_2(CO)_9]$ with $P(C_6H_5)_2R$ $[R = Ru(\pi\text{-}C_5H_5)(CO)_2]$ leads to the formation of the neutral mixed-metal derivatives $[FeRu(\pi\text{-}C_5H_5)(CO)_6P(C_6H_5)_2]$ and $[FeRu(\pi\text{-}C_5H_5)(CO)_5P(C_6H_5)_2]$.

## INTRODUCTION

It has been previously established that the tertiary phosphine $P(C_6H_5)_2R$ $[R = Fe(\pi\text{-}C_5H_5)(CO)_2]$, like triphenylphosphine, reacts with $[Fe_2(CO)_9]$ in benzene at room temperature to yield a monosubstituted product of the type $[Fe(CO)_4$(Ligand)$]$[2]. However, whereas $[Fe(CO)_4P(C_6H_5)_3]$ is photochemically inert, irradiation of $[Fe(CO)_4P(C_6H_5)_2R]$ $[R = Fe(\pi\text{-}C_5H_5)(CO)_2]$ [(I); $M = M' = Fe$] with UV light results in the formation of the bridged carbonyl complex $[Fe_2(\pi\text{-}C_5H_5)(CO)_5P(C_6H_5)_2]$ [(II); $M = M' = Fe$][2]. The reactions of $[Fe(\pi\text{-}C_5H_5)(CO)_2P(C_6H_5)_2]$, as well as $[Ru(\pi\text{-}C_5H_5)(CO)_2P(C_6H_5)_2]$, with $[M'(\pi\text{-}C_5H_5)(CO)_2Cl]$ $(M' = Fe$ or Ru) have now been investigated to determine whether these unusual phosphines are capable of halogen displacement, and furthermore whether $[MM'(\pi\text{-}C_5H_5)_2(CO)_4P(C_6H_5)_2]^+$, if obtainable, may be degraded to $[MM'(\pi\text{-}C_5H_5)_2(CO)_3P(C_6H_5)_2]^+$ photochemically.

## RESULTS AND DISCUSSION

Triphenylphosphine is known to react with $[Fe(\pi\text{-}C_5H_5)(CO)_2Cl]$ in solution

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* For Part XIII see ref. 1.

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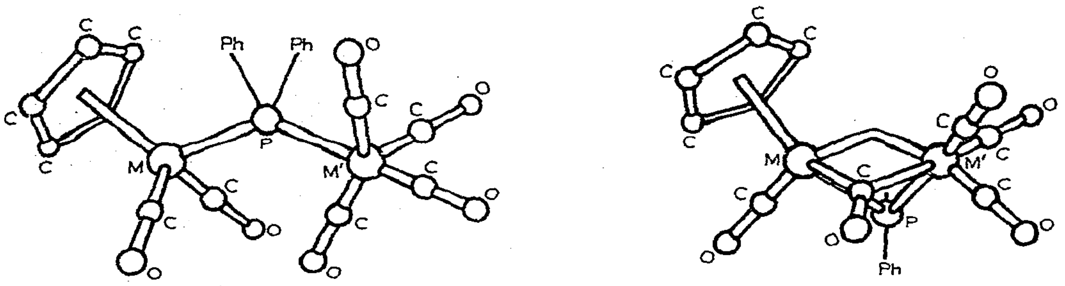
to afford, as the major product, the ionic complex $[Fe(\pi\text{-}C_5H_5)(CO)_2P(C_6H_5)_3]Cl$. The neutral species $[Fe(\pi\text{-}C_5H_5)(CO)P(C_6H_5)_3Cl]$ is also formed, but its yield is low, particularly if ionising solvents such as ethanol are employed[3-5]. It is now found that the ligand $P(C_6H_5)_2R$ $[R = Fe(\pi\text{-}C_5H_5)(CO)_2]$ likewise displaces the chloro group in $[Fe(\pi\text{-}C_5H_5)(CO)_2Cl]$, to give the cationic species $[Fe(\pi\text{-}C_5H_5)(CO)_2P(C_6H_5)_2R]^+$ [(III); M = M' = Fe].

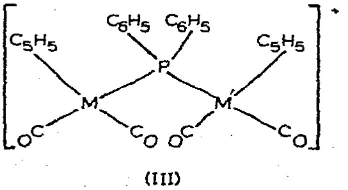


(I) (II)

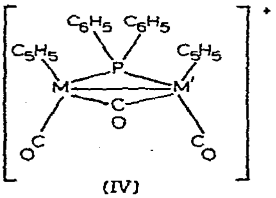
Fig. 1. Proposed structures of $[MM'(\pi\text{-}C_5H_5)(CO)_6P(C_6H_5)_2]$ [(I); M = M' = Fe; M = Ru, M' = Fe] and $[MM'(\pi\text{-}C_5H_5)(CO)_5P(C_6H_5)_2]$ [(II); M = M' = Fe; M = Ru, M' = Fe] showing the stereochemistry of the metal atoms only.

The latter was isolated and characterised as the tetraphenylborate salt. Similarly the reaction of $[Fe(\pi\text{-}C_5H_5)(CO)_2P(C_6H_5)_2]$ with the ruthenium complex $[Ru(\pi\text{-}C_5H_5)(CO)_2Cl]$ in the presence of $NaB(C_6H_5)_4$ affords the mixed-metal derivative $[FeRu(\pi\text{-}C_5H_5)_2(CO)_4P(C_6H_5)_2]B(C_6H_5)_4$ [(III); M = Fe, M' = Ru]. This compound could not however, be isolated completely free of the $\{[Fe(\pi\text{-}C_5H_5)(CO)_2]_2P(C_6H_5)_2\}B(C_6H_5)_4$, and $\{[Ru(\pi\text{-}C_5H_5)(CO)_2]_2P(C_6H_5)_2\}B(C_6H_5)_4$, also formed. It is relevant to note at this point that the reaction of $Pn_2(CH_3)_4$ (Pn = P or As) with $[Fe(\pi\text{-}C_5H_5)(CO)_2Br]$ has been previously reported[6] to yield the complex $\{[Fe(\pi\text{-}C_5H_5)(CO)_2]_2Pn(CH_3)_2\}Br$. On the basis of the results presented above it is suggested that the formation of this product results from the interaction of the intermediate $[Fe(\pi\text{-}C_5H_5)(CO)_2P(CH_3)_2]$ with $[Fe(\pi\text{-}C_5H_5)(CO)_2Br]$.

The ruthenium complex $[Ru(\pi\text{-}C_5H_5)(CO)_2P(C_6H_5)_2]$ has also been employed as a ligand, and shown to give products analogous to those obtained with $[Fe(\pi\text{-}C_5H_5)(CO)_2P(C_6H_5)_2]$. Thus treatment of $[Ru(\pi\text{-}C_5H_5)(CO)_2Cl]$ with this ligand in benzene/methanol in the presence of $NaB(C_6H_5)_4$ gave the bridged ionic derivative $\{[Ru(\pi\text{-}C_5H_5)(CO)_2]_2P(C_6H_5)_2\}B(C_6H_5)_4$ [(III); M = M' = Ru]. Furthermore reaction of $[Ru(\pi\text{-}C_5H_5)(CO)_2P(C_6H_5)_2]$ with a suspension of $[Fe_2(CO)_9]$ in benzene gave the bridged neutral complex $[FeRu(\pi\text{-}C_5H_5)(CO)_6P(C_6H_5)_2]$ [(I); M = Ru, M' = Fe].



(III)



(IV)

As found previously[2] for $[Fe_2(\pi\text{-}C_5H_5)(CO)_6P(C_6H_5)_2]$ [(I); M = M′ = Fe], irradiation of the mixed-metal complex $[FeRu(\pi\text{-}C_5H_5)(CO)_6P(C_6H_5)_2]$ [(I); M = Ru, M′ = Fe] with UV light led to the displacement of a carbonyl group and the formation of a species which spontaneously rearranges to a bridging carbonyl derivative, in this case $[FeRu(\pi\text{-}C_5H_5)(CO)_5P(C_6H_5)_2]$ [(II); M = Ru, M′ = Fe]. In contrast, irradiation of $[MM'(\pi\text{-}C_5H_5)_2(CO)_4P(C_6H_5)_2]B(C_6H_5)_4$ [(III); M, M′ = Fe and/or Ru] in tetrahydrofuran did not give $[MM'(\pi\text{-}C_5H_5)_2(CO)_3P(C_6H_5)_2]B(C_6H_5)_4$ [(IV); M, M′ = Fe and/or Ru] but gave instead the dimer $[M(\pi\text{-}C_5H_5)(CO)_2]_2$ (M = Fe or Ru).

The ionic derivatives $[MM'(\pi\text{-}C_5H_5)_2(CO)_4P(C_6H_5)_2]B(C_6H_5)_4$ were char-

TABLE 1

COLOURS AND CONDUCTIVITY AND ANALYTICAL DATA

| *Compound* | *Colour* | *Conductivity*[a] | *Analysis found (calcd.) (%)* | | |
|---|---|---|---|---|---|
| | | | *C* | *H* | *P* |
| $\{[Fe(\pi\text{-}C_5H_5)(CO)_2]_2P(C_6H_5)_2\}B(C_6H_5)_4$ | Yellow | 91 | 69.8<br>(70.0) | 4.7<br>(4.7) | 3.8<br>(3.7) |
| $\{[Ru(\pi\text{-}C_5H_5)(CO)_2]_2P(C_6H_5)_2\}B(C_6H_5)_4$ | Yellow | 93 | 63.2<br>(63.3) | 4.3<br>(4.3) | 3.4<br>(3.3) |
| $[FeRu(\pi\text{-}C_5H_5)_2(CO)_4P(C_6H_5)_2]B(C_6H_5)_4$[b] | Yellow | 91 | 66.6<br>(66.5) | 4.5<br>(4.5) | 3.5<br>(3.4) |
| $[FeRu(\pi\text{-}C_5H_5)(CO)_5P(C_6H_5)_2]$[c] | Red | 2.1 | 48.4<br>(48.3) | 2.9<br>(2.8) | 5.5<br>(5.7) |

[a] $Ohm^{-1}\cdot cm^2\cdot mole^{-1}$; $1\text{–}10\times10^{-4}$ *M* solutions in acetone. [b] Found: Fe, 6.8. Calcd.: Fe, 6.2%. [c] Found: Fe, 10.1. Calcd.: Fe, 10.2%.

TABLE 2

IR AND NMR SPECTROSCOPIC DATA

| *Compound* | *C–O stretching frequencies* ($cm^{-1}$)[a] | $C_5H_5$ *proton resonances*[b,c] |
|---|---|---|
| $\{[Fe(\pi\text{-}C_5H_5)(CO)_2]_2P(C_6H_5)_2\}B(C_6H_5)_4$ | 2046 s, 2031 s, 1996 s, (br)[d] | 5.45 s[e] |
| $\{[Ru(\pi\text{-}C_5H_5)(CO)_2]_2P(C_6H_5)_2\}B(C_6H_5)_4$ | 2059 s, 2047 s, 2010 s (br)[d] | 4.59 s[f] |
| $[FeRu(\pi\text{-}C_5H_5)_2(CO)_4P(C_6H_5)_2]B(C_6H_5)_4$ | 2053 s, 2039 s, 2004 s (br)[d] | 5.22 s, 5.55 d [*J*(P–H) 1.5 Hz][e] |
| $[FeRu(\pi\text{-}C_5H_5)(CO)_6P(C_6H_5)_2]$ | 2051 m (sh), 2032 s, 1974 m (br) 1949 vs, 1930 m (sh)[d] | |
| $[FeRu(\pi\text{-}C_5H_5)(CO)_5P(C_6H_5)_2]$ | 2037 ms, 1986 s, 1968 s (sh), 1958 s, 1807 ms[g] | 4.70 s, br[h] |
| $[Fe_2(\pi\text{-}C_5H_5)(CO)_6P(C_6H_5)_2]$ | 2045 m (sh), 2032 s, 1991 s, 1957 m, 1920 vs[d] | 4.98 s, br[h] |
| $[Fe_2(\pi\text{-}C_5H_5)(CO)_5P(C_6H_5)_2]$ | 2035 ms, 1980 s, 1970 ms (sh)[h] 1956 ms, 1797 m[g] | 4.19 s, 5.07[h] |

[a] Abbreviations: vs, very strong; s, strong; ms, medium strong; m, medium; (sh), shoulder; (br), broad. [b] τ scale (TMS reference) measured at 38°. [c] Abbreviations: s, singlet; d, doublet; br, broad. [d] Measured in $CH_2Cl_2$. [e] Measured in $CD_2Cl_2$. [f] Measured in $CD_3COCD_3$. [g] Measured in cyclohexane. [h] Measured in $CDCl_3$.

acterized by elemental analysis, and were shown to be 1/1 electrolytes in acetone. The NMR spectra of $\{[M(\pi\text{-}C_5H_5)(CO)_2]_2P(C_6H_5)_2\}B(C_6H_5)_4$ (M = Fe or Ru) contain a single cyclopentadienyl proton resonance while two resonances associated with these protons are observed in the spectrum of $[FeRu(\pi\text{-}C_5H_5)_2(CO)_4P(C_6H_5)_2]B(C_6H_5)_4$. The band patterns in the C–O stretching region in the IR spectra of these derivatives are typical of compounds of the type $\{[Fe(\pi\text{-}C_5H_5)(CO)_2]_2\ X\}$ Anion [X = Cl, Br, I or $PnY_2$ (Pn = P, As or Sb; Y = Cl or Br)] consistent with the proposed formulation[7-9].

$[FeRu(\pi\text{-}C_5H_5)(CO)_5P(C_6H_5)_2]$ was characterised by elemental analysis, while $[FeRu(\pi\text{-}C_5H_5)(CO)_6P(C_6H_5)_2]$ which could not be isolated pure, was identified by means of IR spectroscopy only. The NMR spectrum of $[FeRu(\pi\text{-}C_5H_5)(CO)_5P(C_6H_5)_2]$ contains a single cyclopentadienyl proton resonance demonstrating that this compound, unlike $[Fe_2(\pi\text{-}C_5H_5)(CO)_5P(C_6H_5)_2]$, exists either as a single isomer or as more than one isomer in dynamic equilibrium in solution. Both bridging and terminal carbonyl stretching modes are observed in the IR spectrum of this mixed-metal derivative. The frequencies and relative intensities of these bands are very similar to those of the corresponding bands observed in the spectrum of $[Fe_2(\pi\text{-}C_5H_5)(CO)_5P(C_6H_5)_2]$. On the basis of this IR evidence, it is suggested that the structure of $[FeRu(\pi\text{-}C_5H_5)(CO)_5P(C_6H_5)_2]$ (or its major isomer) is analogous to that previously proposed[2] for $[Fe_2(\pi\text{-}C_5H_5)(CO)_5P(C_6H_5)_2]$ in the crystalline state [(II); M = Ru, M′ = Fe].

## EXPERIMENTAL

The compounds $[Fe_2(CO)_9]$, $[Fe(\pi\text{-}C_5H_5)(CO)_2Cl]$ and $[Ru(\pi\text{-}C_5H_5)(CO)_2Cl]$ were synthesised according to established procedures[7,10-12]. All experiments were performed under nitrogen. The photochemical reactions employed a Hanovia medium pressure arc photochemical reactor. The chromatographic separations were effected on an alumina column (50 × 1.5 cm; Merck acid washed alumina, activity III). The IR and NMR spectra were recorded on a Perkin–Elmer model 21 and on the Varian HA-100D instruments respectively. Conductivities were determined using a Metrohm E365B conductoscope. The elemental analyses were obtained by the Alfred Bernhardt Micro-analytical Laboratory, Elbach-über-Engelskirchen, West-Germany.

### *Synthesis of* $[Fe_2(\pi\text{-}C_5H_5)_2(CO)_4P(C_6H_5)_2]B(C_6H_5)_4$ *and* $[FeRu(\pi\text{-}C_5H_5)_2(CO)_4P(C_6H_5)_2]B(C_6H_5)_4$

A benzene solution (ca. 25 ml) of $[Fe(\pi\text{-}C_5H_5)(CO)_2P(C_6H_5)_2]$ (0.72 g, 2.0 mmol), prepared *in situ* from equimolar quantities of $NaP(C_6H_5)_2$ and $[Fe(\pi\text{-}C_5H_5)(CO)_2I]$, was added dropwise to a stirred solution of $[Fe(\pi\text{-}C_5H_5)(CO)_2Cl]$ (0.42 g, 2.0 mmol) or $[Ru(\pi\text{-}C_5H_5)(CO)_2Cl]$ (0.52 g, 2.0 mmol) in benzene (ca. 30 ml) and the resultant solution stirred for 5 min. $NaB(C_6H_5)_4$ (0.85 g, 2.5 mmol) in methanol (ca. 10 ml) was added and the mixture stirred for a further 5 min. The solvent was removed under reduced pressure and the residue washed with benzene, crystallised from acetone/methanol and recrystallised from acetone/petroleum ether. Yields: $[Fe_2(\pi\text{-}C_5H_5)_2(CO)_4P(C_6H_5)_2]B(C_6H_5)_4$, ca. 75%; $[FeRu(\pi\text{-}C_5H_5)_2(CO)_4P(C_6H_5)_2]B(C_6H_5)_4$, ca. 45%.

*Synthesis of* $[Ru_2(\pi\text{-}C_5H_5)_2(CO)_4P(C_6H_5)_2]B(C_6H_5)_4$

A benzene solution (ca. 25 ml) of $[Ru(\pi\text{-}C_5H_5)(CO)_2P(C_6H_5)_2]$ (0.81 g, 2.0 mmol), prepared *in situ* from equimolar quantities of $Na[Ru(\pi\text{-}C_5H_5)(CO)_2]$ and $P(C_6H_5)_2Cl$, was added dropwise to a stirred solution of $[Ru(\pi\text{-}C_5H_5)(CO)_2Cl]$ (0.52 g, 2.0 mmol) and $NaB(C_6H_5)_4$ (0.85 g, 2.5 mmol) in benzene (ca. 40 ml) and methanol (ca. 10 ml) and the resultant solution stirred for 1 h. The solvent was removed under reduced pressure to afford a yellow residue which was washed with benzene and then extracted with dichloromethane. The product isolated from the filtered dichloromethane extract was crystallised from dichloromethane/petroleum ether. Yield ca. 40%.

*Synthesis of* $[FeRu(\pi\text{-}C_5H_5)(CO)_5P(C_6H_5)_2]$

A solution of $[Ru(\pi\text{-}C_5H_5)(CO)_2P(C_6H_5)_2]$ (0.81 g, 2.0 mmol) in benzene (ca. 25 ml) was added dropwise to a stirred suspension of $[Fe_2(CO)_9]$ (0.73 g, 2.0 mmol) in benzene (ca. 100 ml) and the resultant solution irradiated with UV light for 5 h. The solution was filtered, concentrated to a very small volume and transferred to an alumina column. Elution with benzene afforded a red band which was collected. The product isolated from this solution was crystallised from benzene/petroleum ether. Yield ca. 10%.

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