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REACTIONS OF METAL CARBONYL DERIVATIVES

XVI*. A COMPARATIVE STUDY OF THE REACTIVITY OF CHLORODICARBONYL-η-CYCLOPENTADIENYLRUTHENIUM AND CHLOROBIS(TRIPHENYLPHOSPHINE)-η-CYCLOPENTADIENYLRUTHENIUM TOWARDS CERTAIN NUCLEOPHILES

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Summary

While $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$ shows no evidence for dissociation in alcohol, $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ reveals considerable ionic behaviour. Consistent with this the latter compound reacts far more readily than the former with nucleophiles in alcohol to yield cationic or neutral species of the type $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2L]^x$ (x = +1 or 0) where L = a neutral or anionic ligand respectively. Reactions studied include those involving the ligands carbon monoxide, dinitrogen, the tetraphenylborate anion, the triphenylcyanoborate anion and the trihydridocyanoborate anion. The nitrile derivatives $[Ru(\eta\text{-}C_5H_5)L_2\text{-}NCBX_3]$ (L = CO or $P(C_6H_5)_3$, X = H or C_6H_5) are found to rearrange readily affording either the metal cyanide $[Ru(\eta\text{-}C_5H_5)L_2CN]$ or the isonitrile species $[Ru(\eta\text{-}C_5H_5)L_2CNBX_3]$.

Introduction

Previous studies [2, 3] from these and other laboratories have revealed that in general reaction of $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ with nucleophilic ligands takes place

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in one of two ways viz. (i) substitution of one or both carbonyl groups by the reagent or (ii) ligand replacement of the chloro group as a chloride ion. Two further types of reaction are possible although thus far they have not been reported as being applicable to $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$. One involves nucleophilic attack on a coordinated carbonyl group by the ligand, as illustrated by the reaction of $[Fe(\eta\text{-}C_5H_5)(CO)_3]^+$ with methoxide ions to give $[Fe(\eta\text{-}C_5H_5)(CO)_2\text{-}COOCH_3]$ [4], and the other nucleophilic attack on the cyclopentadienyl ring, as depicted by the reaction of $[Fe(\eta\text{-}C_5H_5)(CO)_2P(C_6H_5)_3]^+$ with hydride ions to afford $[Fe(C_5H_6)(CO)_2P(C_6H_5)_3]$ [5]. The mode of reaction of $[Fe(\eta\text{-}C_5H_5)\text{-}(CO)_2Cl]$ is very dependent on the nature of the ligand under consideration. Thus for neutral strongly π-acidic ligands such as $P(OC_6H_5)_3$ for instance, carbonyl replacement is effected whereas for more basic ligands such as $P(C_2H_5)_3$, chloride displacement occurs [2].

At the outset of this work $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$ and its substituted derivative $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ had received very little attention. A comparative study of these compounds was thus initiated with the object of establishing the influence of replacing the carbonyl groups by the stronger donor $P(C_6H_5)_3$ ligands. Subsequent reports have revealed that the triphenylphosphine in compounds of the type $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2X]$ is labile and readily removed and this has led to the synthesis of a number of novel derivatives [6-9].

Results and discussion

Both $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$ and $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ are non-electrolytes in acetone, as established by conductivity measurements. Likewise $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$ is also a non-electrolyte in methanol but $[Ru(\eta\text{-}C_5H_5)\text{-}\{P(C_6H_5)_3\}_2Cl]$ shows appreciable ionic behaviour in this solvent indicating that, whereas the equilibrium:

$$[Ru(\eta\text{-}C_5H_5)L_2Cl] + CH_3OH \rightleftharpoons [Ru(\eta\text{-}C_5H_5)L_2(CH_3OH)]^+ + Cl^-$$

lies far to the left for L = CO, it is considerably more to the right for L = $P(C_6H_5)_3$. Consistent with this observation addition of a methanol solution of sodium tetraphenylborate to a refluxed solution of $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ in methanol led to the separation of $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2(CH_3OH)]B(C_6H_5)_4$. However a similar type of product could not be isolated from the corresponding reaction involving $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$. Solvento species of the type $[Ru(\eta\text{-}C_5H_5)L_2(\text{solvent})]^+$ (L = CO or $P(C_6H_5)_3$) where solvent can be acetone as well as alcohol are best obtained in situ by addition of silver salts such as $AgSbF_6$ to $[Ru(\eta\text{-}C_5H_5)L_2Cl]$ in the appropriate solvent. Although $[Ru(\eta\text{-}C_5H_5)\text{-}\{P(C_6H_5)_3\}_2(CH_3OH)]B(C_6H_5)_4$ was isolated as a relatively stable yellow microcrystalline product, it could not be obtained analytically pure. It was identified by means of IR and NMR spectroscopy* and shown to be a 1/1 electrolyte in acetone by conductivity measurements. In contrast the acetonitrile derivative $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2(CH_3CN)]B(C_6H_5)_4$ can be isolated in an analytically

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* Resonances readily assigned to cyclopentadienyl, phenyl and methoxy protons were observed in the NMR spectrum of $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2(CH_3OH)]B(C_6H_5)_4$ but the presence of other peaks prevented any unique assignment.

pure state [6]. Also it can be obtained directly in high yields by refluxing a solution of $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ and $NaB(C_6H_5)_4$ in acetonitrile for a short period [6].

Not unexpectedly, on the basis of the above equilibrium, passage of carbon monoxide through an ethanol solution of $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ led to the formation of $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2(CO)]^+$, best isolated as the tetraphenylborate salt. This reaction contrasts with the previously reported reaction of $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ with carbon monoxide under pressure using benzene as solvent, in which it was found that the product is neutral $[Ru(\eta\text{-}C_5H_5)(CO)P(C_6H_5)_3Cl]$ [6]. Treatment of a methanol solution of $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$ and $NaB(C_6H_5)_4$ with carbon monoxide at room temperature did not produce $[Ru(\eta\text{-}C_5H_5)(CO)_3]^+$, consistent with the inability of $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$ to form the solvento species $[Ru(\eta\text{-}C_5H_5)(CO)_2(CH_3OH)]^+$ on dissolution in methanol. $[Ru(\eta\text{-}C_5H_5)(CO)_3]^+$ is obtained by carbonylation of $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$ in methanol at a high temperature and under a high pressure of carbon monoxide, however. Both $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2(CO)]B(C_6H_5)_4$ and $[Ru(\eta\text{-}C_5H_5)(CO)_3]B(C_6H_5)_4$ have been synthesized previously, the former by reaction of $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ with carbon monoxide under pressure in acetone solution in the presence of $NaB(C_6H_5)_4$ [6] and the latter by high pressure carbonylation of $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$ in acetone in the presence of $NaB(C_6H_5)_4$ [10].

In view of the ready reaction of carbon monoxide with $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ in alcohol, attempts were made to effect a similar chloride displacement with dinitrogen. However no dinitrogen product could be detected in this or in the reaction of $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2(CH_3OH)]^+$ with dinitrogen under pressure. Some interaction between dinitrogen and $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2\{(CH_3)_2CO\}]^+$ was indicated by the appearance of bands in the N_2 stretching region of the IR spectrum of their reaction mixture*, but no dinitrogen-containing product could be isolated from solution.

Although $[Ru(\eta\text{-}C_5H_5)(CO)_3]B(C_6H_5)_4$ was not formed in the atmospheric pressure carbonylation of $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$ in methanol in the presence of sodium tetraphenylborate, a reaction was shown to occur. The product, formed in far higher yield by refluxing a methanol solution of $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$ and $NaB(C_6H_5)_4$ or $[Ru(\eta\text{-}C_5H_5)(CO)_2(CH_3OH)]B(C_6H_5)_4$ in methanol for a few hours, was characterised as the σ-phenyl derivative $[Ru(\eta\text{-}C_5H_5)(CO)_2C_6H_5]$, also obtained by treatment of $[\{Ru(\eta\text{-}C_5H_5)(CO)_2\}_2X]^+$ (X = Cl or Br) with $B(C_6H_5)_4^-$ [11]. Although not a well documented reaction, extraction of a phenyl group from $B(C_6H_5)_4^-$ by a transition metal has also previously been reported for $[Ni(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2]^+$ [12], $[Pt\{P(CH_3)_2C_6H_5\}_2(CH_3OH)CH_3]^+$ [13] and *cis*-$[Pt\{P(C_2H_5)_3\}_2Cl_2]$ [14]. Treatment of $[Ru(\eta\text{-}C_5H_5)(CO)_2\{(CH_3)_2CO\}]^+$ with $B(C_6H_5)_4^-$ did not lead to the σ-phenyl product but resulted in its reduction to $[Ru(\eta\text{-}C_5H_5)(CO)_2]_2$. The reducing properties of $B(C_6H_5)_4^-$ have been noted previously , with $IrCl_6^{2-}$ and $[Fe(\eta\text{-}C_5H_5)(CO)SCH_3]_2^{2+}$ for instance being readily reduced to $IrCl_6^{3-}$ and $[Fe(\eta\text{-}C_5H_5)(CO)SCH_3]_2^+$ respectively [1, 15].

The behaviour of $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ towards $B(C_6H_5)_4^-$ in alcohol

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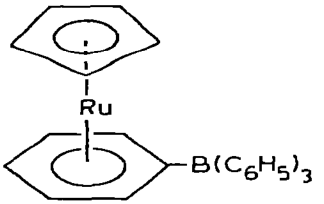
* These peaks were not observed in the spectrum of the reaction mixture for the corresponding reaction performed under argon.

under reflux conditions contrasted with that of [Ru(η-C_5H_5)$(CO)_2Cl$] in that both phosphine ligands as well as the chloro group were replaced. The product, shown to be neutral in solution, was characterised as [Ru(η-C_5H_5){η-C_6H_5B-$(C_6H_5)_3$}]. The IR spectrum of this compound contains five bands in the 1500-1350 cm^{-1} region. This band pattern has been proposed as being indicative of the presence of a phenyl group of $B(C_6H_5)_4^-$ being π-bonded to a metal [16]. Owing to the low solubility of this compound a well-resolved NMR spectrum, and thus confirmation of the above mode of bonding, could not be obtained. However, as well as a sharp resonance at τ 5.24 and a complex pattern at τ 2.80, two broad resonances at τ 3.78 and 4.39 which can be assigned to the protons of a π-bonded phenyl ring were apparent in the spectrum.

With a view to obtaining a more soluble analogue, [Ru(η-$CH_3C_5H_4$)-{$P(C_6H_5)_3$}$_2$Cl] was reacted with $NaB(C_6H_5)_4$ in methanol under reflux to give [Ru(η-$CH_3C_5H_4$){η-$C_6H_5B(C_6H_5)_3$}]. The NMR spectrum of this compound contains resonances at τ 5.28 and 5.39, each of relative intensity 2 and assigned to the cyclopentadienyl protons, a single sharp resonance at τ 8.30 of relative intensity 3 (assigned to the methyl protons), a complex resonance pattern of relative intensity 15 centered at τ 2.82 and two complex resonance patterns of relative intensity 5 at τ 3.88 and 4.49 respectively. The latter were assigned to protons associated with a phenyl ring π-bonded to the ruthenium. On the basis of the IR and NMR spectroscopic evidence the sandwich structure represented below was proposed for these compounds.



A recent crystal structure determination has confirmed this proposal [17]. It has also been established that the tetraphenylborate anion is bonded to a transition metal through one of its phenyl rings in a number of rhodium and iridium derivatives of the type [ML_2{η-$C_6H_5B(C_6H_5)_3$}] (M = Rh or Ir, L = ligand) [16, 18] and in a ruthenium complex of stoichiometry [RuH{$P(C_6H_5)_3$}$_2${η-C_6H_5B-$(C_6H_5)_3$}] [19]. Similar to [Ru(η-C_5H_5)$(CO)_2$(solvent)]$^+$ (solvent = alcohol or acetone), the solvento species [Ru(η-C_5H_5){$P(C_6H_5)_3$}$_2$(solvent)]$^+$ (solvent = alcohol or acetone) also showed contrasting behaviour towards $B(C_6H_5)_4^-$. Thus, whereas refluxing of a suspension of [Ru(η-C_5H_5){$P(C_6H_5)_3$}$_2$(CH_3OH)]$B(C_6H_5)_4$ in methanol gave [Ru(η-C_5H_5){η-$C_6H_5B(C_6H_5)_3$}], addition of $B(C_6H_5)_4^-$ to [Ru(η-C_5H_5){$P(C_6H_5)_3$}$_2$ {$(CH_3)_2CO$}]$^+$ in acetone produced unstable products which could not be identified.

The anion $B(C_6H_5)_3CN^-$ was shown to react differently to $B(C_6H_5)_4^-$ with [Ru(η-C_5H_5)$(CO_2)_2Cl$] in alcohol under reflux. Neither [Ru(η-C_5H_5)$(CO)_2C_6H_5$] nor [Ru(η-C_5H_5){η-$C_6H_5B(C_6H_5)_2CN$}] but [Ru(η-C_5H_5)$(CO)_2CN$], characterised by standard procedures as well as by comparison with the product obtained by metathetical reaction of [Ru(η-C_5H_5)$(CO)_2Cl$] with KCN, was formed. However addition of $B(C_6H_5)_3CN^-$ to [Ru(η-C_5H_5)$(CO)_2$(solvent)]$^+$ (solvent = methanol or acetone) in the appropriate solvent at room temperature gave the zwitterionic species [Ru(η-C_5H_5)$(CO)_2$NCB$(C_6H_5)_3$]. Characterisation of this complex as a nitrile and not an isonitrile derivative of ruthenium was on the basis of IR spectroscopic evidence [20]. The C—N stretching frequency for this compound (2203 cm^{-1}, measured in dichloromethane) is approximately 35 cm^{-1} higher than the frequency of the corresponding mode for B$(C_6H_5)_3CN^-$, which is consistent with the trend normally observed on coordination of a nitrile ligand to a transition metal [20]. The compound is unstable to heat and readily decomposes to [Ru(η-C_5H_5)$(CO)_2$CN]. It is thus apparent that it is an intermediate in the formation of the latter from [Ru(η-C_5H_5)$(CO)_2$Cl] and B$(C_6H_5)_3CN^-$ in alcohol under reflux. [Ru(η-C_5H_5)$(CO)_2$NCB$(C_6H_5)_3$] has previously been reported as a product of the reaction of [{Ru(η-C_5H_5)$(CO)_2$}$_2$X]$^+$ (X = Cl or Br) with B$(C_6H_5)_3CN^-$ [11].

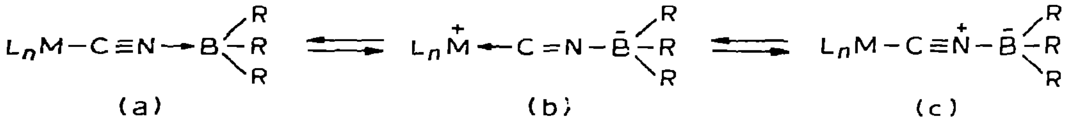
Addition of B$(C_6H_5)_3CN^-$ to an acetone solution of [Ru(η-C_5H_5){P$(C_6H_5)_3$}$_2$-{$(CH_3)_2$CO}]$^+$ produced a yellow crystalline compound of stoichiometry [Ru(η-C_5H_5){P$(C_6H_5)_3$}$_2$CNB$(C_6H_5)_3$]. The C—N stretching frequency for this compound viz. 2134 cm^{-1} was not that expected for a nitrile derivative of ruthenium but corresponded to a value expected for an isonitrile species. Consistent with this, treatment of [Ru(η-C_5H_5){P$(C_6H_5)_3$}$_2$CN] (prepared by metathetical reaction of [Ru(η-C_5H_5){P$(C_6H_5)_3$}$_2$Cl] with KCN) with B$(C_6H_5)_3$ in solution at room temperature gave the same compound. Careful monitoring of the reaction of [Ru(η-C_5H_5){P$(C_6H_5)_3$}$_2${$(CH_3)_2$CO}]$^+$ with B$(C_6H_5)_3CN^-$ in acetone by means of IR spectroscopy revealed the presence of a peak at 2203 cm^{-1} which decreased in intensity with increase in intensity of the band at 2134 cm^{-1}. It is assumed that the higher frequency mode corresponds to [Ru(η-C_5H_5){P$(C_6H_5)_3$}$_2$NCB-$(C_6H_5)_3$] and that an extremely novel isomerism involving the conversion of a nitrile to an isonitrile derivative has been effected.

In view of the contrasting linkage isomerism behaviour of [Ru(η-C_5H_5)-$(CO)_2$SCN] and [Fe(η-C_5H_5)$(CO)_2$SCN] [11, 21, 22], the mode of reaction of B$(C_6H_5)_3CN^-$ with [Fe(η-C_5H_5)$(CO)_2${$(CH_3)_2$CO}]$^+$ was studied. Reaction of the two afforded the nitrile product [Fe(η-C_5H_5)$(CO)_2$NCB$(C_6H_5)_3$] which unlike its ruthenium analogue was found not to degrade to [Fe(η-C_5H_5)$(CO)_2$CN] on heating in acetone solution. A preference for the iron derivative to be *N*-bonded is again observed.

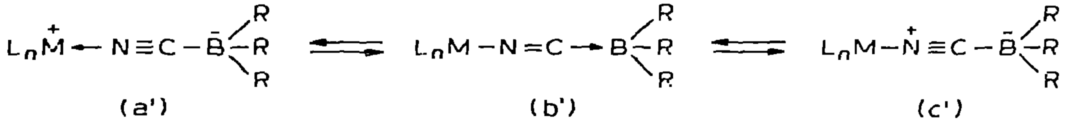
A previous study [6] has revealed that $NaBH_4$ reacts with [Ru(η-C_5H_5)-{P$(C_6H_5)_3$}$_2$Cl] in tetrahydrofuran to afford [Ru(η-C_5H_5){P$(C_6H_5)_3$}$_2BH_4$] in which the BH_4 group is bonded to the ruthenium through two of its hydrogen atoms. On the other hand treatment of [Ru(η-C_5H_5)$(CO)_2$Cl] with BH_4^- has been found to give the simple hydride [Ru(η-C_5H_5)$(CO)_2$H] [23]. The cyanoborohydride BH_3CN^- thus has the potential of behaving as a ligand in which it bonds to a metal through its hydrogen atoms or of acting as a source of hydride ions, as well as functioning as a simple nitrile ligand. A further possibility is as a bridging ligand in which both the nitrile group and a hydrogen atom are involved in bonding to the metals, as found for instance in [Cu{P$(C_6H_5)_3$}$_2BH_3CN$]$_2$ [20, 24]. Reaction of BH_3CN^- with [Ru(η-C_5H_5){P$(C_6H_5)_3$}$_2${$(CH_3)_2$CO}]$^+$ in acetone was found to afford primarily [Ru(η-C_5H_5){P$(C_6H_5)_3$}$_2$CN] on the basis of IR evidence [ν(C—N) 2083 cm^{-1}, measured in dichloromethane]. A second peak in the spectrum of the reaction mixture at 2141 cm^{-1} was assigned to

$[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2CNBH_3]$ but separation of the two products could not be effected. Monitoring of the reaction by means of IR revealed the formation of a third compound $[\nu(C{-}N)\ 2203\ cm^{-1}]$ which is assumed to be $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2NCBH_3]$, but this rapidly decomposed. Interaction of $[Ru(\eta\text{-}C_5H_5)(CO)_2\{(CH_3)_2CO\}]^+$ with BH_3CN^- in acetone led to brown-black decomposed products even at low temperatures. Some $[Ru(\eta\text{-}C_5H_5)(CO)_2]_2$ was observed, but in very small quantity. Its formation would probably be through the hydride species $[Ru(\eta\text{-}C_5H_5)(CO)_2H]$. The iron derivative $[Fe(\eta\text{-}C_5H_5)(CO)_2CNBH_3]$ has been obtained previously but by interaction of $[Fe(\eta\text{-}C_5H_5)(CO)_2CN]$ with diborane [25].

Complexes containing BR_3NC bonded as an isonitrile ligand have in general lower C—N stretching frequencies than corresponding compounds in which the ligand is bonded to the metal through the nitrogen [20]. The principal canonical forms describing the bonding of $CNBR_3$ and $NCBR_3$ to transition metals are represented below (M = metal; L = ligand).



Isonitrile bonding



Nitrile bonding

The lower C—N frequencies for isonitrile derivatives is indicative of canonical form b contributing more to the overall structure of isonitrile compounds than form b' to the overall structure for the nitrile derivatives.

The frequency of the C—N stretching mode for $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2CN]$ is considerably less than that for $[Ru(\eta\text{-}C_5H_5)(CO)_2CN]$. This is attributed to a greater π-back-donation from the ruthenium to the anti-bonding orbitals of the cyanide group in the case of $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2CN]$ due to the presence of the stronger $(\sigma{-}\pi)$ donor $P(C_6H_5)_3$ ligands. The observed increase in the C—N stretching frequency on formation of adducts of the type $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2CNBR_3]$ ($R = H$ or C_6H_5) is explained in terms of an effective depopulation of the C—N anti-bonding orbitals as a result of the bonding of the nitrogen to the boron. A similar increase in the frequency of the C—N stretching modes of some Mn^{I}, Ni^{II} and Fe^{II} cyano complexes on formation of their BF_3 and BH_3 adducts has been reported [26, 27].

With a view to establishing the mechanism of formation of $[Ru(\eta\text{-}C_5H_5)\{\eta\text{-}C_6H_5B(C_6H_5)_3\}]$ from $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ and $B(C_6H_5)_4]^-$ in alcohol, $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ was reacted with various arene derivatives in the hope of isolating products of the type $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2(1\text{-}2\text{-}\eta\text{-arene})]^+$, $[Ru(\eta\text{-}C_5H_5)P(C_6H_5)_3(1\text{-}4\text{-}\eta\text{-arene})]^+$ and $[Ru(\eta\text{-}C_5H_5)(1\text{-}6\text{-}\eta\text{-arene})]^+$. These reactions were prompted by the ease of removal of one or both $P(C_6H_5)_3$ ligands in $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2X]$ (X = Cl, H or CH_3) by various ligands as illustrated by the products $[Ru(\eta\text{-}C_5H_5)P(C_6H_5)_3(CO)Cl]$ [6], $[Ru(\eta\text{-}C_5H_5)P(C_6H_5)_3\text{-}C(CF_3)=C(CF_3)C(CF_3)=CH(CF_3)]$ [8], $[Ru\{(C_6H_5)_2PC_6H_4\text{-}\eta\text{-}C_5H_4\}C_6F_4N=NC_6F_5]$ [9] and $[Ru(\eta\text{-}C_5H_5)\{\eta\text{-}C_6H_5B(C_6H_5)_3\}]$, the stability of the latter compound and the previous isolation of $[Pt\{P(C_2H_5)_3\}_2\{1\text{-}2\text{-}\eta\text{-}C_6(CF_3)_6\}]$, [28], $[Rh(\eta\text{-}C_5H_5)\{1\text{-}4\text{-}\eta\text{-}C_6(CF_3)_6\}]$ [29] and $[Ru\{1\text{-}6\text{-}\eta\text{-}C_6(CH_3)_6\}\{1\text{-}4\text{-}\eta\text{-}C_6(CH_3)_6\}]$ [30]. However none of the above reactions involving the arenes, benzene, mesitylene, hexamethylbenzene or hexafluorobenzene and performed in the presence of a large counterion such as PF_6^- gave any indication of affording the required products. Further, no 1-2-η-, 1-4-η- or 1-6-η- arene bonded derivatives could be detected in the reactions of $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2(CH_3OH)]SbF_6$, or $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2\{(CH_3)_2CO\}]SbF_6$ with the appropriate arene. Irradiation of a solution of $[Ru(\eta\text{-}C_5H_5)(CO)_2\{(CH_3)_2CO\}]SbF_6$ and the arene also proved negative.

Experimental

The compounds $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$ and $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ were synthesized according to literature methods [10, 31]. All experiments were performed under nitrogen. The photochemical reactions employed a Hanovia medium pressure arc photochemical reactor. Chromatographic separations were carried out 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 a Varian HA-100D instrument respectively. Conductivities were determined using a Metrohm E365B conductoscope. The elemental analyses were obtained by the Alfred Bernhardt Microanalytical Laboratory, Elbach-uber-Engelskirchen, West Germany. Table 1 shown colours, analytical and conductivity data for the compounds considered and Table 2 IR and NMR data.

(i). $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2(CH_3OH)]B(C_6H_5)_4$. A solution of $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ (0.5 g, 0.69 mmol) in methanol (60 ml) was refluxed for 8 h. The solution was filtered and $NaB(C_6H_5)_4$ (0.48 g, 1.4 mmol) in methanol (10 ml) was added to the filtrate. The yellow precipitate which separated from solution was isolated, washed with water, methanol and petroleum ether and dried. Yield 20%.

(ii) $[Ru(\eta\text{-}C_5H_5)L_2(CO)]B(C_6H_5)_4$, ($L = P(C_6H_5)_3$ *or* CO). A solution of $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ (0.50 g, 0.69 mmol) or $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$ (0.18 g, 0.70 mmol) in methanol (100 ml) was kept under an atmosphere of carbon monoxide in an autoclave at a temperature of 45°C and at a pressure of 250 psi for 60 h. The solution was filtered and $NaB(C_6H_5)_4$ (0.36 g, 1.05 mmol) in methanol (20 ml) was added to the filtrate. Concentration of the solution effected the separation of a yellow or white precipitate, which was isolated and washed with methanol and petroleum ether. $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2(CO)]B(C_6H_5)_4$ was recrystallised from dichloromethane/petroleum ether. Yield 50%. $[Ru(\eta\text{-}C_5H_5)(CO)_3]B(C_6H_5)_4$ was not further purified. Yield 30%.

$[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2(CO)]B(C_6H_5)_4$ is also obtained in lower yield by passage of carbon monoxide through a methanol solution of $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ in the presence of $NaB(C_6H_5)_4$.

TABLE 1

COLOURS, ANALYTICAL AND CONDUCTIVITY DATA

Compound[a]	Colour	Analyses found (calcd.) (%)				
		C	H	P or N	Others	Conductivity[b] (Ohm^{-1} $cm.^2$ mol^{-1})
$[RuCp(PPh_3)_2(CO)]BPh_4$	Yellow	76.2 (76.4)	5.3 (5.3)	5.9 (P) (6.0)		92
$[RuCp(CO)_2Ph]$	Orange	52.1 (52.2)	3.4 (3.4)		10.9 (O) (10.7)	0.1
$[Ru(MeCp)(PPh_3)_2Cl]$	Yellow	68.3 (68.2)	5.2 (5.0)	7.8 (P) (8.4)	4.6 (Cl) (4.8)	0.4
$[RuCpBPh_4]$	Brown	71.9 (71.8)	5.3 (5.2)		2.0 (B) (2.2)	1.2
$[Ru(MeCp)BPh_4]$	Brown	72.1 (72.2)	5.5 (5.5)		2.0 (B) (2.2)	0.8
$[RuCp(CO)_2NCBPh_3]$	White	63.6 (63.7)	4.2 (4.1)	2.9 (N) (2.9)	2.1 (B) (2.2)	0.1
$[RuCp(PPh_3)_2CNBPh_3]$	Yellow	75.4 (75.2)	5.2 (5.3)	6.6 (P) (6.5) 1.6 (N) (1.5)	1.0 (B) (1.1)	0.4
$[RuCp(CO)_2CN]$	White	38.9 (38.7)	2.2 (2.0)	5.5 (N) (6.6)		0.1
$[FeCp(CO)_2NCBPh_3]$	Yellow	70.0 (70.1)	4.5 (4.5)	3.2 (N) (3.1)		0.7
$[RuCp(PPh_3)_2CN]$	Yellow	70.6 (70.2)	5.0 (4.9)	2.0 (N) (2.0)		0.3

[a] Abbreviations: Me, CH_3; Ph, C_6H_5; Cp, η-C_5H_5. [b] For ca 10^{-3} *M* solutions in acetone.

TABLE 2

IR AND NMR SPECTROSCOPIC DATA

Compound	IR data (cm^{-1})		NMR data (τ, ppm)[a]	
	C—O stretching frequencies	Other modes	C_5H_5 resonances	Other resonances
$[RuCp(CO)_2(Me_2CO)]SbF_6$	2070 s, 2021 s[b]			
$[FeCp(CO)_2(Me_2CO)]SbF_6$	2078 s, 2031 s[b]			
$[RuCp(PPh_3)_2(CO)]BPh_4$	1981[c]		4.73[c]	
$[RuCp(CO)_3]BPh_4$	2119 ms, 2064 s(br)[d]			
$[RuCp(CO)_2Ph]$	2029 s, 1963 s[c]		4.67[f]	2.55; 3.02[f,g] (phenyl)
$[Ru(MeCp)(PPh_3)_2Cl]$			6.02 (b); 6.68 (b)[f]	
$[RuCpBPh_4]$		1481 m, 1442 m, 1430 m, 1415 m, 1393 mw[d]	5.24[f]	3.78; 4.39[f] (bonded phenyl)
$[Ru(MeCp)BPh_4]$		1480 m, 1451 m(sh), 1442 m, 1428 m, 1390 mw[d]	5.28; 5.39[f]	3.88; 4.49[f] (bonded phenyl)
$[RuCp(CO)_2NCBPh_3]$	2080 s, 2036 s[c]	2203[c] (ν(C—N))	4.08[e]	
$[FeCp(CO)_2NCBPh_3]$	2079 s, 2039 s[c]	2203[c] (ν(C—N))	4.41[e]	
$[RuCp(PPh_3)_2CNBPh_3]$		2134[c] (ν(C—N))	5.49[f]	
$[RuCp(CO)_2CN]$	2061 s, 2014 s[c]	2126[c] (ν(C—N))	4.50[f]	
$[RuCp(PPh_3)_2CN]$		2083[c] (ν(C—N))	5.61[f]	
$NaBPh_4$		1478 m, 1428 m[d]		

[a] TMS reference; measured at 38°C. [b] Measured in acetone. [c] Measured in CH_2Cl_2. [d] Measured as nujol mull. [e] Measured in CD_3COCD_3. [f] Measured in $CDCl_3$. [g] Centres of broad complex multiplets.

(iii). $[Ru(\eta\text{-}C_5H_5)(CO)_2C_6H_5]$. A solution of $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$ (0.50 g, 1.9 mmol) and $NaB(C_6H_5)_4$ (0.99 g, 2.9 mmol) in methanol (50 ml) was refluxed for 10 h. The solvent was removed under reduced pressure and the residue extracted with benzene. The extract was filtered through a short alumina column (10 cm). Removal of the solvent under reduced pressure afforded $[Ru(\eta\text{-}C_5H_5)(CO)_2C_6H_5]$ as an orange oil. Yield 50%.

(iv). $[Ru(\eta\text{-}CH_3C_5H_4)\{P(C_6H_5)_3\}_2Cl]$. A solution of $[Ru\{P(C_6H_5)_3\}_3Cl_2]$ (2.0 g, 2.1 mmol) and 5.0 ml of freshly distilled methylcyclopentadiene in benzene (150 ml) was stirred for 2 days. The solvent was removed under reduced pressure, the residue extracted with a minimum of benzene and the extract transferred to an alumina column. Elution with chloroform produced a yellow band which was collected. The product, isolated from the eluate, was crystallized from chloroform/petroleum ether. Yield 60%.

(v). $[Ru(\eta\text{-}RC_5H_4)\{\eta\text{-}C_6H_5B(C_6H_5)_3\}]$, $(R = H \text{ or } CH_3)$. A solution of $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ (0.50 g, 0.69 mmol) or $[Ru(\eta\text{-}CH_3C_5H_4)\{P(C_6H_5)_3\}_2Cl]$ (0.51 g, 0.69 mmol) and $NaB(C_6H_5)_4$ (0.48 g, 1.4 mmol) in methanol (500 ml) was refluxed for 14 h. The solution was filtered, concentrated to 400 ml and allowed to stand. The brown crystals which separated from solution over a period of 24 h were isolated and washed with methanol and petroleum ether. Yields: $[Ru(\eta\text{-}C_5H_5)\{\eta\text{-}C_6H_5B(C_6H_5)_3\}]$, 20%; $[Ru(\eta\text{-}CH_3C_5H_4)\{\eta\text{-}C_6H_5B(C_6H_5)_3\}]$, 10%.

(vi). $[Ru(\eta\text{-}C_5H_5)(CO)_2NCB(C_6H_5)_3]$ *and* $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2CNB(C_6H_5)_3]$. A solution of $AgClO_4$ (0.143 g, 0.69 mmol) in acetone (20 ml) was added dropwise to a stirred solution of $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$ (0.18 g, 0.69 mmol) or $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ (0.50 g, 0.69 mmol) in acetone (40 ml). A white precipitate of AgCl separated. The solution was filtered and added dropwise to a stirred solution of $NaB(C_6H_5)_3CN$ (0.41 g, 1.40 mmol) in acetone (40 ml). The solvent was removed from the resultant reaction mixture under reduced pressure and the residue extracted with dichloromethane. The extract was filtered and evaporated to dryness. The products were crystallised from dichloromethane/petroleum ether. Yields: $[Ru(\eta\text{-}C_5H_5)(CO)_2NCB(C_6H_5)_3]$, 55%; $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2CNB(C_6H_5)_3]$, 30%.

(vii). $[Fe(\eta\text{-}C_5H_5)(CO)_2NCB(C_6H_5)_3]$. A solution of $AgSbF_6$ (1.18 g, 3.44 mmol) in acetone (20 ml) was added dropwise to a stirred solution of $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ (0.61 g, 1.72 mmol) in acetone (100 ml) and the solution stirred for a further 5 min. The solution was filtered and the filtrate added dropwise to a stirred solution of $NaB(C_6H_5)_3CN$ (1.11 g, 3.81 mmol) in acetone (50 ml). Stirring was continued for a further 30 min. The solvent was removed under reduced pressure and the residue extracted with dichloromethane. The extract was filtered, the filtrate concentrated and the product allowed to crystallise. Yield: 60%.

(viii). $[Ru(\eta\text{-}C_5H_5)L_2CN]$, $(L = CO \text{ or } P(C_6H_5)_3)$. A solution of $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$ (0.18 g, 0.69 mmol) or $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2Cl]$ (0.50 g, 0.69 mmol) and KCN (0.09 g, 1.40 mmol) in methanol (60 ml) was refluxed for 2 h. The solvent was removed under reduced pressure and the residue extracted with benzene. The extract was filtered and the product isolated from the filtrate was crystallised from dichloromethane/petroleum ether. Yields: $[Ru(\eta\text{-}C_5H_5)(CO)_2CN]$, 60%; $[Ru(\eta\text{-}C_5H_5)\{P(C_6H_5)_3\}_2CN]$, 45%.

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