Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTIONS OF π-BENZENERUTHENIUM(II) COMPLEXES WITH ALKYLATING REAGENTS

R. A. ZELONKA and M. C. BAIRD
Department of Chemistry, Queen's University, Kingston, Ontario (Canada)

(Received May 8th, 1972)

SUMMARY

The compounds $(\pi\text{-}C_6H_6)Ru(R)Cl(PPh_3)$ ($R = CH_3$, C_6H_5), $(\pi\text{-}C_6H_6)RuCl(\pi\text{-}C_3H_5)$ and $[(\pi\text{-}C_6H_6)Ru(\pi\text{-}C_5H_5)]Cl$ are described. The ^{31}P NMR spectra of a series of tertiary phosphine complexes of the π-benzeneruthenium system are also reported.

INTRODUCTION

Since the discovery of ferrocene, the aromatic π-cyclopentadienyl ligand has been shown to stabilize an extremely wide variety of transition metal complexes[1]. In contrast, although many of the isoelectronic complexes of benzene and benzene derivatives have long been known[2], the diversity which characterizes π-cyclopentadienyl complexes has seemingly been absent in the chemistry of π-arene systems.

Recently, however, a number of reports have suggested that a great deal of chemistry is to be associated with the chemistry of π-arene complexes of for instance, iron[3], manganese[4] and molybdenum[5]. In addition, π-arene complexes are interesting as possible intermediates in the platinum(II)-catalyzed H–D exchange of aromatics[6,7].

We have recently shown[7,8] that the $(\pi\text{-}C_6H_6)Ru^{II}$ moiety forms a variety of stable complexes in which the ruthenium generally coordinates three other ligands. The chloride ions in the dimeric complex, $[(\pi\text{-}C_6H_6)RuCl_2]_2$, are readily substituted by a number of nucleophiles in water, dimethylsulphoxide (DMSO) and acetonitrile (MeCN), while the coordinated benzene is attacked by cyanide and hydride ions in DMSO to yield cyclohexadienyl and 1,3-cyclohexadiene complexes, respectively. We now report compounds in which the chlorine is substituted by alkyl and aryl groups, and also the ^{31}P NMR spectra of tertiary phosphine complexes of the type $(\pi\text{-}C_6H_6)RuXX'(PR_3)$ ($X,X' = Cl$, Br, I, SCN, CH_3, C_6H_5).

EXPERIMENTAL

The complex, $[(\pi\text{-}C_6H_6)RuCl_2]_2$, was prepared from $RuCl_3 \cdot 3\,H_2O$ and 1,3-cyclohexadiene in aqueous ethanol[7]. The organomercury and organotin compounds were prepared using standard procedures[9,10], while thallium cyclopentadienide was prepared by the method of Fischer[11].

$(\pi\text{-}C_6H_6)Ru(CH_3)Cl(PPh_3)$

Dimethylmercury (0.8 ml) was added to a suspension of $[(\pi\text{-}C_6H_6)RuCl_2]_2$ (0.2 g) in 20 ml acetonitrile and the mixture was stirred under nitrogen for 1 h. As the reaction proceeded, the suspension slowly dissolved. After 1 h triphenylphosphine (0.4 g) was added, the reaction was stirred for a further 20 min, and the solution was eluted through an activated alumina column with acetonitrile. Two coloured fractions were collected, the first (yellow) containing the product; the second (orange) containing $(\pi\text{-}C_6H_6)RuCl_2(PPh_3)$[7]. The solvent was removed from the former *in vacuo* at room temperature, leaving an oil which solidified on the addition of 5 ml of ethyl ether. The product was recrystallized from acetonitrile/ether to give orange-yellow crystals in 63% yield. The complex can also be prepared by using tetramethyltin or trimethyltin chloride in place of dimethylmercury. It is soluble in polar solvents such as chloroform and acetonitrile, but insoluble in ether and hexane.

Analytical data are shown in Table 1, ^{1}H NMR data in Table 2.

TABLE 1
ANALYTICAL DATA

Compound	*M.p.*[a] (°C)	*Found*			*Calcd.*		
		C	*H*	*Mol.wt.* (*CHCl*$_3$)	*C*	*H*	*Mol.wt.*
$(\pi\text{-}C_6H_6)Ru(CH_3)Cl(PPh_3)$	139	60.83	4.77	511	61.04	4.92	492
$(\pi\text{-}C_6H_6)Ru(Ph)Cl(PPh_3)$	150	65.20	4.78	568	65.04	4.73	554
$(\pi\text{-}C_6H_6)RuCl(\pi\text{-}C_3H_5)$	176	42.43	4.24	261	42.27	4.34	256
$[(\pi\text{-}C_6H_6)Ru(\pi\text{-}C_5H_5)]Cl$[b]	161	47.30	4.05		47.25	3.97	

[a] Compounds decompose without melting. [b] 1/1 electrolyte in MeCN ($\Lambda_M = 107$ ohm$^{-1}\cdot$cm$^2\cdot$mol^{-1}).

TABLE 2
^{1}HNMR DATA ($CDCl_3$)

Compounds	$\pi\text{-}C_6H_6$ (τ)[a]	*Other resonances* (τ)[a]
$(\pi\text{-}C_6H_6)Ru(Me)Cl(PPh_3)$	4.88 (d), J(PH) 0.6 Hz	Me (d) 8.83, J(PH) 8.4 Hz PPh_3 (m), 2.62
$(\pi\text{-}C_6H_6)Ru(Ph)Cl(PPh_3)$	4.66 (d), J(PH) 0.5 Hz	Ph (m) 4.23, PPh_3 (m) 2.73
$[(\pi\text{-}C_6H_6)Ru(\pi\text{-}C_5H_5)]Cl$[b]	3.88 (s)	C_5H_5 (s) 4.65
$(\pi\text{-}C_6H_6)RuCl(\pi\text{-}C_3H_5)$	4.47 (s)	C_3H_5[c]

[a] s=singlet, d=doublet, m=multiplet. [b] In acetonitrile. [c] See discussion.

$(\pi\text{-}C_6H_6)Ru(Ph)Cl(PPh_3)$

This compound was prepared as above by reacting $[\pi\text{-}C_6H_6)RuCl_2]_2$ and diphenylmercury in acetonitrile for 3 h at room temperature. It was obtained as yellow-brown crystals in 51% yield, and has much the same solubility properties as the methyl compound.

Similar reactions with diethylmercury resulted in total decomposition, possibly via an ethylruthenium complex. No reactions were observed with dibenzylmercury or tetrabenzyltin, or Grignard and alkyllithium reagents, even at elevated temperatures.

$(\pi\text{-}C_6H_6)RuCl(\pi\text{-}C_3H_5)$

Tetraallyltin (1.5 ml) was added to a solution of $[(\pi\text{-}C_6H_6)RuCl_2]_2$ in 50 ml of acetonitrile. The reaction was stirred under nitrogen at room temperature for 1 h, and then eluted through an alumina column with acetonitrile. The solvent was removed *in vacuo*, the residue was washed with ether to remove any unreacted tetraallyltin and recrystallized from acetonitrile/ether to give yellow platelets of the product in 72% yield. The compound is soluble in polar organic solvents.

No reaction was observed with tetramethallyltin.

$[(\pi\text{-}C_6H_6)Ru(\pi\text{-}C_5H_5)]Cl$

Thallium cyclopentadienide (0.21 g) was added to a solution of $[(\pi\text{-}C_6H_6)RuCl_2]_2$ (0.2 g) in 70 ml acetonitrile to give, after 45 min, a precipitate of thallium chloride. The reaction mixture was filtered and the solvent was removed *in vacuo* at room temperature. The resulting residue was recrystallized from acetonitrile/ether to give the pale brown product in 83% yield.

Physical measurements

IR spectra were obtained on Beckman IR-10 and Perkin–Elmer 180 IR spectrometers, mass spectra on a Jeolco JMS-OISC high resolution mass spectrometer and NMR spectra on a Bruker HX60 spectrometer with internal TMS lock. Melting points were determined on a Gallenkamp melting point apparatus and are corrected. Molecular weights were determined in chloroform at 37° using a Hewlett Packard 302B vapour pressure osmometer, while conductivity measurements were carried out using a Philips PR9501 conductivity bridge.

The 220 MHz spectrum was run at the Canadian 220 MHz NMR Centre, Ontario Research Foundation, Sheridan Park, Ontario.

DISCUSSION

Although Grignard and alkyllithium reagents would be expected to displace one or more of the very labile[7] chloride ions from $[(\pi\text{-}C_6H_6)RuCl_2]_2$, no reactions were observed in solvents such as ether or tetrahydrofuran. The starting material was invariably recovered in good yield, and it seems likely that it is too insoluble to be reactive. Unfortunately the monomeric complexes $(\pi\text{-}C_6H_6)RuCl_2(PR_3)$ were also quite unreactive, although they are suitably soluble in tetrahydrofuran. Possibly these six-coordinate low-spin d^6 systems are kinetically inert, and we find that substitution of chloride by iodide also does not occur.

We do find, however, that $[(\pi\text{-}C_6H_6)RuCl_2]_2$ in acetonitrile [present as the monomer, $(\pi\text{-}C_6H_6)RuCl_2(NCMe)$[7]] reacts readily with electrophilic alkylating reagents such as dimethyl- and diphenylmercury, reactions which can be monitored by NMR. Thus addition of a ten-fold molar excess of dimethylmercury to a solution of $(\pi\text{-}C_6H_6)RuCl_2(MeCN)$ in acetonitrile results in a decrease in intensity of the arene resonance of the latter at τ 4.30 and the appearance of a new arene resonance at τ 4.78. New methyl resonances at τ 9.10 and τ 8.90, attributable to methylmercuric chloride and a methylruthenium species, respectively, also appear. Similarly, the reaction with diphenylmercury results in a new resonance at τ 4.68, attributable to a phenylruthenium compound. Addition of triphenylphosphine to these solutions yields the monomeric complexes (π-C_6H_6)Ru(Me)Cl(PPh_3) and (π-C_6H_6)Ru(Ph)Cl(PPh_3), respectively, and thus the species in solution are presumably (π-C_6H_6)Ru(Me)Cl(MeCN) and (π-C_6H_6)Ru(Ph)Cl(MeCN).

Similar reactions of chloroplatinum(II) complexes have been shown to yield methyl- and phenylplatinum complexes[12], *i.e.*:

$$cis\text{-}PtCl_2(PMe_2Ph)_2 + Ph_2Hg \rightleftarrows trans\text{-}Pt(Ph)Cl(PMe_2Ph)_2 + PhHgCl$$
$$cis\text{-}PtCl_2(PBu_3)_2 + Me_2Hg \rightleftarrows trans\text{-}Pt(Me)Cl(PBu_3)_2 + MeHgCl$$

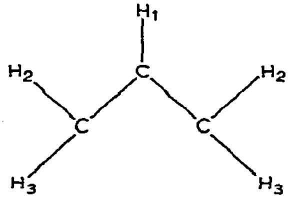
However, whereas an oxidative–addition mechanism could not be excluded in the platinum series[12], such a mechanism seems very unlikely for the ruthenium alkylations. Instead a bimolecular electrophilic substitution mechanism, as has already been well-established for many other reactions of alkylmercuruals[13], seems much more probable.

The IR spectra of the methyl and phenyl compounds had bands at 274 cm^{-1} and 284 cm^{-1}, respectively, which may be assigned to ν(RuCl). A variety of arene–ruthenium compounds exhibit terminal ν(RuCl) in this region[7]. The IR spectrum of the methyl compound also exhibits ν(CH) at 2888 cm^{-1} while the phenyl compound has bands at 1465 cm^{-1} and 1452 cm^{-1} which are not attributable to either the benzene ring or the triphenylphosphine. In addition, although no parent ion cluster was observed in the mass spectrum of the methyl complex, lines were observed due to the species CH_x^+ ($x = 1$–4). These lines are not observed in the mass spectra of any other ruthenium π-arene complexes[7].

The reaction with diethylmercury appears to give an unstable ethylruthenium complex, but only dark decomposition products were obtained. The only other ethylruthenium complex which we are aware of, $C_2H_5RuCl(PPh_3)_3$[14], is also unstable, spontaneously losing ethylene at one atmosphere pressure to yield the corresponding hydride. No reaction with dibenzylmercury was observed. As there seems to be no reason why a benzylruthenium complex should be unstable, and indeed as no decomposition was observed, but only (π-C_6H_6)$RuCl_2$(PPh_3) was isolated, it seems likely that the anticipated bimolecular reaction was somehow hindered sterically.

The compound [(π-C_6H_6)Ru(π-C_5H_5)]Cl is a 1/1 electrolyte in acetonitrile and is presumably a sandwich complex similar to the isoelectronic ruthenocene[15]. The IR spectrum is consistent with the presence of a π-cyclopentadienyl group[16], with bands at 1411, 816, 714 and 396 cm^{-1}. There is no band in the ruthenium–chlorine stretching region.

The IR spectrum of the complex (π-C_6H_6)RuCl(π-C_3H_5) has a terminal ν(RuCl) at 265 cm^{-1} as well as bands at 2910, 2870, 1201, 992, 969, 944, 910, 784 and 582 cm^{-1}, characteristic of a π-allyl group[17], (I). The NMR spectrum shows a single benzene



(I)

resonance, suggesting the presence of only one isomer, but the allyl resonances at approximately τ 5.8 and τ 7.66 (relative intensities 3/2) are too complex at 60 MHz to analyze satisfactorily.

The 220 MHz NMR spectrum in the allyl region is shown in Fig. 1. It is clearly not a simple A_2M_2X-type[18] spectrum, but rather an AB_2X_2-type[19]; the only significant changes on going from 60 MHz to 220 MHz were expansion of the multiplet at ~τ 5.8 and resolution of the doublet structure (~0.5 Hz) of the main peak of that multiplet. By analogy with other π-allyl systems[18], the resonance centred at τ 7.66 may be assigned to H_3, the 10.6 Hz separation corresponding to the *trans* spin–spin coupling with H_1. The resonance is clearly very complex, however, although not all of the expected[19] sixteen lines could be resolved.

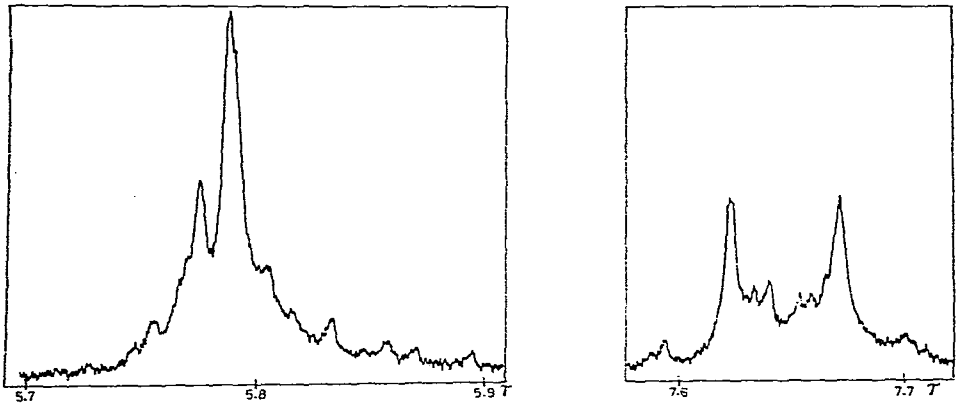


Fig. 1. 220 MHz NMR spectrum in the allyl region of $(\pi\text{-}C_6H_6)RuCl(\pi\text{-}C_3H_5)$.

The strong doublet at τ 5.78 can be assigned to H_2, coupled weakly (*J* 0.5 Hz) with H_1, while the resonance of H_1 would theoretically be a sixteen line multiplet. The very small coupling between H_1 and H_2 is surprising, but a similar observation has been made for one isomer of $(\pi\text{-}C_3H_5)_2Pt$[20]. The near coincidence of the resonances of H_1 and H_2 is also unusual, but a variety of chemical shifts have been reported for other π-allylruthenium(II) complexes[21,22], while coincidence of these two resonances has been reported for $(\pi\text{-}C_5H_5)Pt(\pi\text{-}C_3H_5)$[23].

No variation in the NMR spectrum in the temperature range −65° to +50° was found to occur.

Table 3 lists the ^{31}P chemical shifts of a series of benzeneruthenium complexes[7]. The presence of the three resonances in the spectrum of the thiocyanate complex is a result of coordination isomerism of the ligand[7]; in the case of the diphosphine complex, the chemical shift of the uncoordinated phosphorus[7] is quite clearly to higher field than the chemical shift of the free ligand.

In the present state of the theory of ^{31}P chemical shifts, very little can be said of the data in Table 3. As is generally observed[24], coordination of a tertiary phosphine results in a downfield shift of the ^{31}P resonance, while coordination of a phosphite results in an upfield shift. Also, as has been reported for complexes of platinum[24] and rhodium[25], the chemical shifts decrease in the order $I^- > Br^- > Cl^-$, and on substituting Cl^- by methyl.

TABLE 3

^{31}P CHEMICAL SHIFTS[a]

Complex	*δ (Complex)*	*δ (Free ligand)*[b]	*Δδ*
$(\pi\text{-}C_6H_6)RuCl_2(PPh_3)$	−27.2	+7.0	−34.2
$(\pi\text{-}C_6H_6)RuBr_2(PPh_3)$	−23.3	+7.0	−30.3
$(\pi\text{-}C_6H_6)RuI_2(PPh_3)$	−21.5	+7.0	−28.5
$(\pi\text{-}C_6H_6)Ru(NCS)_2(PPh_3)$	−29.7, −31.9, −33.1	+7.0	−36.7, −38.9, −40.1
$(\pi\text{-}C_6H_6)Ru(Ph)Cl(PPh_3)$	−38.0	+7.0	−45.0
$(\pi\text{-}C_6H_6)Ru(Me)Cl(PPh_3)$	−40.7	+7.0	−47.7
$(\pi\text{-}C_6H_6)RuCl_2(PMePh_2)$	−22.2	+27.7	−49.9
$(\pi\text{-}C_6H_6)RuCl_2(PMe_2Ph)$	−19.7	+47.6	−67.3
$(\pi\text{-}C_6H_6)RuCl_2(PBu_3)$	−21.1	+32.7	−53.8
$(\pi\text{-}C_6H_6)RuCl_2(PEt_3)$	−27.7	+20.1	−47.8
$(\pi\text{-}C_6H_6)RuCl_2(Ph_2PCH_2PPh_2)$	−25.9, +28.1	+22.6[c]	−48.5, +5.5
$(\pi\text{-}C_6H_6)RuCl_2[P(OMe)_3]$	−116.6	−141.0	+24.4
$(\pi\text{-}C_6H_6)RuCl_2[P(OEt)_3]$	−112.2	−138[d]	+25.8
$(\pi\text{-}C_6H_6)RuCl_2[P(OPh)_3]$	−108.3	−128[d]	+19.7

[a] Ppm relative to 85% H_3PO_4, downfield shifts negative. [b] Ref. 26 unless otherwise stated. [c] This work. [d] Ref. 24.

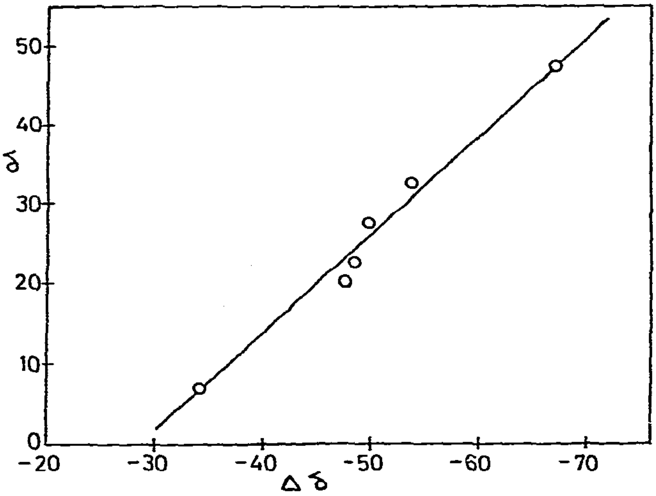


Fig. 2. Plot of ^{31}P chemical shifts of the free ligands *vs.* the change in the ^{31}P chemical shift on coordination.

Interestingly, a plot of δ (free ligand) *vs.* Δδ for the six dichloro complexes gives a reasonably good straight line (Fig. 2), as has been reported for an extensive series of rhodium complexes[26]. We have no explanation at present for this relationship.

ACKNOWLEDGEMENTS

We thank the National Research Council of Canada for financial assistance and the International Nickel Company of Canada for a scholarship to R.A.Z.

REFERENCES

1 R. B. King, *Transition-Metal Organometallic Chemistry*, Academic Press, New York and London, 1969.
2 H. Zeiss, P. J. Wheatley and H. J. S. Winkley, *Benzenoid–Metal Complexes*, Ronald Press, New York, 1966.
3 I. U. Khand, P. L. Pauson and W. E. Watts, *J. Chem. Soc. C*, (1969) 2024.
4 P. J. C. Walker and R. J. Mawby, *Inorg. Chem.*, 10 (1971) 404.
5 M. L. H. Green, J. Knight, L. C. Mitchard, G. G. Roberts and W. E. Silverthorn, *Chem. Commun.*, (1971) 1619.
6 J. L. Garnett, *Catal. Rev.*, 5 (1971) 229.
7 R. A. Zelonka and M. C. Baird, *Can. J. Chem.*, in press.
8 R. A. Zelonka and M. C. Baird, *J. Organometal. Chem.*, 35 (1972) C43.
9 L. G. Makarova and A. N. Nesmeyanov, *Methods of Elemento-Organic Chemistry*, Vol. 4, North Holland Publishing Company, 1967.
10 M. Dub, *Organometallic Chemistry*, Vol. 2, Springer, New York, 1967.
11 E. O. Fischer, *Angew. Chem.*, 69 (1957) 207.
12 R. J. Cross and R. Wardle, *J. Chem. Soc. A*, (1970) 840.
13 F. R. Jensen and B. Rickborn, *Electrophilic Substitutions of Organomercurials*, McGraw-Hill, New York, 1968.
14 P. S. Hallman, B. R. McGarvey and G. Wilkinson, *J. Chem. Soc. A*, (1968) 3143.
15 G. L. Hardgrove and D. H. Templeton, *Acta Crystallogr.*, 12 (1959) 28.
16 H. P. Fritz, *Advan. Organometal. Chem.*, 1 (1964) 239.
17 E. O. Fischer and H. Werner, *Metal π-Complexes*, Elsevier, New York, 1966, p. 180.
18 G. E. Coates, M. L. H. Green and K. Wade, *Organometallic Compounds*, Vol. 2, Methuen, London, 1968, p. 47.
19 J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Vol. 1, Pergamon, London, 1965.
20 S. O'Brien, *J. Chem. Soc. A*, (1971) 9.
21 G. Sbrana, G. Braca, F. Piacenti and P. Pino, *J. Organometal. Chem.*, 13 (1968) 240.
22 J. Powell and B. L. Shaw, *J. Chem. Soc. A*, (1968) 159.
23 B. L. Shaw and N. Sheppard, *Chem. Ind.*, (1961) 517.
24 J. F. Nixon and A. Pidcock, *Ann. Rev. NMR Spectrosc.*, 2 (1969) 345.
25 T. H. Brown and P. J. Green, *J. Amer. Chem. Soc.*, 92 (1970) 2359.
26 B. E. Mann, C. Masters and B. L. Shaw, *J. Chem. Soc. A*, (1971) 1104.