View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1972. Downloaded by Freie Universitaet Berlin on 22/10/2014 10:24:05.

Reactions of Metal Carbonyl Derivatives. Part XII.[1] The Synthesis of Some Cationic Bridged Halogeno-derivatives of Ruthenium and their Reactivity towards Certain Nucleophiles [2]

By **R. J. Haines,*** Research and Process Development Department, South African Iron and Steel Industrial Corporation Limited, P.O. Box 450, Pretoria, Republic of South Africa

A. L. du Preez, Department of Inorganic and Analytical Chemistry, University of Pretoria, Pretoria, Republic of South Africa

A study of the halogenation of $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2]$ has revealed that while neutral $[Ru(\pi\text{-}C_5H_5)(CO)_2X]$ (X = Cl, Br, or I) is formed in solvents such as dichloromethane and chloroform, salts of the cation $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2X]^+$ separate from those reactions performed in benzene or toluene and in the presence of large counterions such as PF_6^-. It is shown that the cationic species $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2X]^+$ is readily susceptible to attack by halides and pseudo-halides to yield products according to the scheme

$$[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2X]^+ + Y^- \longrightarrow [Ru(\pi\text{-}C_5H_5)(CO)_2X] + [Ru(\pi\text{-}C_5H_5)(CO)_2Y]$$

The mechanism of formation of $[Ru(\pi\text{-}C_5H_5)(CO)_2X]$ from $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2]$ is discussed in terms of this scheme. The cations $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2X]^+$ (X = Cl and Br) also react readily with the anion BPh_4^-. Fission of a boron–carbon bond in BPh_4^- and transfer of a phenyl group to a ruthenium atom is effected, to yield $[Ru(\pi\text{-}C_5H_5)(CO)_2Ph]$ and $[Ru(\pi\text{-}C_5H_5)(CO)_2X]$. The cyanide and not a phenyl group is extracted from BPh_3CN^- on reaction with $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2X]^+$ (X = Cl or Br) in acetone under reflux to give $[Ru(\pi\text{-}C_5H_5)(CO)_2CN]$ and $[Ru(\pi\text{-}C_5H_5)(CO)_2X]$; the zwitterionic species $[Ru^+(\pi\text{-}C_5H_5)(CO)_2NCB^-Ph_3]$ is shown to be an intermediate in the reaction.

THE first reported synthesis of the bridged halogeno-derivatives $[\{Fe(\pi\text{-}C_5H_5)(CO)_2\}_2X]$Anion (X = Cl, Br, or I; Anion = BF_4 or PF_6) involved the treatment of the neutral iron complexes $[Fe(\pi\text{-}C_5H_5)(CO)_2X]$ with strong Lewis acids such as $AlBr_3$ and $BF_3\cdot OEt_2$.[3-5] These cationic species, $[\{Fe(\pi\text{-}C_5H_5)(CO)_2\}_2X]^+$, were shown to be very susceptible to nucleophilic attack. For instance the reactions of $[\{Fe(\pi\text{-}C_5H_5)(CO)_2\}_2Br]PF_6$ with C_5H_5N, C_6H_5CN, and $C_6H_5NH_2$ in solution at room temperature readily afforded $[Fe(\pi\text{-}C_5H_5)(CO)_2C_5H_5N]PF_6$, $[Fe(\pi\text{-}C_5H_5)(CO)_2C_6H_5CN]PF_6$, and $[Fe(\pi\text{-}C_5H_5)(CO)_2C_6H_5NH_2]PF_6$ respectively, according to the scheme: [4]

$$[\{Fe(\pi\text{-}C_5H_5)(CO)_2\}_2X]^+ + \text{Ligand} \longrightarrow [Fe(\pi\text{-}C_5H_5)(CO)_2\text{Ligand}]^+ + [Fe(\pi\text{-}C_5H_5)(CO)_2X] \quad (X = \text{halogen})$$

It has subsequently been established that the bridged species $[\{Fe(\pi\text{-}C_5H_5)(CO)_2\}_2X]^+$ (X = Cl, Br, and I) are intermediates in the halogenation of $[\{Fe(\pi\text{-}C_5H_5)(CO)_2\}_2]$

---

[1] Part XI, J. A. de Beer and R. J. Haines, *J. Organometallic Chem.*, in the press.

[2] Preliminary communication, R. J. Haines and A. L. du Preez, *J. Amer. Chem. Soc.*, 1971, **93**, 2820.

[3] E. O. Fischer and E. Moser, *Z. Naturforsch.*, 1965, **20*b***, 184.

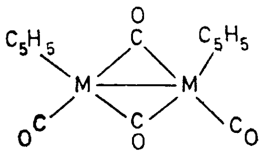
[4] E. O. Fischer and E. Moser, *J. Organometallic Chem.*, 1965, **3**, 16.

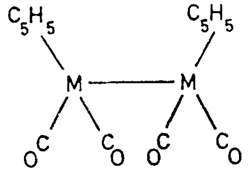
[5] E. O. Fischer and E. Moser, *Z. anorg. Chem.*, 1966, **342**, 156.

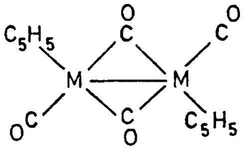
View Article Online

Published on 01 January 1972. Downloaded by Freie Universitaet Berlin on 22/10/2014 10:24:05.

to give $[Fe(\pi\text{-}C_5H_5)(CO)_2X]$ and that under the appropriate experimental conditions they may be isolated from the reaction mixtures.[6-8] The mechanism proposed for the formation of $[Fe(\pi\text{-}C_5H_5)(CO)_2X]$ from $[\{Fe(\pi\text{-}C_5H_5)(CO)_2\}_2]$ involves the bridged carbonyl isomers [9-13] of the latter (I), and (III), as precursors.[6,8] The non-bridged isomer (II) was eliminated as a precursor for this reaction on the basis of certain experimental evidence.[6,8] The relative amount of this isomer in solution is very small however (<1%) [14] and this might account for its inability to influence the overall reaction path. In contrast more than half of the ruthenium derivative $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2]$ is present in solution as the non-bridged isomer.[14]


(I)


(II)


(III)

M = Fe or Ru

A study of the halogenation of $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2]$ has thus been initiated to establish whether, as a result of the non-bridged isomer being present in solution in considerable quantity, the course of this reaction is different to that previously found for $[\{Fe(\pi\text{-}C_5H_5)(CO)_2\}_2]$. The results of this study and those relating to a study of the reactions of $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2X]^+$ (X = Cl, Br, or I) with certain nucleophiles, are reported here.

RESULTS AND DISCUSSION

Treatment of $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2]$ with the halogens X_2 (X = Cl, Br, and I) in dichloromethane or chloroform at room temperature was found to afford the neutral halogeno-derivatives $[Ru(\pi\text{-}C_5H_5)(CO)_2X]$ as the sole products. This observation contrasts with the previous finding that the cationic species $[Fe(\pi\text{-}C_5H_5)(CO)_3]^+$, as well as $[Fe(\pi\text{-}C_5H_5)(CO)_2X]$, is formed in the corresponding bromination and chlorination reactions involving $[\{Fe(\pi\text{-}C_5H_5)(CO)_2\}_2]$.[6,8] Ionic products were found to be formed in high yield when toluene or benzene was utilised as solvent in the reactions of $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2]$ with halogens. The cations of these species, which were isolated as the yellow tetraphenylborate or hexafluorophosphate salts by performing these latter reactions at room temperature in the presence of $NaBPh_4$ or NH_4PF_6 and enough methanol to ensure dissolution of the latter, were characterised as $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2X]^+$ (X = Cl, Br, or I). Significantly if the reactions of $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2]$ with bromine and chlorine in toluene in the presence of NH_4PF_6 are performed at −78°, green and not yellow products as obtained in the room-temperature reactions discussed above, are observed to separate from solution. These derivatives revert rapidly to yellow $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2X]PF_6$ (X = Cl or Br) in solution and attempts to crystallise them were, as a consequence, unsuccessful. They were obtained in impure form by rapid precipitation from dichloromethane solutions at low temperatures. The latter analysed approximately for $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2X]PF_6$ (X = Cl or Br) and gave infrared spectra identical to those of yellow $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2X]PF_6$ (X = Cl or Br). It is thus suggested that these green derivatives are a second isomeric form of $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2X]PF_6$ (X = Cl or Br). Green tetraphenylborate products were also found to be formed in the chlorination and bromination reactions of $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2]$ in toluene at −78° in the presence of $NaBPh_4$ but they proved to be even more unstable than their hexafluorophosphate analogues. Green products were not detected in any of the reactions of $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2]$ with iodine in solution at −78° however.

The bridged halogeno-derivatives $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2X]$Anion (X = Cl, Br, or I; Anion = PF_6 or BPh_4), similar to their iron analogues, are very susceptible to nucleophilic attack and were found to react readily with the corresponding halide ions X^- to yield $[Ru(\pi\text{-}C_5H_5)(CO)_2X]$. This observation suggests that the cationic species $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2X]^+$ are intermediates in the formation of $[Ru(\pi\text{-}C_5H_5)(CO)_2X]$ by halogenation of $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2]$. Confirmation that they are indeed intermediates was achieved by monitoring a reaction of $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2]$ with iodine in dichloromethane at room temperature by means of infrared spectroscopy; CO stretching bands which correspond to the cation $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2I]^+$ were initially observed but these were found to decrease in intensity with increase in intensity of peaks corresponding to $[Ru(\pi\text{-}C_5H_5)(CO)_2I]$.

It is apparent from the above results that apart from their inability to yield $[Ru(\pi\text{-}C_5H_5)(CO)_3]^+$, the halogenation reactions of $[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2]$ are very similar to the corresponding reactions involving $[\{Fe(\pi\text{-}C_5H_5)(CO)_2\}_2]$.[6,8] A mechanism analogous to that previously

---

[6] R. J. Haines and A. L. du Preez, *J. Amer. Chem. Soc.*, 1969, **91**, 769.

[7] D. A. Brown, A. R. Manning, and D. J. Thornhill, *Chem. Comm.*, 1969, 338.

[8] R. J. Haines and A. L. du Preez, *J. Chem. Soc.* (*A*), 1970, 2341.

[9] F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, 1967, **6**, 15.

[10] R. D. Fischer, A. Vogler, and K. Noack, *J. Organometallic Chem.*, 1967, **7**, 135.

[11] A. R. Manning, *J. Chem. Soc.* (*A*), 1968, 1319.

[12] J. G. Bullitt, F. A. Cotton, and T. J. Marks, *J. Amer. Chem. Soc.*, 1970, **92**, 2155.

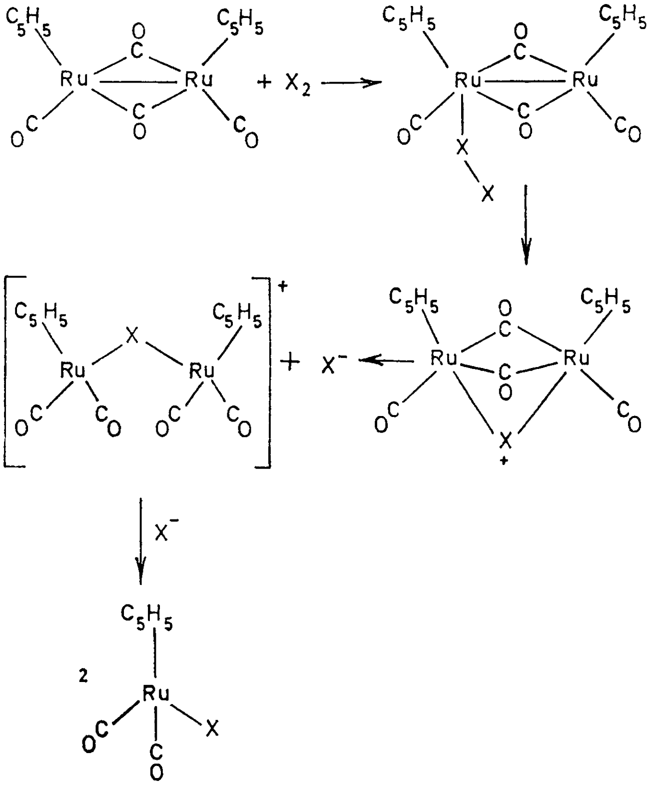
[13] P. McArdle and A. R. Manning, *J. Chem. Soc.* (*A*), 1970, 2128.

[14] K. Noack, *J. Organometallic Chem.*, 1967, **7**, 151.

View Article Online

Published on 01 January 1972. Downloaded by Freie Universitaet Berlin on 22/10/2014 10:24:05.

proposed for the formation of [Fe(π-C_5H_5)$(CO)_2X$] in the reactions of [{Fe(π-C_5H_5)$(CO)_2$}$_2$] with halogens,[6,8] is thus proposed for these halogenations (see Scheme 1).



Scheme 1

The non-bridged isomer of [{Ru(π-C_5H_5)$(CO)_2$}$_2$] was eliminated as a precursor for these reactions on the basis of the arguments used to eliminate the non-bridged isomer of [{Fe(π-C_5H_5)$(CO)_2$}$_2$] as a precursor for the corresponding reactions involving [{Fe(π-C_5H_5)$(CO)_2$}$_2$][6,8].

Table 1

Colours and conductivity and analytical data

Compound	Colour	Conductivities[a] (Ω^{-1} cm^2 mol^{-1})	Analyses (%) Found C	Found H	Found Others	Calculated C	Calculated H	Calculated Others
[{Ru(π-C_5H_5)$(CO)_2$}$_2$Cl]SbF_6	Yellow	133	23·3	1·5	4·9 (Cl); 16·1 (F)	23·5	1·4	5·0 (Cl); 15·9 (F)
[{Ru(π-C_5H_5)$(CO)_2$}$_2$Br]PF_6	Yellow	139	25·3	1·5	12·1 (Br); 4·5 (P)	25·1	1·5	11·9 (Br); 4·6 (P)
[{Ru(π-C_5H_5)$(CO)_2$}$_2$Br]BPh_4	Yellow	95	54·9	3·6	9·3 (Br)	54·1	3·6	9·5 (Br)
[{Ru(π-C_5H_5)$(CO)_2$}$_2$I]PF_6	Yellow	132	23·6	1·5	17·9 (I)	23·5	1·4	17·7 (I)
[{Ru(π-C_5H_5)$(CO)_2$}$_2$I]BPh_4	Yellow	94	51·4	3·4	14·4 (I)	51·3	3·4	14·3 (I)
[Ru(π-C_5H_5)$(CO)_2Cl$]	Yellow	0·1	32·8	2·1	13·7 (Cl)	32·6	2·0	13·8 (Cl)
[Ru(π-C_5H_5)$(CO)_2Br$]	Yellow	0·1	27·7	1·6	26·4 (Br)	27·8	1·7	26·5 (Br)
[Ru(π-C_5H_5)$(CO)_2I$]	Orange	0·1	24·0	1·4	36·4 (I)	24·1	1·4	36·3 (I)
[Ru(π-C_5H_5)$(CO)_2CN$]	White	0·1	38·9	2·2	5·5 (N)	38·7	2·0	5·6 (N)
[Ru(π-C_5H_5)$(CO)_2SCN$]	Yellow	0·1	34·2	1·8	5·1 (N)	34·3	1·8	5·0 (N)
[Ru(π-C_5H_5)$(CO)_2Ph$]	Orange	0·1	52·1	3·4	10·8 (O)	52·2	3·4	10·7 (O)
[Ru(π-C_5H_5)$(CO)_2NCBPh_3$]	White	0·1	63·6	4·1	2·9 (N); 2·1 (B)	63·7	4·1	2·9 (N); 2·2 (B)

[a] For *ca.* 10^{-3}M-solutions in acetone.

The yellow and the green isomers of [{Ru(π-C_5H_5)$(CO)_2$}$_2$X]PF_6 (X = Cl and Br) react readily with the pseudo-halides Y^- = SCN^- and CN^- in solution to yield products according to the scheme

$$[\{Ru(\pi\text{-}C_5H_5)(CO)_2\}_2X]^+ + Y^- \longrightarrow [Ru(\pi\text{-}C_5H_5)(CO)_2X] + [Ru(\pi\text{-}C_5H_5)(CO)_2Y]$$

The presence of a weak peak at 697 cm^{-1} and assigned to ν(C–S) in the infrared spectrum of [Ru(π-C_5H_5)$(CO)_2SCN$] is consistent with the SCN group in this derivative being bonded to the ruthenium through the sulphur atom.[15] [{Ru(π-C_5H_5)$(CO)_2$}$_2$X]$^+$ (X = Cl or Br) is also readily attacked by azide ions but the expected product [Ru(π-C_5H_5)$(CO)_2N_3$] could not be isolated in pure form.

Treatment of yellow or green [{Ru(π-C_5H_5)$(CO)_2$}$_2$X]-PF_6 (X = Cl or Br) with an excess of sodium tetraphenylborate in solution readily effected the fission of a boron–carbon bond in the BPh_4^- anion and the formation of products characterised by elemental analysis and i.r. and n.m.r. spectroscopy as [Ru(π-C_5H_5)$(CO)_2Ph$] and [Ru(π-C_5H_5)$(CO)_2X$]. This BPh_4^- attack accounts for the inability to obtain the yellow tetraphenylborate salts of [{Ru(π-C_5H_5)$(CO)_2$}$_2$X]$^+$ (X = Cl and Br) in pure form in high yield. Although mercury salts are known to cleave boron–carbon bonds, reactions involving the transfer of a phenyl group from boron to a transition-metal atom are not well documented. Isolated examples include the slow formation of *trans*-[Pt$(PEt_3)_2Ph_2$] from *cis*-[Pt$(PEt_3)_2Cl_2$] and $NaBPh_4$ in tetrahydrofuran under reflux[16] and the reaction of [Pt$(PMe_2Ph)_2$(MeOH)Me]$^+$ with $NaBPh_4$ in solution to give *trans*-[Pt$(PMe_2Ph)_2Ph_2$].[17] The decomposition of [Ni(π-C_5H_5)$(PPh_3)_2$]BPh_4 to [Ni(π-C_5H_5)(PPh_3)Ph] in refluxing tetrahydrofuran has also been proposed to involve the transfer of a phenyl group from the tetraphenylborate anion.[18]

The cyanide and not a phenyl group is extracted from BPh_3CN^- on reaction with [{Ru(π-C_5H_5)$(CO)_2$}$_2$X]$^+$ (X = Cl or Br) in acetone or tetrahydrofuran under reflux and the products [Ru(π-C_5H_5)$(CO)_2CN$] and

---

[15] T. E. Sloan and A. Wojcicki, *Inorg. Chem.*, 1968, **7**, 1268.

[16] H. C. Clark and K. R. Dixon, *J. Amer. Chem. Soc.*, 1969, **91**, 596.

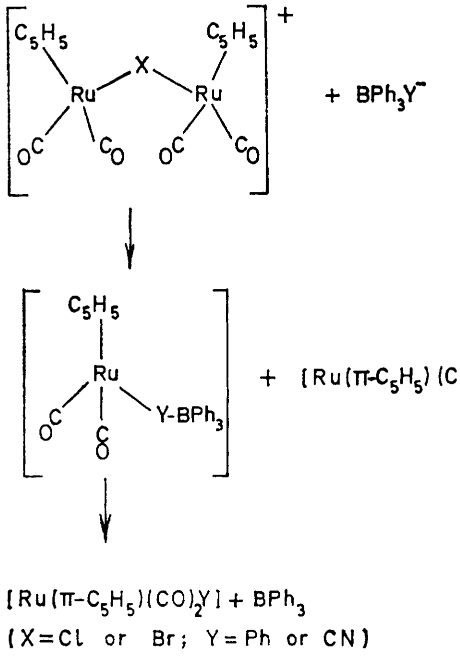
[17] H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, 1970, **9**, 1226.

[18] P. M. Treichel and R. L. Shubkin, *Inorg. Chim. Acta*, 1968, **2**, 485.

View Article Online

Published on 01 January 1972. Downloaded by Freie Universitaet Berlin on 22/10/2014 10:24:05.

$[Ru(\pi-C_5H_5)(CO)_2X]$ obtained. The corresponding room-temperature reaction did not afford $[Ru(\pi-C_5H_5)(CO)_2CN]$ but gave together with $[Ru(\pi-C_5H_5)(CO)_2X]$, a compound whose infrared spectrum exhibited peaks of frequency *ca.* 20 cm^{-1} higher than the corresponding bands in the spectrum of $[Ru(\pi-C_5H_5)(CO)_2CN]$. Attempts to separate this compound from $[Ru(\pi-C_5H_5)(CO)_2X]$ by means of column chromatography resulted in its decomposition to $[Ru(\pi-C_5H_5)(CO)_2CN]$. It was isolated in high yield from the reaction of BPh_3CN^- with $[Ru(\pi-C_5H_5)(CO)_2(Me_2CO)]^+$ however. The latter was synthesised by addition of Ag^+ ions to $[\{Ru(\pi-C_5H_5)(CO)_2\}_2]$ in acetone. The n.m.r. spectrum of this derivative was shown to contain as well as a sharp cyclopentadienyl resonance, peaks readily assigned to phenyl protons and of relative intensity 3 : 1 with respect to the former. Conductivity data were consistent with the compound being a non-electrolyte in acetone while the elemental analyses corresponded with the stoicheiometry $C_{26}H_{20}O_2NBRu$. On the basis of the above results it is apparent that the compound is the zwitterionic species $[Ru^+(\pi-C_5H_5)(CO)_2NCB^-Ph_3]$. The frequency of the C–N stretching mode observed in its infrared spectrum is very similar to the corresponding bands found in the spectra of derivatives containing the cyanotrihydridoboron anion as ligand.[19,20] It is thus proposed that the BPh_3CN^- anion is bonded to the ruthenium in $[Ru^+(\pi-C_5H_5)(CO)_2NCB^-Ph_3]$ through the nitrogen atom. $[Ru^+(\pi-C_5H_5)(CO)_2NCB^-Ph_3]$ decomposes to $[Ru(\pi-C_5H_5)(CO)_2CN]$ on heating in solution suggesting that it is an intermediate in the formation of the latter from $[\{Ru(\pi-C_5H_5)(CO)_2\}_2X]^+$ (X = Cl or Br).



SCHEME 2

The mechanism outlined in Scheme 2 is thus proposed for the reactions of $[\{Ru(\pi-C_5H_5)(CO)_2\}_2X]^+$ (X = Cl and Br) with BPh_4^- and BPh_3CN^- in solution.

The σ-phenyl derivative $[Ru(\pi-C_5H_5)(CO)_2Ph]$ is also formed on treatment of $[Ru(\pi-C_5H_5)(CO)_2Cl]$ with BPh_4^- in alcohol under reflux. A previous study has revealed that donor ligands L readily displace the chloro-group in $[Ru(\pi-C_5H_5)(CO)_2Cl]$ to give $[Ru(\pi-C_5H_5)(CO)_2L]^+$ when alcohol is employed as solvent.[21] The above reaction involving $[Ru(\pi-C_5H_5)(CO)_2Cl]$ and BPh_4^- is thus readily explained in terms of this chloride displacement and the mechanism depicted in Scheme 2.

TABLE 2

I.r. and n.m.r. spectroscopic data

Compound	C–O Stretching frequencies [a,b] (cm^{-1})	C_5H_5 Proton resonances (τ)
$[\{Ru(\pi-C_5H_5)(CO)_2\}_2Cl]SbF_6$	2073s,b, 2026s	4·05 [c]
$[\{Ru(\pi-C_5H_5)(CO)_2\}_2Br]PF_6$	2067s,b, 2021s	4·13 [c]
$[\{Ru(\pi-C_5H_5)(CO)_2\}_2Br]BPh_4$	2067s,b, 2024s	4·24 [c]
$[\{Ru(\pi-C_5H_5)(CO)_2\}_2I]PF_6$	2062s,b, 2017s	4·05 [c]
$[\{Ru(\pi-C_5H_5)(CO)_2\}_2I]BPh_4$	2064s,b, 2021s	4·10 [c]
$[Ru(\pi-C_5H_5)(CO)_2Cl]$	2059s, 2008s	4·48 [d]
$[Ru(\pi-C_5H_5)(CO)_2Br]$	2055s, 2005s	4·57 [d]
$[Ru(\pi-C_5H_5)(CO)_2I]$	2048s, 1997s	4·46 [d]
$[Ru(\pi-C_5H_5)(CO)_2CN]$	2061s, 2014s [e]	4·50 [d]
$[Ru(\pi-C_5H_5)(CO)_2SCN]$	2061s, 2012s [f]	4·50 [d]
$[Ru(\pi-C_5H_5)(CO)_2Ph]$	2029s, 1963s	4·67 [d]
$[Ru(\pi-C_5H_5)(CO)_2NCBPh_3]$	2080s, 2036s [g]	4·08 [c]

[a] Measured in dichloromethane. [b] Abbreviations: s, strong; b, broad. [c] Measured in $[^2H_6]$acetone. [d] Measured in deuteriochloroform. [e] ν(C–N) = 2125 cm^{-1}. [f] ν(C–N) = 2118 cm^{-1}; ν(C–S) = 697 cm^{-1} (nujol). [g] ν(C–N) = 2203 cm^{-1}.

EXPERIMENTAL

The compound $[\{Ru(\pi-C_5H_5)(CO)_2\}_2]$ was synthesised according to a method previously reported.[22] All experiments were performed under a nitrogen atmosphere. The chromatographic separations were effected on an alumina column (50 × 1·5 cm; Merck acid-washed alumina, activity III). I.r. and n.m.r. spectra were recorded on a Perkin-Elmer model 21 spectrophotometer and on the Varian A60A and HA100 instruments respectively. Conductivities were determined using a Metrohm E365B conductoscope. The elemental analyses were obtained by the Alfred Bernhardt Microanalytical Laboratory, Elbach-über-Engelskirchen, West Germany.

Reactions of $[\{Ru(\pi-C_5H_5)(CO)_2\}_2]$.—(a) *With halogens in dichloromethane.* An equimolar amount of the halogen (chlorine, bromine, or iodine) in carbon tetrachloride (*ca.* 5 ml) or dichloromethane (*ca.* 30 ml) was added dropwise to a stirred solution of $[\{Ru(\pi-C_5H_5)(CO)_2\}_2]$ (0·50 g, 1·1 mmol) in dichloromethane (*ca.* 60 ml) at room temperature and the resultant solution was stirred for 30 min. The solvent was removed under reduced pressure and the product, $[Ru(\pi-C_5H_5)(CO)_2X]$ (X = Cl, Br, or I) was crystallised from dichloromethane–light petroleum; yield 70—80%.

(b) *With halogens in toluene at* 0° *in the presence of large counterions.* An equimolar amount of the halogen (chlorine, bromine, or iodine) in carbon tetrachloride (*ca.* 10 ml) or

---

[19] S. J. Lippard and P. S. Welcker, *Chem. Comm.*, 1970, 515.
[20] P. C. Ford, *Chem. Comm.*, 1971, 7.
[21] A. L. du Preez, unpublished results.
[22] T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1968, 2158.

View Article Online

Published on 01 January 1972. Downloaded by Freie Universitaet Berlin on 22/10/2014 10:24:05.

toluene (*ca.* 30 ml) was added dropwise to a stirred solution of [{Ru(π-C_5H_5)$(CO)_2$}$_2$] (0·50 g, 1·1 mmol) and $NaBPh_4$ or NH_4PF_6 (2·2 mmol) in toluene (*ca.* 60 ml) and methanol (*ca.* 5—10 ml) at 0°. The yellow (orange) product which separated from solution was crystallised from either dichloromethane–light petroleum or acetone–light petroleum. Yields varied between 25 and 75% depending on the compound.

The bridged chloro-species was best isolated as the hexafluoroantimonate salt synthesised by addition of [Ru(π-C_5H_5)$(CO)_2$$(Me_2CO)$]$SbF_6$ to an equimolar amount of [Ru(π-C_5H_5)$(CO)_2$Cl]. The acetone complex was prepared *in situ* from [{Ru(π-C_5H_5)$(CO)_2$}$_2$] and $AgSbF_6$.

Treatment of [{Ru(π-C_5H_5)$(CO)_2$}$_2$] with halogens by the procedure described in (b) but at a temperature of −78° resulted in the separation of deep green products. Attempts to purify these derivatives proved unsuccessful.

Reaction of [{Ru(π-C_5H_5)$(CO)_2$}$_2$X]PF_6 (X = Cl *or* Br) *with* Y^- = CN^-, SCN^-, BPh_4^-, *and* BPh_3CN^-.—A slight excess of KCN, NH_4SCN, $NaBPh_4$, or $NaBPh_3CN$ in acetone (*ca.* 30 ml) was added to a solution of [{Ru(π-C_5H_5)$(CO)_2$}$_2$X]PF_6 (X = Cl or Br) (1·0 mmol) in dichloromethane (*ca.* 40 ml) and the resultant solution was stirred for 15 h. Separation of the two products which formed was effected by means of column chromatography. [Ru^+(π-C_5H_5)$(CO)_2$$NCB^-Ph_3$] decomposed rapidly to [Ru(π-C_5H_5)$(CO)_2$CN] on the column however and the latter compound was thus isolated. [Ru(π-C_5H_5)$(CO)_2$CN] and [Ru(π-C_5H_5)$(CO)_2$SCN] were crystallised from dichloromethane–light petroleum and benzene–light petroleum respectively while [Ru(π-C_5H_5)$(CO)_2$Ph] was isolated as a yellow oil; yields *ca.* 60%.

[Ru(π-C_5H_5)$(CO)_2$CN] and [Ru(π-C_5H_5)$(CO)_2$Ph] were also obtained by refluxing a methanol solution of [Ru(π-C_5H_5)$(CO)_2$Cl] and KCN and an alcohol solution of [Ru(π-C_5H_5)$(CO)_2$Cl] and $NaBPh_4$ respectively.

Synthesis of [Ru^+(π-C_5H_5)$(CO)_2$$NCB^-Ph_3$].—[Ru($\pi$-$C_5H_5$)$(CO)_2$$(Me_2CO)$]$ClO_4$ (3·4 mmol) in acetone (*ca.* 40 ml) was added dropwise to a stirred solution of $NaBPh_3CN$ (1·0 g, 3·4 mmol) in acetone (*ca.* 60 ml) and the resultant solution was stirred for 5 min. The solvent was removed under reduced pressure and the residue was crystallised from acetone–light petroleum; yield *ca.* 55%.

The authors thank Dr. K. G. R. Pachler, National Chemical Research Laboratory, C.S.I.R., Pretoria for the measurement of the n.m.r. spectra. One of us (A. L. du Preez) thanks the Industrial Development Corporation of South Africa, the South African Council for Scientific and Industrial Research, and the University of Pretoria for financial support.

[1/1702 *Received*, 17*th September*, 1971]