Facile Preparation of π-Arene Complexes of Ruthenium [(η^5-C_5Me_5)Ru(Arene)]X including a π-Pyridine and the First π-Furan Derivatives

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Zinc reduction of $(Cp^*RuCl_2)_n$(Cp^* = η^5-C_5Me_5) in tetrahydrofuran or acetone affords '$(Cp^*RuCl)_n$' which reacts smoothly with arenes with or without KPF_6, even at −50 °C, to give the π-complexes [Cp*Ru(arene)]X (arene = benzene, 3-methylthiophene, pyridine, 2,6-lutidine, 3,5-lutidine, or furan) including the first detected π-furan complex in solution and a rare example of a π-pyridine complex; the latter is proposed as a model for pyridine co-ordination in hydrodenitrogenation reactions, however, the mode of pyridine co-ordination is highly dependent on the polarity of the solvent.

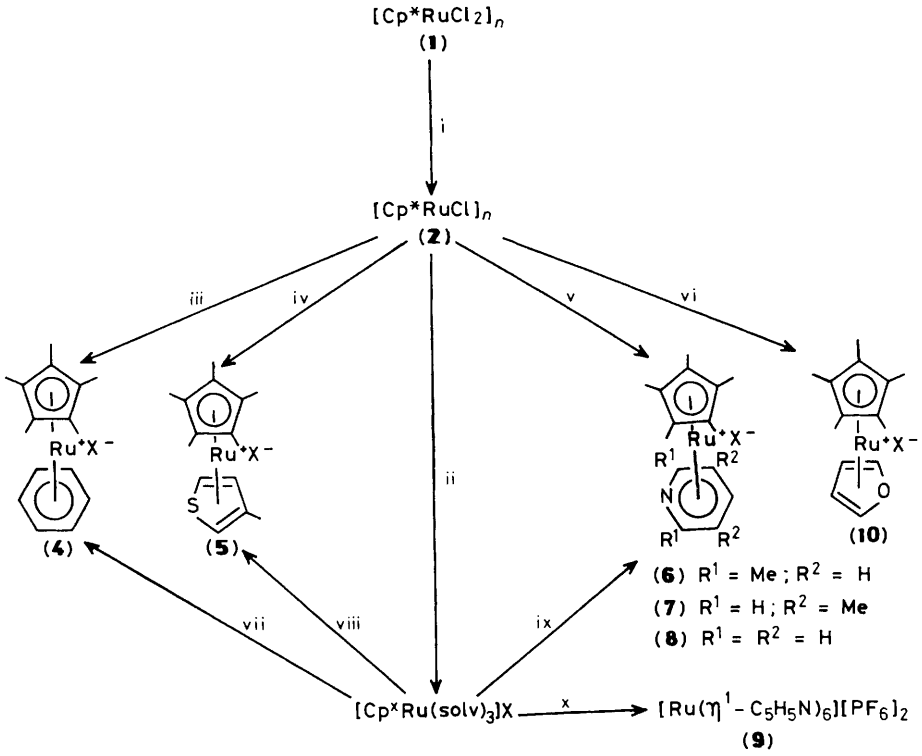
There is presently a great deal of interest in the modelling of industrial hydro-treatment processes such as hydrodesulphurization (HDS)[1] or hydrodenitrogenation (HDN).[2] It now seems clear that co-ordination of the heterocycle to the surface is a 'three-point' (π) co-ordination.[1] However, the number of relevant organometallic models remains limited.[3—8] In the case of HDS, Angelici *et al.* have studied π-thiophene complexes of Mn[3] and Ru.[4] For $[CpRu(C_4H_4S)]^+$ they found a rupture of the C–S bond upon reaction with electrophiles.[1,4c] Furthermore, they found that the 2- and 5-positions of the thiophene are rendered more active, for instance,[4a,b] for deuteriation. This complex thus represents the best homogeneous HDS model so far. However, preparation of these complexes is not straightforward and cannot be extended to other heterocycles such as pyridines for which the σ-co-ordination is preferred. π-Complexes of substituted pyridines are quite rare, except for those of 2,6-lutidine.[6] In the case of pyridine itself, only two such complexes, namely $Cr(CO)_3(\eta^6$-$C_5H_5N)$[7] and $Mo(\eta^6$-$C_5H_5N)(PMePh_2)_3$,[8] are known but they are not easily prepared. Also, there is no readily accessible half-sandwich ruthenium complex able to react smoothly with arenes even at low temperature.

Two independent syntheses of the polymeric complex $[Cp^*RuCl]_n$ (Cp^* = η^5-C_5Me_5)[9,10] have recently led to considerable development in the chemistry of half-sandwich ruthenium complexes.[11]

As part of a study of their reactivity,[12] we have found a facile preparation of complexes of the type $[Cp^*RuCl]_n$ and $[Cp^*Ru(solv.)_3]X$ (solv. = tetrahydrofuran (THF), H_2O, Me_2CO; X = Cl, PF_6), both excellent precursors for $[Cp^*Ru(\eta^6$-Ar)]X derivatives (Ar = arene = benzene, 3-methylthiophene, pyridine, 2,6-lutidine, 3,5-lutidine, furan). These include the first π-furan complex and a rare example of a π-pyridine one.

Zinc reduction of a suspension of $[Cp^*RuCl_2]_n$ (**1**) leads to rapid dissolution of the ruthenium complex and appearance of a green colouration which totally disappears after 15 min. The red complex obtained, tentatively formulated as $[Cp^*RuCl]_n$ (**2**), can react further with KPF_6 to give a yellow solution from which $[Cp^*Ru(Me_2CO)(H_2O)_2]PF_6$ (**3**) can be isolated. Complexes (**2**) and (**3**) react readily with benzene to give the known $[Cp^*Ru(\eta^6$-$C_6H_6)]PF_6$ (**4**)[12] in quantitative yield.

Complex (**2**) also reacts readily with 3-methylthiophene at room temperature to give $[Cp^*Ru(\eta^5$-(3-Me)$C_4H_3S)]PF_6$ (**5**),



Scheme 1. Preparation of some cationic pentamethylcyclopentadienylarene derivatives. *Reagents*: i, Zinc, acetone or THF; ii, acetone (X = Cl, KPF_6); iii, benzene in THF with or without KPF_6; iv, 3-methylthiophene, THF, KPF_6; v, substituted pyridine, THF (R^1 = Me, R^2 = H or R^1 = H, R^2 = Me in the presence of KPF_6, R^1 = R^2 = H no KPF_6); vi, furan, CH_2Cl_3, vii, benzene; viii, thiophene; ix, 2,6- or 3,5-lutidine; x, pyridine, acetone.

which can be isolated in 60% yield as red brown crystals upon recrystallization from CH_2Cl_2–Et_2O. The same reaction was carried out with substituted pyridines and, after similar workup, pale yellow crystals of [Cp*Ru(η^6-2,6-lutidine)]PF_6 (**6**) and creamy white crystals of [Cp*Ru(η^6-3,5-lutidine)]PF_6 (**7**) were isolated in 80 and 70% yield, respectively.

In the case of pyridine itself, the reaction is more complicated since it is highly dependent upon the polarity of the solvent used. Reaction of (**2**) with pyridine (1 equiv.) at −50 °C or at room temperature leads to little colour change and affords a pale yellow precipitate (**8**) in 50—60% yield. The complex is even less soluble than (**6**) and (**7**), and was identified as [Cp*Ru(η^6-C_5H_5N)]Cl. In acetone, a more polar solvent, addition of pyridine leads, even at low temperature, to an immediate colour change to deep yellow and, upon similar work-up to that described above, yields bright yellow crystals of [Ru(η^1-C_5H_5N)$_6$][PF_6]$_2$ (**9**).[14]

This difference in behaviour is quite interesting and probably results from the variable nature of the ruthenium centre. [Cp*RuCl]$_n$ is probably a soft complex for which the π-co-ordination of pyridine is preferred. However, in the more polar acetone, in the presence of KPF_6, the cationic ruthenium centre formed is hard and favours the σ-co-ordination of pyridine. The substitution of Cp* by pyridine, when using only one equivalent of pyridine is puzzling, particularly since the fate of the Cp* ligand is unknown.

It is equally surprising to observe that, when furan is reacted with [Cp*RuCl]$_n$ in CH_2Cl_2, it forms a π-co-ordinated complex [Cp*Ru(η^6-C_5H_4O)]Cl (**10**), which we believe to be the first π-complex of furan reported.[15] However, this compound is unstable and was only observed in solution; it should also be noted that the reaction does not proceed in THF or acetone, presumably because these solvents are better σ-ligands than furan is a π-ligand.

All the π-complexes are yellow crystalline salts, except the methylthiophene derivative which is brown. They are soluble, although only slightly, in polar solvents such as CH_2Cl_2 or acetone. They have been characterized by ^{1}H n.m.r. spectroscopy and, in particular, a shift of *ca.* δ 1 to high field is observed for the arene signals† especially for the protons in the *ortho*-position with respect to the hetero-atom. We obtained ^{13}C n.m.r. spectra for complexes (**4**), (**5**), and (**7**), but the others were too insoluble to provide clear data. Satisfactory i.r. spectra and microanalytical data (C, H, and N) were also obtained.

In conclusion, we describe a very easy one-pot preparation of a series of π-arene complexes from the readily accessible

† *Spectroscopic data* for (**3**)—(**10**): Cp* indicates shifts of H and C in the complex's pentamethylcyclopentadienyl group; Ar, shifts of the arene group H and C. Spectra were measured in [^{2}H]-acetone, except for (**3**) in CD_2Cl_2 and (**6**) in $CDCl_3$.

[Cp*Ru(MeCO)(H_2O)$_2$][PF_6] (**3**): ^{1}H n.m.r. δ 1.28 (s, 15H, Cp*), 2.21 (s, 6H, Me_2CO), 2.72 (s, 4H, $2H_2O$). (**4**) (Ar = η^6-C_6H_6): δ 2.20 (s, 15H, Cp*), 6.18 (s, 6H, Ar); ^{13}C n.m.r. δ 87.0 (C_5Me_5), 12.1 (C_5Me_5), 106.9 (Ar). (**5**) [Ar = η^5-(3-Me)C_4H_3S]: ^{1}H n.m.r. δ 2.02 (s, 15H, Cp*), 6.14 (m, 1H, 4-H Ar), 5.93 (m, 2H, 2- and 5-H Ar), 2.26 (s, 3H, Me, Ar); ^{13}C n.m.r. δ 95.9 (C_5Me_5), 10.7 (C_5Me_5), 102.3 (3-C Ar), 89.0 (4-C Ar), 78.7 and 78.5 (2- and 5-C Ar), 9.9 (Me Ar). (**6**) (Ar = η^6-2,6-lutidine): ^{1}H n.m.r. δ 2.12 (s, 15H, Cp*), 6.43 (m, 3H, 3-, 3'-, and 4-H Ar), 2.59 (s, 6H, 2Me Ar). (**7**) (Ar = η^6-3,5-lutidine): ^{1}H n.m.r. δ 2.14 (s, 15H, Cp*), 7.11 (d, 2H, J_{HH} 1.4 Hz, 2- and 2'-H Ar), 6.47 (t, 1H, 4-H Ar), 2.48 (s, 6H, 2Me Ar); ^{13}C n.m.r. δ 92.9 (C_5Me_5), 10.9 (C_5Me_5), 105.0 (2- and 2'-C Ar), 100.3 and 98.0 (3-, 3'- and 4-C Ar), 16.2 (Me Ar). (**8**) (Ar = η^6-C_5H_5N): ^{1}H n.m.r. δ 2.23 (s, 15H, Cp*), 6.70 (m, 5H, 2-, 3-, and 4-H Ar). (**9**) (Ar = η^1-C_5H_5N): ^{1}H n.m.r. δ 8.94 (m, 2H, 2-H Ar), 8.30 (m, 1H, 4-H Ar), 7.88 (m, 2H, 3-H Ar). (**10**) (Ar = η^5-C_4H_4O): ^{1}H n.m.r. δ 2.14 (s, 15H, Cp*), 6.10 (m, 2H, 2-H Ar), 5.73 (m, 2H, 3-H Ar).

complex $(Cp^*RuCl_2)_n$. Our method is much simpler and leads to higher yields than the method previously described.[13] The reaction conditions allow the preparation of unusual complexes such as those of pyridine and furan, and can also allow co-ordination to ruthenium of thermosensitive molecules containing arene groups. The pyridine and lutidine derivatives may prove to be suitable organometallic models for HDN.

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