Aromatic Polyether Synthesis *via* Activated Substitution in a Ruthenium(II) Complex of *p*-Dichlorobenzene

John A. Segal
New Science Group, Imperial Chemical Industries PLC, P.O. Box 11, The Heath, Runcorn, Cheshire WA7 4QE, U.K.

Nucleophilic substitution of $[(C_5H_5)Ru(p\text{-}C_6H_4Cl_2)]^+$ by bis-aryloxy anions leads to the formation of aromatic organoruthenium polymers of poly-ether or -ether-ketone type; metal-free polymer is obtained by arene-displacement in a co-ordinating solvent.

The activation of *p*-dichlorobenzene to nucleophilic substitution by aryloxy anions is a goal of value in aromatic polymer synthesis. At present, the dichloro compounds used commercially to form aromatic ether linkages are based on more complex and, therefore, more costly bis-aryl systems which contain electron-withdrawing groups to facilitate substitution.[1] Even in the Ullmann ether reaction, where copper compounds promote the reactivity of the Ar–X bond, the yields from dichlorobenzenes are insufficient[2] to produce polyethers of significant molecular weight.[3] An alternative approach to Ar–Cl activation is *via* η-arene co-ordination to a metal centre, such as $Cr(CO)_3$,[4] $Mn(CO)_3^+$,[5] or η-cpFe^+,[6] (cp = cyclopentadienyl). However, the synthetic utility of halogen substitution in co-ordinated arenes by aromatic oxygen nucleophiles has been little studied.[7] In fact, it appears that only reactions with phenoxide itself are known.† In the present work, di-substitution of co-ordinated $p\text{-}C_6H_4Cl_2$ has been developed to provide a novel route to organometallic polyethers and their metal-free analogues.

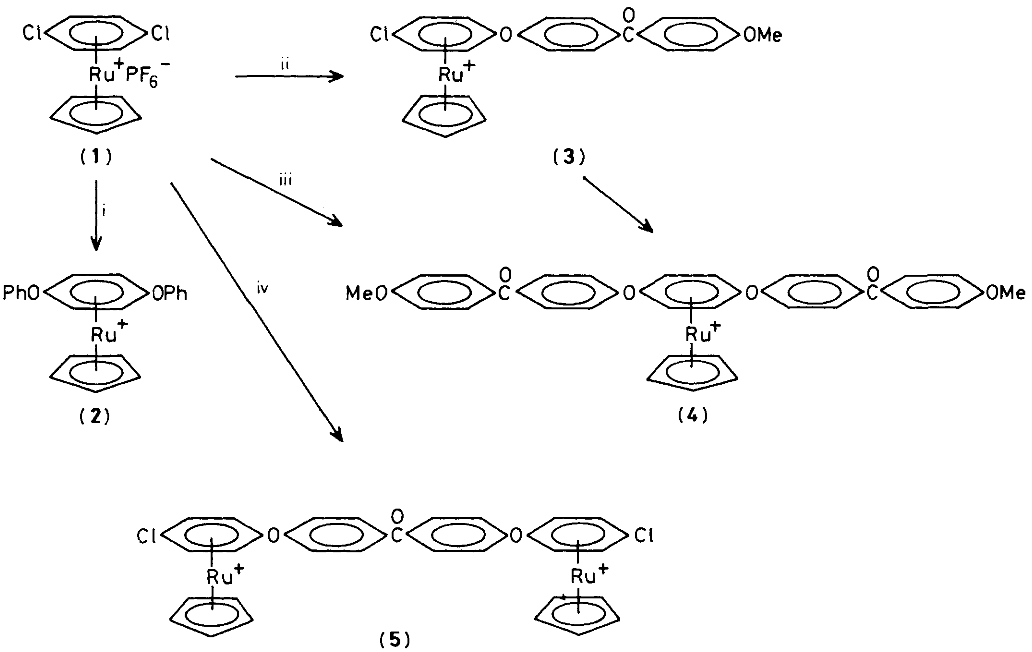
Cation (**1**)‡ (see Scheme 1) was found to react smoothly not only with phenoxide in acetone to give the 3-ring bis-phenoxy derivative (**2**),§ but also with the monosodium salt of 4-hydroxy-4′-methoxybenzophenone to give both the 3-ring mono- and the 5-ring di-substitution products (**3**) and (**4**). Also, the reaction of (**1**) with the disodium salt of dihydroxybenzophenone, taken in 2 : 1 ratio, led to formation of the diruthenium system (**5**). These results demonstrate the linking of two bis-phenol units by the organometallic species, and the linking of two organometallic units by the bis-phenol. They imply that polymer formation should be possible.

Reaction of the disodium salt of 4,4′-dihydroxybenzophenone with an equimolar quantity of (**1**) in dimethylformamide (DMF) or dimethyl sulphoxide (DMSO) at 85—90 °C (Scheme 2) led to formation of the soluble organometallic ether-ketone polymer (**6**) which was isolated as a buff solid {^{1}H n.m.r. ([$^2H_6$]DMSO) δ 5.66 (s, 5H, C_5H_5); 6.48 (s, 4H, OC_6H_4O); 7.48, 7.97 ($|J_{AX} + J_{AX'}|$ 9 Hz, 8H, OCC_6H_4O)}. The metal-free poly(ether-ether-ketone), PEEK, was obtained from (**6**) by an arene-displacement reaction either photochemically in MeCN or, better, thermally at 160 °C in DMSO. The free PEEK polymer is insoluble, by contrast with its organometallic derivative, and it precipitated leaving $[cpRu(OSMe_2)_3]^+$ in solution. An unoptimised small-scale reaction based on (**1**) (200 mg) gave a 75% yield of PEEK with inherent viscosity (I.V.) 0.21 (in H_2SO_4), and differential scanning calorimetry showed T_g 144, T_m 335 °C, as expected for this polymer;[9] {^{1}H n.m.r. (CF_3SO_3H solution + [$^2H_6$]DMSO capillary) δ 7.21, 8.02 ($|J_{AX} + J_{AX'}|$ 8 Hz, 8H, OCC_6H_4O); 7.24 (s, 4H, OC_6H_4O)}. From a similar reaction of (**1**) with the dipotassium salt of bis-phenol A, the analogous organometallic polyether (**7**) was isolated {^{1}H n.m.r. ([$^2H_6$]DMSO) δ 1.70 (s, 6H, CMe_2); 5.54 (s, 5H, C_5H_5); 6.23 (s, 4H, OC_6H_4O); 7.17, 7.39 ($|J_{AB} + J_{AB'}|$ 8.5 Hz, 8H, OC_6H_4C)}. Again displacement of ruthenium in DMSO led to the free polymer which was precipitated by the addition of water, leaving the tris-DMSO complex in the aqueous solution. This polymer, obtained in 70% yield, gave I.V. 0.29 (in $CHCl_3$) with T_g 115 °C [^{1}H n.m.r. ($CDCl_3$) δ 1.67 (s, 6 H, CMe_2); 6.86, 7.16 ($|J_{AX} + J_{AX'}|$ 8.8 Hz, 8H, CC_6H_4O); 6.97

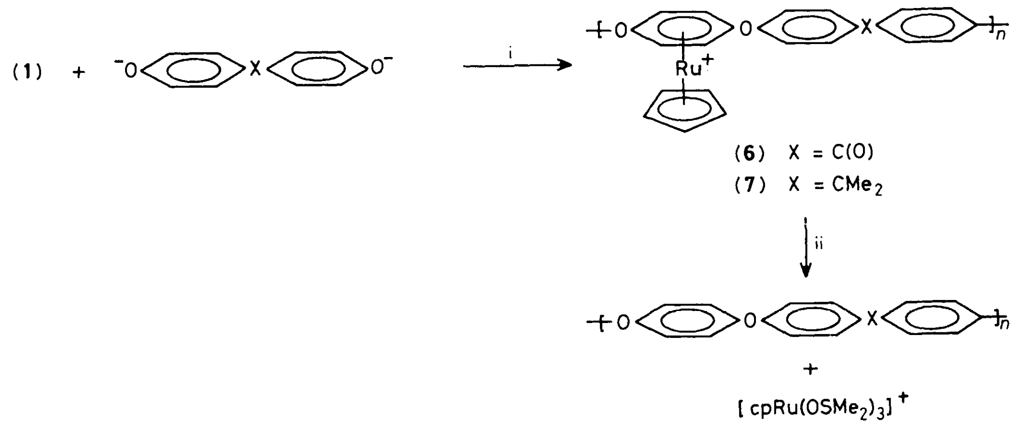
† These reactions are with aryl *mono*halides only, see refs. 4—7, and refs. therein.

‡ Obtained by the general route from $[cpRu(NCMe)_3]PF_6$, ref. 8.

§ All new compounds gave satisfactory elemental analysis.



Scheme 1. *Reagents:* i, NaOPh in acetone, 40 °C, 10 min; ii, $NaOC_6H_4C(O)C_6H_4OMe$, 1:1 ratio with (**1**), in DMF, 50 °C, 10 min; iii, $NaOC_6H_4C(O)C_6H_4OMe$, 2:1 ratio with (**1**), in DMF, 85 °C, 20 min; iv, $NaOC_6H_4C(O)C_6H_4ONa$, 1:2 ratio with (**1**), in DMF, 70 °C, 1 h.



Scheme 2. *Reagents:* i, Na or K bis-phenate, 1:1 ratio with (**1**), in DMSO, 85—90 °C, 1.5 h; ii, DMSO, 160 °C, 1.5 h.

(s, 4H, OC_6H_4O)]. Gel permeation chromatography (in 1,2-$C_2H_4Cl_2$ *vs.* standard polystyrenes) gave M_n 6170, M_w 15600.

The use of the $cpRu^+$ unit allows formation of the chloroarene complex from a tris-solvent species $[cpRuL_3]^+$, L = NCMe, and then displacement of the product poly-arene to regenerate a tris-solvent species $[cpRuL_3]^+$, L = $OSMe_2$ or NCMe. The system is therefore in principle a cyclic one, and it demonstrates the feasibility of forming polymers from simple chloroarenes co-ordinated to transition metals. The intermediate organometallic polymer need not even be isolated from solution in DMSO, since the $cpRu^+$ unit can be removed *in situ* by simple thermolysis. This type of approach may ultimately lead to new catalytic pathways for the synthesis of the commercially important aromatic polyethers.

I thank Dr. H. M. Colquhoun for valuable discussions, and I.C.I. PLC for permission to publish.

Received, 10th June 1985; Com. 808

References

1 *E.g.* R. N. Johnson, A. G. Farnham, R. A. Clendinning, W. F. Hale, and C. N. Merrian, *J. Polym. Sci., Part A*-1, 1967, **5**, 2375.
2 A. A. Moroz and M. S. Shvartsberg, *Russ. Chem. Rev. (Engl. Transl.)*, 1974, **43**, 679; see also *e.g.* G. Soula and L. Linguenheld, E. P. 21868 (1981).
3 J. A. Segal, unpublished work.
4 J. F. Bunnett and H. Herrmann, *J. Org. Chem.*, 1971, **36**, 4081, and refs. therein.
5 P. L. Pauson and J. A. Segal, *J. Chem. Soc., Dalton Trans.*, 1975, 1677.
6 A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Dokl. Akad. Nauk SSSR*, 1967, **175**, 606.
7 W. E. Watts, The Organic Chemistry of Metal-Coordinated Cyclopentadienyl and Arene Ligands, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, 1982, vol. 8, p. 1013, and refs. therein.
8 T. P. Gill and K. R. Mann, *Organometallics*, 1982, **1**, 485.
9 *Cf.* T. E. Attwood, P. C. Dawson, J. L. Freeman, R. J. Hoy, J. B. Rose, and P. A. Staniland, *Polymer*, 1981, **22**, 1096.