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 $[(C_5H_5)Ru(p-C_6H_4Cl_2)]^+$ 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 insufficient² to produce polyethers of significant molecular weight.³ An alternative approach to Ar-Cl activation is via n-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 $p-C_6H_4Cl_2$ 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. ([2 H₆]DMSO) δ 5.66 (s, 5H, C₅H₅); 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 H₂SO₄), and differential scanning calorimetry showed T_g 144, T_m 335 °C, as expected for this polymer;⁹ {¹H n.m.r. (CF₃SO₃H solution + [²H₆]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. ([2 H₆]DMSO) δ 1.70 (s, 6H, CMe₂); 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 CHCl₃) with T_g 115 °C [¹H n.m.r. (CDCl₃) δ 1.67 (s, 6 H, CMe₂); 6.86, 7.16 ($|J_{AX} + J_{AX}'|$ 8.8 Hz, 8H, CC₆H₄O); 6.97

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

 $[\]ddagger$ 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, NaOC₆H₄C(O)C₆H₄OMe, 1:1 ratio with (1), in DMF, 50 °C, 10 min; iii, NaOC₆H₄C(O)C₆H₄OMe, 2:1 ratio with (1), in DMF, 85 °C, 20 min; iv, NaOC₆H₄C(O)C₆H₄ONa, 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 = OSMe₂ 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.

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