# Ruthenium-containing Organometallic Dendrimers

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Convergent methodology is used to build up the first organotransition metal dendrimers and these contain ruthenium–carbon σ-bonds exclusively as surface functions on the growing macromolecules.

Inorganic and organometallic polymers are of increasing interest[1] although only very recently have polymers been synthesized that contain a metal–carbon σ-bond, and these were chain-type polymers.[2–4] The highly branched macromolecules called dendrimers, arborols or cascade molecules are also of growing interest.[5–8] However, the majority are organic in nature. One exception is a metal complex containing 22 ruthenium atoms held together by coordinate bonds to
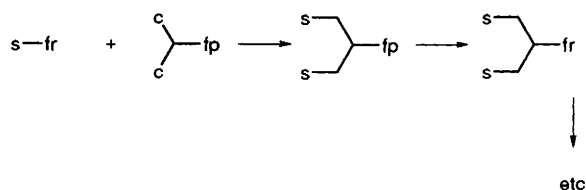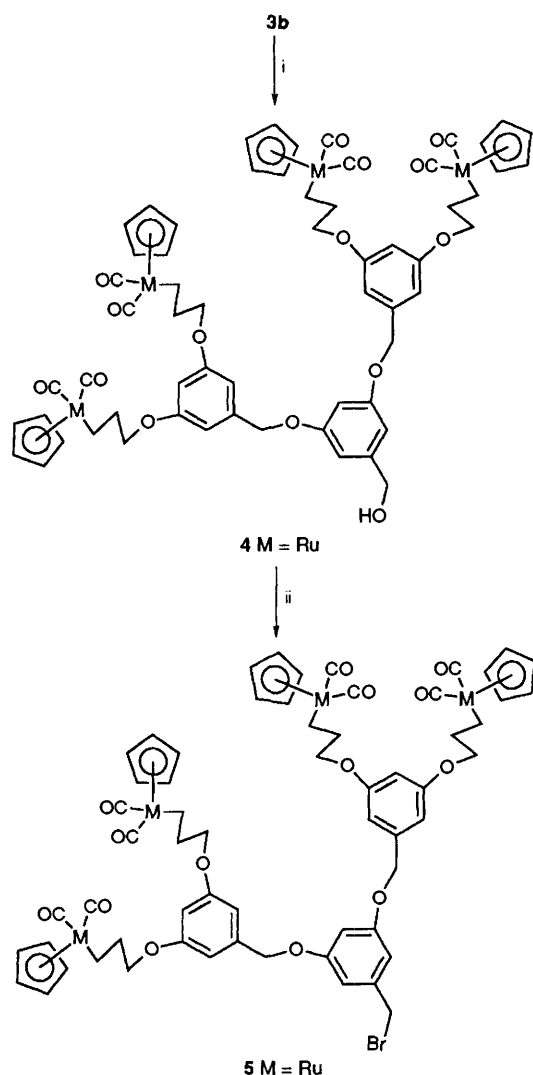
Scheme 1
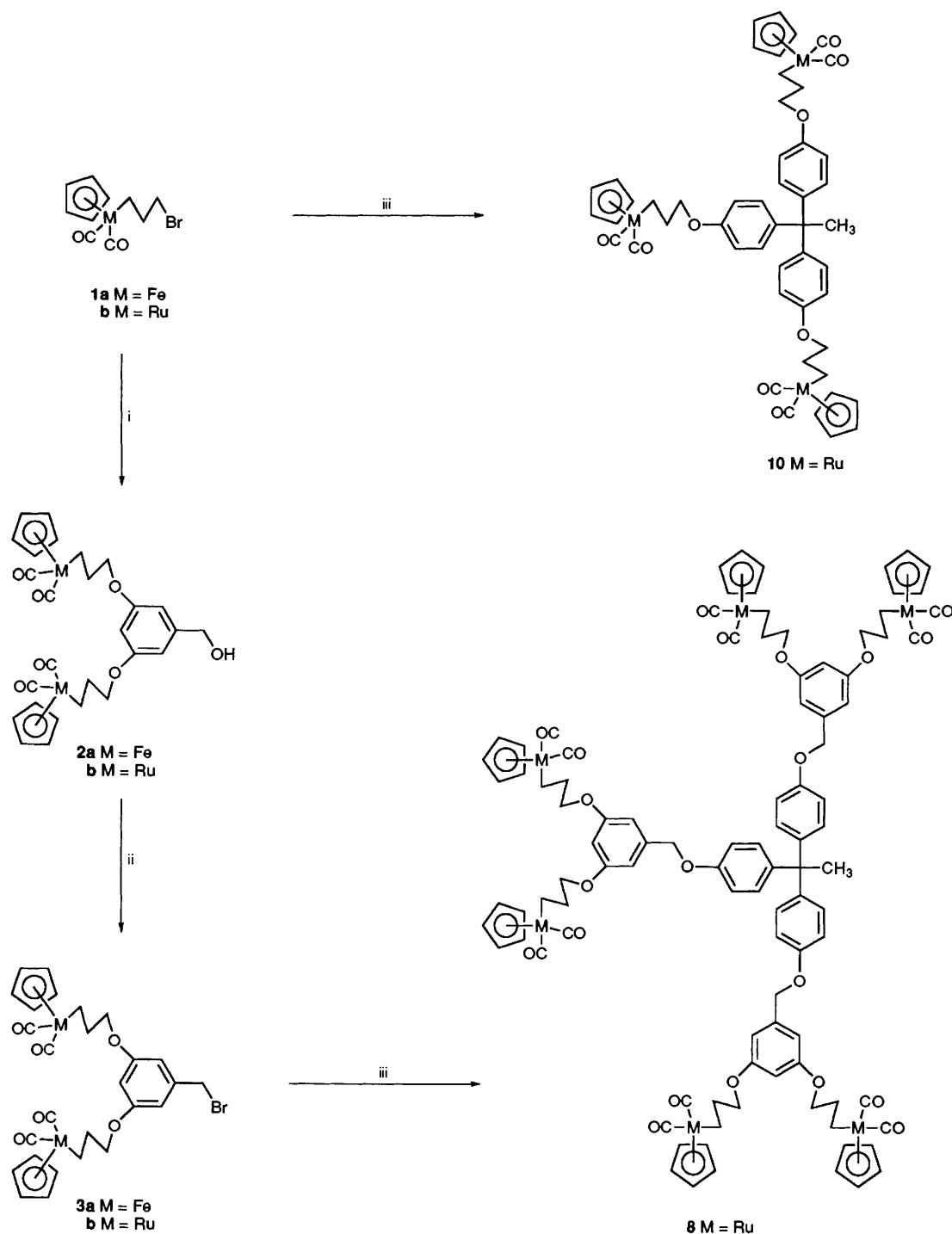
Scheme 2 *Reagents and conditions*: i, 3,5-dihydroxybenzyl alcohol, K_2CO_3, 18-crown-6, reflux acetone 48 h; ii, CBr_4, PPh_3, THF, room temp. 20 min; iii, 1,1,1-tris(4-hydroxyphenyl)ethane, K_2CO_3, 18-crown-6, reflux acetone, 48 h

nitrogen donor ligands.[9] We now describe a convergent synthesis of the first series of organotransition metal dendrimers that contain metal–carbon σ-bonds on the periphery of the molecules. Such compounds may show interesting properties as a result of their novel molecular architectures.

In our approach, we have used the methodology developed by Hawker and Fréchet[10] but we have included a metal in the functionalized monomer (s-fr). The metal alkyl group is then incorporated in the growing macromolecule, see Scheme 1. In this procedure the metal, with its ligand system, will then end

up as the surface functionality (s) of the dendritic macromolecule. We used the bromoalkyl complexes $CpM(CO)_2$-{$(CH_2)_3Br$} (where M = Fe[11] **1a** or Ru[12] **1b** and Cp = η^5-C_5H_5) as the functionalized monomers (s-fr). We have previously found that the metal with its ligand system in these,[13] and related complexes[14] are relatively inert and that reactions of the haloalkyl complexes can be directed to the halofunction.[13] We were also encouraged in our belief that large molecules could be built up containing metal–carbon σ-bonds since we have found that the stability of several

3b

4 M = Ru

5 M = Ru

Scheme 3 *Reagents and conditions*: i, 3,5-dihydroxybenzyl alcohol, K_2CO_3, 18-crown-6, reflux acetone 48 h; ii, CBr_4, PPh_3, THF, room temp. 20 min

classes of alkyl complexes, including $CpM(CO)_2R$ (M = Fe or Ru)[15] and $Mn(CO)_5R$,[16] increased as the number of carbon atoms in the *n*-alkyl chain (R) increased. Thus, the bromoalkyl iron or ruthenium complexes (**1a** or **1b**) react with 3,5-dihydroxybenzyl alcohol in the presence of potassium carbonate and 18-crown-6 over 2 days in refluxing acetone to give the new ether complexes **2a** and **2b** in reasonable yield (40 and 70%, respectively) as shown in Scheme 2.

Complexes **2a** and **2b** were purified by column chromatography and are the first generation benzyl alcohols; they were characterized by IR, ¹H NMR, ¹³C NMR, mass spectrometry and microanalysis.† Compound **2a** is a yellow oil and **2b** is a colourless crystalline solid (mp 95 °C). Both compounds are relatively air and thermally stable. Conversion of **2a** and **2b** to the corresponding benzyl bromides **3a** and **3b** was accomplished using PPh_3/CBr_4[10] (Scheme 2).

The first generation benzyl bromides were obtained in good yields and also characterized by standard methods.‡ The iron compound **3a** was, however, relatively unstable and showed significant decomposition even under N_2 at room temperature. Attempts to react compound **3a** with 3,5-dihydroxybenzyl alcohol in refluxing acetone led only to decomposition and none of the desired second generation benzyl alcohol could be detected.

The ruthenium compound **3b** was, however, stable at room temperature. Reaction of **3b** with 3,5-dihydroxybenzyl alcohol resulted in the formation of the anticipated second generation benzyl alcohol **4** (70% yield) and the reaction of **4** with PPh_3/CBr_4 gave the second generation benzyl bromide **5** (Scheme 3).

Compounds **4** and **5** are white and glassy in appearance and were characterized by standard methods.§ Reaction of **5** with 3,5-dihydroxybenzyl alcohol gave the third generation benzyl alcohol **6**, which is an 8 metal system and can be converted to the corresponding benzyl bromide **7**.

We have now built up a series of dendritic wedges that still contain a reactive functional group *viz*. the compounds **3**, **5** and **7**; these compounds are 2-, 4- and 8-metal systems, respectively.

In the convergent approach,[10] the dendritic wedges are attached to a polyfunctional core. Thus, reaction of the first generation benzyl bromide, **3b** with the core molecule 1,1,1,-tris(4-hydroxyphenyl)ethane, gave a good yield of the 6 metal system **8**¶ (Scheme 2). Similarly, reaction of the second generation benzyl bromide **5** with the same core gave the expected 12 metal system **9**‖ (Scheme 4). We also show that the bromoalkyl compound **1b** will react with the core to give **10** (Scheme 2).

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† *Selected data* for **2b**: $IR(CH_2Cl_2)$ $v(CO)$ 2012, 1948 cm⁻¹; ¹H NMR $\delta(CDCl_3)$ 6.49 (d, *J* 2 Hz, 2H Ar); 6.38 (t, *J* 2.4 Hz, 1H, Ar), 5.25 (s, 10H, Cp), 4.61 (d, *J* 6 Hz, 2H, $ArCH_2OH$), 3.86 (t, *J* 6.6 Hz, 4H, CH_2OAr), 2.01 (m, 4H, $CH_2CH_2CH_2$), 1.69 (m, 4H, $RuCH_2$); ¹³C NMR $\delta(CDCl_3)$ 202.09 (CO), 160.6, 143.14, 105.07, 100.51 (Ar), 88.54 (Cp), 71.05 (CH_2OAr), 65.53 ($ArCH_2OH$), 38.50 ($CH_2CH_2CH_2$), −9.33 ($RuCH_2$).

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‡ *Selected data* for **3b**: $IR(CH_2Cl_2$ $v(CO)$ 2012, 1948 cm⁻¹; ¹H NMR $\delta(CDCl_3)$ 6.50 (d, *J* 2.4 Hz, 2H, Ar), 6.38 (t, *J* 2.2 Hz, 1H, Ar), 5.25 (s, 10H, Cp), 4.41 (s, 2H, $ArCH_2Br$), 3.85 (t, *J* 6.8 Hz, 4H, CH_2OAr), 2.01 (m, 4H, $CH_2CH_2CH_2$), 1.69 (m, 4H, $RuCH_2$); ¹³C NMR $\delta(CDCl_3)$ 202.06 (CO), 160.46, 139.46, 107.42, 101.42 (Ar), 88.55 (Cp), 71.09 (CH_2OAr), 38.46 ($CH_2CH_2CH_2$), 32.92 ($ArCH_2Br$), −9.37 ($RuCH_2$); mass spectrum (FAB) *m/z* 731 (P + 1).

§ *Selected data* for **5**: $IR(CH_2Cl_2)$ $v(CO)$ 2012, 1948 cm⁻¹; ¹H NMR $\delta(CDCl_3)$ 6.55 (d, *J* 2 Hz, 2H, Ar^{II}), 6.47 (d, *J* 2.4 Hz, 5H, Ar^{II} + Ar^{I}), 6.34 (t, *J* 2 Hz, 2H, Ar^{I}), 5.18 (s, 20H, Cp), 4.88 (s, 4H, Ar^{I}CH_2O), 4.34 (s, 2H, Ar^{II}CH_2Br), 3.80 (t, *J* 6.8 Hz, 8H, CH_2OAr^{I}), 1.94 (m, 8H, $CH_2CH_2CH_2$), 1.63 (m, 8H, $RuCH_2$); ¹³C NMR δ $(CDCl_3)$ 202.08 (CO), 160.57, 160.06, 139.66, 138.74, 108.16, 105.69, 102.24, 100.82 (Ar^{I} + Ar^{II}), 88.55 (Cp), 71.06 (CH_2OAr^{I}), 70.22 (Ar^{I}CH_2O), 38.47 ($CH_2CH_2CH_2$); 33.66 (Ar^{II}CH_2Br); −9.32 ($RuCH_2$); mass spectrum (FAB) *m/z* 1445 (P-2CO).

¶ *Selected data* for **8**: $IR(CH_2Cl_2)$ $v(CO)$ 2012, 1947 cm⁻¹; ¹H NMR δ $(CDCl_3)$ 6.99 (d, *J* 8.8 Hz, 6H, Ar^{CORE}), 6.85 (d, *J* 9.2 Hz, 6H, Ar^{CORE}), 6.55 (d, *J* 2 Hz, 6H, Ar), 6.40 (t, *J* 2.2 Hz, 3H, Ar), 5.25 (s, 30H, Cp), 4.96 (s, 6H, $ArCH_2O$), 3.86 (t, *J* 6.6 Hz, 12H, CH_2OAr), 2.10 (s, 3H, CCH_3), 2.02 (m, 12H, $CH_2CH_2CH_2$), 1.70 (m, 12H, $RuCH_2$); ¹³C NMR δ $(CDCl_3)$ 202.10 (CO), 160.54, 142.00, 105.69, 100.71 (Ar), 156.87, 139.33, 129.63, 114.02 (Ar^{CORE}), 88.56 (Cp), 71.05 (CH_2OAr), 70.11 ($ArCH_2O$), 50.66 (CCH_3), 38.49 ($CH_2CH_2CH_2$), −9.31 ($RuCH_2$); mass spectrum (FAB) *m/z* 2195 (P-2CO).

‖ *Selected data* for **9**: IR (CH_2Cl_2) $v(CO)$ 2012, 1947 cm⁻¹; ¹H NMR $\delta(CDCl_3)$ 7.01 (d, *J* 9.2 Hz, 6H, Ar^{CORE}), 6.86 (d, *J* 8.8 Hz, 6H, Ar^{CORE}), 6.67 (d, *J* 2 Hz, 6H, Ar^{II}), 6.55 (d, *J* 2.4 Hz, 15H, Ar^{II} + Ar^{I}), 6.40 (t, *J* 2.4 Hz, 6H, Ar^{I}), 5.22 (s, 60H, Cp), 4.95 (s, 12H, Ar^{I}CH_2O), 4.94 (s, 6H, Ar^{II}CH_2O), 3.86 (t, *J* 6.6 Hz, 24H, CH_2OAr^{I}), 2.11 (s, 3H, CMe), 2.01 (m, 24H, $CH_2CH_2CH_2$), 1.68 (m, 24H, $RuCH_2$); ¹³C NMR $\delta(CDCl_3)$ 202.11 (CO), 160.55, 160.14, 138.93, 129.67, 114.01, 106.51, 106.49, 105.71, 100.79, (Ar^{I} + Ar^{II} + Ar^{CORE}), 88.55 (Cp), 71.04 (CH_2OAr^{I}), 70.18 (Ar^{I}CH_2O), 38.47 ($CH_2CH_2CH_2$), −9.31 ($RuCH_2$); mass spectrum (FAB) *m/z* 4509 (P-2CO).

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9 M = Ru
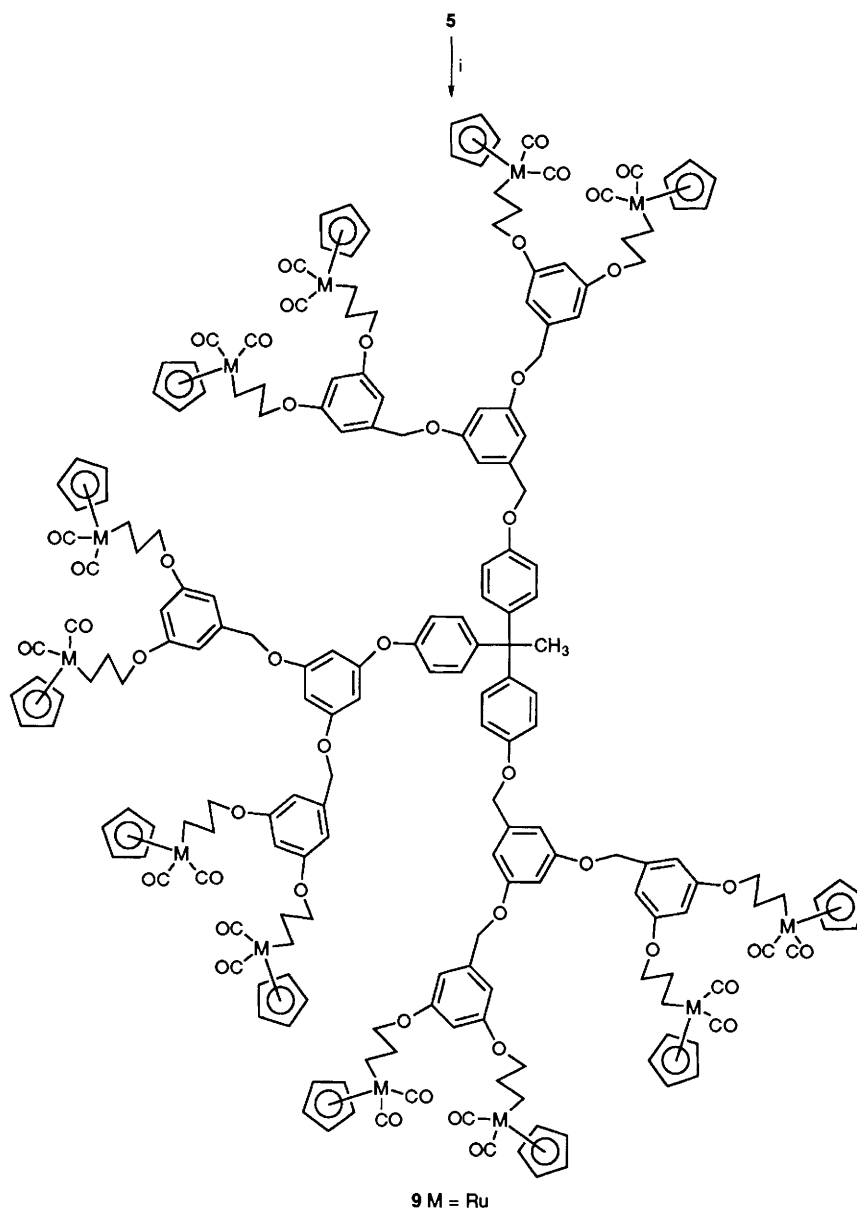
Scheme 4 *Reagents and conditions*: i, 1,1,1-tris(4-hydroxyphenyl)ethane, K₂CO₃, 18-crown-6, reflux acetone 48 h

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