Dithiocarbamate-Functionalized Dendrimers as Ligands for Metal Complexes

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Received January 22, 1998

Zeroth- and first-generation poly(amido)amine dendrimers have been functionalized with dithiocarbamate end groups and reacted with ruthenium complexes, to form metallodendrimers. Monomeric ruthenium dithiocarbamate complexes were also prepared as model compounds and their spectroscopic data compared with those of the metallodendrimers. The novel compounds were characterized using NMR spectroscopy (^{1}H and ^{13}C) and mass spectrometry. The compound [Ru(S_2CNMe_2)(PPh_3)(η^5-C_5H_5)] has also been characterized crystallographically.

Introduction

The beauty and complexity of Nature's dendritic arrays have inspired synthetic chemists to mimic such structures at the molecular level. These dendritic polymers, or dendrimers, are currently generating a great deal of excitement as new applications are being proposed for them.[1−3] Recently, the synthesis of metallodendrimers has become an important focus of activity.[4−13] Much of this interest has been stimulated by their use as carriers for catalysts.[13−16] Since solute molecules with diameters greater than 20 Å can be removed from solution by ultrafiltration techniques, dendrimers have the potential to solve the problem of catalyst recovery in homogeneous systems.

Dendrimers have highly branched treelike structures with multiple chain ends, and although the presence of internal functionalities may have an influence, dendrimer reactivity is largely determined by the nature of the end groups. Hence, in our quest for catalyst-carrying materials, the bulk of the dendrimer may be viewed principally as a structural support for the important outer surface of the molecule. Therefore, we have chosen to develop methods for the covalent bonding of metal complexes to functionalized end groups of known dendrimers. To date, attention has been centered on the synthesis of phosphine-terminated dendrimers and their metal complexes.[10−13] With a view to expanding the range of ligand groups available, we report herein (i) the formation of a novel class of dithiocarbamate-terminated dendrimers and (ii) their use as ligands for the formation of ruthenium(II) complexes.

Our approach has been based on the use of the well-known and well-characterized poly(amido)amine (PAMAM) dendrimers[17] to provide the structural framework for our molecules. These dendrimers were then functionalized to give dithiocarbamate salts ($RR'NCS_2^-$, where R = Me and R′ = dendrimer), which were then used to bind to the metal centers.

Experimental Section

Methanol and dichloromethane were distilled before use, *N*-methylethylenediamine and the dichloro(*p*-cymene)ruthenium(II) dimer were purchased from Aldrich, and cyclopentadienylbis(triphenylphosphine)-ruthenium(II) chloride was prepared as described in the literature.[18]

^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-EX 270-MHz and Bruker DRX 400-MHz spectrometers, IR spectra were recorded on a Research Series FTIR spectrometer, and microanalysis was performed by Imperial College and University of North London analytical services. Mass spectra were recorded by the Imperial College mass spectrometry service (FAB-MS and −ve ES-MS), the Birmingham University mass spectrometry service (FAB-MS and MALDI), the University of Warwick mass spectrometry service (+ve ES-MS), and The National Mass Spectrometry Service Centre, The University of Wales (+ve and −ve ES-MS).

The nomenclature used for the dendrimers is that originally suggested by Newkome et al.[19] In the listings of spectral data for the dendrimers, subscripts "int" and "ext" refer to internal and external moieties, where the signals do not coincide.

Preparation of 3-Cascade 2. A solution of triester **1** (1.59 g, 5 mmol) in MeOH (15 cm^3) was added to a solution of *N*-methylethyl-

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S0020-1669(98)00067-6 CCC: $15.00
Published on Web 07/10/1998

enediamine (18.52 g, 0.25 mol) in MeOH (20 cm^3). The mixture was stirred for 10 days at room temperature. The solvent and excess reagent were removed in vacuo, yielding the tris(amine) **2** as a pale yellow oil. Yield: 2.01 g. Selected IR absorption maxima: ν (cm^{-1}) = 3282 (s), 3081 (m), 2937 (s), 2852 (m), 1646 (s) (C═O), 1552 (s), 1450 (m), 1363 (w), 1290 (w), 1259 (w), 1124 (m). ^{1}H NMR (D_2O): δ (ppm) = 3.21 (t, 6H, ^3J(H,H) = 6.3 Hz, NHC**H**$_2$), 2.69 (t, 6H, ^3J(H,H) = 7.2 Hz, NC**H**$_2$), 2.57 (t, 6H, ^3J(H,H) = 6.3 Hz, C**H**$_2$NHCH$_3$), 2.32 (t, 6H, ^3J(H,H) = 7.2 Hz, C**H**$_2$CO), 2.22 (s, 9H, NHC**H**$_3$). ^{13}C NMR (D_2O): δ (ppm) = 175.4 (**C**O), 49.4 (**C**H$_2$NH), 48.9 (N**C**H$_2$), 38.8 (NH**C**H$_2$), 34.7 (**C**H$_3$NH), 33.1 (**C**H$_2$CO). +ve FAB-MS: *m*/*z* 402 (M + 1).

Preparation of 3-Cascade 3. A solution of the tris(amine) **2** (200 mg, 0.497 mmol) in water (5 cm^3) was added to a solution of NaOH (60 mg, 1.49 mmol) in water (10 cm^3). Carbon disulfide (0.11 g, 1.49 mmol) was added and the mixture stirred overnight. The solvent was removed in vacuo to yield a pale yellow hygroscopic solid. Yield: 335 mg. Selected IR absorption maxima: ν (cm^{-1}) = 2933 (m), 1639 (s) (C═O), 1554 (s), 1479 (s) (CN), 1434 (m), 1375 (s), 1257 (sh, s), 1205 (s), 1108 (m), 1062 (w), 977 (s). ^{1}H NMR (D_2O): δ (ppm) = 4.19 (t, 6H, ^3J(H,H) = 6.1 Hz, NHC**H**$_2$), 3.47 (t, 6H, ^3J(H,H) = 6.1 Hz, C**H**$_2$N), 3.39 (s, 9H, NC**H**$_3$), 2.74 (t, 6H, ^3J(H,H) = 7.5 Hz, NC**H**$_2$), 2.37 (t, 6H, ^3J(H,H) = 7.5 Hz, C**H**$_2$CO). ^{13}C NMR (D_2O): δ (ppm) = 210.7 (**C**S$_2$), 175.4 (**C**O), 55.2 (**C**H$_2$NCH$_3$), 49.0 (N**C**H$_2$), 43.6 (N**C**H$_3$), 37.7 (NH**C**H$_2$), 33.2 (**C**H$_2$CO). −ve FAB-MS: *m*/*z* 672 (M − Na). −ve ES-MS: *m*/*z* 672 (M − Na), 325 [(M − 2Na)/2], 209 [(M − 3Na)/3].

Preparation of 6-Cascade 5. A solution of hexaester **4** (0.959 g, 1 mmol) in MeOH (5 cm^3) was added directly to a solution of *N*-methylethylenediamine (27.43 g, 0.37 mol) in MeOH (10 cm^3). The reaction mixture was stirred for 14 days. The solvent and excess reagent were removed in vacuo to yield **5** as a yellow oil. Yield: 1.127 g. Selected IR absorption maxima: ν (cm^{-1}) = 3288 (s), 3079 (s), 2937 (s), 2850 (s), 1639 (s) (C═O), 1560 (s), 1459 (s), 1361 (m), 1286 (m), 1259 (m), 1149 (m), 1085 (w), 1041 (m). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.78 (br t, 3H, CONH$_{int}$), 7.69 (br t, 6H, CONH$_{ext}$), 3.31 (q, 12H, NHC**H**$_{2,ext}$), 3.19 (br, 6H, NHC**H**$_{2,int}$), 2.70 (br, 30H, NC**H**$_2$, C**H**$_2$-NHCH$_3$), 2.49 (br t, 6H, C**H**$_2$N(CH$_2$)$_2$), 2.40 (s, 18H, NC**H**$_3$), 2.30 (br, 18H, C**H**$_2$CO), 1.87 (br s, 6H, N**H**CH$_3$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 173.1, 172.7 (**C**O), 52.9, 50.7, 50.5, 49.8, 38.43, 37.8, 35.6 (**C**H$_2$), 34.5 (**C**H$_3$), 34.01 (**C**H$_2$). +ve FAB-MS: *m*/*z* 1128 (M + 1).

Preparation of 6-Cascade 6. A solution of the hexamine **5** (1.0 g, 0.886 mmol) in water (10 cm^3) was added to a solution of NaOH (0.213 g, 5.32 mmol) in water (3 cm^3). Carbon disulfide (0.404 g, 5.32 mmol) was added and the mixture stirred overnight. The solvent was removed in vacuo to yield a yellow hygroscopic solid. Yield: 1.52 g. Selected IR absorption maxima: ν (cm^{-1}) = 3276 (s), 3058 (s), 2927 (s), 1658 (s) (C═O), 1544 (s), 1467 (sh, s) (CN), 1367 (s), 1255 (sh, s), 1201 (s), 1105 (m), 1058 (w), 975 (s). ^{1}H NMR (D_2O): δ (ppm) = 4.20 (br, 12H, NHC**H**$_{2,ext}$), 3.47 (t, 12H, ^3J(H,H) = 6.0 Hz, C**H**$_2$NCH$_3$), 3.39 (s, 18H, NC**H**$_3$), 3.27 (br, 6H, NHC**H**$_{2,int}$), 2.81 (br, 18H, NC**H**$_2$), 2.65 (br, 6H, C**H**$_2$N(CH$_2$)$_2$), 2.41 (br, 18H, C**H**$_2$CO). ^{13}C NMR (D_2O): δ (ppm) = 210.8 (**C**S$_2$), 175.1, 174.8 (**C**O), 55.0, 51.7, 49.4, 49.2, 49.0 (**C**H$_2$), 43.5 (**C**H$_3$), 37.7, 37.1, 32.9 (**C**H$_2$). −ve ES-MS: *m*/*z* 835.3 [(M − 2Na)/2], 549.2 [(M − 3Na)/3].

Preparation of 3-Cascade 7. The dithiocarbamate **3** (76 mg, 0.109 mmol) and the dichloro(*p*-cymene)ruthenium(II) dimer (100 mg, 0.163 mmol) were stirred in dichloromethane (25 cm^3) and MeOH (5 cm^3) for 12 h. The solvent was removed in vacuo, the residue extracted with dichloromethane, the extract filtered to remove NaCl, and the solvent removed in vacuo. The product was isolated by size exclusion chromatography (SEC) (Bio-Beads, S-X3; dichloromethane). Yield: 120 mg, 76.5%. Selected IR absorption maxima: ν (cm^{-1}) = 3276 (m), 3054 (m), 2960 (s), 2925 (m), 2867 (m), 1660 (s) (C═O), 1508 (sh, s) (CN), 1469 (m), 1440 (m), 1265 (m), 1214 (s), 1124 (m), 1056 (w), 1031 (w), 998 (w). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.29 (m, 3H, CONH), 5.48 and 5.29 (t, 12H, C$_6$H$_4$), 3.96 (m, 3H, NHC**H**), 3.52 and 3.39 (m, 9H, NHC**H** and C**H**$_2$NCH$_3$), 3.16 (s, 9H, NC**H**$_3$), 2.81 (sept, 3H, ^3J(H,H) = 6.9 Hz, ArC**H**(CH$_3$)$_2$), 2.65 (br, 6H, NC**H**$_2$), 2.31 (m, 6H, C**H**$_2$CO), 2.23 (s, 9H, ArC**H**$_3$), 1.27 (d, 18H, ^3J(H,H) = 6.9 Hz, ArCH(C**H**$_3$)$_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 211.7 (**C**S$_2$), 172.8 (**C**O), 102.8, 98.9, 83.6, 83.5, 82.5, 82.4 (**C**$_6$H$_4$), 50.1, 49.7 (**C**H$_2$), 37.2 (N**C**H$_3$), 36.6, 33.4 (**C**H$_2$), 31.5 (**C**H), 22.7 (Ar**C**H$_3$), 19.1 (ArCH-(**C**H$_3$)$_2$). +ve FAB-MS: *m*/*z* 1440 (M + 1), 1402 (M − Cl), 1270 (M − Cl − cymene), 1103 (M − Cl − cymene − Ru − S$_2$), 1066 (M − 2Cl − cymene − Ru − S$_2$), 964 (M − Cl − cymene − Ru − branch), 929 (M − 2Cl − cymene − Ru − branch). +ve ES-MS: *m*/*z* 1440 (M), 1269 [(M − Cl − cymene), 617 [(M − 2Cl − cymene)/2]. Anal. Found: C, 42.37; H, 5.37; N, 6.96. Calcd for $C_{51}H_{78}Cl_3N_7O_3Ru_3S_6$: C, 42.55; H, 5.47; N, 6.81.

Table 1. Crystal Data for [Ru(S_2CNMe_2)(PPh_3)(η^5-C_5H_5)] Complexes

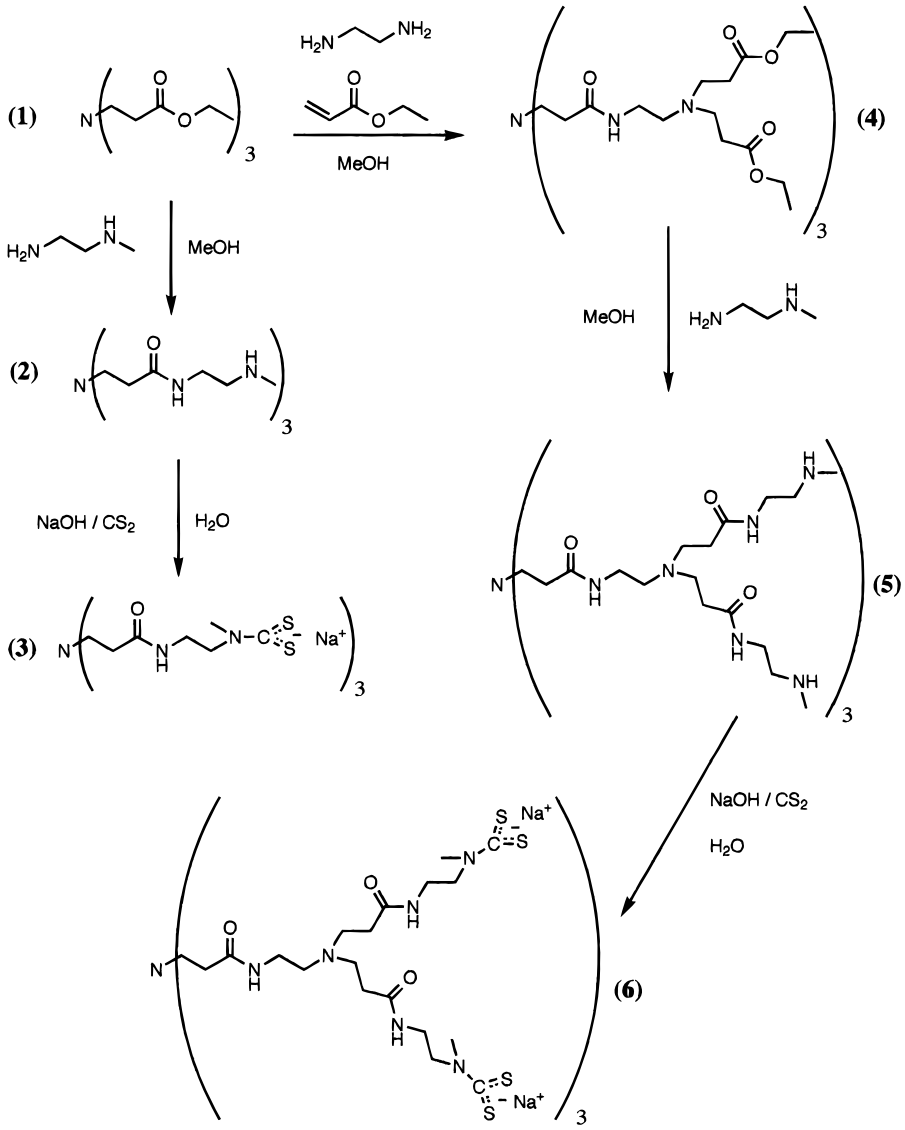
formula	$C_{26}H_{26}NPS_2Ru$	$C_{26}H_{26}NPS_2Ru$
fw	548.6	548.6
lattice type	monoclinic	triclinic
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
a/Å	27.352(1)	10.048(1)
b/Å	9.538(1)	10.335(1)
c/Å	18.956(1)	13.227(1)
α/deg		98.29(1)
β/deg	107.59(1)	95.83(1)
γ/deg		115.61(1)
V/Å^3	4714.3(4)	1204.8(2)
Z	8	2
ρ_{calc}/g cm^{-3}	1.546	1.512
F(000)	2240	560
μ(Cu Kα)/mm^{-1}	7.78	7.61
R_1[a]	0.040	0.041
wR_2[b]	0.093	0.100

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Preparation of 3-Cascade 9. The dithiocarbamate **3** (77 mg, 0.11 mmol) and [RuCl(PPh_3)$_2$(η^5-C_5H_5)] (218 mg, 0.3 mmol) were heated to reflux in MeOH (20 cm^3) for 30 min. The red residue was extracted with dichloromethane, the extract was filtered to remove impurities and NaCl, and the solvent was removed in vacuo. The product was isolated by SEC (Bio-Beads, S-X3; dichloromethane). Yield: 110 mg, 52.4%. Selected IR absorption maxima: ν (cm^{-1}) = 3309 (m), 3040 (m), 2921 (m), 1658 (s) (C═O), 1481 (sh, s) (CN), 1432 (s), 1392 (s), 1267 (m), 1213 (s), 1120 (m), 1089 (s), 1025 (w), 997 (m), 827 (w), 796 (w), 746 (m), 696 (s), 530 (s), 430 (m). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.52 and 7.29 (m, 45H, PC$_6$H$_5$), 6.60 (s, 3H CONH), 5.29 (s, 1H, C**H**$_2$Cl$_2$), 4.35 (s, 15H, C$_5$H$_5$), 3.57 (m, 3H, NHC**H**), 3.19−3.02 (m, 9H, NHC**H** and C**H**$_2$NCH$_3$), 2.80 (s, 9H, NC**H**$_3$), 2.62 (m, 6H NC**H**$_2$), 2.21 (m, C**H**$_2$CO). ^{13}C NMR ($CDCl_3$): δ (ppm) = 216.0 (**C**S$_2$), 172.6 (**C**O), 137.4 (d, ^1J(C,P) = 38.3 Hz), 134.0 (d, ^2J(C,P) = 10.6 Hz), 128.7 (s), 127.1 (d, ^3J(C,P) = 9.1 Hz) (P**C**$_6$H$_5$), 75.9 (**C**$_5$H$_5$), 54.0 (**C**H$_2$Cl$_2$), 49.5 (two coinciding signals), 37.0 (**C**H$_2$), 36.4 (**C**H$_3$), 33.8 (**C**H$_2$). ^{31}P NMR ($CDCl_3$): δ (ppm) = 54.5 (s, **P**Ph$_3$). +ve FAB-MS: *m*/*z* 1913 (M + 1), 1783 (M − 2cp), 1652 (M − PPh$_3$), 1388 (M − 2PPh$_3$), 1126 (M − 3PPh$_3$), 1061 (M − 3PPh$_3$ − cp), 998 (M − 3PPh$_3$ − 2cp), 933 (M − 3PPh$_3$ − 3cp). +ve ES-MS: *m*/*z* 637 [(M/3)$^+$]. Found: C, 55.25; H, 4.87; N, 4.93. Calcd for $C_{90}H_{96}N_7O_3P_3Ru_3S_6$·0.5$CH_2Cl_2$: C, 55.60; H, 5.01; N, 5.02.

Preparation of 6-Cascade 8. The dithiocarbamate **6** (51 mg, 0.03 mmol) and the dichloro(*p*-cymene)ruthenium(II) dimer (55 mg, 0.09 mmol) were stirred in dichloromethane (15 cm^3) and MeOH (2 cm^3) for 12 h. The solvent was removed in vacuo, the residue extracted with dichloromethane, the extract filtered to remove NaCl, and the solvent removed in vacuo. The product was isolated by SEC (Bio-Beads, S-X1; dichloromethane). Yield: 66 mg, 68.9%. Selected IR absorption maxima: ν (cm^{-1}) = 3276 (w), 2956 (w), 1660 (s), 1515 (s), 1438 (m), 1400 (m), 1261 (m), 1209 (m), 1114 (w), 1054 (w), 1033 (w). ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.2−7.8 (br, 9H CONH), 5.46 (d, 12H, C$_6$H$_4$), 5.28 (m, 16H, C$_6$H$_4$, 2C**H**$_2$Cl$_2$), 4.00 (br, 6H, NHC**H**$_{ext}$), 3.40−3.23 (br, 24H, NHC**H**$_{int+ext}$, C**H**$_2$N$_{int+ext}$), 3.16 (s, 18H, NC**H**$_3$), 2.91 (br, 12H, NC**H**$_{2,ext}$), 2.78 (m, 6H, ArC**H**), 2.70 (br, 6H, NC**H**$_{2,int}$), 2.48 (br, 18H, C**H**$_2$CO), 2.20 (s, 18H, ArC**H**$_3$), 1.24 (d, 36H, 3J(H,H) = 6.9 Hz, ArCH(C**H**$_3$)$_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 211.6 (**C**S$_2$), 172.4 (CO), 102.9, 99.0, 83.8, 83.5, 82.6, 82.4 (**C**$_6$H$_4$), 54.2 (**C**H$_2$Cl$_2$), 52.4, 50.3, 50.2, 48.7 (**C**H$_2$), 37.1 (**C**H$_3$), 36.6, 33.5 (two coinciding signals) (**C**H$_2$), 31.6 (Ar**C**H), 22.7 (Ar**C**H$_3$), 19.2 (ArCH-

Scheme 1. Synthesis of Sodium Dithiocarbamate-Terminated Dendrimers



($\mathbf{C}H_3)_2$). Anal. Found: C, 41.79; H, 5.61; N, 7.77. Calcd for $C_{117}H_{183}Cl_6N_{19}O_9Ru_6S_{12}\cdot 2CH_2Cl_2$: C, 42.35; H, 5.60; N, 7.89.

Preparation of 6-Cascade 10. The dithiocarbamate **6** (189 mg, 0.11 mmol) and [RuCl(PPh_3)$_2$(η^5-C_5H_5)] (436 mg, 0.6 mmol) were heated to reflux in MeOH (20 cm^3) for 12 h. The red residue was extracted with dichloromethane, the extract was filtered to remove impurities and NaCl, and the solvent was removed in vacuo. The product was isolated by SEC (Bio-Beads, S-X1; dichloromethane). Yield: 188 mg, 41.3%. Selected IR absorption maxima: ν (cm^{-1}) = 3288 (s), 3050 (m), 2923 (m), 2831 (m), 1648 (s) (C=O), 1535 (s), 1481 (s) (CN), 1432 (s), 1392 (s), 1265 (m), 1213 (s), 1122 (m), 1089 (s), 1027 (w), 997 (m), 796 (w), 746 (m), 696 (s), 530 (s), 421 (w). ^{1}H NMR ($CDCl_3$); δ (ppm) = 7.51 and 7.27 (m, 90H, $C_6\mathbf{H}_5$), 7.16−7.06 (m, 9H, CON**H**), 5.29 (s $C\mathbf{H}_2Cl_2$), 4.34 (s, 30H, $C_5\mathbf{H}_5$), 3.61 and 3.30−3.05 (m, 30H, NHC$\mathbf{H}_2$ and C$\mathbf{H}_2$NCH_3), 2.79 (s, 18H, NC$\mathbf{H}_3$), 2.68−2.27 (m, 42H, NC$\mathbf{H}_2$, C$\mathbf{H}_2$CO, and C$\mathbf{H}_2$N(CH_2)$_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 215.8 (**C**S_2), 172.8 and 172.2 (**C**O), 137.4 (d, ^1J(C,P) = 38.3 Hz), 133.9 (d, ^2J(C,P) = 10.6 Hz), 128.5 (s), 127.0 (d, ^3J(C,P) = 8.9 Hz) (P$\mathbf{C}_6H_5$), 75.9 ($\mathbf{C}_5H_5$), 53.4 ($\mathbf{C}H_2Cl_2$), 52.2, 49.9 (coinciding signals), 49.5, 36.9 (br **C**H_2), 36.4 (**C**H_3), 34.0 (two coinciding signals) (**C**H_2). ^{31}P NMR ($CDCl_3$): δ (ppm) = 54.6 (s, **P**Ph_3). +ve FAB-MS: *m*/*z* 4150.5 (M), 4021.6 (M − 2cp), 3648 (M − PPh_3 − cp − Ru − CS_2), 3520 (M − branch), 2576 (M − 6PPh_3), 2335 (M − 6PPh_3 − cp − Ru − CS_2). Anal. Found: C, 55.03; H, 5.55; N, 6.72. Calcd for $C_{195}H_{219}N_{19}O_9P_6Ru_6S_{12}\cdot CH_2Cl_2$: C, 55.57; H, 5.27; N, 6.28.

Preparation of [RuCl(S_2CN**M**e**$_2$)(*p*-cym)], 11.** Sodium dimethyldithiocarbamate (32 mg, 0.22 mmol) and the dichloro(*p*-cymene)ruthenium(II) dimer (61 mg, 0.1 mmol) were stirred in dichloromethane (10 cm^3) for 12 h. The solvent was removed in vacuo, the residue extracted with dichloromethane, the extract filtered to remove NaCl, and the solvent removed in vacuo. The product was isolated by SEC (Bio-Beads, S-X3; dichloromethane). Yield: 63 mg, 81%. Selected IR absorption maxima: ν (cm^{-1}) = 3058 (m), 2958 (s), 2923 (s), 2865 (m), 1531 (s, CN), 1467 (m), 1440 (m), 1394 (s), 1253 (m), 1153 (s), 1051 (m), 985 (m), 919 (w), 860 (m), 804 (w), 723 (w). ^{1}H NMR ($CDCl_3$): δ (ppm) = 5.45 (d, ^3J(H,H) = 5.9 Hz, 2H, $C_6\mathbf{H}_4$), 5.25 (d, ^3J(H,H) = 5.9 Hz, 2H, $C_6\mathbf{H}_4$), 3.14 (s, 6H, NC$\mathbf{H}_3$), 2.84 (quintet, ^3J(H,H) = 6.9 Hz, 1H, ArC**H**), 2.24 (s, 3H, ArC$\mathbf{H}_3$), 1.27 (d, ^3J(H,H) = 6.9 Hz, 6H, ArCH(C$\mathbf{H}_3$)$_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 211.1 (**C**S_2), 103.2, 98.9, 83.7, 82.6 ($\mathbf{C}_6H_4$), 38.6 (N**C**H_3), 31.7 (**C**H), 22.9 (Ar**C**H_3), 19.3 (ArCH(**C**H_3)$_2$). +ve FAB-MS: *m*/*z* 391 (M + 1). Anal. Found: C, 39.63; H, 4.88; N, 3.43. Calcd for $C_{13}H_{20}ClNRuS_2$: C, 39.93; H, 5.17; N, 3.58.

Preparation of [Ru(S_2CN**M**e**$_2$)(P**P**h**$_3$)(η_5-C_5H_5)], 12.** Sodium dimethyldithiocarbamate (73 mg, 0.5 mmol) and [RuCl(PPh_3)$_2$(η^5-C_5H_5)] (290 mg, 0.4 mmol) were heated to reflux in MeOH (15 cm^3) for 30 min. The orange solid was isolated by filtration and washed with methanol and ether. Yield: 184 mg, 84%. Selected IR absorption maxima: ν (cm^{-1}) = 3050 (s), 2919 (s), 1511 (s, CN), 1479 (s), 1432 (s), 1386 (s), 1257 (m), 1139 (s), 1089 (s), 985 (m), 792 (m), 742 (m),

694 (s), 530 (s), 458 (m), 428 (m), 322 (w). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.46 and 7.19 (m, 15H, $PC_6\mathbf{H}_5$), 4.28 (s, 5H, $C_5\mathbf{H}_5$), 2.69 (s, 6H, $NC\mathbf{H}_3$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 215.0 ($\mathbf{C}S_2$), 137.5 (d, ^1J(C,P) = 38.4 Hz), 134.1 (d, ^2J(C,P) = 10.9 Hz), 128.6 (s), 126.9 (d, ^3J(C,P) = 9.1 Hz, $P\mathbf{C}_6H_5$), 75.9 ($\mathbf{C}_5H_5$), 37.7 ($\mathbf{C}H_3$). ^{31}P NMR ($CDCl_3$): δ (ppm) = 55.0 (s, $\mathbf{P}Ph_3$). +ve FAB-MS: *m*/*z* 549 (M + 1). Anal. Found: C, 56.72; H, 4.66; N, 2.56. Calcd for $C_{26}H_{26}NPRuS_2$: C, 56.91; H, 4.79; N, 2.55.

X-ray Crystallography. Crystallographic data are summarized in Table 1. Intensity data were collected in the ω-scan mode, for the monoclinic polymorph an orange rhomb of dimensions 0.40 × 0.30 × 0.27 mm and for the triclinic polymorph an orange platy needle of dimensions 0.30 × 0.30 × 0.10 mm, both at 203 K on a Siemens P4/RA diffractometer using Cu Kα radiation (1.541 78 Å) to a maximum 2θ value of 120°. The structures were solved by direct methods. In the triclinic polymorph, the cyclopentadienyl ring was found to be disordered, and this was resolved into two partial-occupancy orientations, the major-occupancy portions of which were refined anisotropically. In both complexes, the phenyl rings of the phosphine ligands were refined as optimized rigid bodies and the remaining non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$ [$U(H) = 1.5U_{eq}(C-Me)$], and were allowed to ride on their parent carbon atoms. Computations were performed by full-matrix least-squares techiques based on F^2 to give for the monoclinic (triclinic) polymorphs $R_1 = 0.040$ (0.041), w$R_2 = 0.093$ (0.100) for 2987 (3083) independent, observed, absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$] using the SHELXTL PC program system, version 5.03.

Results and Discussion

Syntheses. The PAMAM dendrimers (**1** and **4**) were prepared by following literature methods. The ester-terminated dendrimers **1** and **4** were reacted with excess *N*-methylethylenediamine to obtain the new compounds **2** and **5** with secondary amines on the surface of the polymer (Scheme 1). Longer reaction times and a greater excess of the amine reagent than were used in the literature were necessary to ensure complete reaction. The ^{1}H NMR spectra of **2** and **5** show only one resonance each for the *N*-methyl protons. This confirms that the primary amine of *N*-methylethylenediamine reacts preferentially with the ester-terminated dendrimers and that the surface is constituted only of secondary amine groups. This difference in reactivity of the primary and secondary amine moieties also suggests that, in this special case, chain termination of the growing dendrimer via ring closure is extremely unlikely. There was no evidence in our results for such species.

Further reaction of **2** and **5** with CS_2 and NaOH gave the sodium dithiocarbamate salts **3** and **6** as pale yellow hygroscopic solids (Scheme 1), which were characterized by infrared and ^{1}H and ^{13}C NMR spectroscopy.

Due to the hygroscopic nature of **3** and **6**, they were reacted without further purification to form the desired metallodendrimers, which could then be readily purified by size exclusion chromatography (SEC). The dendritic dithiocarbamate was treated with a suitable metal precursor to chelate the metal directly via halide metathesis. The bidentate nature of the dithiocarbamate ligand results in strong metal−ligand binding, conferring considerable stability on the product. Reaction of **3** and **6** with the dichloro(*p*-cymene)ruthenium(II) dimer [Ru(μ-Cl)$_2$Cl$_2$(*p*-cym)$_2$] gave **7** (Figure 1) and **8**, respectively, whereas reaction with chlorocyclopentadienylbis(triphenylphosphine)-ruthenium(II), [RuCl(PPh_3)$_2$(η^5-C_5H_5)], resulted in **9** and **10** (Figure 2). The metal complexes were purified by size exclusion chromatography (Bio-Beads S-X3 and S-X1; eluent dichloromethane) to give orange/brown solids for **7** and **8** and yellow/orange solids for **9** and **10**.

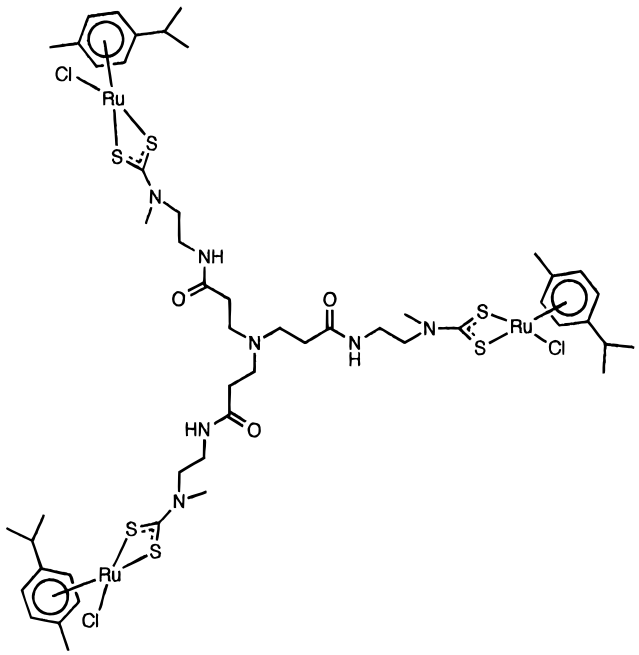


Figure 1. 3-Cascade **7**.

^{1}H and ^{13}C{^{1}H} NMR Spectra. The *N*-methyl proton and carbon resonances in the NMR spectra of the novel compounds are listed in Table 2. Carbon DEPT experiments were performed to confirm the position of the *N*-methyl carbon signal in all cases. The *N*-methyl resonances in the ^{1}H NMR spectra are observed at 2.22 and 2.40 ppm for the zeroth- and first-generation amines (**2** and **5**), respectively, and at 3.39 ppm for the respective dendrimer dithiocarbamate salts (**3** and **6**). The equivalent resonances in the ^{13}C{^{1}H} NMR spectra are observed at 34.5 ppm for **2** and **5** and 43.5 ppm for **3** and **6**. New resonances at ca. 211 ppm are observed which can be attributed to the CS_2^- moieties. Hence, incorporation of the CS_2^- moiety in the formation of the dithiocarbamates can be inferred by a downfield shift ($\Delta\delta$ = ca. 1.0 ppm) of the methyl resonances in the ^{1}H NMR spectra and an upfield shift ($\Delta\delta$ = ca. 9.0 ppm) plus the presence of additional signals at ca. 211 ppm in the ^{13}C{^{1}H} NMR spectra. Similar chemical shift changes are observed for the ^{1}H NMR resonances arising from the external ethylene spacer groups, but little change is seen for the internal groups.

Coordination of the ruthenium center to the dithiocarbamate ligand leads to an upfield shift of the *N*-methyl proton and carbon resonances in the NMR spectra of the zeroth- and first-generation metallodendrimers. In the ^{1}H NMR spectra, the observed shift is greater for the methyl signals of **9** and **10** ($\Delta\delta$ = ca. 0.6 ppm) than for those of **7** and **8** ($\Delta\delta$ = ca. 0.2 ppm). The *N*-methyl resonances in the ^{13}C{^{1}H} NMR spectra have shifted upfield ($\Delta\delta$ = ca. 5−7 ppm compared to those of **3** and **6**) upon the formation of the metallodendrimers. Conversely, the CS_2 signals are shifted downfield. Notably, no signals are seen in the spectra of compounds **7**−**10** that could be assigned to partially metalated dendrimers. Again, only small changes were seen in the chemical shifts arising from the internal ethylene groups of the dendrimers.

The simple dimethyldithiocarbamate complexes were also prepared, and their spectroscopic data were compared with those of the metal-complexed dendrimers. The chemical shift values for the *N*-methyl and CS_2 resonances of the monomers [RuCl(S_2CNMe_2)(*p*-cym)] and [Ru(S_2CNMe_2)(PPh_3)(η^5-C_5H_5)] were found to be almost identical to those values obtained for

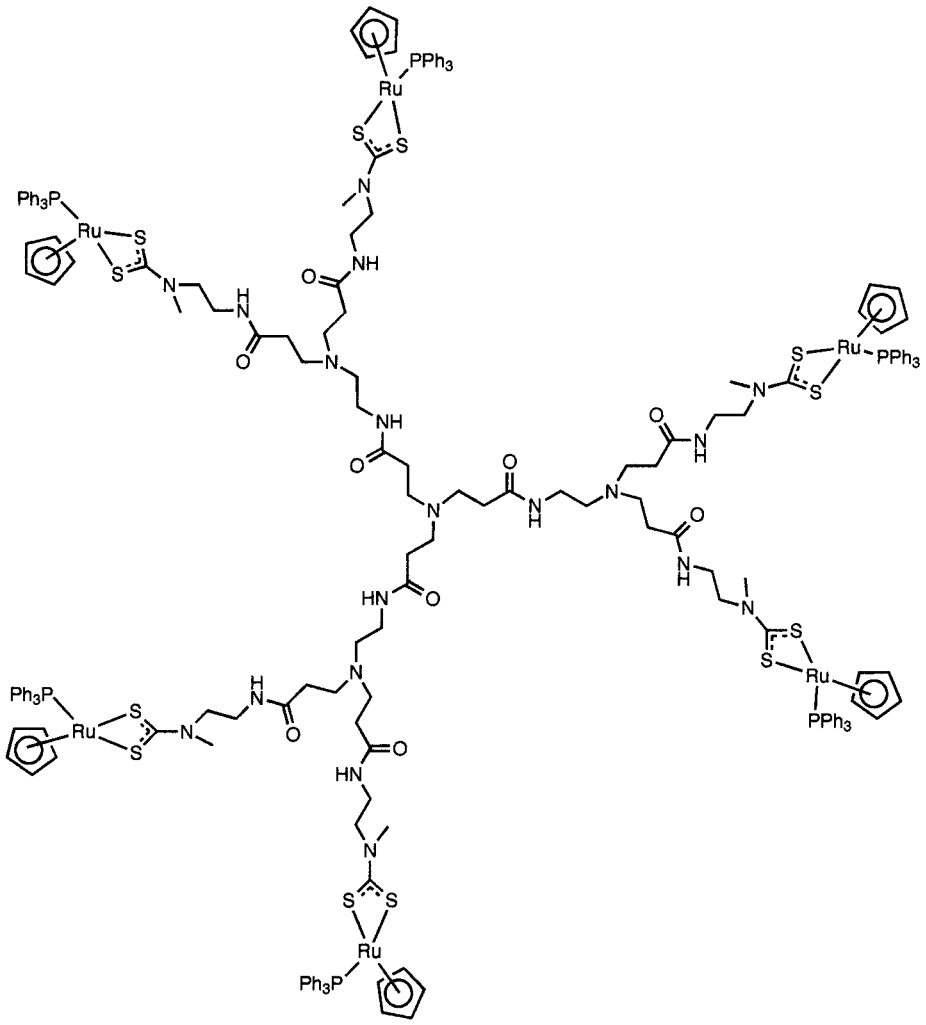


Figure 2. 6-Cascade **10**.

Table 2. Selected ^{1}H and ^{13}C NMR Data

	δ/ppm (N**C**H$_3$)		
compd	^{1}H	^{13}C	δ/ppm (**C**S$_2$)
2	2.22	34.7	
5	2.40	34.5	
3	3.39	43.6	210.7
6	3.39	43.5	210.8
11	3.14	38.6	211.1
7	3.16	36.6	211.7
8	3.16	37.1	211.6
12	2.69	37.7	215.0
9	2.80	36.4	216.0
10	2.79	36.4	215.8

the respective zeroth- and first-generation dendrimers **7**, **8** and **9**, **10**. These results indicate that the ^{1}H and ^{13}C{^{1}H} NMR data can be used as diagnostic tools for the successful formation of each of the metal−dendrimer complexes.

The metallodendrimers are present as geometrical isomers due to the restricted rotation about the CN bond. The data collected for the crystal structure of **12** shows that the CN bond has considerable double-bond character when the dithiocarbamate ligand is coordinated with a metal. The signals observed in the ^{1}H NMR spectra for the CH_2 protons are multiplets and not triplets as would be expected for one isomer. However, the relative ratio of aliphatic protons to aromatic protons indicated that the dendrimers were monodisperse.

The *N*-methyl proton and carbon resonances in the NMR spectra of the novel compounds can be compared and used as indicators of successful reactions (Table 2).

Infrared Spectra. The infrared spectra of **2**−**6** were recorded as thin films on NaCl plates in the region 4000−600 cm^{-1}, and those of **7**−**12** were recorded as KBr pellets in the region 4000−400 cm^{-1}.

The 1450−1550 cm^{-1} region of the IR spectra of dithiocarbamates is associated with the R_2N-CS_2 stretching vibrations.[20] This CN vibration is observed at 1479 cm^{-1} for dithiocarbamate **3** and at 1467 cm^{-1} for **6**. This compares to a value of 1480 cm^{-1} for the simple sodium dimethyldithiocarbamamte.[21] Upon coordination of the metal centers to the ligands, shifts in ν_{CN} to 1508 and 1515 cm^{-1} for metal complexes **7** and **8**, respectively, and to 1481 cm^{-1} for both of the metal complexes **9** and **10** are seen. This is entirely consistent with the expected increase of double-bond character of the CN group, resulting in higher vibrational frequencies.[22] The ν_{CN} frequencies are lower than those of the simple dimethyldithiocarbamate ligands which can be seen at 1531 cm^{-1} for **11** and 1511 cm^{-1} for **12**. This can be attributed to the increased size of the substituent (R) on the dithiocarbamate.[23]

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Other vibrations of note are those due to the ν_{CO} stretch which is present in the amide functionalities of the dendrimer. This has been observed in the region 1639−1660 cm^{-1} for all of the compounds **7**−**10**, confirming that the dendrimer branch units are present in the metal complexes.

Mass Spectra. The amines **2** and **5** were characterized by positive-ion fast atom bombardment (FAB) mass spectrometry. Protonated molecular ions are observed at 402 for **2** and 1128 for **5** (all values are *m*/*z*). There are no peaks present which could be attributed to partially aminated compounds (i.e., for **2**, peaks at 374 and 346 would be due to the di- and monoamines, respectively; and for **5**, peaks at 1100, 1072, 1044, 1016, 988, and 960 would correspond to the penta- to monoamines, respectively). The zeroth-generation sodium dithiocarbamate **3** was characterized by negative-ion FAB and electrospray (ES) mass spectrometry. In the FAB-MS, a peak at 672, attributed to (M − Na), was observed. In the ES-MS, peaks were seen that could be attributed to the ions (M − Na), [(M − 2Na)/2], and [(M − 3Na)/3]. The first-generation dithiocarbamate **6** was successfully characterized by negative-ion ES-MS, showing clear peaks attributable to the ions [(M − 2Na)/2] and [(M − 3Na)/3]. Attempts to characterize dithiocarbamate **6** by negative-ion FAB-MS were unsuccessful due to the mass of the ion being beyond the range of the instruments used.

Several attempts were made to characterize the metallodendrimers **7**−**10**, by FAB, ES, and MALDI-TOF mass spectrometries. In no case did the MALDI-TOF provide useful results, possibly as a consequence of the strong absorption of the laser light by the metal complexes themselves. Positive-ion ES-MS of the zeroth-generation metallodendrimers showed peaks due to (M/3) for **9** and (M), [(M − Cl − cymene)], and [(M − 2Cl − cymene)/2] for **7**. However, no useful results were obtained for the higher generation dendrimers, **8** and **10**, despite several attempts, using a variety of different machines.

The positive-ion FAB mass spectra for **7**, **9**, and **10** showed the expected protonated molecular ions. Peaks were not observed in the regions corresponding to partially metalated dendrimers; i.e., for **7** peaks would have been present at 1193 and 945 for the dimetalated and trimetalated species, respectively, for **9** peaks would have been present at 1508 and 1103, and for **10** peaks would have been present at 3745, 3340, 2935, 2530, and 2125 for the penta-, tetra-, tri-, di-, and monometalated products! Attempts to characterize **8** by positive-ion FAB mass spectrometry were unsuccessful.

X-ray Crystal Structure. **12** crystallized as a mixture of both orange needles and rhombs in an approximate 10:1 ratio. X-ray analysis showed the needles to be the already established triclinic form of the complex[24] (Figure 3). The rhombs were found to be monoclinic, and a single-crystal structural analysis showed them to be chemically identical and hence to be a new polymorphic form. The conformations of the two polymorphs do not exhibit any major differences, though the packing density of the new monoclinic form is significantly greater with a ρ_{calc} of 1.546 g cm^{-3}; cf. 1.512 g cm^{-3} for the triclinic polymorph (both values corresponding to structures determined at −70 °C). The feature of interest in the context of the development of subsequent dendritic structures is the degree of double-bond character present in the central C−N bond in the dithiocarbamate ligand. In both polymorphs, this bond exhibits significant partial double-bond character [1.332(7) and 1.330(6) Å in the triclinic and monoclinic polymorphs, respectively], the ligands in each case being planar to within 0.03 Å.

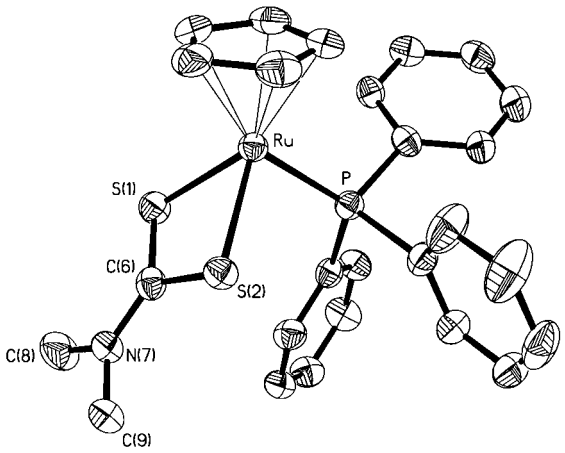

Figure 3. Molecular structure of **12** (monoclinic polymorph, 50% probability ellipsoids).

Conclusions

We have clearly demonstrated the synthesis of dithiocarbamate-terminated dendrimers and their subsequent reactions to form ruthenium dithiocarbamate complexes. We have shown that both IR and NMR (^1H and ^{13}C) spectra provide useful indicators of metal complex formation. We have also shown that both FAB and ES mass spectrometry are useful characterizational tools although, as the dendrimers become heavier, results become more difficult to obtain.

Acknowledgment. We thank the EPSRC for a studentship (F.J.S.) and Johnson Matthey for their generous loan of $RuCl_3$. We are indebted to the following people for their expertise in mass spectrometry characterization: Mr. G. P. Tucker, Mr. J. Barton, and Dr. C. Ball at Imperial College, Mr. P. R. Ashton at Birmingham University, Ms. M. O'Sullivan at the University of Warwick, and Dr. J. A. Ballantine at the University of Wales, Swansea.

IC980067B

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