

Synthesis and characterization of a first generation organorhenium dendrimer

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Dedicated to Professor Fausto Calderazzo on his 70th birthday.

Abstract

A new, more efficient route to the functionalized Cp compound $[\eta^5\text{-(C}_5\text{H}_4\text{)CH}_2\text{CH}_2\text{CH}_2\text{I}]\text{Re(CO)}_3$, (**2**) is reported. The reaction of **2** with $[(\text{LiC}_5\text{H}_4)\text{Re(CO)}_3]$ yields the new binuclear complex $(\text{CO})_3\text{Re}[(\eta^5\text{-C}_5\text{H}_4)(\text{CH}_2)_3(\eta^5\text{-C}_5\text{H}_4)]\text{Re(CO)}_3$ (**3**). The crystal structure of **3** has been determined. Crystals of **3** are triclinic, space group $P\bar{1}$, with $a = 8.241(1)$ Å, $b = 11.154(1)$ Å, $c = 11.699(1)$ Å, $\alpha = 106.383(10)^\circ$, $\beta = 102.512(10)^\circ$, $\gamma = 105.067(10)^\circ$, $Z = 2$ and $R = 0.045$. Compound **2** has also been used to build up a first generation organometallic dendrimer containing six rhenium units by the convergent method. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Dendrimer; Rhenium; Convergent synthesis

1. Introduction

Recent advances in dendritic molecules have established synthetic strategies for the systematic construction of various organometallic dendrimers [1]. Lately the focus has shifted from the synthetic aspects to their properties and applications. Synthesis of dendrimers with components of specific functions have been targeted [2]. Properties are being modified increasingly with functional centers. The multiplication of functional components attached to a dendritic skeleton moves into the forefront, not the dendrimer itself, and new materials with specific properties are anticipated [3].

A wide range of organometallic dendrimers have been synthesized in the past decade with varying molecular architecture incorporating different metal atoms. It has been demonstrated that the metal atom can be incorporated at the periphery [4] or at the core [5] or throughout the dendritic skeleton [6]. We have been successful in our laboratory in the past to build up various organometallic dendrimers incorporating differ-

ent organometallic units including Fe, Ru and Co functionalities [1,7]. Having established the generality that can be adopted for the construction of organometallic dendrimers we have turned our attention to the synthesis of cascade molecules for possible applications. The rich chemistry of various oxo-rhenium compounds in homogeneous catalysis is well documented [8]. Our first aim was to investigate the feasibility of synthesizing a first generation dendrimer with CpRe(CO)_3 (**1**) units in the dendritic wedges and to attempt subsequently the oxidation of the carbonyl groups to generate oxo-rhenium units in the dendritic periphery.

2. Experimental

2.1. General procedures

All reactions were carried out under a purified nitrogen atmosphere using standard Schlenk line techniques. Solvents were distilled from appropriate drying agents under nitrogen prior to use. Potassium carbonate was dried before use and $\text{Re}_2(\text{CO})_{10}$ (Strem), 3,5-dihydroxybenzyl alcohol (Aldrich), 1,1,1-tris(4-hydroxy-

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phenyl)ethane (Aldrich), *n*-BuLi (1.5 M hexane solution, Merck) were used as received. Diiodopropane (Aldrich) was refluxed over CaH_2 and was distilled (under reduced pressure) prior to use. $\text{CpRe}(\text{CO})_3$ (**1**) was synthesized by literature methods [9]. Silica gel (Merck, 60) was used for column chromatography eluting the products with appropriate solvents/solvent mixtures. NMR spectra were recorded at ambient temperature on a Varian Unity-400 spectrometer in CDCl_3 at the following frequencies: ^1H , 399.952 MHz; ^{13}C , 100.577 MHz. Chemical shifts are reported relative to the residual signals of CDCl_3 . Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer as hexane or CH_2Cl_2 solutions. Mass spectra were obtained on a VG-70SEQ mass spectrometer using xenon gas in the FAB mode and a Voyager-DE PRO machine was used for MALDI TOF analysis.

2.2. Synthesis of $[(\eta^5\text{-C}_5\text{H}_4)(\text{CH}_2)_3\text{I}]\text{Re}(\text{CO})_3$ (**2**)

n-BuLi (0.62 ml, 1.5 M, 1.0 mmol) was added to a degassed THF (15 ml) solution of $\text{CpRe}(\text{CO})_3$, (0.28 g, 0.83 mmol) at -78°C and was stirred at that temperature for 3 h. Diiodopropane (0.2 ml, 1.7 mmol) was added and the reaction mixture brought to room temperature. It was then stirred for an additional 2 h at this temperature. Solvent was removed under vacuum and the residue dissolved in CH_2Cl_2 . The CH_2Cl_2 solution was filtered and the volume reduced to ~ 10 ml. Silica gel (1 g) was added into the solution and the solvent pumped off. The residue was then loaded onto a column of silica gel prepared with hexane. Excess diiodopropane was removed by first eluting the column with hexane. Unreacted **1** was then collected with 5% CH_2Cl_2 /hexane and compound **2** was eluted with 10% CH_2Cl_2 /hexane. Small amounts of the dimer (**3**) were also collected in the last fraction on eluting with 20% CH_2Cl_2 /hexane mixture. Compound **2** was obtained by adding pentane to a CH_2Cl_2 solution of the residue obtained above to give the required product as a colorless oil. Yield 0.21 g (50%). IR (CH_2Cl_2) ν (CO) 2021, 1924 cm^{-1} ; ^1H -NMR δ 5.26 (m, 4H Cp), 3.19 (t, $J(\text{H,H}) = 6.79$ Hz, 2H, $-\text{CH}_2\text{I}$), 2.55 (m, 2H, CpCH_2-), 1.99 (m, 2H, $-\text{CH}_2\text{CH}_2\text{I}$); ^{13}C -NMR δ 194.2 (CO), 108.9 (*ipso*-Cp), 83.8 (Cp), 83.2 (Cp) 34.9 (CpCH_2-), 28.8 ($-\text{CH}_2-$), 5.2 ($-\text{CH}_2\text{I}$).

2.3. Synthesis of compound **4**

A mixture of **2** (0.23 g, 0.45 mmol), 3,5-dihydroxybenzyl alcohol (0.031 g, 0.22 mmol), K_2CO_3 (0.18 g, 1.3 mmol), 18-crown-6 (0.014 g, 0.053 mmol) was refluxed in acetone (15 ml) for 72 h. The reaction was monitored periodically by TLC. The solvent was evaporated under reduced pressure and the residue was extracted with CH_2Cl_2 (3×10 ml). The combined CH_2Cl_2 extracts

were chromatographed using the procedure described in Section 2.2 but using a silica gel column prepared with 10% ethylacetate/hexane. After eluting the column with 10% ethylacetate/hexane, compound **4** was then eluted with 30% ethyl acetate/hexane. Mononuclear **5** was collected as the last fraction eluting with 50% ethyl acetate/hexane mixture. Compound **4** was obtained by adding pentane to a CH_2Cl_2 solution of the residue obtained above to give the required product as a colorless oil. Yield, 0.15 g (74%). IR (CH_2Cl_2), ν (CO), 2021, 1924 cm^{-1} ; ^1H -NMR δ 6.51 (d, $J(\text{H,H}) = 1.6$ Hz, 2H, Ar), (t, $J(\text{H,H}) = 1.99$ Hz, 1H, Ar), 5.26 (m, 8H, Cp), 4.63 (s, Ar- CH_2OH), 3.98 (t, $J(\text{H,H}) = 5.99$ Hz, 4H, $-\text{CH}_2\text{O}-$), 2.63 (m, 4H, CpCH_2-), 1.96 (m, 4H, $-\text{CH}_2\text{CH}_2\text{O}-$); ^{13}C -NMR δ 194.2 (CO), 160.0 (Ar), 143.4 (Ar), 110.2 (*ipso*-Cp), 105.1(Ar), 100.5 (Ar), 83.6 (Cp), 83.0 (Cp), 66.5 ($-\text{CH}_2\text{O}-$), 65.2 ($-\text{CH}_2\text{OH}$), 31.0 (CpCH_2-), 24.7 ($-\text{CH}_2-$); MS (FAB) m/z 890 (M^+), 862 ($\text{M}-\text{CO}^+$), 806 ($\text{M}-3\text{CO}^+$), 778 ($\text{M}-4\text{CO}^+$), 750 ($\text{M}-5\text{CO}^+$), 722 ($\text{M}-6\text{CO}^+$). Anal. Calc. for $\text{C}_{29}\text{H}_{26}\text{O}_9\text{Re}_2\cdot\text{CH}_2\text{Cl}_2$: C 36.92, H 2.89. Found: C 36.76, H 2.76.

Solvent was removed from the last fraction and the compound (**5**) was obtained by adding pentane into a CH_2Cl_2 solution of the residue obtained: Yield, 0.047 g (20%); IR (CH_2Cl_2), ν (CO), 2021, 1924 cm^{-1} ; ^1H -NMR δ 6.48 (s, 1H, Ar), 6.45 (s, 1H, Ar), 6.31 (t, 1H, $J(\text{H,H}) = 2.19$ Hz, Ar), 5.26 (m, 4H, Cp), 4.61 (s, 2H, Ar CH_2-), 3.96 (t, 2H, $\text{CH}_2\text{CH}_2\text{O}-$, $J(\text{H,H}) = 5.98$ Hz), 2.62 (m, CpCH_2- , 2H, $J(\text{H,H}) = 7.59$ Hz), 1.96 (m, $-\text{CH}_2\text{CH}_2\text{O}$, 2H); ^{13}C -NMR δ 194.2 (CO), 160.2 (Ar), 156.8 (Ar), 143.6 (Ar), 110.2 (Ar), 109.2 (*ipso*-Cp), 106.2 (Ar), 105.1 (Ar), 101.0 (Ar), 83.6 (Cp), 83.0 (Cp), 66.5 ($-\text{CH}_2\text{O}-$), 65.0($-\text{CH}_2\text{OH}$), 31.0 (CpCH_2-), 24.7 ($-\text{CH}_2-$); MS (FAB) m/z 516 (M^+), 488 ($\text{M}-\text{CO}^+$), 460 ($\text{M}-2\text{CO}^+$), 432 ($\text{M}-3\text{CO}^+$).

2.4. Synthesis of compound **6**

Bromination of **4** was carried out using $\text{CBr}_4/\text{PPh}_3$. The hydroxy wedge **4** (0.13 g, 0.14 mmol) was stirred with a mixture of CBr_4 (0.064 g, 0.19 mmol) and PPh_3 (0.051 g, 0.19 mmol) in THF (10 ml). The reaction was monitored by TLC. Additional amounts of $\text{CBr}_4/\text{PPh}_3$ (2×0.19 mmol) were added to drive the reaction to completion. The reaction was then quenched by adding few drops of distilled water. Solvent was evaporated under vacuum and the residue extracted with CH_2Cl_2 (3×10 ml). The combined extracts were chromatographed using a procedure described in Section 2.2 but using a silica gel column prepared with hexane. The column was first eluted with hexane and the benzyl bromide **6** was eluted with 20% ethyl acetate/hexane mixture. Solvent was removed under reduced pressure and compound **6** was obtained by adding pentane to a CH_2Cl_2 solution of the residue obtained to give the

required product as a colorless oil. Yield, 0.13 g (92%). IR (CH_2Cl_2), ν (CO), 2021, 1924 cm^{-1} ; $^1\text{H-NMR}$ δ 6.52 (d, 2H, $J(\text{H,H}) = 2.39$ Hz, Ar), 6.36 (t, $J(\text{H,H}) = 2.39$ Hz, 1H, Ar), 5.26 (m, 8H, Cp), 4.40 (s, 2H, $-\text{CH}_2\text{Br}$), 3.97 (t, $J(\text{H,H}) = 5.59$ Hz, 4H, $-\text{CH}_2\text{O}-$), 2.62 (m, $J(\text{H,H}) = 7.59$ Hz, 4H, CpCH_2-), 1.96 (m, 4H, $\text{CH}_2\text{CH}_2\text{O}-$); $^{13}\text{C-NMR}$ δ 194.2 (CO), 159.9 (Ar), 139.8 (Ar), 110.2 (*ipso*-Cp), 107.5 (Ar), 101.4 (Ar), 83.6 (Cp), 83.0 (Cp), 66.6 ($-\text{CH}_2\text{O}-$), 33.4 (ArCH_2Br), 31.0 (CpCH_2-), 24.7 ($-\text{CH}_2-$); MS (FAB) m/z , 954 (M^+), 926 ($\text{M}-\text{CO}^+$), 870 ($\text{M}-3\text{CO}^+$), 842 ($\text{M}-4\text{CO}^+$), 814 ($\text{M}-5\text{CO}^+$), 786 ($\text{M}-6\text{CO}^+$); Anal. Calc. for $\text{C}_{29}\text{H}_{25}\text{O}_8\text{BrRe}\cdot 2\text{CH}_3\text{COOC}_2\text{H}_5$: C 39.19, H 3.64. Found: C 39.49, H 2.72.

2.5. Synthesis of compound 7

A mixture of **6** (0.10 g, 0.10 mmol), 1,1,1-tris(4-hydroxyphenyl)ethane (0.010 g, 0.033 mmol), K_2CO_3 (0.05 g, 0.36 mmol) and 18-crown-6 (0.010 g, 0.038 mmol) was refluxed in acetone (15 ml) for 72 h. The reaction was monitored by TLC. The solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 (3×10 ml). The combined extracts were chromatographed using a procedure described in Section 2.2 but using a silica gel column prepared with 10% ethylacetate/hexane. The column was first eluted with 10% ethylacetate/hexane and the first generation rhenium dendrimer was then eluted with 35% ethylacetate/hexane. Solvent was removed under reduced pressure and the compound **7** was obtained by adding pentane to a CH_2Cl_2 solution of the residue obtained, to give the required product as a colorless oil. Yield 0.084 g, (82%). IR (CH_2Cl_2), ν (CO), 2021, 1924 cm^{-1} ; $^1\text{H-NMR}$ δ 7.00 (d, $J(\text{H,H}) = 8.79$ Hz, 6H, Ar), 6.84 (d, $J(\text{H,H}) = 8.79$ Hz, 6H, Ar), 6.49 (d, $J(\text{H,H}) = 2.39$ Hz, 6H, Ar), 6.39 (t, $J(\text{H,H}) = 1.99$ Hz, 3H, Ar), 5.26 (m, 24H, Cp), 4.95 (s, $\text{ArCH}_2\text{O}-$, 6H), 3.97 (t, $J(\text{H,H}) = 5.59$ Hz, 12H, $-\text{CH}_2\text{O}-$), 2.62 (m, $J(\text{H,H}) = 7.59$ Hz, 12H, CpCH_2-), 2.17 (s, 3H, $-\text{CCH}_3$), 1.96 (m, 12H, $\text{CH}_2\text{CH}_2\text{O}-$); $^{13}\text{C-NMR}$, δ 194.3 (CO), 160.0 (Ar), 156.7 (Ar), 142.0 (Ar), 139.6 (Ar), 129.5 (Ar), 113.9 (Ar), 110.3 (*ipso*-Cp), 105.8 (Ar), 100.7 (Ar), 83.6 (Cp), 83.11 (Ar), 69.8 ($-\text{CH}_2\text{O}-$), 66.6 ($\text{ArCH}_2\text{O}-$), 53.7 ($-\text{CCH}_3$), 31.0 (CpCH_2-), 29.2 ($-\text{CCH}_3$), 24.7 ($-\text{CH}_2-$); MS (MALDI TOF) 3083 ($\text{M}-\text{CO} + \text{matrix}^+$), 3214 ($\text{M}-3\text{CO} + 2\text{matrix}^+$), 3345 ($\text{M}-5\text{CO} + 3 \text{matrix}^+$).

2.6. Synthesis of compound 3

The compound $\text{CpRe}(\text{CO})_3$ (0.25 g, 0.74 mmol) was reacted with *n*-BuLi (0.6 ml, 1.5 M, 0.96 mmol) at -78°C in THF (15 ml). The reaction mixture was stirred at this temperature for 2.5 h and diiodopropane (0.04 ml, 0.37 mmol) was added. The reaction mixture

was warmed to room temperature and stirred for an additional 2 h. The solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 (3×10 ml). The combined extracts were then chromatographed using a procedure described in Section 2.2. Complex **3** was eluted with 20% CH_2Cl_2 /hexane and the solvent removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and white crystals of **3** were obtained by the slow diffusion of pentane into the CH_2Cl_2 solution. Yield 0.053 g (22%). m.p.: $108-110^\circ\text{C}$; IR (CH_2Cl_2), ν (CO), 2021, 1924 cm^{-1} ; $^1\text{H-NMR}$ δ 5.25 (m, 8H, Cp), 2.47 (t, $J(\text{H,H}) = 7.99$ Hz, 4H, CpCH_2-), 1.70 (m, $-\text{CH}_2-$, 2H); $^{13}\text{C-NMR}$, δ 194.2 (CO), 110.0 (*ipso*-Cp), 83.6 (Cp), 82.9 (Cp) 33.5 ($-\text{CH}_2-$), 27.6 (CpCH_2-); MS (FAB) m/z 710 (M^+), 682 ($\text{M}-\text{CO}^+$), 654 ($\text{M}-2\text{CO}^+$), 626 ($\text{M}-3\text{CO}^+$), 598 ($\text{M}-4\text{CO}^+$), 570 ($\text{M}-5\text{CO}^+$), 542 ($\text{M}-6\text{CO}^+$);

2.7. Crystal structure determination of 3

A colorless crystal selected from a batch obtained by slow diffusion of pentane into a CH_2Cl_2 solution of compound **3** at -30°C , was used for the X-ray diffraction study. Crystal and refinement data is given in Table 1. Data were collected at room temperature using a Nonius Kappa CCD with 1.5 kW graphite monochromated Mo radiation. The strategy for the data collection was evaluated using the COLLECT Software [10]. Exposure times of 80 s per frame and scan widths of 1° were used throughout the data collection. Four sets of data were collected: a $180^\circ \varphi$ scan and 3 ω scans. The four sets of data were scaled and reduced using Denzo-SMN [11]. Unit cell dimensions were refined on all data. The data were treated for absorption corrections using the program SORTAV [12]. The structure was solved and refined using SHELX97 [13]. Hydrogen atoms were placed in calculated positions and included in the model during later stages of the refinement.

3. Results and discussion

Scheme 1 depicts the synthetic strategy involved in the build-up of a first generation dendrimer containing six $\text{CpRe}(\text{CO})_3$ units at the periphery.

Previously we have synthesized organometallic dendrimers in which the metal atom is σ -bonded to the dendritic skeleton at the periphery. Using this strategy we have synthesized dendrimers containing up to 48 metal atoms at the dendritic periphery [7a]. Recently we prepared a first generation dendrimer in which the linking unit is primarily derived from one of the ancillary ligands which is π -bonded to the metal atom (see Scheme 1). Herein we report the systematic construction of a first generation organometallic rhenium den-

dimer using standard convergent methodology [14] to investigate the potential of the rhenium functionality incorporated in the dendrimer.

3.1. Synthesis of $[(\eta^5\text{-C}_5\text{H}_4)\text{CH}_2\text{CH}_2\text{CH}_2\text{I}]\text{Re}(\text{CO})_3$ (**2**) and $(\text{CO})_3\text{Re}[(\eta^5\text{-C}_5\text{H}_4)(\text{CH}_2)_3(\eta^5\text{-C}_5\text{H}_4)]\text{Re}(\text{CO})_3$ (**3**)

Compound **2** had been synthesized previously by Casey and coworkers [15] from $\text{CpRe}(\text{CO})_3$ by introducing an allyl unit on the Cp ring and subsequently converting the double bond of the allyl group into a halo-alkyl functionality. We find that this compound can be synthesized in a single step and with better overall yields. Thus **2** was synthesized by the addition of excess of diiodopropane to a THF solution of $[\text{Li}(\text{C}_5\text{H}_4)\text{Re}(\text{CO})_3]$ (**1a**) [16] Eq. (1).

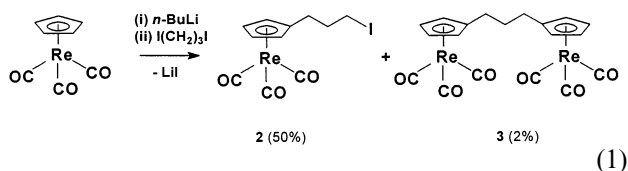


Table 1
Crystallographic and structure refinement data for compound **3**

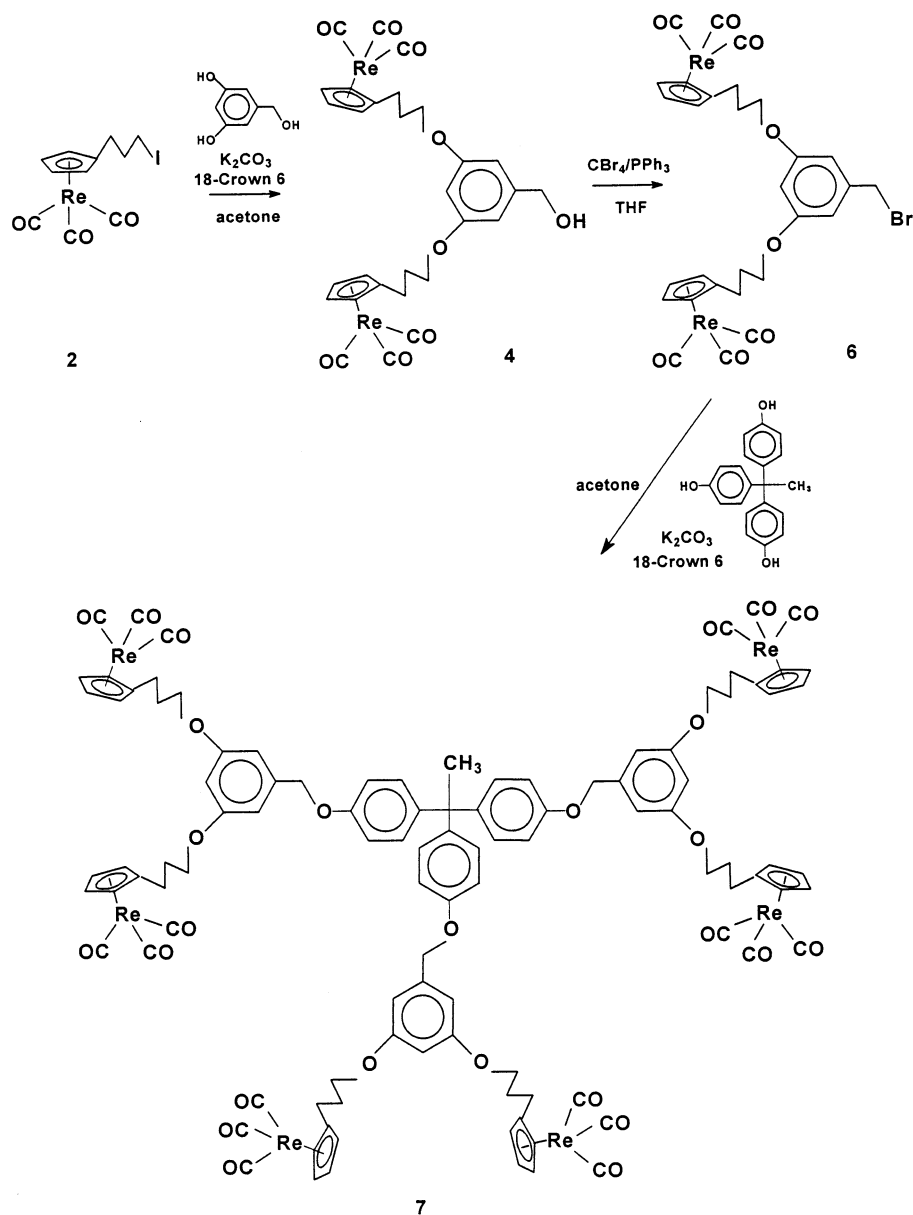
Empirical formula	$\text{C}_{19}\text{H}_{14}\text{O}_6\text{Re}_2$
Formula weight	710.70
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	8.241(1)
b (Å)	11.154(1)
c (Å)	11.699(1)
α (°)	106.38(1)
β (°)	102.51(1)
γ (°)	105.07(1)
V (Å ³)	946.2(2)
Z , Calculated density (Mg m ⁻³)	2, 2.495
Temperature (K)	293(2)
Wavelength (Å)	0.71070
Absorption coefficient (mm ⁻¹)	12.814
$F(000)$	652
Crystal size (mm)	0.23 × 0.35 × 0.45
Diffractometer	Enraf–Nonius Kappa CCD
Data collection method	1° φ and ω scans
Theta range for data collection (°)	1.91 to 30.53
Index ranges	$-11 < h < 11, -15 < k < 5, -16 < l < 16$
Reflections collected/unique	13452/5635 [$R_{\text{int}} = 0.047$]
Completeness to $2\theta = 30.53$	97.3%
Absorption correction	Numerical (SORTAV)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5635/0/245
Goodness-of-fit on F^2	0.982
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.045, wR_2 = 0.1173$
R indices (all data)	$R_1 = 0.0513, wR_2 = 0.1245$
Extinction coefficient	0.0106(9)
Largest different peak and hole	6.12 and $-3.35 \text{ e } \text{\AA}^3$

Compound **2** was formed in 50% yield along with small amounts ($\sim 2\%$) of the dimer $(\text{CO})_3\text{Re}[(\eta^5\text{-C}_5\text{H}_4)(\text{CH}_2)_3(\eta^5\text{-C}_5\text{H}_4)]\text{Re}(\text{CO})_3$ (**3**). Compound **3** can be independently synthesized in 22% yield by treating the lithiated species **1a** with 0.5 equivalents of diiodopropane.

Both **2** and **3** have been characterized by spectroscopic methods. The two bands observed in the CO stretching region of the IR spectra of both **2** and **3** are in similar positions to those of the parent compound **1**. Three sets of methylene protons at δ 3.19, 2.55 and 1.99 ppm and a multiplet due to the Cp ring at δ 5.26 ppm are seen in the ¹H-NMR spectrum of **2**, and as expected, six peaks are observed in the ¹³C-NMR spectrum. Two sets of multiplets from the methylene protons at δ 2.47 and 1.70 ppm and a multiplet arising from the Cp ring is observed at δ 5.25 ppm in the ¹H-NMR spectrum of **3**. In the ¹³C-NMR spectrum five signals are seen. In the mass spectrum a molecular ion peak is observed at 710 corresponding to M^+ and peaks due to subsequent loss of CO groups are in agreement with a molecular formula $(\text{CO})_3\text{Re}(\text{C}_5\text{H}_4)(\text{CH}_2)_3(\text{C}_5\text{H}_4)\text{Re}(\text{CO})_3$ for **3**. Crystals of **3** suitable for X-ray analysis were grown by the diffusion of pentane into a CH_2Cl_2 solution of **3**. An X-ray crystal structure determination confirms the molecular structure of the dimer formed. The bond angles and bond lengths are comparable with the parent compound **1** [17] and other related compounds [18]. The average Re–C(Cp) bond length (2.304 Å) is slightly longer than the average Re–C(Cp) bond length (2.284 Å) in **1**. However it is similar to the related compounds having substitution at the Cp ring (see Ref. [12]). A PLATON diagram of **3** shown in Fig. 1 depicts its molecular structure.

3.2. Synthesis of $\{(CO)_3\text{Re}(C_5H_4)(CH_2)_3(O)\}_2(C_6H_3)CH_2OH$ (**4**)

In previous experiments to synthesize organometallic dendrimers we have made use of a haloalkyl chain which is σ -bonded to the metal atom as the linking unit in the ‘wedge’ synthesis [7]. Dendrimers up to generation four have been made in our laboratory using the organometallic synthon $\text{CpRu}(\text{CO})_2(\text{CH}_2)_3\text{Br}$. The haloalkyl substituent in our current procedure is not directly σ -bonded to the metal as in the earlier cases, but is a substituent on the Cp ligand which is π -bonded to the metal atom. Related organometallic dendrimers where the organometallic fragments are bonded to the dendrimer via a substituent on the Cp ligand have been reported before. Ferrocene terminated dendrimers [19] and ruthenium terminated dendrimers [20] have thus been prepared by using appropriate organometallic units in which the metal units are linked to the polyaromatic ether skeleton via an alkyl chain derived from the π -bonded Cp ring.



Scheme 1.

The reaction of **2** with 3,5-dihydroxybenzyl alcohol in the presence of potassium carbonate and 18-crown-6 in refluxing acetone for 72 h yielded **4**. The reaction was periodically monitored by TLC and the product formed was isolated by column chromatography as a colorless oil (yield ~80%). Small amounts of the monosubstituted product, $(\text{CO})_3\text{Re}(\text{C}_5\text{H}_4)(\text{CH}_2)_3\text{O}(\text{C}_6\text{H}_3)(\text{OH})(\text{CH}_2\text{OH})$ (**5**) were also formed in the reaction. Both products were identified by ^1H -NMR spectroscopy. Two resonances arising from the aromatic protons of the benzylic group are observed at δ 6.51 and 6.35 ppm in the ratio 2:1 for compound **4**. Whereas three resonances are observed at δ 6.48, 6.45 and 6.31 ppm in the ratio 1:1:1 for compound **5** for the same group. The triplet at δ 4.63 ppm, which is due to one of the CH_2

groups of the C_3 chain, is shifted downfield compared to the parent organometallic unit **2**. The ratio of the methylene protons to that of the aromatic protons and the CH_2 protons of the benzylic group confirm the formation of the bis-substituted hydroxy wedge **4**. The relative intensities of all the protons in compound **5** are also in good agreement with the formation of the monosubstituted product.

Both **4** and **5** are further characterized by ^{13}C -NMR, IR and mass spectral analyses. As expected, five additional peaks are seen in the ^{13}C -NMR spectrum of **4** and seven additional peaks in the case of **5** compared with the starting organometallic compound **2**. There is no change in $\nu(\text{CO})$ from precursor to products in the IR spectra. A peak corresponding to the molecular ion

was observed at m/z 890 (M^+) in the FAB mass spectrum of **4**. Peaks corresponding to subsequent loss of CO groups provide further support for the formation of the hydroxy dendritic wedge. FAB mass spectrum of **5** also conclusively support the formation of the mono-substituted compound. Peaks corresponding to the molecular ion (m/z 516, M^+) and subsequent loss of CO groups are observed in the spectrum.

3.3. Synthesis of compound **6**

The bis-substituted hydroxy 'wedge' **4** was converted to the corresponding benzyl bromide complex **6** in high yield (90%) by treatment with CBr_4/PPh_3 in THF (see Scheme 1). The reaction was monitored by TLC and it was found that excess of brominating reagent is required for the completion of the reaction. The product formed was separated by column chromatography and was isolated as a colorless oil.

Compound **6** was characterized by various spectroscopic methods. The notable change in the proton, as well as carbon spectrum, are that due to the CH_2 signals from the benzylic group. An upfield shift of the CH_2 protons (δ 4.40 ppm) of the benzylic group provide ample support for the formation of the brominated product. A similar shift was seen in the ^{13}C -NMR spectrum for the benzylic CH_2 carbon resonance. A molecular ion peak at m/z 954 (M^+) and peaks corresponding to subsequent loss of CO groups in the FAB mass spectrum further support the formation of the brominated product.

3.4. A first generation dendrimer containing six rhenium atoms

Reaction of three molar equivalents of the benzyl bromide wedge **6** with one molar equivalent of the core

molecule 1,1,1-tris(4-hydroxyphenyl)ethane (CORE) in the presence of potassium carbonate and 18-crown-6 in refluxing acetone for 72 h produced the anticipated first generation dendrimer **7** containing six rhenium atoms at the periphery in good yields (82%). The reaction was monitored by TLC. Additional resonances in the 1H -NMR spectrum of **7** support the formation of the first generation rhenium containing organometallic dendrimer. Two sets of peaks, at δ 7.00 and 6.84 ppm arising from the CORE molecule, are in agreement with the resulting dendrimer. The benzylic CH_2 protons show a downfield shift to δ 4.95 ppm. Furthermore, the relative intensities of various resonances in the 1H -NMR spectrum of **7** are in good agreement with the expected number of protons and thus provide ample support for the proposed dendrimer. Six carbon resonances due to the CORE molecule, in addition to the peaks due to the 'wedge', are seen in the ^{13}C -NMR spectrum of **7**. The shift observed for the benzylic CH_2 carbon atom is as expected due to the replacement of the bromine atom by the ethereal oxygen from the CORE molecule. Our attempts to observe a molecular ion peak in the FAB and electrospray mass spectral experiments carried out thus far have been unsuccessful. However, the fragmentation peaks observed in some of the experiments provide valuable information. The peak observed at m/z 872 in the chemical ionization process corresponds to the dendritic wedge $[(CO)_3Re(C_5H_4)(CH_2)_3(O)_2(C_6H_5)CH_2]^+$ and provides some support for the suggested first generation dendrimer. We further carried out a MALDI TOF experiment on **7** in an effort to obtain a molecular ion peak, using indoleacrylic acid (IAA) as the matrix. Even though we could not observe the expected molecular ion peak at m/z 2922, a number of peaks were detected in the mass range close to it. Three

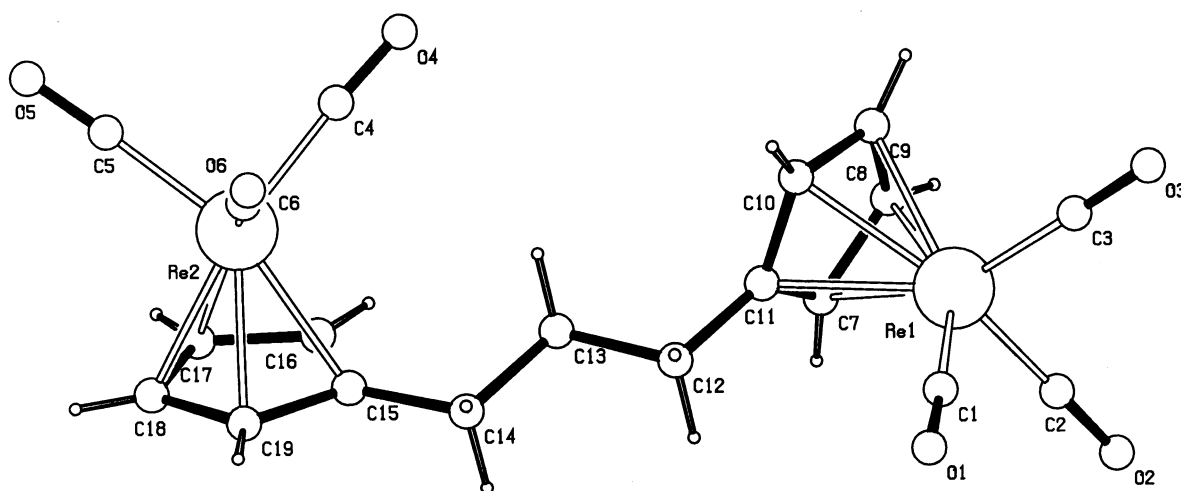


Fig. 1. Molecular structure of **3**.

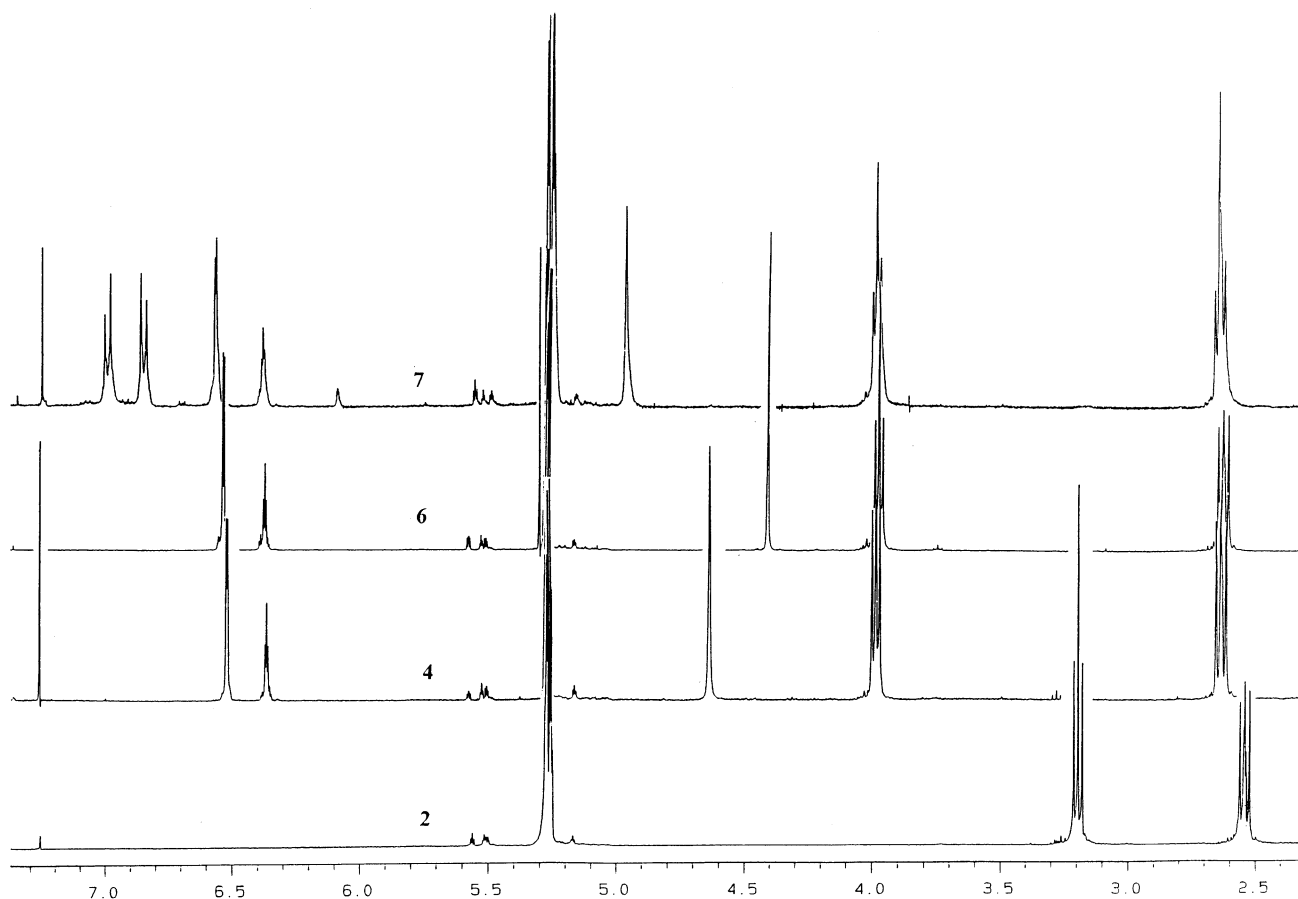


Fig. 2. Selected portions of ^1H -NMR spectra of **2**, **4**, **6** and **7**.

distinct peaks were observed at m/z 3083, 3214 and 3341 with the peak at m/z 3083 showing the highest intensity of these three peaks. These peaks observed may be due to adducts formed with the matrix. Thus the peaks at 3083, 3214 and 3341 can be assigned to $(\text{M}-\text{CO} + \text{matrix})^+$, $(\text{M}-3\text{CO} + 2\text{matrix})^+$ and $(\text{M}-5\text{CO} + 3 \text{ matrix})^+$, respectively.

We carried out additional MALDI TOF experiments with different matrices. A similar pattern of multiple adduct formation was observed with hydroxypicolinic acid (HPA) and anthranilic acid matrices. Furthermore, the spectrum obtained for **7** with anthranilic acid as the matrix showed a peak at 3034 corresponding to $(\text{M}-\text{CO} + \text{matrix})^+$ and peaks at 3006, 2978, 2950 and 2922 due to subsequent CO losses. Thus, MALDI TOF experiments along with spectroscopic data strongly support the formation of the proposed first generation dendrimer **7**.

Multinuclear NMR is particularly useful for the characterization of the various dendritic 'wedges' and dendrimers. Fig. 2 illustrates the changes that can be followed in the ^1H -NMR spectra in the systematic construction of the dendrimer using the convergent approach. The chemical shift changes occur primarily

to the nuclei at the reaction sites. In the first step, the triplet due to the $-\text{CH}_2\text{I}$ group shifts downfield when the halogen atom is replaced by the oxygen atom from the building block 3,5-dihydroxybenzyl alcohol. The three CH_2 protons from the C_3 chain on the Cp ring show more or less similar chemical shift, in the remaining steps of the dendrimer construction. The reaction site now is the CH_2 of the benzylic group and it can be seen from the spectra, that the peaks due to these CH_2 protons shift upfield or downfield in the subsequent steps, depending on the functionality attached to this CH_2 group. Similar changes can be observed in the ^{13}C -NMR as well, and can be effectively used to monitor the progression of the reaction in each step of the dendrimer build up.

We made several attempts to obtain good elemental analyses for the compounds reported. However, in most cases the percentage carbon and hydrogen found were not in good agreement with calculated values. This we believe is due to the presence of small amounts of impurities, or solvents, which we could not remove by repeated column chromatography or prolonged drying. However, IR and NMR spectroscopic data along with FAB and MALDI TOF mass spectrometry experiments

strongly support the suggested formulation for all the new compounds reported.

Having prepared the first generation dendrimer we turned our attention to its oxidation. Our initial attempts to oxidize the carbonyl groups on the metal atom in the dendrimer were unsuccessful. We are pursuing alternative methods to generate oxo-rhenium functionalities at the periphery of the dendrimer.

4. Conclusions

A first generation organometallic dendrimer containing six rhenium atoms at the periphery can be synthesized by convergent methodology in good yields. By using an alternative route, we have prepared **2** in good yields. A dinuclear rhenium compound **3** was formed during the synthesis of **2** in small quantities. Although our initial attempts to oxidize the carbonyl groups on the rhenium dendrimer **7** were unsuccessful, alternative strategies may be incorporated to synthesize the oxidation products.

5. Supplementary material

Atomic coordinates, thermal parameters, and bond lengths and angles for compound **3** are available from the authors.

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