

Supporting Information Available

for

Introduction of the Cluster Fragment $\text{Ru}_3(\text{CO})_{11}$ at the Periphery of Phosphine Dendrimers Catalyzed by the Electron-Reservoir Complex $[\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{Me}_6)]$

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Experimental procedures and spectroscopic data for the reactions of the di- and dendritic phosphine ligands $\text{CH}_3(\text{CH}_2)_2\text{N}(\text{CH}_2\text{PPh}_2)_2$, **3**, DAB-*dendr*-G3- $[\text{N}(\text{CH}_2\text{PPh}_2)_2]_{16}$, **2**, and DAB-*dendr*-G4- $[\text{N}(\text{CH}_2\text{PPh}_2)_2]_{32}$, **6**, with $[\text{Ru}_3(\text{CO})_{12}]$ in the presence of the catalyst $[\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{Me}_6)]$, **1**.

- **1. General:** Chemicals were purchased from Aldrich and Strem, and were used as received. THF was distilled under $\text{Na}/\text{Ph}_2\text{CO}$ under nitrogen and dried over molecular sieves (4 Å) prior to use. ^1H NMR: Bruker 250 MHz; ^{13}C NMR: Bruker 62.9 MHz; ^{31}P NMR: Bruker 81 MHz. The phosphine dendrimers were synthesized according to Reetz (ref. 8) and the data for the new dendritic phosphine DAB-*dendr*-G4- $[\text{N}(\text{CH}_2\text{PPh}_2)_2]_{32}$, **6**, are detailed below. These dendritic polyphosphines were prepared from the commercial poly(propyleneimine) dendrimers with 16 and 32 primary amino groups at the periphery provided by Aldrich. $[\text{Ru}_3(\text{CO})_{12}]$ was purchased from Strem chemicals. The model diphosphine $\text{CH}_3(\text{CH}_2)_2\text{N}(\text{CH}_2\text{PPh}_2)_2$ was also synthesized according to the procedure reported in reference 8 of Reetz's communication (see ref. 8 of the present paper); all the spectroscopic data were checked and found to be in agreement with those noted in that publication.

- **2. Reaction between $\text{CH}_3(\text{CH}_2)_2\text{N}(\text{CH}_2\text{PPh}_2)_2$, **3**, and $[\text{Ru}_3(\text{CO})_{12}]$ in the ratio: 1/4 with 0.01 equiv. $[\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{Me}_6)]$, **1**. Synthesis and characterization of $[\text{CH}_3(\text{CH}_2)_2\text{N}(\text{CH}_2\text{PPh}_2)_2\{\text{Ru}_3(\text{CO})_{11}\}_2]$, **4****

The diphosphine $\text{CH}_3(\text{CH}_2)_2\text{N}(\text{CH}_2\text{PPh}_2)_2$, **3** (0.13 g, 0.28 mmol) and $[\text{Ru}_3(\text{CO})_{12}]$ (0.73 g, 1.14 mmol) were dissolved in THF in an inert atmosphere at 20°C, and the green complex

[Fe^ICp(C₆Me₆)], **1** (0.025 M, 0.01 mmol) in THF was added by cannula. The initially orange solution immediately turned dark red upon addition of **1**, and the mixture was stirred for 15 min. at 20°C and the THF was removed under vacuum. Ether was added to the solid red residue, then pentane was added, the solution was filtered, and crystallization at -20°C yielded 0.342 g (0.20 mmol, 73%) of red crystalline bis-cluster product **4** after drying for two days under vacuum to remove the residual solvent. The hexanuclear complex **4** is highly soluble in chlorinated solvents and decomposes on a silica column. Otherwise, **4** is air stable for several weeks, but is very sun-light sensitive (thus, it should always be protected from visible light).

IR (CH₂Cl₂, ν, cm⁻¹): 2095 (w), 2043 (m), 2029 (s), 2008 (s), 1990 (s);

¹H NMR (CDCl₃, δ, ppm): 0.80 (t, 3H, CH₃), 1.45 (m, 2H, CH₃CH₂), 2.75 (t, 2H, CH₂CH₂N), 3.70 (dd, ²J_{P-H} = 3.1 Hz, 4H, CH₂P), 7.75-8.15 (m, 20, Ph).

¹³C{¹H} NMR (CDCl₃, δ, ppm): 11.2 (CH₃), 22.0 (CH₂), 62-61 (m, CH₂N + CH₂P), 128.9, 130.9, 132.0, 133.5 (Ph), 210 (CO).

³¹P {¹H} NMR (CDCl₃, δ, ppm): 33.47 (s)

Elemental analysis: see ref. 12.

FAB(+) mass spectrum: most intense peaks at 1482.82: [M - 7 CO + H⁺], 1454.90: [M - 8 CO + H⁺], 1427.11: [M - 9 CO + H⁺]. The theoretical distribution corresponding to the presence of the Ru₆ fragment agrees with the experimental one. The MALDI TOF mass spectrum, which only shows the fragments 583.34 (Ru₃(CO)₁₀) and 557.18 (Ru₃(CO)₉) for the cluster [Ru₃(CO)₁₂], shows the following fragments for **4** under the same conditions: 799.68 [M - 17 CO + H⁺], 770.43 [M - 18 CO + H⁺], 742.42 [M - 19 CO + H⁺], 714.97 [M - 20 CO + H⁺], 686.26 [M - 21 CO + H⁺], and another group of less intense peaks: 613.58 [M - Ru-20 CO + H⁺], 585.06 [M - Ru - 21 CO + H⁺], 557.99 [M - Ru - 22 CO + H⁺]. For each peak, the experimental isotopic distribution corresponds to the theoretical one.

3. Reaction between CH₃(CH₂)₂N(CH₂PPh₂)₂, **3**, and [Ru₃(CO)₁₂] in the ratio: 1/1.05 with 0.1 equiv. [Fe^ICp(C₆Me₆)], **1**.

CH₃(CH₂)₂N(CH₂PPh₂)₂, **3** (0.136 g, 0.30 mmol) and [Ru₃(CO)₁₂] (0.20 g, 0.31 mmol) were dissolved in THF in an inert atmosphere at 20°C, and the green complex [Fe^ICp(C₆Me₆)], **1**

(0.025 M, 0.03 mmol) in THF was added by cannula. The initially orange solution immediately turned dark red upon addition of **1**, the mixture was stirred for 15 min. at 20°C, and the THF was removed under vacuum. This crude reaction mixture was submitted to ^{31}P NMR spectrum, which gave three signals at 33.65, 33.47 and 21.71 ppm corresponding to the chelate $[\text{CH}_3(\text{CH}_2)_2\text{N}(\text{CH}_2\text{PPh}_2)_2\cdot\text{Ru}_3(\text{CO})_{10}]$, **4** (only one singlet), the monodentate monocluster $[\text{CH}_3(\text{CH}_2)_2\text{N}(\text{CH}_2\text{PPh}_2)_2\cdot\text{Ru}_3(\text{CO})_{11}]$ (two signals) and the bis-cluster $[\text{CH}_3(\text{CH}_2)_2\text{N}(\text{CH}_2\text{PPh}_2)_2\cdot\{\text{Ru}_3(\text{CO})_{11}\}_2]$, **4** (only one signal). The infrared spectrum shows the disappearance of the band at $\nu = 2058\text{ cm}^{-1}$ (CH_2Cl_2) corresponding to $[\text{Ru}_3(\text{CO})_{12}]$, but shows the following bands: 2094 (w), 2073 (w), 2043 (s), 2029 (s), 2011 (s), 1990 (s); the band at 2073 cm^{-1} has previously been attributed by Bruce^{11b} to the chelate complex $[\text{L}_2\cdot\text{Ru}_3(\text{CO})_{10}]$, L_2 being a diphosphine. The thin-layer chromatography confirms the absence of $[\text{Ru}_3(\text{CO})_{12}]$ and the presence of **4** in the mixture, the two other compounds being the chelate and monodentate complexes as disclosed by the ^{31}P NMR and infrared spectra.

An additional experiment using the ratio $\text{CH}_3(\text{CH}_2)_2\text{N}(\text{CH}_2\text{PPh}_2)_2 / [\text{Ru}_3(\text{CO})_{12}]$: 1/1.05 with 0.1 equiv. $[\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{Me}_6)]$ also gave a mixture of the same three compounds. This type of result has already been obtained by Bruce's group with other diphosphines.^{11b}

4. Synthesis and characterization of DAB-*dendr*- $[\text{N}\{\text{CH}_2\text{PPh}_2\text{Ru}_3(\text{CO})_{11}\}_2]_{16}$, **5**.

DAB-*dendr*-G3- $[\text{N}(\text{CH}_2\text{PPh}_2)_2]_{16}$, **2** (0.10 g, 0.012 mmol) and $[\text{Ru}_3(\text{CO})_{12}]$ (0.51 g, 0.80 mmol) were mixed in 40 mL THF under an inert atmosphere at 20°C, and a THF solution of $[\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{Me}_6)]$, **1** (0.025M, 0.008 mmol) was added by cannula. The initially orange solution immediately turned dark red and the reaction mixture was stirred overnight at 20°C. Then, it was concentrated under reduced pressure to 10 mL and kept at 5°C for 24h. The orange precipitate of $[\text{Ru}_3(\text{CO})_{12}]$ was removed by cannula transfer of the solution to another Schlenk flask, THF was removed under vacuum, and the red residue was dissolved in 50 mL pentane. Slow concentration of this solution to 10 mL allowed to crystallize the remaining $[\text{Ru}_3(\text{CO})_{12}]$ (characterized by TLC). Removal of the pentane under vacuum for two days gave 0.16 g of **5** (0.006 mmol, 50% yield) as a red powder. See the elemental analysis in ref. 15.

Infrared (KBr, cm^{-1} , ν): 2096 (w), 2038 (m), 2017 (s), 1998 (s), 1980 (m), 1970 (m); weak band at $\nu = 2058 \text{ cm}^{-1}$ indicating the presence of traces of $[\text{Ru}_3(\text{CO})_{12}]$.

^{31}P NMR (CDCl_3): $\delta = 33.13 \text{ ppm}$ vs. H_2SO_4 (s); ^1H NMR (CDCl_3 , ppm): broad signals around 2.6 ($\text{CH}_2\text{-CH}_2\text{N}$) and 3.2-3.8 (NCH_2 and NCH_2P) in the aliphatic region; broad phenyl massif between 7 and 8; ^{13}C NMR (CDCl_3 , ppm, 10000 scans): $\delta = 199$ (sharp s, CO), 128 (very weak, C_{phenyl}), 33 (very weak, C_{aliph}); the reduced solubility is limiting for the ^{13}C NMR.

5. Synthesis and characterization of DAB-dendr-G4- $[\text{N}(\text{CH}_2\text{PPh}_2)_2]_{32}$, **6**.

The 64-branch dendritic phosphine DAB-dendr-G4- $[\text{N}(\text{CH}_2\text{PPh}_2)_2]_{32}$, **6**, was synthesized in the same way as the known dendritic phosphine DAB-dendr-G3- $[\text{N}(\text{CH}_2\text{PPh}_2)_2]_{16}$ following a procedure analogous to that used by Reetz⁸, applied to commercial DAB-dendr-G4-NH₂, **2** and PPh_2OH . Analysis for $\text{C}_{1016}\text{H}_{1136}\text{P}_{64}\text{N}_{62}$ ($M = 16\,199$ dalton): C 75.33, H 7.06, N 5.36; found C 74.01, H 6.79, N 5.03. The discrepancy is believed to be due to the inclusion of methanol molecules within the dendritic cavities; these impurities are not removed even under vacuum. This problem is frequently encountered in dendrimer chemistry (for other cases and discussion, see for instance ref. 14b). ^{31}P NMR (CDCl_3): $\delta_{\text{ppm}} = -28.68 \text{ ppm}$ vs. H_2SO_4 . ^1H NMR (CDCl_3): $\delta_{\text{ppm}} = 1\text{-}4$ (m, 492 H, 246 CH_2); 7-8 (m, 640 H, 128 C_6H_5), integration ratio: $\text{H}_{\text{aromatic}}/\text{H}_{\text{aliphatic}} = 1.30$; found 1.32. ^{13}C NMR (CDCl_3): $\delta_{\text{ppm}} = 21.40$ (s), 21.48 (s), 23.83 (b), 23.83 (b), 51.69 (b), 54.62 (b), 128.33 (b, phenyl), 131.13 (d, phenyl), 133.04 (d, $J_{\text{P-C}} = 17.9 \text{ Hz}$, phenyl), 138.20 (d, $J_{\text{P-C}} = 13.03 \text{ Hz}$, phenyl). Infrared (KBr, ν , cm^{-1}) 3067 ($\text{C-H}_{\text{phenyl}}$), 3050 ($\text{C-H}_{\text{phenyl}}$), 2943 ($\text{C-H}_{\text{NCH}_2}$), 1480 ($\text{C-H}_{\text{phenyl}}$), 1469 ($\text{C-H}_{\text{phenyl}}$), 1433 ($\text{C-H}_{\text{phenyl}}$), 735 ($\text{C-H}_{\text{phenyl}}$), 689 ($\text{C-H}_{\text{phenyl}}$).

6 is highly soluble in CDCl_3 and very air sensitive, the oxidation of the phosphine groups RPPH_2 in air to phosphine oxide groups $\text{R-P(Ph)}_2\text{=O}$ being characterized by the appearance of new proton signals shifted downfield from their phosphine position. Also, when the phosphine is partly oxidized to phosphine oxide, the ^{31}P NMR spectrum shows the additional signals at $\delta = 26\text{-}28 \text{ ppm}$ vs. H_2SO_4 corresponding to the phosphine oxide groups.

6. Synthesis and characterization of DAB-dendr-G4- $[\text{N}(\text{CH}_2\text{PPh}_2\text{Ru}_3(\text{CO})_{11})_2]_{32}$, **7**.

DAB-*dendr*-G4-[N(CH₂PPh₂)₂]₃₂, **6** (0.19 g, 0.012 mmol) and [Ru₃(CO)₁₂] (0.98 g, 1.54 mmol) were mixed in 40 mL THF under an inert atmosphere at 20°C, and a THF solution of [Fe^ICp(C₆Me₆)], **1** (0.025 M, 0.01 mmol) was added by cannula. The initially orange solution immediately turned dark red and the reaction mixture was stirred overnight at room temperature. Extraction was carried out as above for the synthesis of **5**, providing 0.152 g (0.003 mmol, 23% yield) of **7** as a CDCl₃ soluble dark-red powder.

Analysis for C₁₇₂₀H₁₁₃₆N₆₂P₆₄Ru₁₉₂O₇₀₄ (M = 55324): C 37.34, H 2.07, N 1.57; found: C 39.80, H 2.51, N 1.78. The discrepancy is at least in its major part due to the inclusion of a large amount of THF molecules (observed in the ¹H NMR spectrum) which are not removed even under vacuum for several days; given the observed reduced solubility of **7** in CDCl₃, it is believed that the steric bulk at the periphery is very large, and is responsible for this THF inclusion in the dendritic cavities in the course of the metallation reaction. With 32 scans, the ¹H NMR spectrum (CDCl₃) only shows the phenyl and THF signals; after 260 scans, the aliphatic structure is finally also apparent under the form of large signals (see the data of the ¹H NMR spectrum of **5** above); ³¹P NMR spectrum (CDCl₃): 33.39 ppm (s).