

# 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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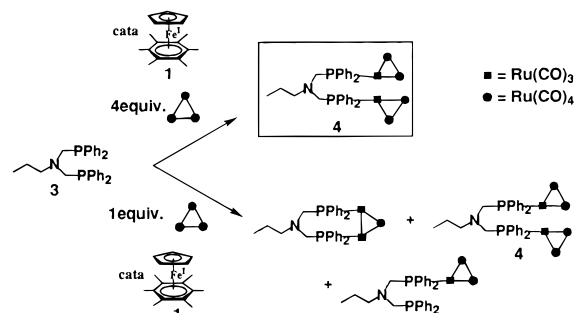
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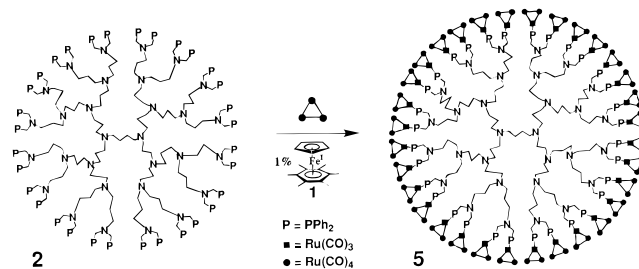
Catalysis is one of the most promising applications of metal-lodendrimers.<sup>1</sup> It is remarkable, however, that the plethora of metalodendrimers published up to now<sup>2,3</sup> and functionalized with metals at the periphery usually contain only one metal at each terminus.<sup>3,4</sup> The clean introduction of transition-metal clusters<sup>5</sup> at the branch termini of dendrimers represents a challenge whose achievements would add a new dimension to the dendrimer field including perspectives in catalysis, molecular electronics, and materials science. It is probable that the lack of report in this area is mostly due to the fact that, under standard thermal conditions, ligand-exchange reactions between cluster-bonded carbonyls and phosphines lead to mixtures. We have sought to circumvent this problem using electron-transfer-chain (ETC) catalysis<sup>6</sup> with the electron-reservoir complex  $[\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{Me}_6)]$ , **1**, as the catalyst.<sup>6,7</sup> The advantage of this technique is the selectivity related to the huge kinetic gain obtained at the radical level due to the exergonic, thus fast, electron transfer in the cross redox chain step when the catalyst is correctly chosen. The stable genuine 19-electron complex **1** is a clean reservoir of electrons which has a sufficiently negative oxidation potential ( $E^\circ = -1.94\text{V}$  vs  $\text{FeCp}_2^{0/+}$  in THF) and can be easily made, stored and handled, and weighed accurately.<sup>7</sup> Using this technique, we now report the first synthesis of dendrimers whose branches are functionalized with a transition-metal cluster.

We chose  $[\text{Ru}_3(\text{CO})_{12}]$ , a classic example of cluster chemistry, whose catalytic properties have recently been emphasized.<sup>5b</sup> The dendritic ligand is the 32-branch dendritic phosphine **2** synthesized by Reetz<sup>8</sup> using the double phosphinomethylation of Meijers's

## Scheme 1



## Scheme 2



1,4-diaminobutane-poly-(trimethyleneamine) dendrimer of generation 3 (DAB-G3)<sup>9</sup> with  $\text{PPh}_2\text{CH}_2\text{OH}$ .<sup>10</sup> To start, however, we used the diphosphine  $\text{CH}_3(\text{CH}_2)_2\text{N}(\text{CH}_2\text{PPh}_2)_2$ , **3**,<sup>8</sup> as a simple, model ligand. The reaction between **3** and  $[\text{Ru}_3(\text{CO})_{12}]$ <sup>11</sup> (molar ratio: 1/1.05) in the presence of 0.1 equiv of **1** in THF at 20 °C led to the complete disappearance of  $[\text{Ru}_3(\text{CO})_{12}]$  in a few minutes and the appearance of a mixture of chelate  $[\text{3} \cdot \text{Ru}_3(\text{CO})_{10}]$ , monodentate  $[\text{3} \cdot \text{Ru}_3(\text{CO})_{11}]$  and bis-cluster  $[\text{3} \cdot \{\text{Ru}_3(\text{CO})_{11}\}_2]$ , **4**. This type of reaction was reported by Bruce with simple diphosphines.<sup>6b,11b</sup> It is easily monitored by thin-layer chromatography and infrared and <sup>31</sup>P NMR spectroscopies and visualized by the rapid color change from orange to dark red. On the other hand, the reaction of **3** with  $[\text{Ru}_3(\text{CO})_{12}]$  in excess (1/4) and only 0.01 equiv of **1** in THF at 20 °C led, in 20 min, to the formation of the air-stable, light-sensitive bis-cluster **4** as the only reaction product (Scheme 1). Excess  $[\text{Ru}_3(\text{CO})_{12}]$  was removed by crystallization upon addition of ether, and **4** was obtained in 73% yield of red crystals after recrystallization from a pentane–ether mixture at –20 °C.<sup>12</sup>

Given the simplicity of the above characterization of the reaction product by <sup>31</sup>P NMR<sup>13</sup> and the excellent selectivity of

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(8) Reetz, M. T.; Lohmer, G.; Schwickardi, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1526; in this paper, Reetz also reported the synthesis of Pd, Ir, Rh, and Ni complexes of **2**, some of which proved very efficient for the catalysis of Heck-type reactions.

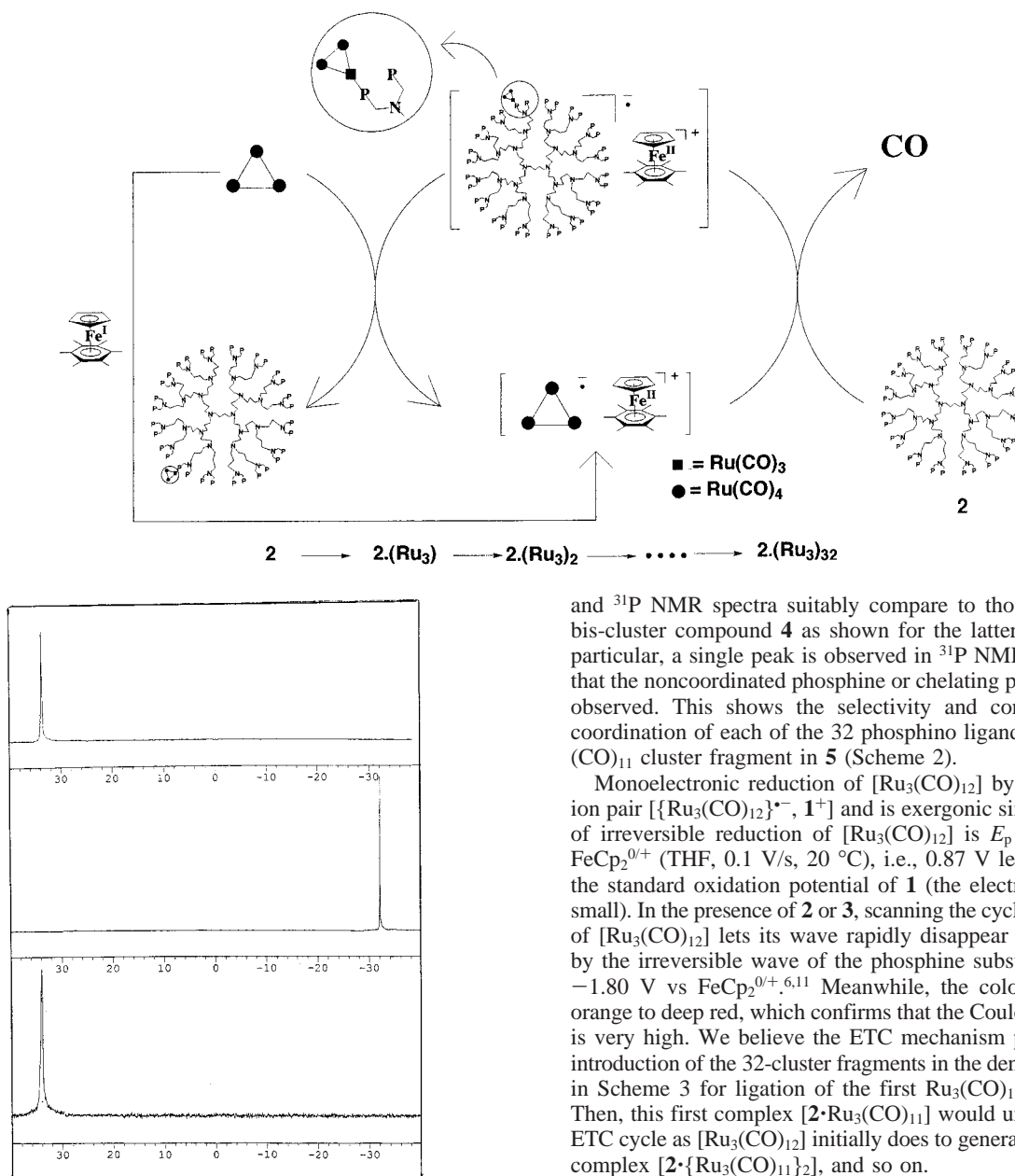
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(11) ETC-catalyzed substitution of carbonyl ligands by phosphines in  $[\text{Ru}_3(\text{CO})_{12}]$  has been pioneered by Bruce's group. See ref 6b and: (a) Bruce, M. I.; Shaw, G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 442. (b) Bruce, M. I.; Hambley, T. W.; Nicholson, B. K.; Snow, M. R. *J. Organomet. Chem.* **1982**, *235*, 83 and 2094. (c) Bruce, M. I.; Matison, J. G.; Wallis, R. G.; Patrick, J. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 2365 and 2375. (d) Bruce, M. I.; Matison, J. G.; Nicholson, B. K. *J. Organomet. Chem.* **1983**, *247*, 321.

(12) Analysis of **4**. Calcd for  $\text{C}_{51}\text{H}_{31}\text{N}_2\text{P}_2\text{Ru}_6\text{O}_{22}$ : C, 36.50; H, 1.86; N, 0.83. Found: C, 36.48; H, 1.95; N, 0.82. Major peaks in the FAB(+) mass spectrum:  $[\text{M} - 7\text{CO}]$ ,  $[\text{M} - 8\text{CO}]$  and  $[\text{M} - 9\text{CO}]$ . See Figure 1 for the <sup>31</sup>P NMR spectrum and the Supporting Information for the synthetic procedures and spectroscopic data. The characteristic chelate band at  $\nu = 2078\text{ cm}^{-1}$  is not observed in the IR spectrum, contrary to the spectrum of the reaction with only 1 equiv of  $[\text{Ru}_3(\text{CO})_{12}]$ . For similar observations and assignments with other diphosphines, see ref 11b.

## Scheme 3



**Figure 1.**  $\{^1\text{H}\}^{31}\text{P}$  NMR spectra of  $[\text{CH}_3(\text{CH}_2)_2\text{N}(\text{CH}_2\text{PPh}_2)_2 \cdot \{\text{Ru}_3(\text{CO})_{11}\}_2]$ , **4** (top), DAB-*dendr*-G3- $[\text{N}(\text{CH}_2\text{PPh}_2)_{16}]_{16}$ , **2** (middle) and DAB-*dendr*- $[\text{N}\{\text{CH}_2\text{PPh}_2\text{Ru}_3(\text{CO})_{11}\}_2]_{16}$ , **5** (bottom);  $\delta$  (ppm vs  $\text{H}_3\text{PO}_4$ , 81 MHz,  $\text{CDCl}_3$ ).

this model reaction when excess  $[\text{Ru}_3(\text{CO})_{12}]$  was used, we could more confidently envisage the same reaction between the phosphine dendrimers such as **2** and  $[\text{Ru}_3(\text{CO})_{12}]$ . This reaction, catalyzed by 1% equiv of **1**, was carried out in THF at 20 °C for 12 h using 0.1 g (0.012 mmol) of **2** and 0.51 g (0.80 mmol) of  $[\text{Ru}_3(\text{CO})_{12}]$ . Excess  $[\text{Ru}_3(\text{CO})_{12}]$  was then removed likewise after several crystallizations, although the infrared spectrum indicated that traces were retained in the metallodendrimer **5**. It is now a well-recognized feature that most large dendrimers retain various hosts tenaciously.<sup>14,15</sup> The dendrimer-cluster assembly **5** was obtained as a very air- and light-sensitive red powder in 50% yield after drying under vacuum for several days.<sup>15</sup> Its infrared

and  $^{31}\text{P}$  NMR spectra suitably compare to those of the model bis-cluster compound **4** as shown for the latter in Figure 1; in particular, a single peak is observed in  $^{31}\text{P}$  NMR, and it is clear that the noncoordinated phosphine or chelating phosphine are not observed. This shows the selectivity and completion of the coordination of each of the 32 phosphino ligands of **3** to a  $\text{Ru}_3(\text{CO})_{11}$  cluster fragment in **5** (Scheme 2).

Monoelectronic reduction of  $[\text{Ru}_3(\text{CO})_{12}]$  by **1** generates the ion pair  $\{[\text{Ru}_3(\text{CO})_{12}]^{\cdot-}, \mathbf{1}^+\}$  and is exergonic since the potential of irreversible reduction of  $[\text{Ru}_3(\text{CO})_{12}]$  is  $E_p = -1.07$  V vs  $\text{FeCp}_2^{0/+}$  (THF, 0.1 V/s, 20 °C), i.e., 0.87 V less negative than the standard oxidation potential of **1** (the electrostatic factor is small). In the presence of **2** or **3**, scanning the cyclic voltammogram of  $[\text{Ru}_3(\text{CO})_{12}]$  lets its wave rapidly disappear and be replaced by the irreversible wave of the phosphine substituted cluster at  $-1.80$  V vs  $\text{FeCp}_2^{0/+}$ .<sup>6,11</sup> Meanwhile, the color changes from orange to deep red, which confirms that the Coulombic efficiency is very high. We believe the ETC mechanism proceeds for the introduction of the 32-cluster fragments in the dendrimer as shown in Scheme 3 for ligation of the first  $\text{Ru}_3(\text{CO})_{11}$  fragment to **2**. Then, this first complex  $[\mathbf{2} \cdot \text{Ru}_3(\text{CO})_{11}]$  would undergo the same ETC cycle as  $[\text{Ru}_3(\text{CO})_{12}]$  initially does to generate the bis-cluster complex  $[\mathbf{2} \cdot \{\text{Ru}_3(\text{CO})_{11}\}_2]$ , and so on.

Finally, the 64-branch phosphine DAB-*dendr*-G4- $[\text{N}(\text{CH}_2\text{PPh}_2)_{32}]_{32}$ , **6**, analogously reacts with  $[\text{Ru}_3(\text{CO})_{12}]$  and 1% **1** (20 °C, THF, 20 min) to give the dark red complex  $\{[\mathbf{6} \cdot \{\text{Ru}_3(\text{CO})_{11}\}_{64}]\}$ , **7**, which is slightly soluble in  $\text{CDCl}_3$ ; **7** showed the expected peak in  $^{31}\text{P}$  NMR at 33.1 ppm and no peak for noncoordinated ( $-28.7$  ppm) or chelating phosphines (33.6 ppm) and its IR spectrum showed the absence of band at  $\nu = 2078$   $\text{cm}^{-1}$  for chelating phosphines. Due to surface bulk, **7** also retains a large amount of THF molecules (observed in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra) even after several days under vacuum.

The use of **1** as an ETC catalyst for the introduction of other clusters onto dendrimers is being investigated.

**Supporting Information Available:** Syntheses and analytical and spectroscopic data for the new compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(14) See ref 1 and: (a) Lange, P.; Schier, A.; Schmidbauer, H. *Inorg. Chem.* **1996**, *35*, 637. (b) Archut, A.; Vögtle, F.; De Cola, L.; Azellini, G. C.; Balzani, V.; Ramanujan, P. S.; Berg, R. H. *Chem. Eur. J.* **1998**, *4*, 699.

(15) Analysis of **5**. Calcd for  $\text{C}_{856}\text{H}_{560}\text{N}_{30}\text{P}_{32}\text{Ru}_{96}\text{O}_{352}$ : C, 37.26; H, 2.04; N, 1.52. Found: C, 36.01; H, 1.87; N, 1.39; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ) 2096 (w), 2038 (m), 2017 (s), 1998 (s), 1980 (s), 1970 (m), a tiny residual band at 2058  $\text{cm}^{-1}$  and the elemental analysis indicate the presence of traces of  $[\text{Ru}_3(\text{CO})_{12}]$  entrapped in the dendrimer;  $^{31}\text{P}$  NMR:  $\delta = 33.13$  ppm vs  $\text{H}_3\text{PO}_4$ , see Figure 1.