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Dendritic Systems Based on Dinuclear Ruthenium or Rhodium Units Generating Peripheral Catalytic Sites

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Abstract: A series of dendritic cations **1**–**4** containing Ru_2S_3 or Rh_2S_3 units, either in the core or in the dendrons, has been synthesized and characterized. The X-ray crystal structure analysis of **2**-Cl shows a trigonal bipyramidal Rh_2S_3 core with propeller-like *para*-hydroxyphenyl substituents at the sulfur atoms. Reaction of the peripheral OH groups with diphenylphosphino benzoic acid results in the formation of phosphine-functionalized dendritic cations **5**–**8**. The ruthenium-containing cation **5**, with three PPh_2 functions at the periphery, acts as ligand for rhodium(I) and enhances significantly the catalytic activity of $[\{Rh(CO)_2Cl\}_2]$ for the carbonylation of methanol.

Keywords: catalysts · dendrimers · rhodium · ruthenium

Introduction

During the two past decades, there has been a growing interest in the study of dendrimers, a new class of macromolecules that can be considered as monodisperse, precisely ordered, polyfunctional polymers.[1] Placing functional groups at chain ends or in well-defined segments determines the properties of these molecules. Three-dimensional synthetic polymers such as dendrimers can be conditionned to encapsulate reactive sites or provide highly controlled surfaces and interfaces.[2] These molecules are fascinating for their fractal topology or for their applications in material sciences or biology. Nowadays, synthetic strategies are well established in the case of purely organic dendrimers, and the current challenges in this field are the development of the predicted potential applications. On the other hand, metallodendrimers have been synthesized more recently, and a large variety of these compounds is now accessible. Two major classes of metallodendrimers have been characterized: 1) dendrimers with organic skeletons functionalized at the periphery by metal centers[3] and 2) dendrimers built around a metal core[4] or a metal cluster,[5] substituted by organic dendrons. There are also a few reports on the incorporation of metal complexes into the dendron arms,[6] but these examples are rare.

Catalysis is one of the most promising applications of metallodendrimers, because these molecules can combine the advantages of homogeneous and heterogeneous catalysis.[7] One of the major problems in homogeneous catalysis is the catalyst recovery from the product mixture. It can be overcome by using biphasic conditions[8] or by developing soluble polymers functionalized by catalytic metal sites.[9] In the latter case, it is difficult to control the number and the location of the catalytic sites in the polymer. Dendrimers represent an alternative concept in the development of new catalytic materials, because their structures are well defined and all the steps are controlled during their growth.

In this paper, we report a new approach to multifunctional dendritic molecules based on dinuclear arene ruthenium or cyclopentadienyl rhodium units, which are able to fix other metal centers as catalytic sites at the periphery.

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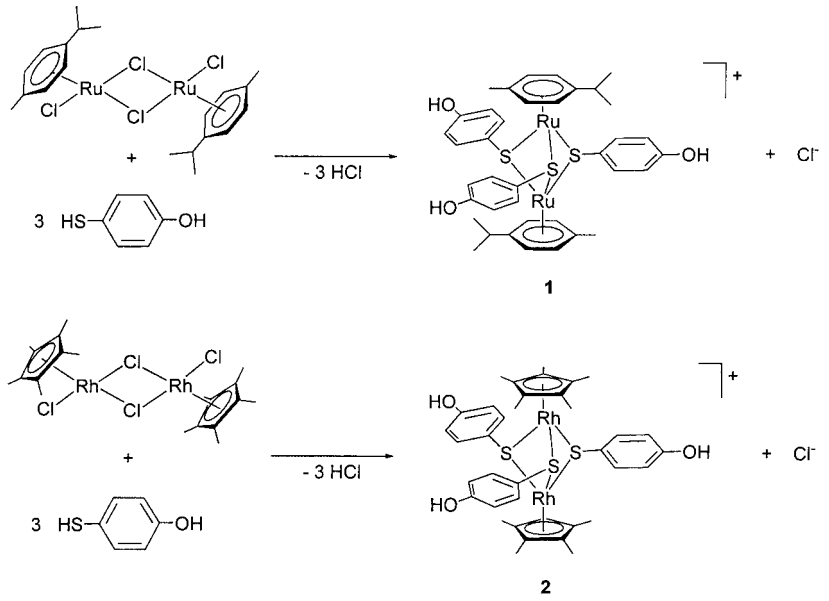
Results and Discussion

Molecular recognition of SH versus OH functions by rhodium or ruthenium: The dinuclear dichloro complexes $[\{Ru(p\text{-}Me\text{-}C_6H_4\text{-}i Pr)Cl_2\}_2]$ and $[\{Rh(C_5Me_5)Cl_2\}_2]$ were found to react in ethanol with *para*-mercaptophenol to give the cationic complexes $[Ru_2(p\text{-}Me\text{-}C_6H_4\text{-}i Pr)_2(p\text{-}S\text{-}C_6H_4\text{-}OH)_3]^+$ (**1**) and $[Rh_2(C_5Me_5)_2(p\text{-}S\text{-}C_6H_4\text{-}OH)_3]^+$ (**2**), which can be isolated in quantitative yield as the chloride salts (Scheme 1).

Both cations **1** and **2** were unambiguously characterized by their MS, IR, ^1H and ^{13}C NMR data as well as by satisfactory elemental analysis data of the chloride salts. The molecular structure of **2** was confirmed by a single-crystal X-ray structure analysis of **2**-Cl: The cation was found to consist of a closed trigonal bipyramid Rh_2S_3 framework, each rhodium atom being coordinated to a η^5-C_5Me_5 ligand and each sulfur atom carrying a *para*-hydroxyphenyl group. The molecular



Scheme 1. Synthesis of the dinuclear cations $[Ru_2(p\text{-Me-}C_6H_4\text{-}i\text{Pr})_2(p\text{-S-}C_6H_4\text{-OH})_3]^+$ (**1**) and $[Rh_2(C_5Me_5)_2(p\text{-S-}C_6H_4\text{-OH})_3]^+$ (**2**).

structure of **2** is shown in Figure 1, important bond lengths and angles are given in Table 1.

Cationic tristhiolato dirhodium and diruthenium complexes of this type, $[M_2L_2(SR)_3]^+$, have already been obtained by Maitlis et al. (M = Rh, L = C_5Me_5, R = C_6F_5;[10a] M = Rh, Ir, L = C_5Me_5, R = C_6F_5, C_6H_4F[10b]) and by Rakowski DuBois et al. (M = Ru, L = C_6Me_6, R = Ph[10c]) from the corresponding $[\{MLCl_2\}_2]$ derivatives and $Pb(SR)_4$ or Me_3SiSR; the structural features of $[Rh_2(C_5Me_5)_2(SC_6F_5)_3]^+$[10a, 10b] and $[Ru_2(C_6Me_6)_2(SPh)_3]^+$[10c] are comparable to those of **2**.

Table 1. Selected bond lengths [Å] and angles [°] for **2**-Cl.

Rh1−Cp*$_{centroid}$	1.798	Rh2−Cp*$_{centroid}$	1.811
Rh1−S1	2.384(2)	Rh2−S1	2.378(2)
Rh1−S2	2.390(1)	Rh2−S2	2.411(2)
Rh1−S3	2.413(2)	Rh2−S3	2.385(2)
Rh1−Rh2	3.236(1)	S1−C21	1.798(6)
S2−C27	1.798(8)	S3−C33	1.787(7)
S1-Rh1-S2	79.70(5)	S1-Rh2-S2	79.39(6)
S1-Rh1-S3	80.06(7)	S1-Rh2-S3	80.74(6)
S2-Rh1-S3	77.89(5)	S2-Rh2-S3	78.03(6)
Rh1-S1-Rh2	85.61(6)	Rh1-S2-Rh2	84.74(5)
Rh1-S3-Rh2	84.81(6)		

Abstract in French: *Nous avons synthétisé et caractérisé les nouveaux cations dendritiques **1**–**4** contenant les unités Ru_2S_3 ou Rh_2S_3. L'analyse de la structure aux rayons X de **2**-Cl montre un coeur Rh_2S_3 à géométrie bipyramide trigonale. La réaction des groupements OH périphériques avec l'acide 2-diphénylphosphinobenzoïque permet la formation des cations dendritiques **5**–**8** fonctionnalisés par des phosphines. Le cation **5** qui contient deux atomes de ruthénium au centre et trois fonctions PPh_2 à la périphérie peut servir de ligand avec le rhodium(I) et permettre d'augmenter significativement l'activité catalytique du précurseur $[\{Rh(CO)_2Cl\}_2]$ pour la carbonylation du méthanol.*

However, these reactions give low yields (12–25%) and are restricted to specific cases only. By contrast, the reactions of $[\{Ru(p\text{-Me-}C_6H_4\text{-}i\text{Pr})Cl_2\}_2]$ and $[\{Rh(C_5Me_5)Cl_2\}_2]$ with *para*-mercaptophenol in ethanol to give **1** and **2**, respectively, are quantitative. The remarkable preference for the SH versus the OH functions of the *para*-mercaptophenol by the dinuclear rhodium or ruthenium units reflects the extraordinary molecular recognition of sulfur by these metals: the reaction is carried out in ethanol with an ethanol/*para*-mercaptophenol ratio of 2000:1, without the OH function of the solvent interfering. Similar reactivity and specificity of the SH versus the OH functions of the *para*-mercaptophenol has been shown by Ashby in the case of iron-carbonyl derivatives.[11] A hydrogen bond involving the chloride and one of the hydroxy groups is observed (O2 ··· Cl 2.947(7) Å, O−H ··· Cl 158.9°). Standard data relating to the X-ray crystal structure of **2** have been deposited in the Cambridge Crystallographic Data Centre.[12]

Complexes **1** and **2** can be used as starting points for the development of dendrimers by either divergent or convergent procedures,[1b] since the OH functions at the aromatic substituents are available for condensation reactions, the

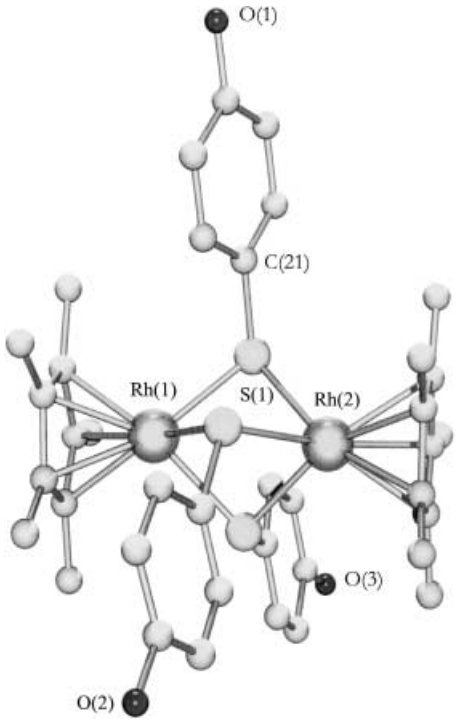


Figure 1. The molecular structure of $[Rh_2(C_5Me_5)_2(p\text{-S-}C_6H_4\text{-OH})_3]^+$ (**2**).

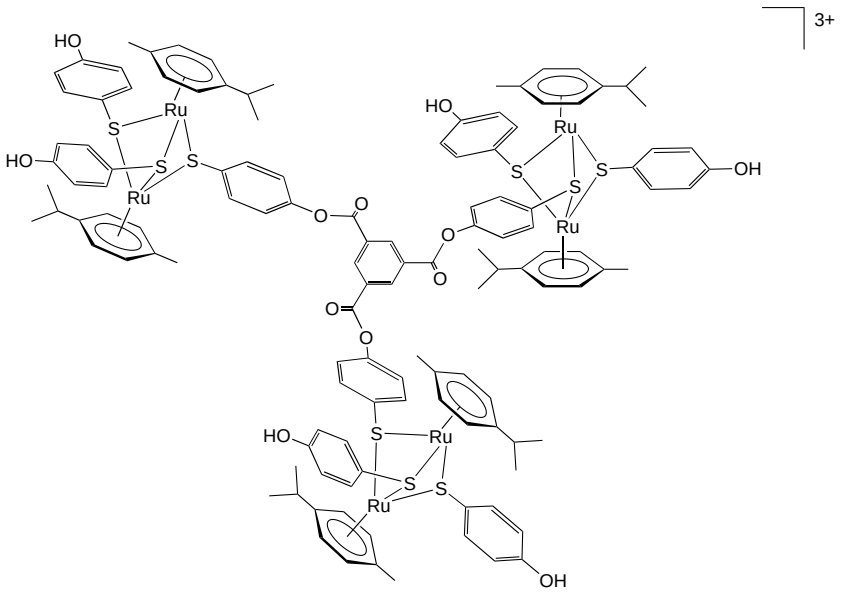
key feature in the build-up of dendritic systems being the molecular recognition of sulfur by rhodium or ruthenium.

Generation of dendrimers containing metallodendrons based on 1 and 2: Condensation of 1,3,5-benzenetricarbonyl trichloride in dichloromethane with **1**-Cl and **2**-Cl in a 1:3 ratio results in the formation of the dendritic cations $[1,3,5\text{-}C_6H_3\{CO_2\text{-}(p\text{-}C_6H_4\text{-}S)Ru_2(p\text{-}Me\text{-}C_6H_4\text{-}i\text{Pr})_2(p\text{-}S\text{-}C_6H_4\text{-}OH)_2\}_3]^{3+}$ (**3**) and $[1,3,5\text{-}C_6H_3\{CO_2(p\text{-}C_6H_4\text{-}S)Rh_2(C_5Me_5)_2(p\text{-}S\text{-}C_6H_4\text{-}OH)_2\}_3]^{3+}$ (**4**) (Scheme 2), which can be isolated in high yield as the chloride salts **3**-Cl_3 and **4**-Cl_3. No cross-linking by-products were isolated after the reaction; this is probably due to our experimental setup (i.e., addition of acid chloride to phenol, see Experimental Section). Cations **3** and **4** give rise to the expected molecular peaks m/z at 903 and 905, respectively, in the ESI mass spectra. The infrared spectra exhibit the characteristic ν_{CO} absorption at 1741 cm^{-1} (**3** and **4**) of the ester functions and the ν_{OH} bands at 3138 cm^{-1} (**3**) and 3411 cm^{-1} (**4**). The NMR spectra of **3** and **4** show the expected signals of all organic groups, the singlet at $\delta = 9.80$ ppm (**3**) or at $\delta = 9.89$ ppm (**4**) being characteristic for the three equivalent protons of the aromatic central core. In the ^{13}C NMR spectra, all resonances observed can be assigned unambiguously (see Experimental Section).

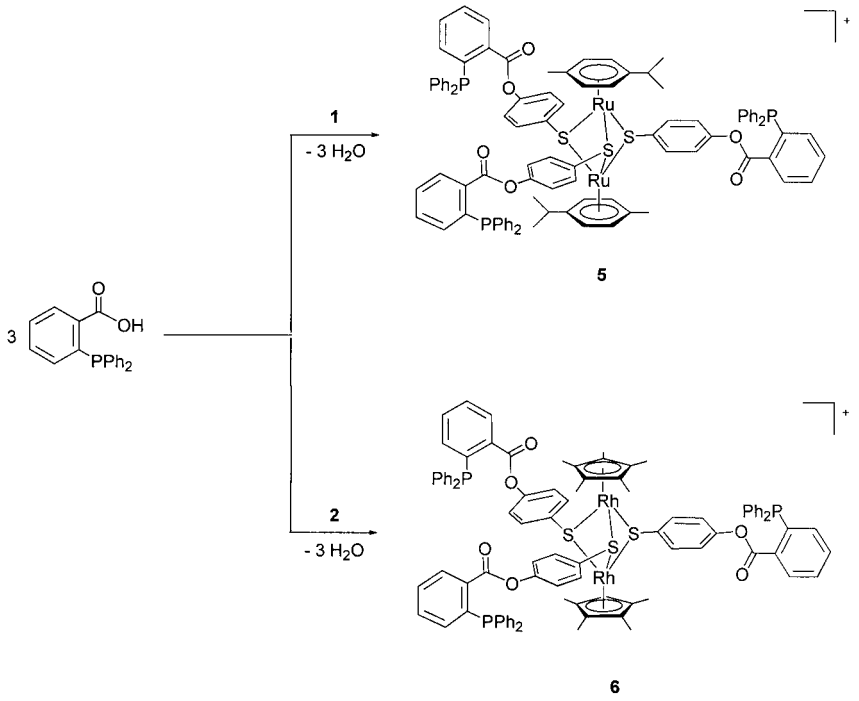
Cations **1**–**4** contain three (**1**, **2**) or six (**3**, **4**) hydroxy functions that are available for esterification by classical condensations reactions; this predisposes these dendritic systems for the introduction of catalytic sites at the periphery.

Peripheral functionalization of the dendritic systems with phosphine groups: The dinuclear cations $[Ru_2(p\text{-}Me\text{-}C_6H_4\text{-}i\text{Pr})_2(p\text{-}S\text{-}C_6H_4\text{-}OH)_3]^+$ (**1**) and $[Rh_2(C_5Me_5)_2(p\text{-}S\text{-}C_6H_4\text{-}OH)_3]^+$ (**2**) react with three equivalents of 2-diphenylphosphinobenzoic acid in dichloromethane, in the presence of condensation agents (*N*,*N*-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), 4-pyrrolidinopyridine (4-ppy)),[13] to give the cationic triphosphine derivatives $[Ru_2(p\text{-}Me\text{-}C_6H_4\text{-}i\text{Pr})_2(p\text{-}S\text{-}C_6H_4\text{-}O\text{-}CO\text{-}o\text{-}C_6H_4\text{-}PPh_2)_3]^+$ (**5**) and $[Rh_2(C_5Me_5)_2(p\text{-}S\text{-}C_6H_4\text{-}O\text{-}CO\text{-}o\text{-}C_6H_4\text{-}PPh_2)_3]^+$ (**6**) (Scheme 3).

Cations **5** and **6** can be isolated as the chloride salts (orange microcrystalline powders) in high yields. The mass spectra show that, in both cations, the three hydroxy functions have indeed been esterified. Accordingly, the $^{31}P\{^1H\}$ NMR spectra of **5** and **6** show one resonance centered at $\delta = -4.7$ ppm for the three equivalent phosphorus atoms. The aromatic ester functions give rise to a characteristic absorption at 1736 cm^{-1} in the infrared spectra of both **5** and **6**. The ^1H and ^{13}C NMR



Scheme 2. Constitution of the dendritic cation **3**, based on $\{Ru_2(p\text{-}Me\text{-}C_6H_4\text{-}i\text{Pr})_2\}$ metallodendron units. In the dendritic cation **4**, the $\{Ru(p\text{-}Me\text{-}C_6H_4\text{-}i\text{Pr})\}$ entities are replaced by $Rh(C_5Me_5)$ entities.



Scheme 3. Build up of peripheric catalytic sites by esterification of the dendritic cation **1** and **2** with phosphine.

data are also in agreement with the constitution of **5** and **6** proposed in Scheme 3.

The same functionalization with peripheral PPh_2 groups also works with the next dendritic generation: Cations **3** and **4** react with 2-diphenylphosphinobenzoic acid in dichloromethane, with DCC, DMAP, and 4-ppy as condensation reagents, to give the cationic dendrimers **7** and **8** containing six PPh_2 groups. Compounds **7** and **8** are isolated as the chloride salts **7**-Cl_3 and **8**-Cl_3, respectively; the spectroscopic (MS, IR, ^1H, ^{13}C, ^{31}P NMR) and analytical data (see Experimental Section) are in agreement with the structure proposed in Scheme 4.

Catalytic potential of the dendritic ligands 5–8 for the carbonylation of methanol: The dendritic cations **5–8**, functionalized by PPh_2 groups at the periphery, were used as auxiliary ligands in the rhodium-catalyzed carbonylation of methanol. The peripheral PPh_2 are able to coordinate rhodium(I) from precursors such as $[\{Rh(CO)_2Cl\}_2]$. The catalytic reaction takes place in a mixture of methanol, iodomethane, and water under a pressure of carbon monoxide (22 bar) at 170 °C [Eq. (1)].

$$CH_3OH + CO \rightarrow CH_3COOH \qquad (1)$$

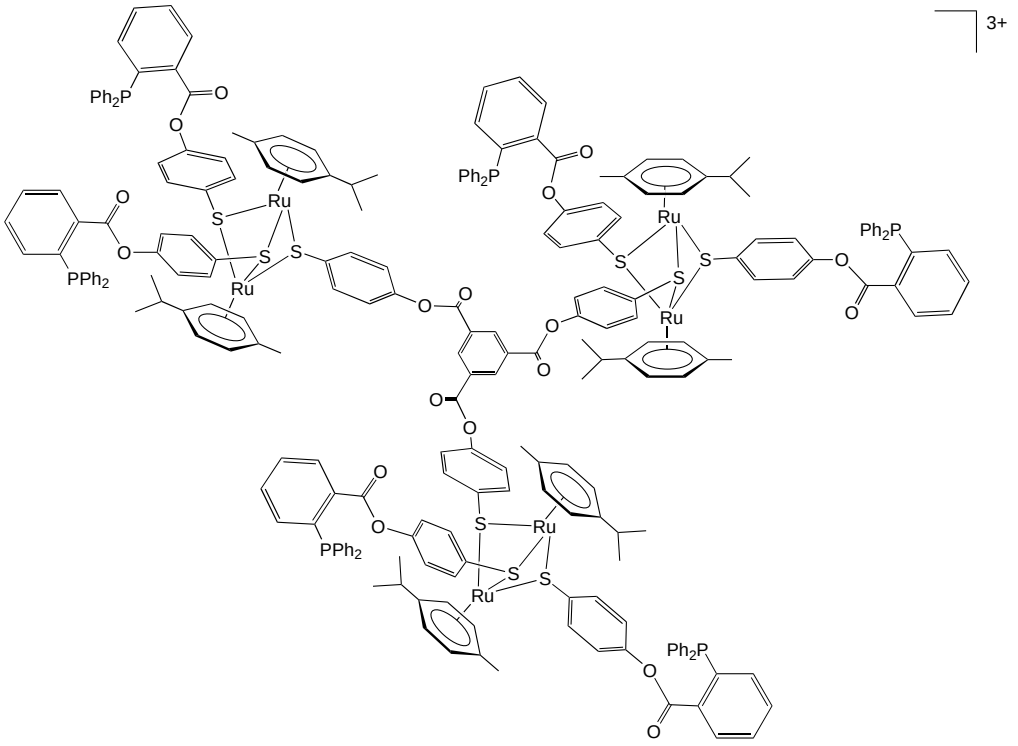
The rhodium-based Monsanto process[14] which works at 150 to 200 °C under CO pressures between 30 and 60 bar does not use auxiliary ligands; the catalytic species formed is the anion $[Rh(CO)_2I_2]^-$, which undergoes oxidative addition of CH_3I to give $[(CH_3)Rh(CO)_2I_3]^-$, rearrangement to $[(CH_3CO)Rh(CO)I_3]^-$, addition of carbon monoxide to $[(CH_3CO)Rh(CO)_2I_3]^-$, and finally reductive elimination of CH_3COI to reform the active species $[Rh(CO)_2I_2]^-$.[15] Phosphine auxiliary ligands have been shown to facilitate the oxidative-addition step.[16] On the other hand, in the iridium-based Cativa™ process,[17] ruthenium co-catalysts facilitate the reductive-elimination step. For this reason, we decided to use the ruthenium-containing phosphine ligands **5** and **7** in combination with a rhodium precursor, $[\{Rh(CO)_2Cl\}_2]$, as the catalytic system and to compare it to the classical Monsanto catalyst.

The results clearly demonstrate that the combination of rhodium (in the catalytic sites) and ruthenium (in the core) improves the catalytic performance for the carbonylation of methanol (Table 2). With respect to the classical Monsanto catalyst (entry 1), the catalytic turnover frequency increases from 20 to 65 min^{-1} by using the combination $[\{Rh(CO)_2Cl\}_2]$/**5**-Cl (entry 2). The combination $[\{Rh(CO)_2Cl\}_2]$/**7**-Cl_3 (entry 3), containing the next dendrimer generation with ruthe-

Table 2. Catalytic carbonylation of methanol.[a]

	Catalyst	Co-catalyst	Ratio	Time	TON[b] [min]	TOF[c] [min^{-1}]
1	$[\{Rh(CO)_2Cl\}_2]$			20	400	20
2	$[\{Rh(CO)_2Cl\}_2]$	**5**-Cl	1:4	20	1300	65
3	$[\{Rh(CO)_2Cl\}_2]$	**7**-Cl_3	3:4	20	180	9
4	$RuCl_3$	**6**-Cl	1:4	20	0	0
5	$RuCl_3$	**8**-Cl_3	3:4	20	0	0
6	solid recovered from entry 2			20	1200	60

[a] Conditions: catalyst/methanol/iodomethane/water 1:2000:200:1000, 22 bar, 170 °C. [b] TON (turnover number) = mol (CH_3COOH + CH_3COOCH_3) per mol rhodium. [c] TOF (turnover frequency) = mol (CH_3COOH + CH_3COOCH_3) per mol rhodium per minute.



Scheme 4. Constitution of the dendritic cation **7**, based on $\{Ru_2(p\text{-Me-}C_6H_4\text{-}i\text{Pr})_2\}$ metallodendron units. In the dendritic cation **8**, the $\{Ru(p\text{-Me-}C_6H_4\text{-}i\text{Pr})\}$ entities are replaced by $Rh(C_5Me_5)$ entities.

nium in the dendrons, also catalyzes the carbonylation of methanol under these conditions, but it is less active, giving a TOF of only 9 min^{-1}. The combinations $RuCl_3$/**6**-Cl (entry 4) and $RuCl_3$/**8**-Cl_3 (entry 5), which contain rhodium only in the core, are found to be completely inactive. These results clearly demonstrate that the carbonylation reaction takes place in the peripheral catalytic sites, while the metal core acts only as a promoter. The combination [{$Rh(CO)_2Cl$}$_2$]/**5**-Cl (entry 2) seems to have the right balance between activity and stability, because the organometallic residue from entry 2 is still active for further runs (entry 6).

Conclusion

In the present study we showed that the remarkable preference for the SH versus OH functions by dinuclear ruthenium and rhodium complexes can be used to build up dendritic cations that contain Ru_2S_3 or Rh_2S_3 units, either in the core or in the dendrons. Thanks to the free peripheral OH groups, these dendritic cations can be functionalized with PPh_2 groups, generating catalytic sites at the periphery in combination with suitable metal atoms. Thus, these phosphine-functionalized dendritic cations serve as ligands and coordinate to rhodium(I).

Catalytic tests that the ruthenium-containing dendritic cation [Ru_2(*p*-Me-C_6H_4-*i*Pr)$_2$(*p*-S-C_6H_4-O-CO-*o*-C_6H_4-PPh_2)$_3$]$^+$ (**5**) increases the catalytic activity of [{$Rh(CO)_2Cl$}$_2$] for the carbonylation of methanol by a factor of three, while the next generation dendrimer **7** is less active as a co-catalyst. A detailed study of the synergistic effects of rhodium and ruthenium in the best combination [{$Rh(CO)_2Cl$}$_2$]/[**5**]Cl is underway.

Experimental Section

General: Solvents were dried and distilled under nitrogen prior to use. All reactions were carried out under nitrogen, by using standard Schlenk techniques. The dinuclear dichloro complexes [{Ru(*p*-Me-C_6H_4-*i*Pr)Cl_2}$_2$] and [{$Rh(C_5Me_5)Cl_2$}$_2$] were synthesized by previously described methods.[18] All other reagents were purchased (Fluka) and used as received. NMR spectra were recorded with a Varian Gemini 200 BB instrument and referenced to the signals of the residual protons in the deuterated solvents. ^{1}H and ^{13}C NMR: internal standard solvent, external standard TMS. Infrared spectra were recorded with a Perkin–Elmer 1720X FT-IR spectrometer. The mass spectra were recorded at the University of Fribourg (Switzerland) by Prof. Titus Jenny. Microanalyses were carried out by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland).

General method for the preparation of 1 and 2: The dinuclear dichloro complex, [{Ru(*p*-Me-C_6H_4-*i*Pr)Cl_2}$_2$] (61 mg, 0.1 mmol) or [{$Rh(C_5Me_5)Cl_2$}$_2$] (62 mg, 0.1 mmol), was refluxed in technical grade ethanol (25 mL). When the complex was completely dissolved, a solution of *p*-mercaptophenol (76 mg, 0.6 mmol) in ethanol (5 mL) was added dropwise to the hot solution. The resulting mixture was refluxed in ethanol for 3 hours. After cooling to 20 °C, the red solution was filtered, and the solvent was removed under reduced pressure. The oil obtained was purified by column chromatography (silica gel, dicholoromethane/ethanol 5:1, R_f close to 0.8). Cations **1** and **2** were isolated in the form of the chloride salts by evaporation of the solvent as red-orange microcrystalline powders in quantitative yields.

[Ru_2(*p*-Me-C_6H_4-*i*Pr)$_2$(*p*-S-C_6H_4-OH)$_3$]$^+$ (1): IR (KBr): $\tilde{\nu}$ = 3438 cm^{-1} (OH); ^{1}H NMR (200 MHz, [D_6]DMSO, 21 °C): δ = 0.74 (d, ^3J = 6.8 Hz, 6H; (CH_3)$_2$CH), 0.85 (d, ^3J = 6.8 Hz, 6H; (CH_3)$_2$CH), 1.55 (s, 6H; CH_3), 1.93 (sept, ^3J = 6.8 Hz, 2H; (CH_3)$_2$*CH*), 5.21 (d, ^3J = 4.9 Hz, 2H; *H-Ar*), 5.26 (d, ^3J = 4.9 Hz, 2H; *H-Ar*), 5.38 (d, ^3J = 4.9 Hz, 2H; *H-Ar*), 5.58 (d, ^3J = 4.9 Hz, 2H; *H-Ar*), 6.80 (d, ^3J = 8.6 Hz, 6H; *H-Ar*), 7.68 (d, ^3J = 8.6 Hz, 6H; *H-Ar*), 9.85 ppm (s, 3H; O*H*); ^{13}C NMR (50 MHz, [D_6]DMSO, 21 °C): δ = 21.31 ((CH_3)$_2$CH), 21.61 ((CH_3)$_2$CH), 30.71 (CH_3), 70.12 ((CH_3)$_2$*CH*), 106.895 (*C-Ar*), 115.73 (*C-Ar*), 125.20 (*C-Ar*), 127.36 (*C-Ar*), 134.10 (*C-Ar*), 158.1 ppm (*C*(*O*)); MS (ESI): *m*/*z*: 846 [M^++H]; elemental analysis calcd (%) for $C_{38}H_{43}ClO_3Ru_2S_3$ (881.54): C 51.77, H 4.92; found: C 51.86, H 4.98.

[Rh_2(C_5Me_5)$_2$(*p*-S-C_6H_4-OH)$_3$]$^+$ (2): IR (KBr): $\tilde{\nu}$ = 3430 cm^{-1} (OH); ^{1}H NMR (200 MHz, [D_6]DMSO, 21 °C): δ = 1.30 (s, 30H; CH_3), 6.79 (d, ^3J = 8.7 Hz, 6H; *H-Ar*), 7.59 (d, ^3J = 8.7 Hz, 6H; *H-Ar*), 9.89 ppm (s, 3H; O*H*); ^{13}C NMR (50 MHz, [D_6]DMSO, 21 °C): δ = 8.99 (*C*H$_3$), 97.63 (*C-Ar*), 116.89 (*C-Ar*), 125.35 (*C-Ar*), 138.03 (*C-Ar*), 146.38 ppm (*C*(*O*)); MS (ESI): *m*/*z*: 853 [M^++H]; elemental analysis calcd (%) for $C_{38}H_{45}Cl_1O_3Rh_2S_3$ (887.22): C 51.44, H 5.11; found: C 51.58, H 5.19.

General method for the preparation of 3 and 4: A solution of 1,3,5-benzenetricarbonyl trichloride (20 mg, 0.07 mmol) and triethylamine (0.03 mL, 0.2 mmol) in CH_2Cl_2 (5 mL) was added slowly to a suspension of the corresponding phenol derivatives, **1**-Cl (200 mg, 0.2 mmol) or **2**-Cl (200 mg, 0.2 mmol), in CH_2Cl_2 (40 mL) at room temperature. The resulting mixture was vigorously stirred for three days. Then the solution was filtered to give the pure dendrimers **3** and **4** as yellow powders, which were dried in vacuo (yield: **3**-Cl_3: 76%, **4**-Cl_3: 75%).

[1,3,5-C_6H_3[CO_2-(*p*-C_6H_4-S)Ru_2(*p*-Me-C_6H_4-*i*Pr)$_2$(*p*-S-C_6H_4-OH)$_2$}$_3$]$^{3+}$ (3): IR (KBr): $\tilde{\nu}$ = 3138 (OH), 1741 cm^{-1} (CO ester); ^{1}H NMR (200 MHz, [D_6]DMSO, 21 °C): δ = 0.74 (d, ^3J = 7.0 Hz, 6H; (CH_3)$_2$CH), 0.85 (d, ^3J = 7.0 Hz, 6H; (CH_3)$_2$CH), 1.56 (s, 6H; CH_3), 1.93 (sept, ^3J = 7.0 Hz, 2H; (CH_3)$_2$*CH*), 5.21 (d, ^3J = 5.8 Hz, 2H; *H-Ar*), 5.28 (d, ^3J = 5.5 Hz, 2H; *H-Ar*), 5.37 (d, ^3J = 5.8 Hz, 2H; *H-Ar*), 5.56 (d, ^3J = 5.5 Hz, 2H; *H-Ar*), 6.79 (d, ^3J = 8.4 Hz, 6H; *H-Ar*), 7.68 (d, ^3J = 8.4 Hz, 6H; *H-Ar*), 9.80 ppm (s, 5H; O*H*); ^{1}H NMR (200 MHz, [D_6]DMSO + D_2O, 21 °C): δ = 0.74 (d, ^3J = 7.0 Hz, 6H; (CH_3)$_2$CH), 0.85 (d, ^3J = 7.0 Hz, 6H; (CH_3)$_2$CH), 1.56 (s, 6H; CH_3), 1.93 (sept, ^3J = 7.0 Hz, 2H; (CH_3)$_2$*CH*), 5.21 (d, ^3J = 5.8 Hz, 2H; *H-Ar*), 5.28 (d, ^3J = 5.5 Hz, 2H; *H-Ar*), 5.37 (d, ^3J = 5.8 Hz, 2H; *H-Ar*), 5.56 (d, ^3J = 5.5 Hz, 2H; *H-Ar*), 6.79 (d, ^3J = 8.4 Hz, 6H; *H-Ar*), 7.68 (d, ^3J = 8.4 Hz, 6H; *H-Ar*), 9.80 ppm (s, 3H; O*H*); ^{13}C NMR (50 MHz, [D_6]DMSO, 21 °C): δ = 21.31 ((CH_3)$_2$CH), 21.61 ((CH_3)$_2$CH), 30.71 (CH_3), 70.12 ((CH_3)$_2$*CH*), 99.75, 106.64 (*C-Ar*), 116.47 (*C-Ar*), 125.35 (*C-Ar*), 127.01 (*C-Ar*), 134.43 (*C-Ar*), 158.14 (*C*(*O*)) 176.15 ppm (CO ester); MS (ESI): *m*/*z*: 899 [M^++H]; elemental analysis calcd (%) for $C_{123}H_{129}Cl_3O_{12}Ru_6S_9$ (2800.71): C 52.75, H 4.64; found: C 52.98, H 4.34.

[1,3,5-C_6H_3[CO_2(*p*-C_6H_4-S)Rh_2(C_5Me_5)$_2$(*p*-S-C_6H_4-OH)$_2$}]$^{3+}$ (4): IR (Kbr): $\tilde{\nu}$ = 3430 (OH), 1741 cm^{-1} (CO ester); ^{1}H NMR (200 MHz, [D_6]DMSO, 21 °C): δ = 1.30 (s, 30H; CH_3), 6.79 (d, ^3J = 8.7 Hz, 6H; *H-Ar*), 7.59 (d, ^3J = 8.7 Hz, 6H; *H-Ar*), 9.89 ppm (s, 5H; O*H*); ^{1}H NMR (200 MHz, [D_6]DMSO + D_2O, 21 °C): δ = 1.30 (s, 30H; CH_3), 6.79 (d, ^3J = 8.7 Hz, 6H; *H-Ar*), 7.59 (d, ^3J = 8.7 Hz, 6H; *H-Ar*), 9.89 ppm (s, 3H; O*H*); ^{13}C NMR (50 MHz, [D_6]DMSO, 21 °C): δ = 9.00 (*C*H$_3$), 97.78 (*C-Ar*), 116.43 (*C-Ar*), 121.01 (*C-Ar*), 125.36 (*C-Ar*), 135.17 (*C-Ar*), 147.13 (*C*(*O*)), 158.84 ppm (*C*O ester); MS (ESI): *m*/*z*: 905 [M^++H]; elemental analysis calcd (%) for $C_{123}H_{135}Cl_3O_{12}Rh_6S_9$ (2817.77): C 52.43, H 4.83; found: C 52.58, H 4.75.

General method for the preparation of 5–8: A solution of 2-diphenylphosphinobenzoic acid (1 g, 3.26 mmol), *N*,*N*-dicyclohexylcarbodiimide (2.7 g, 13.05 mmol), 4-(dimethylamino)pyridine (100 mg, 0.82 mmol), 4-pyrrolidinopyridine (100 mg, 0.68 mmol), and the corresponding phenol derivatives, **1**-Cl (880 mg, 1 mmol), **2**-Cl (880 mg, 1 mmol), **3**-Cl_3 (50 mg), or **4**-Cl_3 (50 mg), in CH_2Cl_2 (40 mL) was allowed to stand at room temperature under nitrogen, until the esterification was completed (three days). The resulting solution was filtered through Celite to remove *N*,*N*-dicyclohexyl urea, and the filtrate was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column (150 g), eluting with acetone. Products **5**–**8** were isolated from the third fraction by evaporation of the solvent, as orange-yellow solids (yields close to 65%).

[Ru_2(*p*-Me-C_6H_4-*i*Pr)$_2$(*p*-S-C_6H_4-O-CO-*o*-C_6H_4-PPh_2)$_3$]$^+$ (5): IR (KBr): $\tilde{\nu}$ = 1735.7 cm^{-1} (CO ester); ^{1}H NMR (200 MHz, [D_6]DMSO, 21 °C): δ =

0.68 (d, $^3J = 6.2$ Hz, 6H; $(CH_3)_2CH$), 0.82 (d, $^3J = 6.2$ Hz, 6H; $(CH_3)_2CH$), 1.52 (s, 6H; CH_3), 1.86 (sept, $^3J = 6.2$ Hz, 2H; $(CH_3)_2CH$), 5.37 (d, $^3J =$ 5.5 Hz, 2H; *H-Ar*), 5.53 (d, $^3J = 5.5$ Hz, 2H; *H-Ar*), 5.67 (d, $^3J = 5.5$ Hz, 2H; *H-Ar*), 5.74 (d, $^3J = 5.5$ Hz, 2H; *H-Ar*), 6.76 – 7.02 (m, 9H; *H-Ar*), 7.09 (d, $^3J = 8.2$ Hz, 6H; *H-Ar*), 7.21 – 7.75 (m, 30H; *H-Ar*), 7.93 (d, $^3J = 8.2$ Hz, 6H; *H-Ar*), 8.28 ppm (m, 3H; *H-Ar*); ^{13}C NMR (50 MHz, [D$_6$]DMSO, 21 °C): $\delta = 21.91$ ($(CH_3)_2CH$), 22.71 ($(CH_3)_2CH$), 31.81 (CH_3), 70.97 ($(CH_3)_2CH$), 106 – 148 (m, *C-Ar*), 159.1 (*C*(*O*)), 165.12 ppm (*C*O ester); ^{31}P NMR (81 MHz, [D$_6$]DMSO, 21 °C): $\delta = -4.72$ ppm; MS (ESI): *m*/*z*: 1711 [M^++H], 1423 [M^++H − $OCOC_6H_4$-*o*-$P(C_6H_5)_2$], 1134 [M^++H − $2\,OCOC_6H_4$-*o*-$P(C_6H_5)_2$]; elemental analysis calcd (%) for $C_{95}H_{82}ClO_6P_3Ru_2S_3$ (1746.38): C 65.04, H 4.73; found: C 65.12, H 4.81.

[$Rh_2(C_5Me_5)_2$(*p*-S-C_6H_4-O-CO-*o*-C_6H_4-PPh_2)$_3$]$^+$ (6): IR (KBr): $\tilde{\nu} =$ 1735 cm^{-1} (CO ester); ^{1}H NMR (200 MHz, [D$_6$]DMSO, 21 °C): $\delta = 1.36$ (s, 30H; CH_3), 7.04 (d, $^3J = 8.8$ Hz, 6H; *H-Ar*), 7.27 – 7.42 (30H, m; *H-Ar*), 7.48 – 7.58 (6H, m; *H-Ar*), 7.73 (d, $^3J = 8.8$ Hz, 6H; *H-Ar*), 8.31 ppm (6H, m; *H-Ar*); ^{13}C NMR (50 MHz, [D$_6$]DMSO, 21 °C): $\delta = 7.96$ (CH_3), 107.6 (*C-Ar*), 116 – 142 (*m*, *C-Ar*), 156.9 pppm (*CO* ester); ^{31}P NMR (81 MHz, [D$_6$]DMSO, 21 °C): $\delta = -3.01$ ppm; MS (ESI): *m*/*z*: 1718 [M^++H], 1430 [M^++H − $OCOC_6H_4$-*o*-$P(C_6H_5)_2$], 1141 [M^++H − $2\,OCOC_6H_4$-*o*-$P(C_6H_5)_2$]; elemental analysis calcd (%) for $C_{95}H_{84}ClO_6P_3Rh_2S_3$ (1752.06): C 65.12, H 4.83; found: C 65.02, H 4.89.

[1,3,5-C_6H_3{CO_2-(*p*-C_6H_4-S)Ru_2(*p*-Me-C_6H_4-*i*Pr)$_2$(*p*-S-C_6H_4-O-CO-*o*-C_6H_4-PPh_2)}$_3$]$^{3+}$ (7): IR (KBr): $\tilde{\nu} = 1733$, 1741 cm^{-1} (CO ester); ^{1}H NMR (200 MHz, [D$_6$]DMSO, 21 °C): $\delta = 0.71$ (d, $^3J = 7.0$ Hz, 18H; $(CH_3)_2CH$), 0.82 (d, $^3J = 7.0$ Hz, 18H; $(CH_3)_2CH$), 1.59 (s, 18H; CH_3), 1.86 (sept, $^3J =$ 7.0 Hz, 6H; $(CH_3)_2CH$), 5.35 (d, $^3J = 5.8$ Hz, 6H; *H-Ar*), 5.47 (d, $^3J =$ 5.5 Hz, 6H; *H-Ar*), 5.54 (d, $^3J = 5.8$ Hz, 6H; *H-Ar*), 5.70 (d, $^3J = 5.5$ Hz, 6H; *H-Ar*), 6.80 – 7.74 (m, 102H; *H-Ar*), 7.92 (d, $^3J = 8.2$ Hz, 6H; *H-Ar*), 8.17 – 8.33 (m, 6H; *H-Ar*), 9.91 ppm (s, 3H; *H-Ar*); ^{13}C NMR (50 MHz, [D$_6$]DMSO, 21 °C): $\delta = 21.31$ ($(CH_3)_2CH$), 21.61 ($(CH_3)_2CH$), 30.71 (CH_3), 70.12 ($(CH_3)_2CH$), 106.64 (*C-Ar*), 116.47 – 160 (*m*, *C-Ar*), 166.38 (CO ester), 176.15 ppm (CO ester); ^{31}P NMR (81 MHz, [D$_6$]DMSO, 21 °C): $\delta =$ − 4.72 ppm; MS (ESI): *m*/*z*: 1475 [M^+ + H].

[1,3,5-C_6H_3{CO_2-(*p*-C_6H_4-S)$Rh_2(C_5Me_5)_2$(*p*-S-C_6H_4-O-CO-*o*-C_6H_4-PPh_2)$_2$}$_3$]$^{3+}$ (8): IR (KBr): $\tilde{\nu} = 1736$, 1741 cm^{-1} (CO ester); ^{1}H NMR (200 MHz, [D$_6$]DMSO, 21 °C): $\delta = 1.30$ (s, 90H; CH_3), 6.80 – 7.74 (m, 102H; *H-Ar*), 7.98 (d, $^3J = 8.2$ Hz, 6H; *H-Ar*), 8.17 – 8.33 (m, 6H; *H-Ar*), 9.97 (s, 3H; *H-Ar*); ^{31}P NMR (81 MHz, [D$_6$]DMSO, 21 °C): $\delta = -3.12$; MS (ESI): *m*/*z*: 1480 [M^+ + H].

X-ray analysis of [$Rh_2(C_5Me_5)_2$(*p*-S-C_6H_4-OH)$_3$]$^+$ (2): An orange crystal of **2** was mounted on a Stoe imaging plate diffractometer system[19] equipped with a one-circle ϕ goniometer and a graphite-monochromator. Data collection was performed at − 120 °C with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). 90 exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with $0 < \phi < 90°$ and with the crystal oscillating through 1° in ϕ. The resolution was $D_{min} - D_{max}$ 12.45 – 0.81 Å. Crystal data and collection paramaters: formula $C_{38}H_{45}ClO_3Rh_2S_3$; M_r 887.19; orthorhombic, space group $P2_12_12_1$; $a = 14.0357(8)$, $b = 14.1433(8)$, $c = 23.670(2)$ Å, $V =$ 4688.7(9) Å^3 $Z = 4$, $F(000) = 1808$, $\rho_{calcd} = 1.257$ g cm^{-1}, $\mu = 0.923$ mm^{-1}, $\theta_{max} = 25.91°$; reflections collected = 16392, number of independent reflections = 7420, $R_{int} = 0.0364$, $wR_2(F^2) = 0.1079$, $R(F) = 0.0389$, parameters = 437, GoF = 1.078. The structure was solved by direct methods by using the program SHELXS-97[20] and refined by full matrix least squares on F^2 with SHELXL-97.[21] The hydrogen atoms were included in calculated positions and treated as riding atoms by using SHELXL-97 default parameters. The figure was drawn with ORTEP-3.[22]

[1] For reviews, see a) S. M. Grayson, J. M. J. Fréchet, *Chem. Rev.* **2001**, *101*, 3189; b) G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendritic Molecules: Concepts, Syntheses, Perspectives*, VCH: New-York, **1996**.

[2] a) J. F. G. A. Jansen, E. M. M. de Brabander van der Berg, E. W. Meijer, *Science* **1994**, *266*, 1226; b) R. H. Jin, T. Aida, S. Inoue, *J. Chem. Soc. Chem. Commun.* **1993**, 1260; c) G. R. Newkome, B. D. Woosley, E. He, C. N. Moorefield, R. Güther, G. R. Baker, G. H. Escamilla, J. Merrill, H. Luftmann, *Chem. Commun.* **1996**, 2737; d) L. Brauge, G. Magro, A. M. Caminade, J. P. Majoral, *J. Am. Chem. Soc.* **2001**, *123*, 6698; e) J. P. Majoral, A. M. Caminade, *Chem. Rev.* **1999**, *99*, 845, and references therein.

[3] a) E. Alonso, D. Astruc, *J. Am. Chem. Soc.* **2000**, *122*, 3222; b) N. Feeder, J. Geng, P. G. Goh, B. F. G. Johnson, C. M. Martin, D. S. Shepard, W. Zhou, *Angew. Chem.* **2000**, *112*, 1727; *Angew. Chem. Int. Ed.* **2000**, *39*, 1661.

[4] P. Weyermann, J. P. Gisselbrecht, C. Boudon, F. Diederich, M. Gross, *Angew. Chem.* **1999**, *111*, 3400; *Angew. Chem. Int. Ed.* **1999**, *38*, 3215.

[5] a) R. Wang, Z. Zheng, *J. Am. Chem. Soc.* **1999**, *121*, 3549; b) C. B. Gorman, W. Y. Su, H. Jiang, M. Watson, P. Boyle, *Chem. Commun.* **1999**, 877; c) C. B. Gorman, B. L. Parkhust, W. Y. Su, K.-Y. Chen, *J. Am. Chem. Soc.* **1997**, *119*, 1141.

[6] a) E. C. Constable, *Chem. Commun.* **1997**, 1073; b) E. C. Constable, O. Eich, C. E. Houscroft, L. A. Johnston, *Chem. Commun.* **1998**, 2661; c) E. C. Constable, O. Eich, C. E. Houscroft, *J. Chem. Soc. Dalton Trans.* **1999**, 1363; d) G. R. Newkome, C. N. Moorefield, F. Vögtle, in *Dendritic Molecules: Concepts, Syntheses, Perspectives*, VCH: New York, **1996**, Chapter 8.

[7] a) D. Astruc, F. Chardac, *Chem. Rev.* **2001**, 101, 2991; b) D.A Tomalia, P. R. Dvornic, *Nature* **1994**, *372*, 617; c) J. W. J. Knapen, A. W van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijkens, D. M. Grove, G. van Koten, *Nature* **1994**, *372*, 659; d) G. Rodriguez, M. Lutz, A. L. Spek, G. van Koten, *Chem. Eur. J.* **2002**, *8*, 45.

[8] G. Süss-Fink, M. Faure, T. R. Ward, *Angew. Chem.* **2002**, *114*, 105; *Angew. Chem. Int. Ed.* **2002**, *41*, 99.

[9] a) L. A. van de Kuil, D. M. Grove, J. W. Zwikker, L. W. Jenneskens, W. Drenth, G. van Koten, *Chem. Mater.* **1994**, *6*, 1675; b) L. A. van de Kuil, H. Luitjes, D. M. Grove, J. W. Zwikker, J. G. M. van der Linden, A. M. Roelofsen, L. W. Jenneskens, W. Drenth, G. van Koten, *Organometallics* **1994**, *13*, 468.

[10] a) J. J. Garcia, H. Torrens, H. Adams, N. A. Bailey, P. M. Maitlis, *J. Chem. Soc. Chem. Commun.* **1991**, 74; b) J. J. Garcia, H. Torrens, H. Adams, N. A. Bailey, A. Shacklady, P. M. Maitlis, *J. Chem. Soc. Dalton Trans.* **1993**, 1529; c) H. T. schacht, R. C. Haltiwanger, M. R. DuBois, *Inorg. Chem.* **1992**, *31*, 1728.

[11] M. T. Ashby, *Inorg. Chem.* **1995**, *34*, 5429.

[12] CCDC-181622 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

[13] a) J. E. Hoots, T. B. Rauchfuss, D. A. Wrobleski, *Inorg. Synth.* **1982**, *21*, 178; b) A. Hassner, L. Krepski, V. Alexanian, *Tetrahedron* **1978**, *34*, 2069; c) A. Hassner, V. Alexanian, *Tetrahedron Lett.* **1978**, *46*, 4475; d) E. F. V. Scriven, *Chem. Soc. Rev.* **1983**, *12*, 129; e) C. M. Thomas, A. Neels, H. Stoeckli-Evans, G. Süss-Fink, *Eur. J. Inorg. Chem.* **2001**, 3005.

[14] a) J. F.Roth, J. H. Craddock, A. Hershman, F. E. Paulik, *Chem. Technol.* **1971**, 600; b) D. Forster, *Adv. Organomet. Chem.* **1979**, *17*, 255.

[15] M. J. Baker, M. F. Giles, A. G. Orpen, M. J. Taylor, R. J. Watt, *J. Chem. Soc. Chem. Commun.* **1995**, 197.

[16] a) K. G. Moloy, R. W. Wegman, *Organometallics* **1989**, *8*, 2883; b) J. Rankin, A. D. Poole, A. C. Benyei, D. J. Cole-Hamilton, *Chem. Commun.* **1997**, 1835; c) J. Rankin, A. C. Benyei, A. D. Poole, D. J. Cole-Hamilton, *J. Chem. Soc. Dalton Trans.* **1999**, 3771; d) J. Yang, A. Haynes, P. M. Maitlis, *Chem. Commun.* **1999**, 179; e) L. Gonsalvi, H. Adams, G. J. Sunley, E. Ditzel, A. Haynes, *J. Am. Chem. Soc.* **1999**, *121*, 11233; f) K. V. Katti, B. D. Santarsiero, A. A.Pinkerton, R. G. Cavell, *Inorg. Chem.* **1993**, *32*, 5919.

[17] J. H. Jones, *Platinum Met. Rev.* **2000**, *44*, 94.

[18] a) R. A.Zelonka, M. C. Baird, *Can. J. Chem.* **1972**, *50*, 3063; b) J. W. Wang, K. Moseley, P. M. Maitlis, *J. Am. Chem. Soc.* **1969**, *91*, 5970; c) M. A. Bennett, A. K. Smith, *J. Chem. Soc. Dalton Trans.* **1974**, 233.

[19] IPDS Software. Stoe & Cie, Darmstadt (Germany), **2000**.

[20] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

[21] G. M. Sheldrick, SHELXL-97, Program for crystal structure refinement, University of Göttingen (Germany9), **1997**.

[22] L. J. Farugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

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