ORGANOMETALLICS
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Rhodicenium Salts: From Basic Chemistry to Polyelectrolyte and Dendritic Macromolecules

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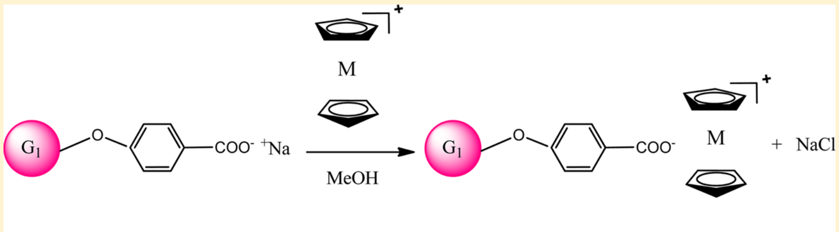
Supporting Information



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M = Rh (**10**) or Co (**12**)

ABSTRACT: A new, facile synthesis of rhodicenium chloride is described, leading to the synthesis of rhodicenium tetraarylborate, the first rhodicenium salt that is soluble in less polar solvents. This opens the route to further chemistry that was prevented by the insolubility of the formerly available rhodicenium salts. This strategy has been extended to the synthesis of water-soluble polyelectrolyte and dendritic macromolecular cobaltocenium and rhodicenium salts.

■ INTRODUCTION

After 60 years of metallocene chemistry, it is remarkable that rhodicenium chemistry has been so little developed. Following Wilkinson's seminal synthesis in 1953 from a cyclopentadienyl salt and tris(acetylacetonato)rhodium(III),[1] the generation of rhodicenium cations was reported in the gas phase by a metal switching reaction[2] and by the gas-phase photoinduced reaction of $RhC_5H_6^+$ with cyclopentane[3] before the use of modern microwave techniques.[4] Rhodicenium cations share with their first-row analogues cobaltocenium cations similar robustness owing to their 18-electron nature. Their salts with mineral acids are all very soluble in water; however, even with very large counteranions they are difficult to precipitate from water. A polarographic study by Wilkinson's group of $[RhCp_2][Cl]$ showed a cathodic wave at −1.53 V vs SCE representing a one-electron reduction; however, the neutral $RhCp_2$ could not be isolated from aqueous solutions. The reaction of anhydrous rhodium chloride with sodium cyclopentadiene produced the diamagnetic compound $RhC_{10}H_{11}$, which was formulated as the Rh^I cyclopentadiene complex $[Rh(\eta^4\text{-}C_5H_6)Cp]$ ($Cp = \eta^5\text{-}C_5H_5$), and the same compound was formed from reduction of $[RhCp_2][Cl]$ in aqueous ethanol by $NaBH_4$.[5] The suggested mechanism involved attack by a hydride either on the Cp ring or intermediately on the metal atom. Oxidation of $RhC_{10}H_{11}$ with HCl gave 50% of the initial rhodicenium cation. A gas also evolved consisting of hydrogen together with C_5 olefinic hydrocarbons. Rhodocene was reported upon reduction of rhodicenium cation with molten sodium and could be trapped only on a liquid-nitrogen-cooled ESR probe,[6] but it decomposed at room temperature with formation of the dimer $[RhCp(\eta^4\text{-}C_5H_5\text{—})]_2$, isolated in 8% yield, in which the η^8,μ_2-dicyclopentadiene ligand bridges the two Rh^I centers.[7] Geiger's group reported the electrochemical reduction of the rhodicenium ion in nonaqueous solvents (CH_3CN and DMF) in two one-electron-reduction processes, and the dimer $[RhCp(\eta^4\text{-}C_5H_5\text{—})]_2$ was isolated by electrolysis of rhodicenium solutions in good yield.[8] This material was quantitatively oxidized back to $[Cp_2Rh][BF_4]$ by $[(C_6H_5)_3C][BF_4]$ in dichloromethane. Rhodocene has been also observed in mass spectral studies of rhodicenium.[9] The instability of this odd-electron rhodocene in comparison to its thermally stable analogue cobaltocene is due to the fact that, in contrast to the first-row 19-electron transition-metal sandwich complexes, for which the orbital of the 19th valence electron is mostly metal based,[10] second- and third-row transition-metal sandwich complexes with one electron in excess vs the 18-electron configuration are ligand-based radicals. The first isolated polysubstituted rhodocene was $[Rh(C_5HPh_4)_2]$, obtained from the reduction of $[Rh(C_5HPh_4)_2]^+$ due to the very large tetraphenylcyclopentadienyl ligands, which inhibited dimerization.[11]

Various rhodicenium complexes with substituted cyclopentadienyl ligands have been reported,[12] including monophosphorylated rhodicenium analogues[13] and functionalized rhodicenium salts containing two acyl and/or imidoyl substituents.[14] Polymethyl rhodicenium complexes have been also reported,[15] including decamethylrhodicenium[16] and nonamethylrhodicenium,[17] imparting greater stability and solubility. Heteronuclear compounds such as rhodocenylferrocene, 1,1′-dirhodocenylferrocene, and 1-cobaltocenyl-1′-rhodocenylferrocene have also been prepared by the statistical nucleophilic

Received: January 13, 2014
Published: February 18, 2014

dx.doi.org/10.1021/om500028e | *Organometallics* 2014, 33, 1259−1265

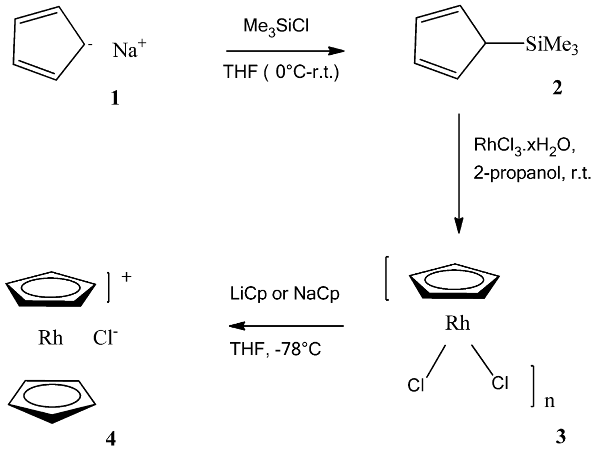
attack of 1,1′-dilithioferrocene on $[CoCp_2][PF_6]$ and $[RhCp_2][PF_6]$, followed by subsequent hydride abstraction with tritylium hexafluorophosphate, yielding the respective termetallocene dications.[18]

Altogether, rhodicenium chemistry is rather limited, and applications are scarce with only some mentions of biomedical usage.[19] Indeed, a major problem is the insolubility of the tetrafluoroborate and hexafluorophosphate salts in common solvents. Therefore, we have reinvestigated the basic rhodicenium chemistry, including an alternative synthesis of rhodicenium chloride from rhodium(III) chloride hydrate, in a two-step reaction which parallels that known for the synthesis of decamethylrhodicenium,[16] and we have disclosed the access to rhodicenium salts, including rhodicenium salts containing polymeric and dendritic macromolecular anions. Finally, the new family of ionic metallocenium dendrimers has been extended to the analogous and comparable cobaltocenium dendrimers.

■ RESULTS AND DISCUSSION

Synthesis of Rhodicenium Chloride. The new synthesis of rhodicenium chloride started from the reaction of (trimethylsilyl)cyclopentadiene[20] with rhodium(III) chloride hydrate in 2-propanol at room temperature, forming the cyclopentadiene rhodium dichloride oligomer[20] that is soluble only in water, DMF, and DMSO. Then, the synthesis of rhodicenium chloride[1] was achieved from the reaction of this oligomer with sodium cyclopentadiene in THF. The product was extracted with hot water, and washing with diethyl ether several times permitted the removal of unreacted organic species. Extraction with nitromethane (in which the other reaction product, NaCl, is insoluble) gave rhodicenium chloride as a yellowish oil (Scheme 1).

Scheme 1. New Synthesis of Rhodicenium Chloride (4)



Access to the rhodicenium hexafluorophosphate 5 was also easily achieved by adding HPF_6 into the aqueous solution of rhodicenium chloride. ^1H NMR is a practical tool allowing comparison among the three rhodium complexes 3−5 (Figure 1).

The protons of the Cp ring of rhodicenium chloride are deshielded by ∼0.1 ppm in comparison to rhodicenium hexafluorophosphate. The complexes 3−5 are soluble only in very polar solvents such as water, DMF, and DMSO, which is a drawback for further reactions of a rhodicenium salt. Therefore, the synthesis of rhodicenium salts with adequate counteranions for a better solubility in less polar solvents was envisaged.

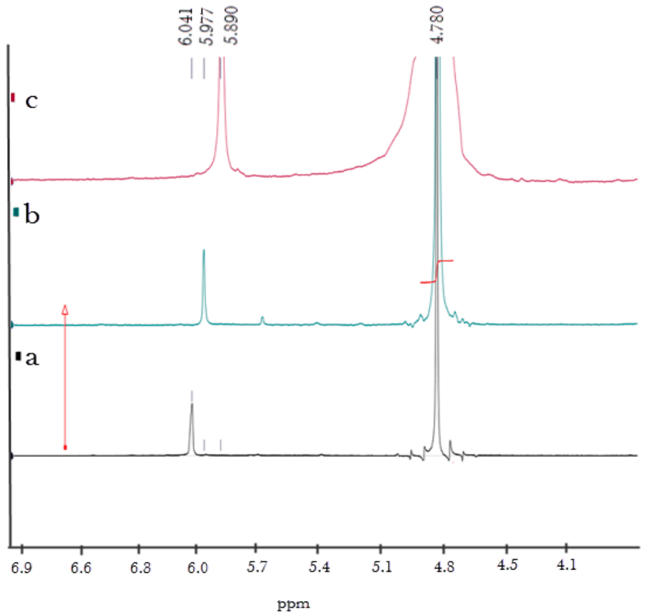
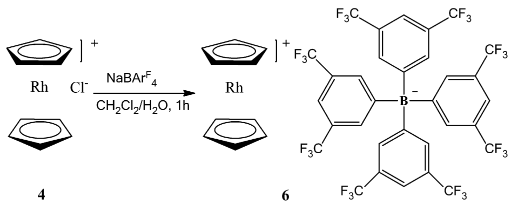


Figure 1. Comparative ^1H NMR spectra in D_2O of $[RhCp(Cl)_2]_n$ (3), $[RhCp_2][Cl]$ (4), and $[RhCp_2][PF_6]$ (5): (a) 3, δ 6.04 ppm (10H, Cp); (b) 4, δ 5.98 ppm (10H, Cp); (c) 5, δ 5.89 ppm (10H, Cp).

Synthesis of a Rhodicenium Tetraarylborate. $Na[BAr^F_4]$ (Ar^F = 3,5-bis(trifluoromethyl)phenyl) was used as a starting material to react with rhodicenium chloride in order to form the salt $[RhCp_2][BAr^F_4]$ (6), in addition to easily removable NaCl (Scheme 2). Extraction of the product in dichloromethane and evaporation of the solvent gave a red-violet powder. ^1H NMR in $CDCl_3$ showed the two typical signals of the aryl groups with the expected 4 and 8 protons and the 10 protons of the two Cp rings, whose signal is now found at 5.63 ppm. This new rhodicenium salt 6 is soluble in lower-polarity solvents such as diethyl ether, dichloromethane, and THF (Table 1). Further reactions of 6 can thus be conveniently achieved in less polar solvents, including hydride addition to rhodicenium salts. For instance, the reaction of 3 with $NaBH_4$ occurs in aqueous ethanol in 30 min,[5] whereas that of 6 proceeds in THF in 5 min followed by extraction with pentane, giving $[Rh(\eta^4\text{-}C_5H_6)Cp]$ (see the Supporting Information). It is likely that 6 will be an appropriate starting material for various nucleophilic reactions with rhodicenium that are impossible with 4 and 5 due to their insolubility in less polar solvents such as THF and dichloromethane, in which 6 is readily soluble.

Scheme 2. Synthesis of a Rhodicenium Tetraarylborate



A sample of the complex 6 in diethyl ether solution was analyzed by FD mass spectrometry, showing the mass peak of

Table 1. Solubilities of the Cyclopentadienylrhodium Dichloride Oligomer 3 and Rhodicenium Complexes 4–6, 8, 10, and 12 as a Function of Their Counteranion, at 25 °C[a]

compd	counteranion	$(C_2H_5)_2O$	CH_2Cl_2	THF	CH_3CN	H_2O	DMSO
3		−	−	−	−	+	+
4	Cl^-	−	−	−	−	+	+
5	PF_6^-	−	−	−	+	+	+
6	$BAr^F{}_4^-$	+	+	+	+	−	−
8	Poly-SO_3^-	−	−	−	−	+	+
10	Dend-COO^-	−	−	−	−	+	+
12	Dend-COO^-	−	−	−	−	+	+

[a] Legend: +, very soluble; −, insoluble.

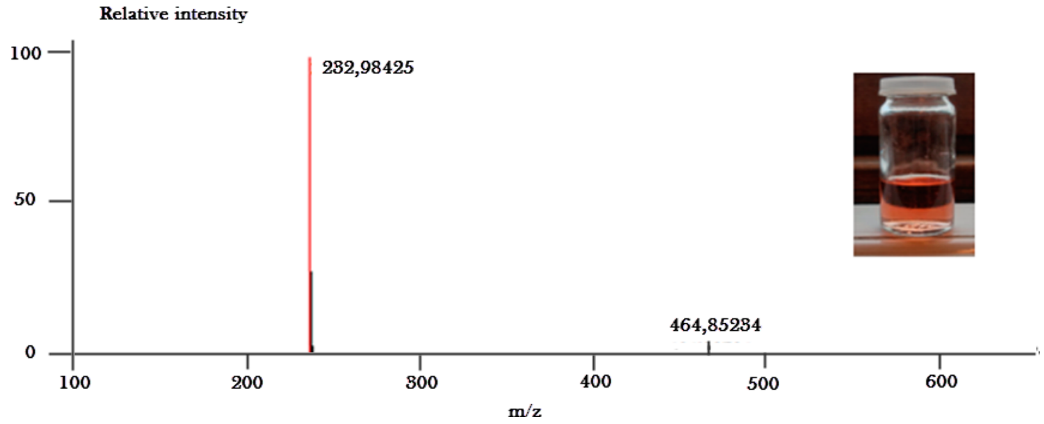


Figure 2. FD MS of $[RhCp_2][BAr^F{}_4]$ (**6**) and photo of the FD MS sample of **6** in diethyl ether.

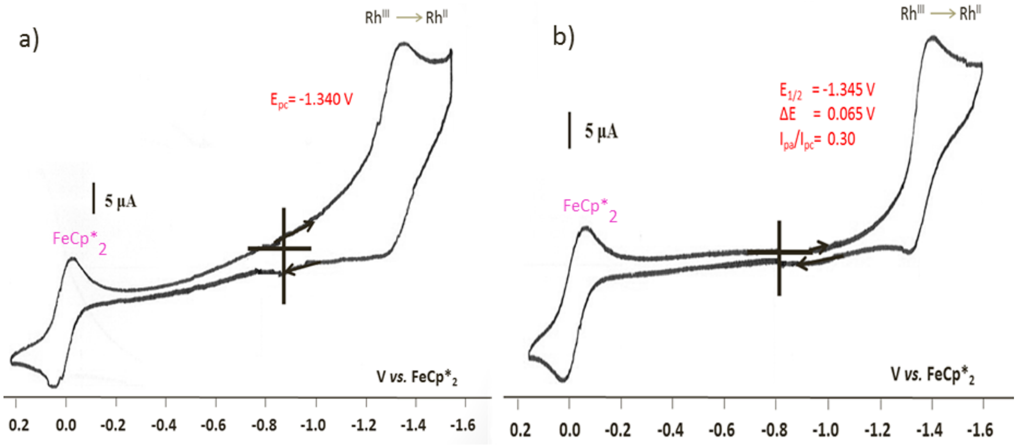


Figure 3. Cyclic voltammetry of $[RhCp_2][BAr^F{}_4]$ (**6**) in THF at (a) 22 °C and (b) −50 °C. The wave at 0.0 V corresponds to the internal reference $[FeCp^*{}_2]$.[22] Conditions: reference electrode, Ag; working and counter electrodes, Pt; scan rate, 0.05 V/s; supporting electrolyte, $[n\text{-}Bu_4N][BAr^F{}_4]$.

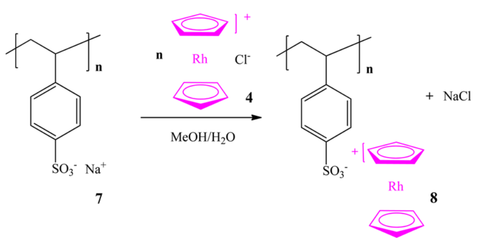
the ionized rhodicenium cation at m/z 232.98 that confirmed the $[RhCp_2][BAr^F{}_4]$ structure (Figure 2).

Product **6** was also characterized by cyclic voltammetry using decamethylferrocene as the internal reference.[22] The cyclic voltammograms were recorded in THF, a very good solubility being accessible with this solvent, at two different temperatures: 22 and −50 °C (Figure 3). At 22 °C an irreversible wave is observed at $E_{pc} = -1.340$ V, due to a one-electron reduction of compound **6** ($Rh^{III/II}$). However, under the same conditions, lowering the temperature to −50 °C allowed the observation of a partial chemical reversibility of the same wave at $E_{1/2} = -1.345$ V. This wave is electrochemically reversible ($\Delta E = 65$ mV) but only partially chemically reversible, as the intensity of the anodic peak is much smaller than that of the cathodic peak ($i_{pa}/i_{pc} = 0.30$). This confirms the results by Geiger et al. including the great instability of the single-electron-transfer product rhodocene, even at −50 °C in THF, and the absence of significant structural rearrangement along the single-electron transfer to the rhodicenium salt **6**.[8]

Synthesis of Water-Soluble Rhodicenium Polystyrene Sulfonate Polymer. Ionic macromolecules such as polymers and dendrimers have been mentioned previously, even though this field of chemistry has not been extensively explored. We envisaged synthesizing ionic rhodicenium polymers and dendrimers in order to study the properties of these new kinds of ionic metallomacromolecules. The starting polymer material sodium polystyrene sulfonate reacted with compound

4 to give the rhodicenium polystyrene sulfonate polymer **8** and NaCl (Scheme 3).

Scheme 3. Synthesis of a Polystyrene Sulfonate Rhodicenium Polymer



The sodium polystyrene sulfonate polymer has an average molecular weight of m/z 70.000; thus, the number of rhodicenium units in polymer **8** is 330 ± 30. The solubility of this new polymer **8** in water is good, being similar to that of its precursor compounds **4** and **7**. The ^{1}H NMR spectrum in water shows the correct ratio between the rhodicenium and polymer protons. The downfield shift of 0.175 ppm for the 10H of Cp of the rhodicenium cation also shows the formation of ionic bonds between the sulfonate anion and the rhodicenium cation (Table 2). Infrared spectroscopy is also a remarkable tool to study the differences in the sulfonate anions between polymers **7** and **8** (Figure 4). The bands at 1191, 1129, and 1042 cm^{-1} of polymer **7** are assignable to sulfonate anions. The change of the band from 1191 to 1216 cm^{-1} in polymer **8** is due to the change of the ionic bond that is now formed between the sulfonate anion and the rhodicenium cation. Another difference is the aromatic C=C bending band that appears at 1633 cm^{-1} in polymer **7** and in polymer **8** changes to 1698 cm^{-1} (Table 2). Finally, DOSY NMR provided the diffusion coefficient of the polymer: $D = [1.38(\pm 0.1)] \times 10^{-10}$ m^2/s. The spectrum is in agreement with rhodicenium being bound to the polymer **7**, providing polymer **8** (Supporting Information).

Table 2. ^{1}H NMR and IR Data for the Metallocenium Complexes 3, 8, and 10−12

complex/ counteranion	Cp (ppm)	Δδ (ppm)	IR in KBr (cm^{-1})
3^a/Cl$^-$	5.977		3104
3^b/Cl$^-$	5.969		3104
8^a/Poly-SO$_3^-$	5.802	0.175^d	1698; 1216; 1129; 1042; 1010
10^b/Dend-COO$^-$	5.957	0.012^e	3107; 1603
11^c/Cl$^-$	5.907		3100
12^c/Dend-COO$^-$	5.823	0.084^f	3099; 1690

^{a}NMR in D$_2$O at 25 °C. ^{b}NMR in methanol-d_4 (1). ^{c}NMR in methanol-d_4 (5). $^d\Delta\delta_{ppm} = \delta$(Cp of **3**) − δ(Cp of **8**). $^e\Delta\delta_{ppm} = \delta$(Cp of **3**) − δ(Cp of **10**). $^f\Delta\delta_{ppm} = \delta$(Cp of **11**) − δ(Cp of **12**).

Synthesis of Water-Soluble G$_1$-Carboxylate Rhodicenium and Cobaltocenium Dendrimers. The supramolecular aspects of dendrimers[23] have been largely considered for various uses such as molecular boxes,[24] exoreceptors,[25] sensors,[25] electron-transfer nanodevices,[26] molecular micelles,[27] nanoreactors,[28] and catalysts.[29] Ionic interactions of dendrimers have been studied previously for different applications such as drug vectors,[30] molecular batteries, and modified electrodes. Polyanionic dendrimers usually display acceptable biocompatibility.[30,31] Therefore, we have synthesized the polybenzoate-terminated dendrimer **9** from a polyiodomethylsilyl precursor.[32] This dendrimer reacted as a sodium salt with complex **4** according to a metathesis ion exchange among the two reacting ion pairs to form a polybenzoate rhodicenium-terminated dendrimer (Scheme 4). Dendrimer **10** (Chart 1) presents a good solubility in methanol and water. Its ^{1}H NMR spectrum discloses the corresponding ratio for the dendritic/peripheral protons (Cp), showing a downfield shift of 0.012 for the 10H of Cp of the rhodicenium cation. The ^{13}C NMR spectrum also confirms the structure of the dendrimeric salt **10**. The nature of the carboxylate anion has changed between dendrimers **9** and **10**, and this is clearly shown by the IR spectrum, in which the absorption due to the carboxylate anion (area 1600−1690 cm^{-1}) in dendrimers **9** and **10** undergoes significant changes (Table 2). Additionally, the DOSY NMR spectrum of **10** provided the diffusion coefficient $D = [4.8(\pm 0.2)] \times 10^{-11}$ m^2/s (Supporting Information).

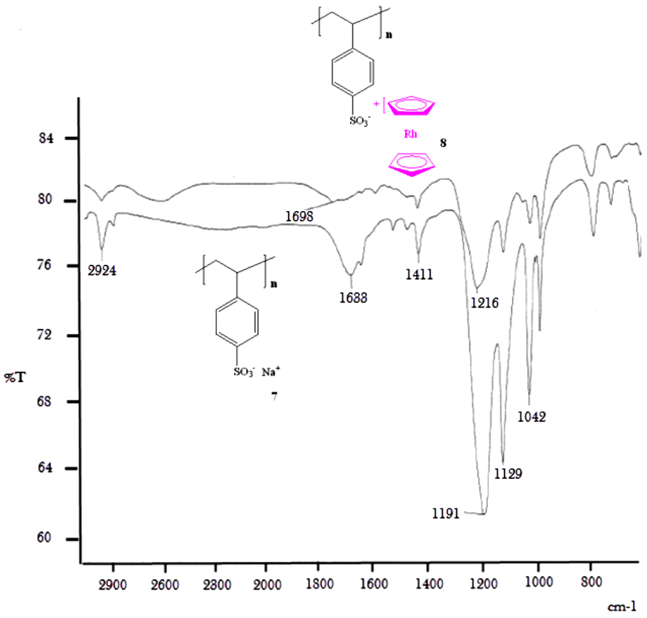


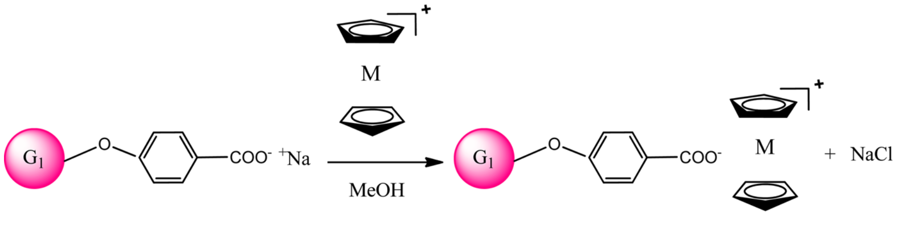
Figure 4. Comparative IR spectra of polymers **7** and **8**.

The expected similar properties of rhodicenium cations and cobaltocenium cations suggest that analogous structures and properties can be obtained for related cobaltocenium salts. Thus, the dendrimer **12** containing cobaltocenium cations in the periphery was also synthesized (Chart 1). Cobaltocenium chloride **11** reacted with the polybenzoate sodium dendrimer **9**, giving the polybenzoate cobaltocenium dendrimer **12** (Scheme 4). The ^{1}H NMR spectrum shows a downfield shift of 0.084 ppm for the 10H of the Cp of the cobaltocenium cation, and the IR spectrum showed a change in the band of the carboxylate anion (Table 2). Finally, the DOSY NMR spectrum of **12** provided the diffusion coefficient $D = [5.5(\pm 0.2)] \times 10^{-11}$ m^2/s (Supporting Information).

■ CONCLUDING REMARKS

The insolubility of classic rhodicenium salts contrasted with the good solubility of rhodium analogues, possibly because the larger inter-ring distance led to more exposed positive charge in rhodicenium than in cobaltocenium, which prevented extension of the organorhodium chemistry. An alternative synthesis of rhodicenium chloride and the preparation of new rhodicenium salts that are soluble in less-polar solvents open the possibilities

Scheme 4. Synthesis of the Rhodicenium and Cobaltocenium Dendrimers[a]



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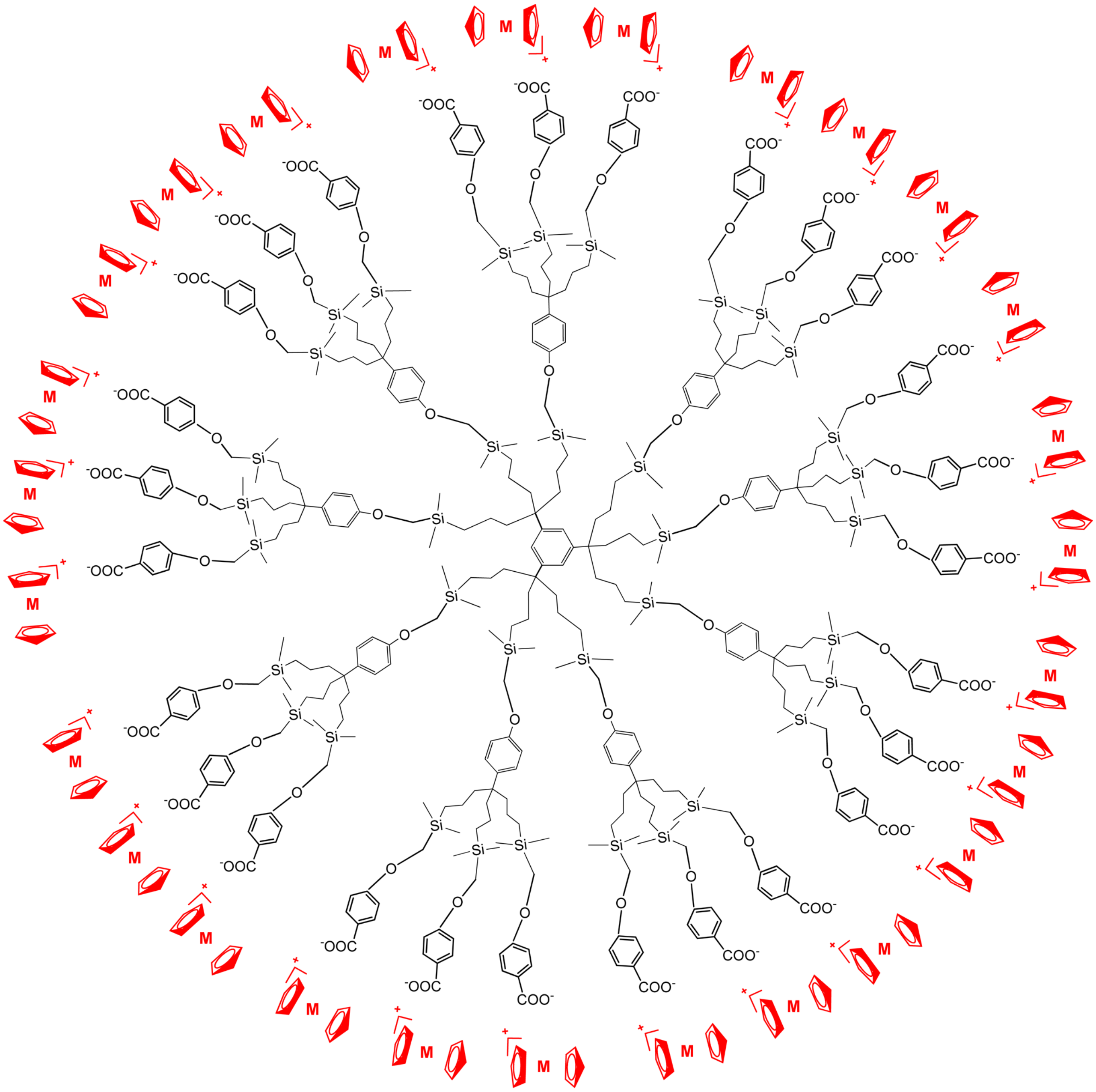
M = Rh (**10**) or Co (**12**)

[a] G_1 stands for a first-generation dendrimer; see the structures in Chart 1.

Chart 1



M = Rh (**10**) or Co (**12**)

of further carrying on organorhodium chemistry. In parallel, ionic water-soluble cobaltocenium and rhodicenium polyelectrolytes and dendrimers with unusual properties have now been made available.

■ EXPERIMENTAL SECTION

General Data. Reagent-grade diethyl ether and tetrahydrofuran (THF) were predried over Na foil and distilled from sodium benzophenone anion under argon immediately prior to use. Dichloromethane (DCM) was distilled over CaH_2 under argon prior to use. All other solvents and chemicals were used as received. The ^{1}H NMR spectra were recorded at 25 °C with a 300 MHz spectrometer. The ^{13}C NMR spectra were obtained in the pulsed FT mode at 75.0 MHz with a 300 MHz spectrometer. All chemical shifts are reported in parts per million (δ, ppm) with reference to Me_4Si (TMS). The infrared (IR) spectra were recorded on a FT-IR spectrophotometer. All electrochemical measurements were recorded under a nitrogen atmosphere. Conditions: dried solvent; temperature, 22 °C; supporting electrolyte, $[n\mathrm{Bu_4N}][\mathrm{BAr^F}_4]$ 0.1 M; working and counter electrodes, Pt; reference electrode, Ag; internal reference, $\mathrm{FeCp^*}_2$ ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$); scan rate, 0.200 V/s. Diffusion measurements were performed at 25 °C with a 400 MHz spectrometer. They were performed using a ^{1}H NMR pulsed-gradient experiment: the simulated spin−echo sequence leads to the measurement of the diffusion coefficient D, where D is the slope of the straight line obtained when $\ln I$ is displayed against the square of the gradient-pulse power according to the equation $\ln I = -\gamma^2 G^2 D \delta^2(\Delta - \delta/3)$, where I is the relative intensity of a chosen resonance, γ is the proton gyromagnetic ratio, Δ is the intergradient delay (150 ms), δ is the gradient pulse duration (5 ms), and G is the gradient intensity. The diffusion constant of water (2.3×10^{-9} m^2/s) was used to calibrate the instrument. The mass spectra were measured by the CESAMO (University of Bordeaux 1, France) on a AccuTOF-GcV instrument which is a GC-TOF. The instrument was equipped with an FD (field desorption) sample introduction system. The elemental analyses were performed by the CESAMO (University of Bordeaux 1, France). The results were obtained with a Thermo Flash 2000 EA instrument. The sample was introduced in a tin container for NCHS analysis.

(Trimethylsilyl)cyclopentadiene.[20] To a solution of sodium cyclopentadienide (1.76 g, 0.02 mol) in 10 mL of THF was added dropwise a solution of trimethylsilyl chloride (2.17 g, 0.02 mol) in 10 mL of THF at 0 °C. The reaction mixture was stirred at 0 °C for 3 h and an additional 2 h at room temperature. Then, the reaction mixture was cautiously treated with cold water and extracted with ether. The organic phase was dried over Na_2SO_4. Further purification was achieved by column chromatography (pentane), and the product was obtained as a colorless liquid (1.8 g, yield 65%).

$[\mathrm{CpRhCl_2}]_n$ (3).[20] To solution of (trimethylsilyl)cyclopentadiene in 7 mL of 2-propanol (0.250 g, 1.81 mmol) was added a solution of hydrated rhodium trichloride (0.161 g, 0.77 mmol) in 7 mL of 2-propanol. The mixture was stirred at room temperature overnight. Pentane was added to the mixture (60 mL), and the precipitate was filtered. The solid was washed several times with dichloromethane. The oligomeric product $[\mathrm{CpRhCl_2}]_n$ was obtained as an orange powder (178.3 mg, yield 97%).

Rhodicenium Chloride (4). The oligomer $[\mathrm{CpRhCl_2}]_n$ (152 mg, 0.64 mmol) was cooled to −78 °C, and then solid CpLi (92 mg, 1.28 mmol) was added slowly. The reaction mixture was stirred for 3 h at −78 °C and then slowly warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure. The solid was extracted with hot water, and the aqueous phase was washed several times with diethyl ether to remove organic impurities. Extraction overnight with nitromethane and filtration gave 106 mg of a yellowish orange powder. Yield: 62%. (Addition of aqueous HPF_6 to product **4** in water and extraction in nitromethane gave 140 mg of rhodicenium hexafluorophosphate (**5**).)

Complex 6. To a solution of rhodicenium chloride (**4**) in 3 mL of water (100 mg, 0.37 mmol) was added $\mathrm{NaBAr^F}_4$ (330 mg, 0.37 mmol) as a solid. The solution was stirred for 1 h. NaCl was added to the water solution until saturation. Product **6** was extracted in dichloromethane. Evaporation of the solvent gave **6** as a reddish violet powder (397 mg, 0.36 mmol). Yield: 98%. ^{1}H NMR of **6** ($CDCl_3$, 300 MHz): δ 7.68 (8H, CF_3CH), 7.52 (4H, CF_3CHCF_3), 5.63 (10H, Cp). ^{13}C NMR of **6** (CD_2Cl_2, 75 MHz): δ 134.9 (CCF_3), 129.0, 128.9, 127.6 (BCCH, $CF_3CCHCCF_3$), 122.1 ($BCCHCCF_3$), 117.5 (CF_3), 87.1 (Cp). FD MS (m/z): calcd for $C_{10}H_{10}Rh^+$ 232.984, found 232.984. Anal. Calcd for $C_{42}H_{22}BF_{24}Rh$: C, 46.01; H, 2.02. Found: C, 45.93; H, 2.08.

Complex 8. To a stirred solution of polymer **7** (20 mg, 0.00028 mmol) in 2 mL of H_2O was added a solution of 2 mL of compound **4** (25.6 mg, 0.096 mmol) in MeOH. The mixture was stirred for $^1/_2$ h. The solvent was removed under vacuum, and the product was extracted twice in nitromethane and filtered. Evaporation of the solvent provided product **8** as a yellowish gel in quantitative yield. ^{1}H NMR of **8** (D_2O, 300 MHz): δ 7.56, 6.62 (4H, CH of Ar of styrenyl), 5.80 (10H of Cp), 1.70 (CH and CH_2 of polymer chain). ^{13}C NMR of **8** (D_2O, 75 MHz): δ 141.6 (Cq of Ar), 128.3 (Cq-CH_2 of Ar), 126.4 and 126.0 (CH of Ar), 86.66 (Cp of rhodicenium), 40.1 (CH and CH_2 of polymeric chain). DOSY NMR: $D = [1.38(\pm 0.1)] \times 10^{-10}$ m^2/s.

Complex 10. To a stirred solution of dendrimer **9** (20 mg, 0.002 mmol) in 2 mL of MeOH was added 2 mL of a solution of compound **4** (15.2 mg, 0.056 mmol) in MeOH. The mixture was stirred for 0.5 h. The solvent was removed under vacuum; the product was extracted twice in nitromethane and filtered. Evaporation of the solvent gave product **10** as a yellow-orange gel in quantitative yield. ^{1}H NMR (CD_3OD, 300 MHz): δ 7.84 and 6.78 (144H, CH arom), 5.96 (270H, Cp), 3.42 (54H, SiCH_2-trz), 1.56 (72H, $CH_2CH_2CH_2Si$), 1.10 (72H, $CH_2CH_2CH_2Si$), 0.49 (72H, $CH_2CH_2CH_2Si$), −0.07 (216H, Si-$(CH_3)_2$). ^{13}C NMR (MeOD, 75 MHz): δ 169.3 (C═O), 163.6 (arom OCq), 131.0 (Cq of arom core), 128.0 and 114.3 (arom CH), 86.9 (Cp), 60.1 (CH_2OAr), 44.0 ($CqCH_2CH_2CH_2Si$), 42.8 ($CqCH_2CH_2CH_2Si$), 17.9 ($CqCH_2CH_2CH_2Si$), 14.4 ($CqCH_2CH_2CH_2Si$), −5.3 ($Si(CH_3)_2$). DOSY NMR: $D = [4.8(\pm 0.2)] \times 10^{-11}$ m^2/s.

Complex 12. To a stirred solution of the dendrimer **9** (20 mg, 0.002 mmol) in 2 mL of MeOH was added a solution of **11** (12.6 mg, 0.056 mmol) in 2 mL of MeOH. The mixture was stirred for $^1/_2$ h. The solvent was removed under vacuum, and the product was extracted twice with nitromethane and filtered. Evaporation of the solvent gave **12** as a yellow gel in quantitative yield. ^{1}H NMR (CD_3OD, 300 MHz): δ 7.88 and 6.86 (144H, CH arom), 5.82 (270H, Cp), 3.46 (54H, SiCH_2-trz), 1.56 (72H, $CH_2CH_2CH_2Si$), 1.12 (72H, $CH_2CH_2CH_2Si$), 0.49 (72H, $CH_2CH_2CH_2Si$), −0.05 (216H, Si-$(CH_3)_2$). ^{13}C NMR (MeOD, 75 MHz): δ 165.3 (C═O), 163.6 (arom OCq), 131.5 (Cq of arom core), 122.3 and 115.5 (arom CH), 84.8 (Cp), 60.4 (CH_2OAr), 42.9 ($CqCH_2CH_2CH_2Si$), 41.7 ($CqCH_2CH_2CH_2Si$), 17.5 ($CqCH_2CH_2CH_2Si$), 14.3 ($CqCH_2CH_2CH_2Si$), −5.5 ($Si(CH_3)_2$). DOSY NMR: $D = [5.5(\pm 0.2)] \times 10^{-11}$ m^2/s.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text giving additional experimental details and figures giving spectroscopic data for all of the new complexes and NMR, IR, and DOSY NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Helpful assistance and discussion with Drs. Jaime Ruiz, Noël Pinaud (DOSY NMR), and Jean-Michel Lanier (NMR) from the CESAMO, Univ. Bordeaux, and financial support from the Univ. Bordeaux, the Centre National de la Recherche Scientifique (CNRS), the Chinese Research Council (CRC), and the Agence Nationale de la Recherche (ANR) are gratefully acknowledged. Dedicated to Prof. Helmut Werner, a distinguished pioneer of organometallic chemistry.

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