Table I. Thermal Transitions for Mesomorphic Compounds 1, 1a-1c, and 2

compd	temp, °C	ΔH,[a] cal/mol	ΔS,[a] cal/(mol K)	transition[a,b]
1	34.5	3690	12.0	$K_1 \rightarrow K_2$
	41	421	1.3	$K_2 \rightarrow K_3$
	46	189	0.6	$K_3 \rightarrow K_4$
	90	1780	4.9	$K_4 \rightarrow D_1$
	149	6390	15.2	$D_1 \rightarrow I$
1a	95	4180	11.3	$K_1 \rightarrow K_2$
	142.5	4340	10.4	$K_2 \rightarrow D_1$
	155	5090	11.9	$D_1 \rightarrow D_2$
	~240 dec			$D_2 \rightarrow I$
1b	106.5	4200	11.1	$K_1 \rightarrow K_2$
	144.5	3820	9.1	$K_2 \rightarrow D_1$
	157	4690	10.9	$D_1 \rightarrow D_2$
	261.5 dec			$D_2 \rightarrow I$
1c	11	3710	13.1	$K_1 \rightarrow D_1$
	34	2860	9.3	$D_1 \rightarrow D_2$
	242.5 dec			$D_2 \rightarrow I$
2	117	4170	10.7	$K \rightarrow S_1$
	137	1090	2.7	$S_1 \rightarrow S_2$
	139.5	1330	3.2	$S_2 \rightarrow I$

[a] Differential scanning calorimetry. [b] From optical microscopy: K = crystal; S = smectic mesophase; D = discotic mesophase; I = isotropic.

Table II. Type of Attractive Interaction vs. Mesophase Range

compd	mesophase range, °C	type of attractive interaction
1	59	hydrophobic
1a	97.5	hydrophobic, cation-radical CT
1b	117	hydrophobic, cation-radical CT
1c	231.5	hydrophobic, cation-radical CT and anion-radical CT

perchlorate **1b** cation-radical salts, on the other hand, show hydrophobic as well as cation-radical/cation-radical charge-transfer (CT) interactions. The TCNQ salt **1c** can show anion-radical/anion-radical CT[12] in addition to hydrophobic and cation-radical/cation-transfer interactions (see Table II).

The cation-radical species also form charge-transfer complexes with **1** in solution. This CT band occurs at 830 nm in CH_2Cl_2, which corresponds to an activation energy (E_a) for self-exchange, i.e., electron transfer between **1** and **1a**, of ~9.2 kcal/mol, with the relationship $E_a = \Delta E_{CT}/4$.[13]

The electronic conductivity of the TCNQ salt **1c** is $<10^{-6}$ Ω^{-1} cm^{-1}.[14] This low conductivity is attributed to the fact that there is complete charge transfer between **1** and TCNQ, as shown by the nitrile stretching frequency[15] (2179 cm^{-1}) in the infrared, and not to the lack of a segregated stacked structure.

In summary, tetraphenyl-$\Delta^{4,4'}$-bi-4*H*-pyran cation radicals with four dodecyl groups have a discotic mesophase over the range 97-230 °C, depending on the counterion. In general, the cation radicals have a mesomorphic range that is considerably larger than that of the neutral species, presumably because of enhanced intermolecular interactions of the charge-transfer type. The observed charge-transfer absorption further suggests the formation of columns of disk-shaped molecules. We suggest that the tendency to form mesomorphic structures may provide valuable information for design of molecular crystals with a predictable structure.

Registry No. **1**, 75817-94-6; **1a**, 81740-35-4; **1b**, 81740-36-5; **1c**, 81740-37-6; **2**, 75818-00-7.

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Anion Receptor Molecules. Chain Length Dependent Selective Binding of Organic and Biological Dicarboxylate Anions by Ditopic Polyammonium Macrocycles†

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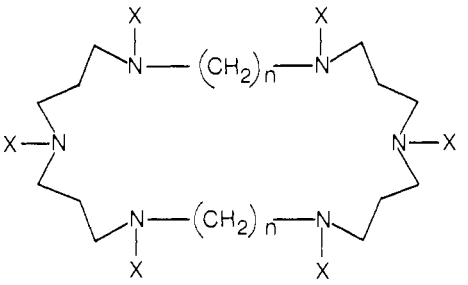
Received February 12, 1982

Anion binding by organic ligands has made significant progress in recent years. Macrocyclic and macropolycyclic polyammonium molecules have been shown to complex strongly and selectively a variety of inorganic and organic anions, thus laying the basis for developing a field of anion coordination chemistry.[1,2] The anion complexation unit of these receptor molecules consists of several positively charged binding sites arranged symmetrically around a cavity defined by the molecular architecture.

Macropolycyclic coreceptors that contain two or more binding subunits may complex two or more substrates, forming di- or polynuclear cryptates;[3] on the other hand, the subunits may cooperate for the multiple binding of a polyfunctional substrate. Thus, cylindrical macropolycycles form selective cryptates of diammonium $^+H_3N-(CH_2)_m-NH_3^+$ cations, bound by each terminal NH_3^+ group, with a stability and a selectively depending on the complementarity between the length of the substrate and the cavity size of the receptor.[4,5]

We have now incorporated such polyfunctional substrate binding features in the design of ditopic coreceptor molecules for *dianionic substrates*. We report here the synthesis of two new hexaazamacrocycles, **1** and **2**, as well as preliminary studies of the remarkable complexation properties of their fully protonated forms **1**-6H$^+$ and **2**-6H$^+$ toward dicarboxylate substrates $^-O_2C-R-CO_2^-$.



1, $n = 7$; X = H
2, $n = 10$; X = H
3, $n = 3$; X = H
16, $n = 7$; X = Ts
17, $n = 10$; X = Ts

The synthesis of **1** and **2** follows a reaction sequence similar to that used earlier for the related macrocycle **3**.[1] Tosylation of 1,7-diaminoheptane yields **4** (mp 144 °C, 97% yield), which is

† ERA No. 265 of the CNRS.

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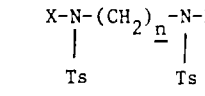


4 (n = 7) and 10 (n = 10), X = H
5 (n = 7) and 11 (n = 10), X = $CH_2CH_2CH_2OH$
6 (n = 7) and 12 (n = 10), X = $CH_2CH_2CH_2OMs$
7 (n = 7) and 13 (n = 10), X = CH_2CH_2CN
8 (n = 7) and 14 (n = 10), X = $CH_2CH_2CH_2NH_2$
9 (n = 7) and 15 (n = 10), X = $CH_2CH_2CH_2NHTs$

converted ($ClCH_2CH_2CH_2OH$, K_2CO_3/DMF, 100 °C) into the diol **5** (68% yield) and then (CH_3SO_2Cl, Et_3N/CH_2Cl_2) into the dimesylate **6** (90% yield); treatment of **4** with acrylonitrile in DMF gives the dinitrile **7** (mp 99 °C; 64% yield), which is reduced (diborane/THF) to the diamine **8** (98% yield) and tosylated (TsCl, Et_3N/THF) to **9** (85% yield). Starting with 1,10-diaminodecane and applying the same sequence of reactions affords the similar **10** (mp 127 °C; 95% yield), **11** (mp 84–86 °C; 73% yield), **12** (95% yield), **13** (mp 130 °C; 80% yield), **14** (98% yield), and **15** (84% yield).

Condensation of **6** with **9** in DMF at 90 °C in the presence of Cs_2CO_3 gives the macrocyclic hexatosylate **16** (glass; 25% yield) after careful purification of the reaction mixture by chromatography (SiO_2 column followed by HPLC on a gel permeation column Waters silica prep PAK). Similarly reaction of **12** with **15** in the same conditions followed by chromatographic purification affords **17** (glass; 25% yield).

Removal of the tosyl groups from **16** and **17** by treatment with 33% HBr/AcOH/phenol at 80 °C for 14 h gives the hydrobromides of the macrocyclic polyamines **1** and **2** in 90% yield. Passing the hydrobromides over an anion-exchange column in the hydroxide form gives the parent hexaamines **1** and **2**; because of its low solubility in water, **2** precipitates on the column and is eluted with ethanol. **1** and **2** are stored as the hydrochlorides **1**–$6H^+$, $6Cl^-$ and **2**–$6H^+$, $6Cl^-$ (colorless powders; mp > 260 °C). All new compounds were fully characterized by their spectral (^1H and ^{13}C NMR, mass) and microanalytical properties.

The pK_a values and the anion-binding properties of the polyammonium macrocycles **1**–$6H^+$ and **2**–$6H^+$ were determined by computer analysis of the pH metric titration curves measured in the presence of a given anion (Table I; Figure 1[6,7]).

(1) Compounds **1** and **2** are new 32- and 38-membered macrocyclic polyamines, containing two di-1,3-propylenetriamine subunits linked by two hydrocarbon bridges. Such bis-chelating macrocycles are in principle able to form dinuclear complexes with transition-metal cations.[3] They are fully protonated around neutral pH to the **1**–$6H^+$ and **2**–$6H^+$ species, which contain two triammonium binding subunits for anions at the poles of the structure. Compounds **1** and **2** may also be considered to incorporate two fragments reminiscent of the natural polyamines, which play an important biological role.[9]

(2) The fully protonated species **1**–$6H^+$ and **2**–$6H^+$ form *strong complexes* with organic dicarboxylate anions $^-O_2C-R-CO_2^-$ in aqueous solution.

(3) The complexation *selectivity* presents a striking structural dependence. Each receptor **1**–$6H^+$ and **2**–$6H^+$ shows a marked selectivity peak among the homologous $^-O_2C-(CH_2)_m-CO_2^-$ substrates (Figure 1). Furthermore, the selectivity peak shifts from m = 2, 3 to m = 5, 6 on going from **1**–$6H^+$ to **2**–$6H^+$ this corresponds to the *same* increase in length, by three CH_2 groups,

Table I. Stability Constants,[a] log K_s (±0.2), for Anion Binding by the Polyammonium Macrocyclic Coreceptors 1-$6H^+$, 2-$6H^+$, and 3-$6H^+$ in Aqueous Solution[6,7]

dicarboxylate anion (m)[c]	macrocyclic ligand[b] 1-$6H^+$	2-$6H^+$	3-$6H^+$
oxalate^{2-} (0)	(3.20)[d]	(6.30)[d]	(3.8)
malonate^{2-} (1)	3.8(2.75)	4.05(3.25)	(3.3)
succinate^{2-} (2)	4.3(3.4)	3.15(3.0)	(2.4)
glutarate^{2-} (3)	4.4(3.4)	3.3(2.9)	(2.35)
adipate^{2-} (4)	3.2(2.3)	3.2(2.95)	(2.35)
pimelate^{2-} (5)	3.1(2.25)	4.4(3.4)	
suberate^{2-} (6)		4.25(3.45)	
azelate^{2-} (7)		3.6(3.2)	
sebacate^{2-} (8)		3.5(3.05)	
maleate^{2-}	4.3		(3.7)
fumarate^{2-}	4.1		(2.2)
butyrate		≲2.0	
N-acetyl-(L)-aspartate^{2-} (2)[e]	4.1	3.35	
N-acetyl-(L)-glutamate^{2-} (3)[e]	4.15	3.25	
N-acetyl-(L)-glutamyl-glycinate^{2-} (6)[e]	3.15	4.3	

[a] The log K_s values are for aqueous solutions containing either 0.01 M NMe_4Cl or 0.1 M NMe_4Cl (values in parentheses). [b] The following pK_a values (±0.1) were determined for compounds 1 and 2: 10.85, 10.60, 9.80, 9.05, 7.40, 6.65 (≥10.7, ~10.7, 9.85, 9.60, 7.90, 7.30) for 1; >10.5, ~10.5, 10.15, 9.45, 7.65, 6.95 (>10.3, ~10.3, 10.10, 9.60, 7.95, 7.30) for 2; aqueous solution at 25 °C, 0.01 M NMe_4Cl (or 0.1 M NMe_4Cl). [c] Chain length in $^-O_2C-(CH_2)_m-CO_2^-$. [d] These higher values probably arise from the presence of 2/1 substrate/receptor species.[7] [e] Number of atoms separating the two terminal carboxylate groups.

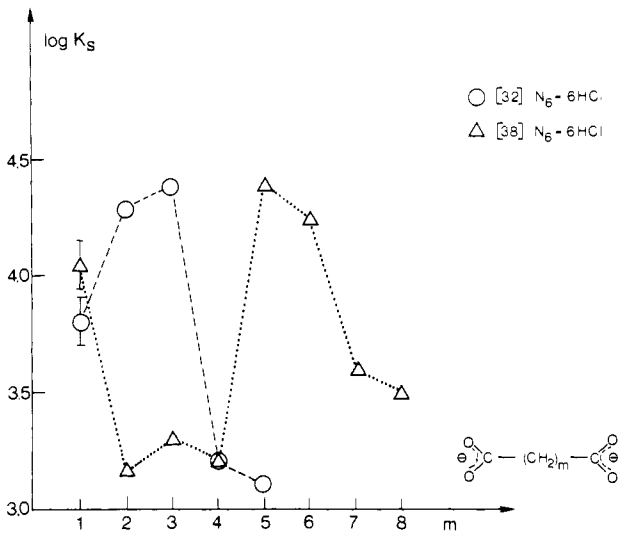


Figure 1. Graphical representation of the stability constants (log K_s) of the complexes formed by the polyammonium macrocycles **1**–$6H^+$ (○) and **2**–$6H^+$ (△) with the dicarboxylates $^-O_2C-(CH_2)_m-CO_2^-$ as a function of chain length m (see also Table I).

(6) The pH metric titration and data analysis procedures were similar to those described earlier. Ligands **1** and **2** were used as their hexahydrochlorides. All measurements were performed on aqueous solutions containing 1×10^{-3} M ligand, 5×10^{-3} M anion, and either 0.1 or 0.01 M supporting electrolyte Me_4NCl. In the former case, the ionic strength is only approximately constant over the titration, so the absolute K_s values are less reliable than the relative ones. Although complexation of chloride is probably weak, it competes with the anion studied; consequently the stability constants determined are apparent constants, the real values for a given anion being even higher than those listed Table I. Indeed, the K_s values are appreciably higher in 0.01 M than in 0.1 M NMe_4Cl, as expected for chloride competition. The fact that the three lowest apparent pK_as of the two ligands are appreciably more basic in 0.1 M than in 0.01 M NMe_4Cl, whereas the three highest ones are almost unaffected, is also indication of chloride binding. This is confirmed by ^{35}Cl NMR studies of the chloride resonance. It is clear that further work is required if more accurate K_s values are to be obtained; especially, other physical methods (heteronuclear NMR of the substrate, calorimetry, electrochemical measurements, anion selective electrodes) may be used to complement and corroborate the pH metric results.

(7) The stoichiometry of the complexes was assumed to be 1/1 in the data analysis procedure. However, the presence of a certain amount of higher order complexes cannot be excluded. This holds especially for the smaller substrates (oxalate, malonate) for which simultaneous binding of a single molecule to the two triammonium sites of the ligand is geometrically unfeasible, unless there is a marked deformation of the macrocycle; the high stability constants calculated for oxalate and malonate, by assuming 1/1 stoichiometry probably result from the presence of 2/1 dianion/hexacation complexes. Further work is required for analyzing this question.

(8) Dietrich, B.; Fyles, D. L.; Fyles, T. M.; Lehn, J. M. *Helv. Chim. Acta* **1979**, *62*, 2763–2787.

(9) See for instance; Tabor, C. W.; Tabor, H. *Annu. Rev. Biochem.* **1976**, *45*, 285–306.

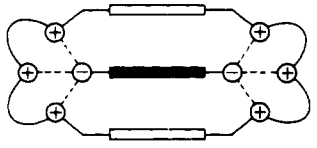
both for the most strongly bound dicarboxylates and for the $(CH_2)_n$ bridges separating the triammonium binding units in **1**-6H$^+$ (n = 7) and in **2**-6H$^+$ (n = 10). The smaller receptor **3**-6H$^+$ (n = 3) binds most strongly the shorter dicarboxylates.[1]

(4) The observation of a selectivity peak as a function of chain length reveals a *dominant structural factor* in dicarboxylate binding. Electrostatic interactions, which favor binding of anions of high charge density, were usually found to dominate both the strength and the selectivity of complexation;[1,2] the effect of ring size was already apparent for ligands of type **3**.[1]

(5) These complexation features may be extended to the selective binding of *biological anionic substrates*, in particular of dicarboxylate species. Thus, **1**-6H$^+$ binds preferentially the dianions *N*-acetyl-(L)-aspartate and *N*-acetyl-(L)-glutamate with respect to the dipeptide *N*-acetyl-(L)-glutamylglycinate, whereas the reverse holds for **2**-6H$^+$, in line with the chain lengths of these substrates.

(6) The high stabilities observed for the optimal coreceptor dicarboxylate substrate pairs results from the incorporation of two binding subunits in the macrocycle and from double (ditopic) carboxylate group-triammonium site binding; this is indicated by the low stabilities found for the single site interactions of butyrate with **2**-6H$^+$ (Table I) and of pimelate^{2-} or butyrate with the subunit reference ligand $^+H_3N(CH_2)_3NH^+_2(CH_2)_3NH_3^+$ (log $K_s \lesssim 2.0$).

(7) The *chain length selection* observed describes a *linear molecular recognition* process analogous to that found for dicationic substrates.[3-5] It may be attributed to *structural* complementarity between the dianionic substrate and the *ditopic coreceptor molecules* **1**-6H$^+$ and **2**-6H$^+$ in which the two binding subunits cooperate for substrate binding. The terminal anionic groups of the dicarboxylate would each interact with a triammonium unit of the coreceptor, the polymethylene chain stretching between the polymethylene bridges of the macrocycle. Highest stability of the complex corresponds to the best fit between substrate length and site separation of the receptor, as schematically represented by **18** and supported by consideration of



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molecular models. Substrates that are either too short or too long form less stable complexes.

In conclusion, the present results demonstrate that it is possible to design coreceptor molecules for the selective multifunctional binding of molecular polyanions, in a way similar to the selective binding of diammonium cations of different chain lengths by macrotricyclic receptor molecules.[3,4] Ligand modification should allow to monitor the *molecular recognition* features, to devise *cocarriers* or *cocatalyst* for the selective transport or the catalytic modification of the bound substrate.[10] Such extensions of the present work are being pursued.

Registry No. 1, 81505-93-3; **1**·6HCl, 81505-94-4; **2**, 81505-95-5; **2**·6HCl, 81505-96-6; **3**·6HCl, 81505-97-7; **4**, 81505-98-8; **5**, 81505-99-9; **6**, 81522-66-9; **7**, 81506-00-5; **8**, 81506-01-6; **9**, 81506-02-7; **10**, 79130-37-3; **11**, 81506-03-8; **12**, 81522-67-0; **13**, 81506-04-9; **14**, 81506-05-0; **15**, 81506-06-1; **16**, 81506-07-2; **17**, 81506-08-3; oxalate^{2-}, 338-70-5; malonate^{2-}, 156-80-9; succinate^{2-}, 56-14-4; glutarate^{2-}, 56-16-6; adipate^{2-}, 764-65-8; pimelate^{2-}, 764-54-5; suberate^{2-}, 764-55-6; azelate^{2-}, 13479-16-8; sebacate^{2-}, 45130-36-7; maleate^{2-}, 142-44-9; fumarate^{2-}, 142-42-7; butyrate, 461-55-2; *N*-acetyl-L-aspartate^{2-}, 3130-81-2; *N*-acetyl-L-glutamate^{2-}, 3130-80-1; *N*-acetyl-L-glutamylglycinate^{2-}, 81506-09-4; 1,7-diaminoheptane, 646-19-5; 1,10-diaminodecane, 646-25-3.

(10) For a recent case of selective functionalization via association of acyclic dications and dianions see: Breslow, R.; Rajagopalan, R.; Schwarz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2905-2907.

Remarkable Dependency of Regioselectivity on the Catalyst Metal Species in the Hydroformylation of Trifluoropropene and Pentafluorostyrene

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Received December 2, 1981

It is well known that the hydroformylation of alkenes is an important reaction for the production of aldehydes.[1] Although precise studies on the mechanism of the reaction as well as applications of the reaction to organic synthesis have been extensively studied, little is known about the reaction of olefins bearing perfluoroalkyl or perfluoroaryl substituents.[2] Recently, it has been shown that the introduction of a trifluoromethyl or pentafluorophenyl group into a biologically active compound often brings about unique physiological activities.[3] For the synthesis of such compounds, 3,3,3-trifluoropropene (TFP) and pentafluorostyrene (PFS) are important fundamental building blocks. Accordingly, we have been studying the hydroformylation of TFP and PFS as one of the possible functionalizations of these building blocks using a variety of transition-metal catalysts and have found unique features of the reaction compared with the hydroformylation of ordinary alkenes. We will describe here unusually high regioselectivities and remarkable dependency of regioselectivity on the structure of catalyst species in the hydroformylation of TFP and PFS.

Hydroformylation of TFP was carried out with $Co_2(CO)_8$, $Ru_3(CO)_{12}$, $Rh_6(CO)_{16}$, and $PtCl_2(DIOP)/SnCl_2$,[4] which are typical hydroformylation catalysts. Results are listed in Table I.

As Table I shows, the reaction of TFP catalyzed by $Co_2(CO)_8$ gave (trifluoromethyl)propanals (TFMPA) in 95% yield where a highly regioselective (93%) formation of "normal" aldehyde, $CF_3CH_2CH_2CHO$ (3-TFMPA) was observed. In sharp contrast with $Co_2(CO)_8$, the rhodium carbonyl cluster $Rh_6(CO)_{16}$ exhibited extremely high catalytic activity and regioselectivity (96%) to give "isoaldehyde", $CF_3(CH_3)CHCHO$ (2-TFMPA). The platinum catalyst $PtCl_2(DIOP)/SnCl_2$ favored the formation of *n*-aldehyde, while $Ru_3(CO)_{12}$ gave isoaldehyde as main product, and in both cases, the formation of considerable amounts of hydrogenated product, $CF_3CH_2CH_3$, was observed. Addition of triphenylphosphine to the cobalt, ruthenium, and rhodium catalyst considerably decreased the catalytic activities but somewhat increases the ratio of isoaldehyde. Because $Rh_6(CO)_{16}$ gave excellent regioselectivity in the formation of 2-TFMPA, several other rhodium catalysts were employed to examine their catalytic activities as well as regioselectivities. Results are also summarized in Table I. The results clearly indicate that the rhodium(I) complexes bearing chlorine as ligand such as $RhCl(PPh_3)_3$ are less active than $HRh(CO)(PPh_3)_3$, Rh-C, and $Rh_6(CO)_{16}$, but the regioselectivity is almost the same in every case examined.

Consequently, it is disclosed that the nature of the central metal of the catalyst plays a key role in determining the regioselectivity of the reaction. Moreover, it should be noted that the metal species

(1) (a) Pino, P.; Piacenti, F.; Bianchi, M. In "Organic Synthesis via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; Vol. 2, pp 43-231. (b) Cornils, B. In "New Syntheses with Carbon Monoxide"; Falbe, J., Ed.; Springer-Verlag: Berlin, 1980; pp 1-225.

(2) Hydroformylation of hexafluoropropene was reported to give a mixture of hexafluoropropane (50%), alcohols (40%), and aldehydes (5-8%). See: Rudkovskii, D. M.; Imyanitov, N. S.; Gankin, V. Yu. *Tr. Vses, Nauchn Issled. Inst. Neftekhim. Protsessov.* **1960**, *121*; *Chem. Abstr.* **1962**, *57*, 10989. A patent claimed the reaction of heptadecafluorodecene, $CF_3(CF_2)_7CH{=}CH_2$, catalyzed by $Co_2(CO)_8$, which gave the corresponding alcohols or aldehydes. See: Roehrscheid, F. (Hoechst A. G.), Ger. Offen. 1973, 2163752; *Chem. Abstr.* **1973**, *79*, 78110m.

(3) For example: (a) Smith, F. A. *Chemtech* **1973**, 422. Filler, R. *Ibid.* **1974**, 722. (b) Lin, T.-S.; Chai, C.; Prusoff, W. H. *J. Med. Chem.* **1976**, *19*, 915.

(4) $PtCl_2(DIOP)/SnCl_2$ was prepared in situ by mixing $PtCl_2(PhCN)_2$, (-)DIOP, and $SnCl_2$ in toluene.

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