interface.[18] Monolayers of **10** can be transferred on to mica to give homogenous films of 3.3 nm thickness with a transfer efficiency greater than 96 %.

In conclusion, we have synthesized a new type of Suzuki monomer that carries G2 hydrophobic and hydrophilic dendrons and shown that it can be polymerized to give the first length-wise (not block-wise) amphiphilically equipped poly(*para*-phenylene) **10**. Polymer **10** differs from known amphiphiles in that it consists of a linear, covalently bound sequence of "little" amphiphiles. It differs from common "polysoaps" because it is much more rigid, which should increase its potential to aggregate, for example, into channels. Langmuir–Blodgett experiments provide the first evidence that the dendritic substituents of **10** segregate lengthwise into hydrophobic and hydrophilic domains (see schematic representation **A**).

Experimental Section

Langmuir monolayers were prepared by spreading 100 μL of solution in $CHCl_3$ (1 gmL^{-1}) on a distilled water subphase in a Langmuir–Blodgett trough (NIMA Ltd.) at room temperature. Compression rates were on the order of one percent per minute. The stability of the monolayers was checked by compressing them to 20 mNm^{-1} and monitoring the area for 20 min.

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[11] **8**: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.38$ (12 H, s), 3.67 (8 H, t), 3.71 (8 H, t), 3.83 (8 H, t), 4.13 (8 H, t), 4.94–5.01 (24 H, seven partially overlapping s), 6.45–6.67 (18 H, eight partially overlapping s), 6.91 (8 H, narrow AA'BB'), 7.31–7.47 (20 H, m), 7.77 (1 H, s), 7.78 (1 H, s); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 58.98$, 67.29, 69.11, 69.55, 69.79, 69.92, 70.30, 70.59, 71.79, 100.92, 101.35, 105.90, 106.18, 115.68, 115.71, 120.85, 127.46, 127.91, 128.47, 132.08, 136.59, 137.53, 138.93, 139.08, 139.49, 139.53, 152.35, 153.23, 153.26, 159.91, 159.99; elemental analysis calcd for $C_{110}H_{116}O_{24}Br_2$: C 66.66, H 5.90; found: C 65.97, H, 5.78. **10**: ^{1}H NMR (500 MHz, $CDCl_3$): all signals are broad, $\delta = 3.31$ (12 H), 3.50 (8 H), 3.65 (8 H), 3.77 (8 H), 4.03 (8 H), 4.82–5.01 (24 H), 6.40–6.63 (20 H), 6.80–6.82 (8 H), 7.28–7.38 (20 H), 7.53–7.68 (4 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 59.00$, 67.30, 68.55, 69.56, 69.76, 69.89, 70.34, 70.59, 71.81, 100.95, 101.38, 105.95, 106.21, 115.59, 115.77, 127.49, 127.91, 128.48, 129.16, 131.38, 134.17, 136.64, 138.98, 139.14, 139.49, 139.59, 140.76, 152.86, 153.07, 159.89, 159.93, 159.99; elemental analysis calcd for $(C_{116}H_{120}O_{24})n$: C 73.40, H 6.37; found: C 72.49, H 6.28.

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The First Efficient Hydroaminomethylation with Ammonia: With Dual Metal Catalysts and Two-Phase Catalysis to Primary Amines[**]

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*Dedicated to Professor Rüdiger Selke
on the occasion of his 65th birthday*

Aliphatic amines are amongst the most important bulk and fine chemicals in the chemical and pharmaceutical industries.[1] Alongside hydroamination,[2] hydroaminomethylation of olefins to amines represents an atom-economic efficient

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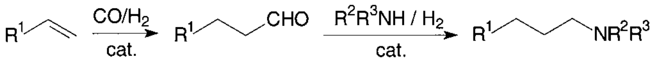
and most elegant synthesis of this class of compounds. In hydroaminomethylation, a reaction sequence of hydroformylation of an olefin to an aldehyde with subsequent reductive amination proceeds in a domino reaction (Scheme 1).[3] In spite of the advantages of hydroaminomethylation, for example availability of starting materials and atom efficiency, comparatively few preparative applications are known. Eilbracht and co-workers in particular have only recently been able to demonstrate the synthetic potential of hydroaminomethylation.[4] Primary and secondary amines were almost exclusively used as amine components. The synthesis of technically important primary amines from ammonia and olefins has only been investigated by Knifton et al.;[5] selectivities of only 32 % with respect to the desired primary amine (based on 85 % conversion) were obtained at extremely low activities (turnover frequency TOF = 9 h^{-1}) and under drastic reaction conditions (200 °C, 140 bar) with a cobalt system. The currently unsolved problems of hydroaminomethylation with ammonia are the unsatisfactory *n*:*iso* selectivity of the hydroformylation stage and the numerous side reactions. In addition to isomerization and hydrogenation of the olefin, there is also the formation of alcohols and aldol condensation products. Moreover, secondary reactions of the primary amine to secondary and tertiary amines occur. An additional difficulty is the catalyst separation in homogeneous, one-phase reaction systems. To solve these problems of the hydroaminomethylation we investigated a combination of the following two systems: 1) a more rapid hydrogenation of the imine to amine and thus fewer side reactions of intermediates should be realized by the use of dual metal catalysts (Rh/Ir), and 2) we sought a simple catalyst separation through phase separation and control of selectivity with respect to the formation of primary, secondary, and tertiary amines[6] by the use of the principle of two-phase catalysis.[7]



Scheme 1. Hydroaminomethylation of olefins ($R^1 - R^3$ = H, alkyl).

The use of dual transition metal catalysts stemmed from the idea that the current hydroaminomethylation catalysts based on rhodium and cobalt are indeed active catalysts for hydroformylation, but with the use of an excess of ligand they are no longer sufficiently active for the hydrogenation of the imine C=N double bond. Since iridium is known to be a very active catalyst for the hydrogenation of C=N double bonds,[8] we used for the first time Rh/Ir catalyst systems for hydroaminomethylation. 1-Pentene was used as the model olefin for the investigation of this catalyst system, and ammonia was used as the only nitrogen source (Table 1).

The aminomethylation of 1-pentene with synthesis gas ($CO:H_2 = 1:5$) and ammonia in the presence of the Rh/Ir/TPPTS (**1**) catalyst system (TPPTS = trisodium 3,3-′,3″-phosphandiyltris(benezenesulfonate)) under standard hydroformylation conditions (130 °C; 120 bar) in an aqueous two-phase system does indeed give amines in 75 % yield. Significantly better selectivities were obtained for the primary amines in comparison to the classical catalyst $[Co_2(CO)_8]$ (91 versus 32 %). Small amounts of the secondary hexylamines di-*n*-hexylamine, di(2-methylpentyl)amine, and *N*-*n*-hexyl-*N*-(2-methylpentyl)amine were formed in addition to the primary hexylamines. Only trace amounts of tertiary amines, imines, enamines, and higher boiling aldol condensation products were formed. Reduction of the reaction temperature to 110 °C led to somewhat lower overall yields (72 %) and to moderately increased selectivities with respect to the primary amine (86:14; Table 1, entry 1). At temperatures above 130 °C ligand degradation and metal leaching occurred.

Both primary and secondary amines can be formed with greater than 90 % selectivity by variation of the olefin:NH_3 ratio (Table 1, entries 2 and 5). This simple selectivity control (Figure 1) is attributable to the competitive reaction of the NH compounds with the newly formed aldehyde. When 0.5 equivalents NH_3 per equivalent of olefin were used, half of

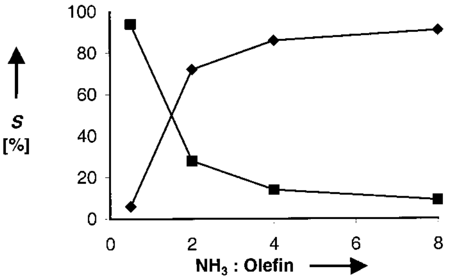


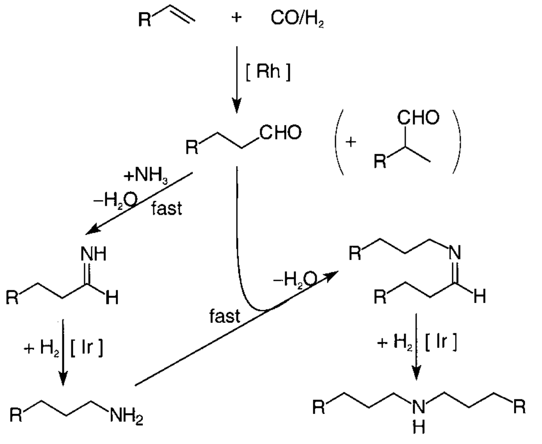
Figure 1. Influence of the NH_3:olefin ratio on selectivity *S* (◆ primary amine, ■ secondary amine).

Table 1. Hydroaminomethylation of 1-pentene with ammonia and the Rh/Ir/TPPTS (**1**) catalyst system.[a]

Entry	*T* [°C]	*t* [h]	Organic solvent	NH_3: olefin	Conversion [%]	Yield [%][b] 2-pentene	amine	high boilers[c]	*n*:*iso* prim.	Prim.:sec. amines
1	110	10	MTBE	8:1	87	12	72	3	86:14	86:14
2	130	5	MTBE	8:1	84	11	69	1	84:16	91:9
3	130	5	MTBE	4:1	90	n.d.	56	1	87:13	86:14
4	130	5	MTBE	2:1	90	n.d.	51	1	87:13	72:28
5	130	5	MTBE	0.5:1	95	n.d.	60	3	84:16	6:94
6	130	10	MTBE	2:1	98	21	78	0	87:13	69:31
7	130	10	anisole	2:1	97	20	76	0	88:12	78:22
8	130	10	toluene	2:1	96	26	69	0	88:12	82:18
9	130	10	MTBE/salt[d]	2:1	96	23	68	0	96:4	76:24

[a] Conditions: *p*(cold) = 78 bar, $CO:H_2 = 1:5$, 0.026 mol% Rh, 0.21 mol% Ir, TPPTS: P:Rh = 425, P:Ir = 52. n.d. = not determined. [b] GC determination (alcohols < 1 %). [c] Higher boiling products (aldol condensation products, tertiary amines, imines). [d] 15 % Na_2SO_4 in the aqueous phase.

the aldehyde reacts with the ammonia and half with the newly formed primary amine, leading to preferential formation of the secondary amine (Scheme 2).



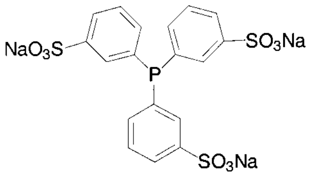
Scheme 2. Formation of primary and secondary amines by hydroaminomethylation of olefins

Different two-phase systems were investigated as reaction medium to improve the selectivity for the primary amine to above 90%. It emerged that by lowering the polarity of the organic phase the selectivity with respect to the primary amine increased (Table 1, entries 6–8). We explain this effect as follows: extraction of the primary amine from the aqueous phase removes it from the catalyst-containing reaction medium so that it no longer competes with ammonia in the aqueous phase during imine formation. The lower the polarity of the organic solvent, the better the more hydrophobic amine is extracted in comparison to ammonia; this leads to an improvement in selectivity. A similar behavior is observed if salt is added to the aqueous phase, as the ionic strength and the polarity difference between the aqueous and organic phases increases (Table 1, entry 9).

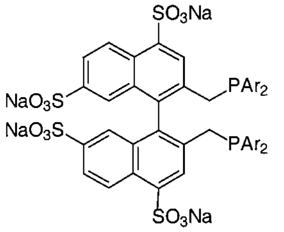
Hydroaminomethylation of the technically highly important olefins propene and 1-butene (Table 2) as well as ethene[10] with ammonia in the two-phase system also affords the products in high yields and selectivities. A significant effect of the olefin chain length on the selectivity of primary amine formation is observed. The fraction of primary amine falls with decreasing olefin chain length. This is correlated with the increased water solubility of the amine formed and thus a lower extraction effect of the organic solvent.

The regioselectivities of the primary amines (*n*:*iso* selectivities 76:24 to 87:13) obtained in the presence of the ligand TPPTS (**1**) are slightly lower than those in the hydroformylation. Higher regioselectivities are not absolutely necessary for industrial applications of this process since branched primary products are also of commercial importance. Nevertheless, it is of fundamental interest to achieve regioselectivities greater than 95%. Since the structure of the phosphane ligand used is the main influencing factor on the *n*:*iso* selectivity of hydroformylations, we used the highly regioselective ligand BINAS (**2**) developed by Herrmann et al.[9] in the hydroaminomethylation of propene, 1-butene, and 1-pentene (Table 2). Excellent *n*:*iso* selectivities of 99:1 were achieved in all cases!

Table 2. Variation of olefins and ligands (TPPTS **1**, BINAS **2**[9]).[a]



TPPTS (1)



Ar = *m*-SO_3Na-C_6H_4

BINAS (2)

Olefin	NH_3: olefin	TPPTS yield. (amine) [%]	TPPTS *n*:*iso*	TPPTS prim.: sec.	BINAS yield. (amine) [%]	BINAS *n*:*iso*	BINAS prim.: sec.
propene	8:1	80	76:24	72:28	90	99:1	77:23
1-butene	8:1	80	85:15	78:22	85	99:1	78:22
1-pentene	8:1	75	84:16	90:10	75	99:1	87:13
propene	0.5:1	90	82:18	20:80	95	99:1	1:99
1-butene	0.5:1	90	87:13	38:62	95	99:1	1:99
1-pentene	0.5:1	85	82:18	48:52	90	99:1	10:90

[a] Conditions: $T = 130\,^{\circ}C$, p(cold) = 78 bar (pentene/butene) or 60 bar (propene), CO:H_2 = 1:5, t = 10 h, 0.026 mol% Rh, 0.21 mol% Ir, TPPTS: P:Rh = 425, P:Ir = 52; BINAS: P:Rh = 140, P:Ir = 18.

We have for the first time described the highly selective hydroaminomethylation of olefins with ammonia to form linear primary and secondary aliphatic amines with a new Rh/Ir system. The method introduced here is of particular importance for the production of industrially important, low molecular weight amines. Thus, the technical application of hydroaminomethylation of olefins appears realizable. An extension of the synthetic method to styrene derivatives and other functionalized olefins is a highly promising prospect and is currently under investigation by us.

Experimental Section

Hydroaminomethylation of 1-pentene (Table 1, entry 2): 1-Pentene (2.5 g, 3.9 mL, 35.7 mmol), [{Rh(cod)Cl}$_2$] (2.3 mg, 4.6 µmol, 0.026 mol%; cod = 1,5-cyclooctadiene), [{Ir(cod)Cl}$_2$] (25.0 mg, 0.037 mmol, 0.21 mol%), aqueous TPPTS solution (7.2 g, 0.55 mol kg^{-1}, 3.96 mmol, P:Rh = 425:1, P:Ir = 52:1), aqueous NH_3 (25%, 21.5 ml, 288 mmol, olefin:NH_3 = 1:8), degassed methyl *tert*-butyl ether (MTBE, 20 mL), and degassed isooctane (internal GC standard, 2.5 mL) were placed under an inert atmosphere into a 200-mL stainless steel autoclave with a glass liner, baffle unit, and magnetic stirrer. The autoclave was sealed, flushed once with synthesis gas, and pressurized to 13 bar CO and 65 bar H_2 (total pressure (cold): 78 bar, CO:H_2 = 1:5), and a reaction temperature of 130 °C was set (total pressure (warm): 120 bar). After a reaction time of 10 h the autoclave was cooled to 0 °C and slowly depressurized. The organic phase was analyzed by gas chromatography (HP5860 series; column: Optima-1, Macherey–Nagel, 50 m, 0.23 mm, 5.0 µm) (pentene quantification), and the aqueous phase was separated, treated with NaOH (0.5 g), and extracted with MTBE (2 × 2 mL). The combined organic phases were analyzed by gas chromatography (amine quantification).

For lower ammonia concentrations the proportionate amounts of standard solutions were used and the volume of the aqueous phase increased to 20 mL with degassed water.

The liquified gasses (ethene, propene, 1-butene) were first condensed into a steel cylinder and then introduced into the autoclave under pressure.

All products were unambiguously identified by GC/MS. After distillation of the products NMR spectra consistent with literature information were obtained.

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[10] The reaction could also be carried out successfully with ethene leading to a selectivity between primary and secondary amine of 38:63 (NH_3:olefin = 8:1) and 5:95 (NH_3:olefin = 0.5:1), respectively. An accurate determination of hydrogenation side reactions was not possible for technical reasons

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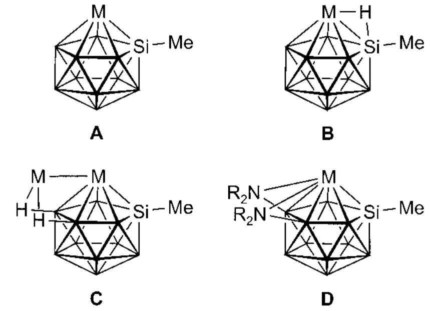
A Novel Coordination Mode of 7-Methyl-7-sila-*nido*-undecaborate(1 −)**

Lars Wesemann,* Michael Trinkaus, and Michael Ruck

The first transition metal complex of a silaborate, 7-methyl-7-sila-*nido*-undecaborate(1 −) ($MeSiB_{10}H_{12}^-$), a derivative of the higher homologue of the carbollide ligand, was described only two years ago.[1] In analogy to the carbon-containing cluster, the silaborate ligand will be referred to as a silollide ligand in the following. The known coordination modes of various complexes of this type that have been characterized by single-crystal structure analyses are depicted in Scheme 1.



Scheme 1. Coordination modes of 7-methyl-7-sila-*nido*-undecaborate(1 −).

Type **A** resembles the typical η^5 coordination mode, as known for many complexes of the dicarbollide (*nido*-$C_2B_9H_{12}^-$)[2] and carbollide (*nido*-$CB_{10}H_{13}^-$)[3, 4] ligands and as is found in the mixed sandwich anions $[Cp^*M(MeSiB_{10}H_{10})]^-$ (M = Co, Rh, Ir)[5] and the carbonyl complexes $[(CO)_3M(MeSiB_{10}H_{10})]^-$ (M = Ru, Fe).[6] Both coordination types **B** and **C** are observed in the dinuclear complex $[NBu_4]_2[\{HFe(MeSiB_{10}H_{10})\}_2]$.[1] Herein we will describe compounds of type **D** which display a hitherto unknown coordination pattern in borane and heteroborane chemistry that results from an unexpected B,H activation.

Jordan[7] and co-workers adapted a method of Chandra and Lappert[8] for the synthesis of dicarbollide complexes from transition metal amides. Application of the same reaction to the silollide ligand yields the highly air- and moisture-sensitive metallasilaborates $[NEt_4][Nb(MeSiB_{10}H_{10})(NMe_2)_3]$ (**1**) and $[NEt_4][Ta(MeSiB_{10}H_{10})(NMe_2)_3]$ (**2**) from $[nido\text{-}MeSiB_{10}H_{12}]^-$ and $[Nb(NMe_2)_5]$ or $[Ta(NMe_2)_5]$ [Eq. (1)]. The reaction is almost quantitative according to NMR spectroscopy.

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