Experimental Section

Standard catalytic system: Prior to use, a mixture of MMA (28 mmol), CCl_4 (104 mmol), and dodecane (internal standard, 8.9 mmol) was degassed thoroughly using the freeze-pump-thaw method. The catalyst (ca. 9.1×10^{-5} mol) in CH_2Cl_2 (ca. 10 mL) was then added at room temperature under an inert atmosphere. The reaction was monitored by withdrawing samples for GC analysis at regular time intervals.

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[1] For recent reviews on dendritic molecules, see a) G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendritic Molecules-Concepts, Synthesis, Perpectives*, VCH, Weinheim, **1996**; b) "Dendrimers": N. Feuerbacher, F. Vögtle, *Top. Curr. Chem.* **1998**, *197*, 1–18; c) M. A. Hearshaw, J. R. Moss, *Chem. Commun.* **1999**, 1–8.

[2] See for example: a) J. W. J. Knapen, A. W. van der Made, J. C. De Wilde, P. W. M. N. van Leeuwen, P. Wijkens, D. M. Grove, G. van Koten, *Nature* **1994**, *372*, 659; b) M. T. Reetz, G. Lohmer, R. Schwickardi, *Angew. Chem.* **1997**, *109*, 1559–1562; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1526–1529.

[3] A. W. Kleij, H. Kleijn, J. T. B. H. Jastrzebski, W. J. J. Smeets, A. L. Spek, G. van Koten, *Organometallics* **1999**, *18*, 268–276.

[4] A. W. Kleij, H. Kleijn, J. T. B. H. Jastrzebski, A. L. Spek, G. van Koten, *Organometallics* **1999**, *18*, 277–285; b) R. A. Gossage, J. T. B. H. Jastrzebski, J. van Ameijde, S. J. E. Mulders, A. J. Brouwer, R. M. J. Liskamp, G. van Koten, *Tetrahedron Lett.* **1999**, *40*, 1461–1464.

[5] G. van Koten, *Pure Appl. Chem.* **1989**, *61*, 1681, and references therein; b) M. P. H. Rietveld, D. M. Grove, G. van Koten, *New J. Chem.* **1997**, *21*, 751.

[6] The nickelated systems are also active in controlled radical polymerization (ATRP). See: a) T. E. Patten, J. Xia, T. Abernathy, K. Matyjaszewski, *Science* **1996**, *272*, 866–868; b) C. Granel, P. Dubois, R. Jérôme, P. Teyssié, *Macromolecules* **1996**, *29*, 8576–8582; c) "*Controlled Radical Polymerization*": K. Matyjaszewski, *ACS Symp. Ser.* **1998**, *685*.

[7] L. A. van de Kuil, H. Luitjes, D. M. Grove, J. W. Zwikker, J. G. M. van de Linden, A. M. Roelofsen, L. W. Jenneskens, W. Drenth, G. van Koten, *Organometallics* **1994**, *13*, 468–477.

[8] a) L. A. van de Kuil, D. M. Grove, R. A. Gossage, J. W. Zwikker, L. W. Jenneskens, W. Drenth, G. van Koten, *Organometallics* **1997**, *16*, 4985–4994; b) R. A. Gossage, L. A. van de Kuil, G. van Koten, *Acc. Chem. Res.* **1998**, *31*, 423–431, and references therein.

[9] C. Valério, J. L. Fillaut, J. Ruiz, J. Guittard, J. C. Blais, D. Astruc, *J. Am. Chem. Soc.* **1997**, *119*, 2588–2589.

[10] Similar protocols have been used for the synthesis of related multiplatinated systems.[3] The nickelated dendrimers **2**–**6**, as well as their ligand precursors, have been characterized by NMR techniques (^{1}H, ^{13}C, ^{29}Si), mass spectrometry (FAB, MALDI-TOF), and microanalyses. Full experimental data will be reported elsewhere.

[11] Nickel incorporation was found to be in the range of 80–89%. This incomplete nickel incorporation (estimated by ^{1}H and ^{13}C NMR spectroscopy, elemental analyses, as well as mass spectrometry) can be ascribed to partial hydrolysis of the C−Li bond(s) during workup. However, this aspect does not hamper the use of these metallodendrimers in catalytic applications. Further details will be reported in a full paper.

[12] Catalytic deactivation of polymeric materials with a high loading of the [NiX(NCN)] complexes has also been observed. See: L. A. van de Kuil, D. M. Grove, J. W. Zwikker, L. W. Jenneskens, W. Drenth, G. van Koten, *Chem. Mater.* **1994**, *6*, 1675–1683.

[13] The X-ray crystal structure determination of **7** will be reported in a forthcoming paper The structural features of **7** are comparable with that of related [$Ni^{III}X_2$(NCN)] species. See, for example: D. M. Grove, G. van Koten, R. Zoet, N. W. Murall, A. Welch, *J. Am. Chem. Soc.* **1983**, *105*, 1379–1380.

[14] We were unable to perform molecular modeling of the G2 derivative **4** with our software (CAChe, MM2) because of the large size of the molecule.

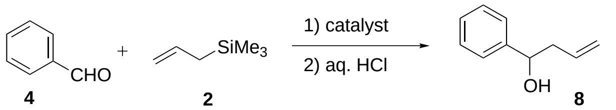
[15] M. Enomoto, T. Aida, *J. Am. Chem. Soc.* **1999**, *121*, 874–875.

[16] L. Fabbrizzi, F. Gatti, P. Pallavicini, E. Zambarbieri, *Chem. Eur. J.* **1999**, *5*, 682–690.

Aluminum Bis(trifluoromethylsulfonyl)amides: New Highly Efficient and Remarkably Versatile Catalysts for C–C Bond Formation Reactions[**]

Andreas Marx and Hisashi Yamamoto[*]

Lewis acids are powerful tools in many different reactions such as Diels–Alder reactions, aldol synthesis, and the Sakurai reaction. The aim is now to develop more-reactive Lewis acidic species that catalytically promote these synthetically valuable transformations.[1] Metal triflates (triflate = OTf) are employed as Lewis acids to promote important carbon–carbon bond formation reactions since the trifluoromethylsulfonyl (Tf) group is one of the strongest neutral electron-withdrawing groups.[1, 2] However, a major limitation of the known metal triflates is the synthesis of highly valuable homoallyl alcohols (for example, **8**) by the Lewis acid promoted reaction of aldehydes with inexpensive and nontoxic allyl trimethylsilane [Eq. (1)]. The formation of such homoallyl alcohols necessitates the use of allyl tin reagents instead.[3, 4]



4 **2** **8** (1)

Attempts to develop more reactive Lewis acidic species for this transformation by modification of the triflate ion with more electron-withdrawing counterions have failed.[5] Herein we report the first successful development of new versatile catalysts derived from the superacid bis(trifluoromethylsulfonyl)amine (Tf_2NH)[6] that promote allylation and other important reactions with unprecedented efficiency.

Recently, ytterbium triflate ($Yb(OTf)_3$) was shown to promote the reaction between aldehydes and allyl tributyltin reagents but that allyl silanes were unaffected by this reagent.[7] Attempts to develop a more-reactive Lewis acid by modification of the triflate ions with the more electron-withdrawing counterion bis(trifluoromethylsulfonyl)amide (bistrifylamide) failed.[5] The desired homoallyl alcohol **8** was only formed in trace amounts and generated $TMSNTf_2$ (TMS = trimethylsilyl) as a side product, which is believed to be the actual promoter for this reaction. This proposal is supported by our finding that catalytic amounts of $TMSNTf_2$[8] or Tf_2NH (**1**), which generates $TMSNTf_2$ in situ through reaction with **2**, form **8** in moderate yield along with substantial amounts of undesired products (Table 1 , entries 1 and 2).

Similar results were obtained when (iPrO)$_2$Ti(NTf$_2$)$_2$[9] and Al(NTf$_2$)$_3$[9] were employed (Table 1, entries 3 and 4). These

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Table 1. Reaction of benzaldehyde and allyl trimethylsilane to give **8** using various catalysts [Eq. (1)].

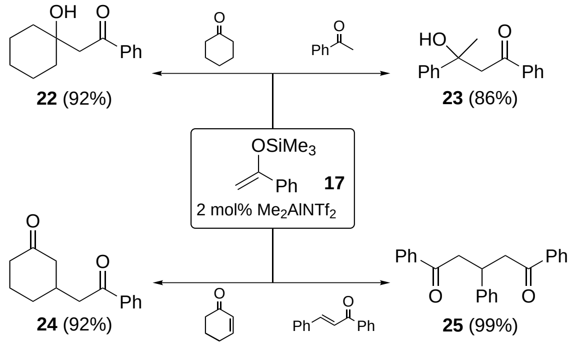
Entry	Catalyst	Conditions	Yield [%][a]
1	TMSNTf$_2$	−20 °C, 3 h	53
2	HNTf$_2$	−20 °C, 3 h	52
3	(iPrO)$_2$Ti(NTf$_2$)$_2$	−78 °C, 3 h	45
4	Al(NTf$_2$)$_3$	−20 °C, 3 h	35[b]
5	Me$_2$AlNTf$_2$	−20 °C, 3 h	93[c]

[a] Yield of isolated products. [b] Precipitation of Al(NTf$_2$)$_3$ at −78 °C. [c] No reaction at −78 °C.

promoters afford an undesired side product in substantial amounts (37 % and 41 %, respectively), which was identified as the recently reported side product formed when BF$_3$ · OEt$_2$ was used as a promoter.[10] By taking mechanistic considerations for the formation of this undesired reaction product into account we suspected that the catalyst must be exhibiting exceedingly high reactivity for a clean promotion of this process. Therefore, a less-reactive catalyst should be more suited for the clean allylation of aldehydes with allyl trimethylsilane. Indeed, we found that 5 mol % of Me$_2$AlNTf$_2$ (**3**), readily prepared by treatment of a solution of Me$_3$Al with one equivalent of commercially available Tf$_2$NH, catalyzes the smooth addition of allyl trimethylsilane (**2**) to benzaldehyde (**4**), and yields **8** in 93 % yield after acidic work-up. We further investigated the scope of the reaction toward the aromatic aldehyde (**5**), the less reactive aliphatic aldehyde hexanal (**6**), and the hindered aldehyde trimethylacetaldehyde (**7**). The results are summarized in Table 2.

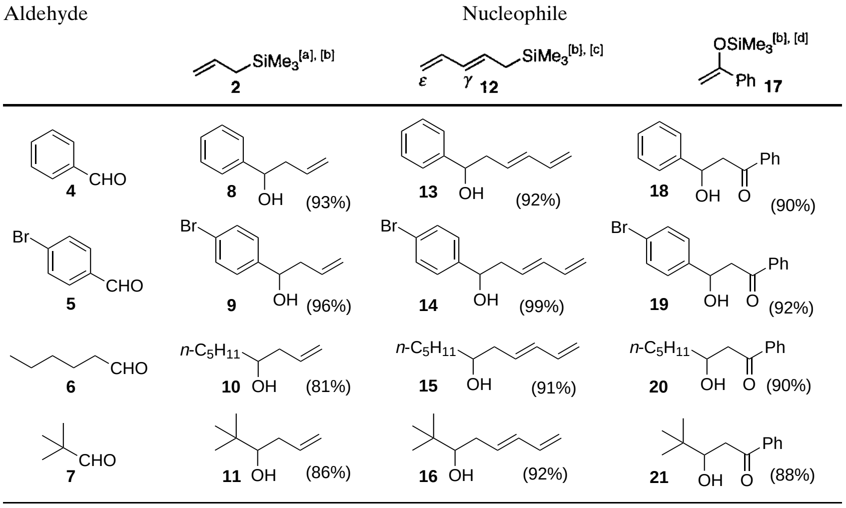
Aromatic aldehydes were allylated in excellent yields and short reaction times. Aliphatic aldehydes were allylated in good yields with the same catalyst loading (5 mol %), but in order to suppress the formation of side products lower reaction temperatures were required, which resulted in longer reaction times.[11]

We further investigated the general scope of Me$_2$AlNTf$_2$ in catalytic C–C bond forming reactions. Catalytic pentadienylation of aldehydes is still a challenging topic in organic synthesis. Strong Lewis acids such as TiCl$_4$ and BF$_3$ · OEt$_2$ applied in stoichiometric amounts commonly yield the desired pentadienylated alcohols **13**–**16** in only moderate yields, and, depending on the applied reaction conditions, mixtures of γ- and ε-substituted products are obtained.[12] However, 5 mol % of **3** is sufficient to effect the addition of 5-trimethylsilyl-1,3-pentadiene (**12**) to aldehydes and gave **13**–**16** (Table 2) in excellent, and up to now unprecedented, yields. Furthermore, the addition proceeds in high selectivity, thus the ε-substituted adducts were formed exclusively. Next, we explored the use of **3** in the catalytic Mukaiyama aldol reaction[13] and found that treatment of various aldehydes with the silyl enol ether **17** in the presence of 2 mol % **3** gave rise to good yields of the desired aldol products **18**–**21** (Table 2). We further investigated the use of this remarkably active catalyst in other addition reactions of **17** and found that **3** supersedes any previously reported Lewis acid. Employment of only 2 mol % allows a smooth cross-aldol reaction between simple ketones to yield the desired adducts **22** and **23** under mild reaction conditions (Scheme 1).[14]



Scheme 1. Cross-aldol reaction between ketones and Michael addition catalyzed by 2 mol % **3**. Reaction conditions: ketone (1 equiv), silyl enol ether **17** (1.1 equiv), 2 mol % **3**, CH$_2$Cl$_2$, −45 °C, 3 h. Desilylation: 1N HCl/THF. The yields in parentheses are of isolated products.

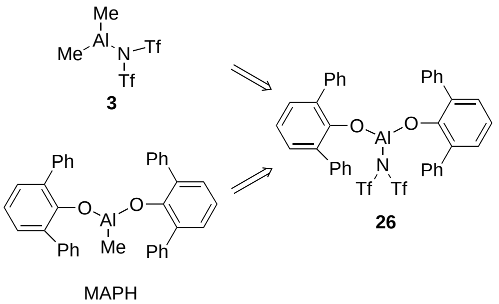
Table 2. Carbon–carbon bond formations catalyzed by Me$_2$AlNTf$_2$



[a] Aldehyde (1 equiv), **2** (1.1 equiv), 5 mol % **3**, CH$_2$Cl$_2$, −20 °C, 3 h (aromatic aldehydes) or −40 °C, 10–20 h (aliphatic aldehydes). Desilylation: 1N HCl/THF. [b] The yields in parentheses are of isolated, purified products. [c] Aldehyde (1 equiv), **12** (1.1 equiv), 5 mol % **3**, CH$_2$Cl$_2$, −78 °C, 3–20 h. Desilylation: tetrabutylammonium fluoride (TBAF) in THF. [d] Aldehyde (1 equiv), **17** (1.1 equiv), 2 mol % **3**, CH$_2$Cl$_2$, −78 °C, 3–20 h. Desilylation: 1N HCl/THF.

Interestingly, when α,β-unsaturated ketones are employed under the same reaction conditions a catalytic 1,4-addition is observed to yield the Michael adducts **24** and **25** in excellent yields without any evidence for 1,2-addition (Scheme 1).[15]

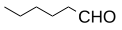
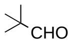
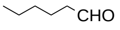
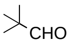
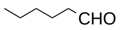
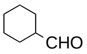
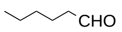
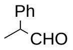
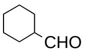
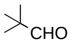
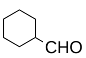
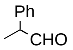
Apart from the remarkable ability of **3** to catalyze C–C bond formation with unprecedented efficiency and versatility, more subtle aspects of this aluminum-derived species appeared. Thus, substitution of both methyl groups in Me$_2$AlNTf$_2$ by suitable ligands should allow the design of tailor-made catalysts. Initially, we aimed to design a suitable catalyst that would recognize and activate a less-shielded carbonyl functionality to undergo chemoselective aldol reaction with the less-shielded substrate. This is a challenging task, since many known promoters of the Mukaiyama aldol reaction trigger the formation of reactive silyl species that catalyze the reaction with loss of selectivity.[13b] A successful achievement of a chemoselective aldol reaction would indicate and favor a Lewis acid catalyzed reaction mechanism over a reaction pathway catalyzed by reactive silyl species. Aluminum 2,6-diphenylphenoxides such as methylaluminum bis(2,6-diphenylphenoxide) (MAPH) have been shown to be suitable for the recognition of less-hindered aldehydes. Thus, compound **26** (Scheme 2) should be suitable for this purpose.[16, 17]



Scheme 2. Design of a catalyst for the chemoselective aldol reaction.

As expected, treatment of an equimolar mixture of hexanal (**6**) and trimethylacetaldehyde (**7**) with **17** in the presence of 5 mol % of **3** effected only a moderate preference for the less-hindered aldehyde (Table 3, entry 1). In marked contrast, the reaction of **17** promoted by **26** yielded the aldol product of the less-hindered aldehyde in 84 % yield, and only trace amounts of the trimethylacetaldehyde-derived product were detected by ^{1}H NMR analysis (Table 3, entry 2). Table 3 further demonstrates that **26** is able to promote the highly selective functionalization of a variety of substrates and exhibits the scope of this process as well as its limitations. While **26** fails to differentiate between hexanal and cyclohexanecarboxaldehyde, higher selectivity is found when the more-hindered 2-phenylpropionaldehyde is employed instead (Table 3, entries 3 and 4). Furthermore, **26** is able to perform the chemoselective aldol reaction between cyclohexanecarboxaldehyde and trimethylacetaldehyde or 2-phenylpropionaldehyde (Table 3, entries 5 and 6, respectively). These findings indicate that the bulky aluminum reagent **26** acts as a highly reactive Lewis acid when it promotes the presented reactions, and thus selectivity can be introduced by suitable ligands.

Table 3. Chemoselective aldol reactions.[a]

Entry	Aldehyde			Cat.	Ratio[b]
1		vs.		**3**	74:26 (–)
2		vs.		**26**	99:1 (84 %)
3		vs.		**26**	57:43 (–)
4		vs.		**26**	93:7 (79 %)
5		vs.		**26**	99:1 (84 %)
6		vs.		**26**	92:8 (67 %)

[a] Aldehydes (1 equiv each), **17** (1 equiv), 5 mol % catalyst, CH_2Cl_2, – 78 °C. Desilylation: 1N HCl/THF [b] Determined by ^{1}H NMR analysis. The yield is given in parentheses.

In conclusion, we have developed a new class of aluminum bis(trifluoromethylsulfonyl)amides as highly reactive and versatile Lewis acidic catalysts for a variety of important C–C bond forming reactions. In addition, we were able to design a ligand scaffold in a rational approach to ensure the selective recognition and activation of a desired substrate, thus indicating that the aluminum species act directly as reactive Lewis acids. Considering the wide applications found for strong electron-withdrawing counterions such as triflates, there is a high probability that metal bistriflylamides will prove to be valuable in the development of new Lewis acids for important organic transformations. The correlation of the catalytic ability of aluminum bistriflylamides with the electronic and steric properties of the ligand sphere should allow the development of Lewis acidic catalysts for enantioselective processes.

Experimental Section

Me_2AlNTf_2 (**3**) was readily prepared by treatment of Me_3Al (100 μL of 0.5M solution in toluene) with 1 equivalent of commercially available Tf_2NH (100 μL of 0.5M solution in CH_2Cl_2) in CH_2Cl_2 (4.0 mL) at room temperature (gas evolution) for 30 min with rigorous exclusion of air and moisture and was used without further purification.

Typical procedure for the reaction of aldehydes with allyl trimethylsilane: Benzaldehyde (**4**, 100 μL, 1.00 mmol) and allyl trimethylsilane (**2**, 175 μL, 1.10 mmol) were added at – 20 °C under argon to a solution of Me_2AlNTf_2 (**3**, 0.05 mmol) in CH_2Cl_2 (4.0 mL). After stirring the reaction mixture for 3 h, 1N HCl (2.0 mL) and THF (2.0 mL) were added and the reaction was allowed to warm to room temperature. The reaction mixture was stirred for 30 min, poured into $NaHCO_3$ solution, and extracted with diethyl ether. The combined organic extracts were dried over $MgSO_4$, concentrated, and the residue was purified by column chromatography on silica gel (EtOAc/hexane, 1/10) to give **8** (138 mg, yield 93 %) as a colorless liquid that shows identical spectral and analytical data with those in ref. [18]

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[1] Recent books: a) *Lewis Acids Reagents* (Ed.: H. Yamamoto), Oxford University Press, New York, **1999**; b) M. Santelli, J.-M. Pons, *Lewis Acids and Selectivity in Organic Synthesis*, CRC Press, New York, **1996**. c) Review: Y. Yamaguchi in *Comprehensive Organic Synthesis, Vol 2* (Eds.: B. M. Trost, I. Fleming, C. H. Heathcock), Pergamon, Oxford, **1991**, p. 325.

[2] a) P. J. Stang, M. Hanack, L. R. Subramanian, *Synthesis* **1982**, 85; b) P. J. Strang, M. R. White, *Aldrichchimica Acta*, **1983**, *16*, 15. For applications of various metal triflates in catalysis see ref. [1].

[3] For general reviews for allylation of aldehydes, see a) J. A. Marshall, *Chem. Rev.* **1996**, *96*, 31; b) Y. Yamamoto, N. Asao, *Chem. Rev.* **1993**, *93*, 2207; c) W. R. Roush in *Comprehensive Organic Synthesis*, *Vol 2* (Eds.: B. M. Trost, I. Fleming, C. H. Heathcock), Pergamon, Oxford, **1991**.

[4] For successful approaches using allyl silanes, see chiral (acyloxy)boranes: K. Ishihara, M. Mouri, Q. Gao, T. Maruyama, K. Furuta, H. Yamamoto, *J. Am. Chem. Soc.* **1993**, *115*, 11 490; chiral Ti^{IV} complexes: D. R. Gauthier, E. M. Carreira, *Angew. Chem.* **1996**, *108*, 2521; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2363.

[5] A. Isshi, O. Kotera, T. Saeki, K. Mikami, *Synlett* **1997**, 1145.

[6] I. A. Koppel, R. W. Taft, F. Anvia, S.-Z. Zhu, L.-Q. Hu, K.-S. Sung, D. D. DesMarteau, L. M. Yagupolski, Y. L. Yagupolski, N. V. Ignatev, N. V. Kondratenko, A. Y. Volkonskii, V. M. Vlasov, R. Notario, P.-C. Maria, *J. Am. Chem. Soc.* **1994**, *116*, 3047.

[7] a) H. C. Aspinall, A. F. Browning, N. Greeves, P. Ravenscroft, *Tetrahedron Lett.* **1994**, *35*, 4639; b) H. C. Aspinall, N. Greeves, E. G. McIver, *Tetrahedron Lett.* **1998**, *39*, 9283.
[8] B. Mathieu, L. Ghosez, *Tetrahedron Lett.* **1997**, *38*, 5497.
[9] K. Mikami, O. Kotera, Y. Motoyama, H. Sakaguchi, M. Maruta, *Synlett* **1996**, 171.
[10] A. Bottoni, A. L. Costa, D. Di Tommaso, I. Rossi, E. Tagliavini, *J. Am. Chem. Soc.* **1997**, *119*, 12131.
[11] A side product formed in substantial amounts at −20 °C was identified as the aldehyde cyclic trimer. See S. E. Denmark, N. G. Alsmstead, *Tetrahedron* **1992**, *48*, 5565.
[12] a) Y. Nishigaichi, Y. Hanano, A. Takuwa, *Chem. Lett.* **1998**, 33, and references therein; b) A. Yanagisawa, Y. Nakatsuka, H. Nakashima, H. Yamamoto, *Synlett* **1997**, 933, and references therein; b) Y. Nishigaichi, M. Fujimoto, A. Takuwa, *J. Chem. Soc. Perkin Trans. 1* **1992**, 2581; d) D. Seyferth, J. Pornet, *J. Org. Chem.* **1980**, *45*, 1722.
[13] a) Reviews: R. Mahrwald, *Chem. Rev.* **1999**, *99*, 1095; E. M. Vogel, H. Gröger, M. Shibasaki, *Angew. Chem.* **1999**, *111*, 1671; *Angew. Chem. Int. Ed.* **1999**, *38*, 1571; b) T. K. Hollis, B. Bosnich, *J. Am. Chem. Soc.* **1995**, *117*, 4570, and references therein.
[14] Cross-aldol reaction with activated trialkylsilylsulfonates: M. Oishi, S. Aratake, H. Yamamoto, *J. Am. Chem. Soc.* **1998**, *120*, 8271; by Reformatsky-type reactions: a) M. Maruoka, S. Hashimoto, Y. Kitagawa, H. Yamamoto, H. Nozaki, *J. Am. Chem. Soc.* **1977**, *99*, 7705; b) L. Weissjohan, H. Wild, *Synthesis* **1997**, 512.
[15] Sc(OTf)$_3$: S. Kobayashi, I. Hachiya, M. Araki, *Synlett* **1993**, 472; TMSCl/SnCl$_2$: N. Iwasawa, T. Mukaiyama, *Chem. Lett.* **1987**, 463; Ph$_3$COTf: S. Kobayashi, M. Murakami, T. Mukaiyama, *Chem. Lett.* **1985**, 953.
[16] MAPH is not catalytically active under the reaction conditions employed. For chemoselective recognition by stoichiometric amounts of MAPH, see K. Maruoka, S. Saito, A. B. Conception, H. Yamamoto, *J. Am. Chem. Soc.* **1993**, *115*, 1183; for use of other aluminum 2,6-diphenylphenoxides, see a) A. Marx, H. Yamamoto, *Synlett* **1999**, 584; b) T. Ooi, Y. Kondo, K. Maruoka, *Angew. Chem.* **1998**, *110*, 3213; *Angew. Chem. Int. Ed.* **1998**, *37*, 3039; c) K. Maruoka, S. Saito, H. Yamamoto, *Synlett* **1994**, 439.
[17] **26** was generated by treatment of MAPH (see ref. [16]) with one equivalent of Tf$_2$NH (gas evolution) and was used without further purification.
[18] K. Iseki, Y. Kuroki, M. Takahashi, Y. Kobayashi, *Tetrahedron* **1997**, *53*, 3513.

Ordered Two-Dimensional Monolayers of Au$_{55}$ Clusters**

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Highly ordered structures of nanoparticles exhibit attractive physical properties for future nanoelectronics.[1–5] Metal particles of 1–4 nm in size are of particular interest because of their special electronic properties, as characterized by their quantum size behavior;[6] their electrons are no longer in a quasi-delocalized three-dimensional state, but are trapped in a “zero-dimensional space”. Ligand-stabilized metal clusters turned out to be ideal objects for studying these effects. With its two freely mobile electrons [Au$_{55}$(PPh$_3$)$_{12}$Cl$_6$] represents something like a “last metal”.[7]

Ordered arrangements of such quantum dots allow correlated single electron tunneling (SET)[8, 9] at room temperature, which has been proposed as a fundamental idea of future nanoelectronics. The realization of such new systems, which require well-defined planar arrays of uniform metal clusters, might open the door to a new generation of computers with a storage capacity raised by a factor of 10^5–10^6 relative to the present state of the art.

Many research groups focus their efforts on reaching this goal.[10–14] Andres et al. reported on perfect layers of alkylthiol-protected gold particles with diameters of 3.7 nm.[15] Another method for generating ordered two-dimensional layers was described by Möller et al. who prepared gold colloids in ordered polymer micelles.[16] In the past we carried out intensive research on the preparation of monolayers by the chemical fixation of ligand-stabilized metal clusters on modified substrates,[17–20] however, we could only observe particles that were at best, densely packed, but not well ordered.

Herein we report the first successful preparation of two-dimensional (2D) hexagonal and cubic lattices of Au$_{55}$ clusters on polymer films by self-assembly. The monolayers were prepared by dipping a poly(ethyleneimine)-covered, carbon-coated copper grid (for transmission electron microscopy) into an aqueous solution of [Au$_{55}$(Ph$_2$PC$_6$H$_4$SO$_3$H)$_{12}$Cl$_6$] clusters (Figure 1). Classical acid–base reactions take place because of the NH functions on the poly(ethyleneimine) (PEI). The strong interactions between clusters and the surface prevent mechanical removal, for example, by washing.

The characterization of the cluster arrangements was performed by transmission electron microscopy (TEM) at

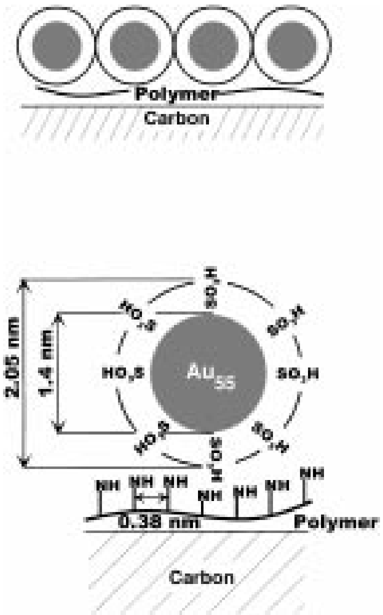

Figure 1. Schematic cross-section of a Au$_{55}$ monolayer on a PEI-modified, carbon-coated copper grid and a magnification of the contact area with characteristic values.

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