determined by NMR spectroscopy. This structure has been reported to produce a triangular prism pocket to bind with the enediyne analogues.[16] Indeed, when the two-base bulge of a 26-mer DNA containing one base (T6) less than the three-base bulge of a 27-mer DNA (**D** in Figure 1) was used as the DNA substrate, enhanced cleavage activity and specificity was observed towards the T7 residue of the 26-mer DNA bulge shown in Figure 2. Thus, the shape and size of the binding pocket of the DNA bulge are probably important controlling factors in the specific recognition by the $[Co^{II}(tfa)_2$-(happ)] complex. The addition of the intercalator $[Pt(terpy)(het)]^+$ to DNA substrate D[12] was, as for DNA substrate A, found to significantly inhibit the cleavage at the bulge site induced by $[Co^{II}(happ)]^{2+}$ in the presence of H_2O_2.

This study provides the first attempt in utilizing a novel Co^{II} complex to show specific targeting and cleavage of a DNA bulge site. No significant reactivity was observed toward the corresponding sequence in a single-stranded DNA region. We assume that the intercalation of the 1,10-phenanthroline ligand of $[Co^{II}(tfa)_2(happ)]$ toward double-stranded DNA is probably inhibited by the two axial ligands in this octahedral complex. On the other hand, it is possible that $[Co^{II}(tfa)_2$-(happ)] recognizes a binding pocket in the DNA bulge of a specific shape and size, and this recognition may be responsible for the observed bulge-specific DNA cleavage by the diffusable hydroxyl radical produced from the reaction between the cobalt(II) complex and H_2O_2.

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Functional Monolayers with Coordinatively Embedded Metalloporphyrins**

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In memory of Jacqueline Libman

The expression of porphyrin functions in supramolecular systems depends on their immediate environment and mutual orientation.[1] Incorporation of porphyrins into artificial bilayers[2] or their assembly onto solid supports[3] neither resulted in uniform orientation of the chromophores, nor

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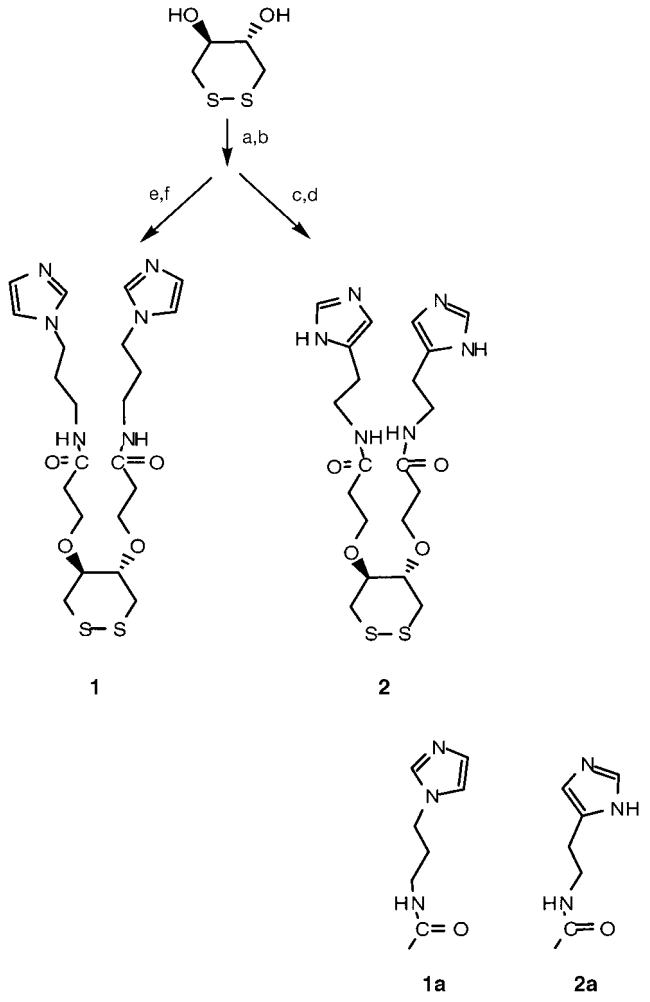
prevented stacking interactions and chromophore aggregation. In nature ligands tend to coordinate axially to metalloporphyrins. It may be that by mimicking these biological trends one could locate the porphyrin in a well-defined environment while avoiding stacking and aggregation. If such an assembly would also retain the capability to transfer electrons to a conducting surface it could be used in future optoelectronic and light-harvesting applications.

Herein we present a novel arrangement of iron porphyrins on gold surfaces. The monolayer prepared differs from other systems in that the metalloporphyrin is not in direct contact with the surface, but rather is held in a perpendicular orientation through an interconnected ligand that also protects its open faces, thus eliminating π stacking to other porphyrin moieties. The bifunctional ligands **1** and **2** (Scheme 1) were



Scheme 1. Schematic representation of the bifunctional ligands **1** and **2** and their respective model compounds **1a** and **2a**. Synthesis: a) acrylonitrile/OH^-; b) HCl; c) pentachlorophenol; d) histamine; e) oxalyl chloride; f) 1-(3-aminopropyl)imidazole.

designed to integrate two essential components: A cyclic disulfide for surface attachment,[4] and two extended imidazolyl residues capable of binding metalloporphyrins in an axial coordination mode.

The cyclic disulfide offers several advantages as an anchor: It prohibits chain segregation even upon possible S–S bond cleavage during self assembly, and reduces the degrees of freedom for tilting of surface-attached molecules towards the S–S axis.[4a] The two imidazole rings provide the "hinges" that hold the porphyrin moiety in a defined orientation, while its axial coordination to the central Fe^{3+} ion masks the porphyrin from neighboring molecules. This molecular arrangement dictates a perpendicular orientation of the metalloporphyrins with respect to the S–S bond as well as to the surface (see Figure 1, bottom). Molecules **1** and **2** differ in the imidazolyl

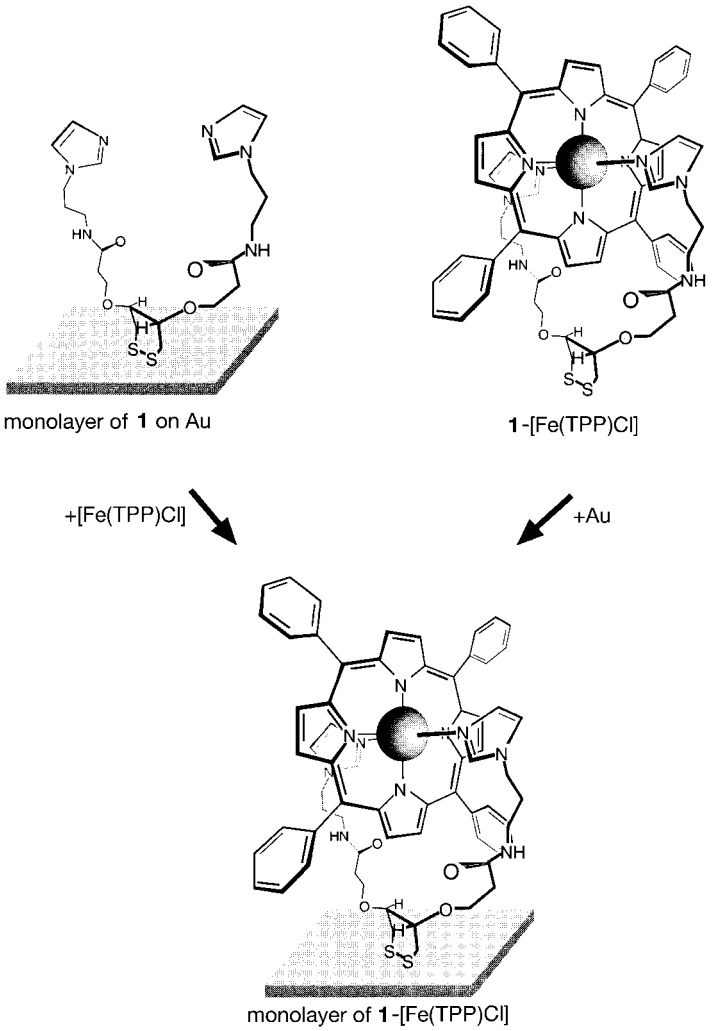


Figure 1. Schematic illustration of the stepwise (left) and preformed (right) methods for the adsorption of the complex **1**-[Fe^{III}(TPP)Cl] onto a gold surface.

residues, possessing either *N*-alkyl (**1**) or free NH groups (**2**), and the length of the chains connecting the cyclic disulfide anchor and the imidazolyl groups.

The formation of metalloporphyrin complexes of **1** and **2** and of their single-chain model compounds **1a** and **2a** was investigated in solution. The UV titration of iron porphyrins with ligands **1**, **1a**, **2**, and **2a** provided the formation constants K_1 and β_2 (Table 1).[5] The β_2 values of the dipodal ligands are higher than those for the model compounds. Titration of iron tetraphenylporphyrin chloride [Fe^{III}(TPP)Cl] with **1** and **2** showed no formation of the monoimidazolyl complex, although such intermediates were observed with the single-stranded *N*-alkylimidazole models **1a** and with *N*-methyl-

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Table 1. Binding constants for the axial coordination of the iron porphyrin [Fe^{III}(TPP)Cl] by imidazole ligands **1**, **1a**, **2**, and **2a** in DMF.

Ligand	K_1 [M^{-1}]	β_2 [M^{-2}]
1a	ca. 50	4.02×10^3
2a	–	1.32×10^4
1	–	1.09×10^4
2	–	2.19×10^4

[a] The binding constants were calculated with respect to the number of imidazolyl residues present in the system.

Table 2. Theoretical and experimental thickness d of monolayers of the bifunctional ligands and their iron porphyrin complexes.

Compound	Adsorption procedure	d [Å] calcd	found
1	–	13 – 14	12 ± 2
1-[Fe^{III}(TPP)Cl]	preformed	17 – 18	17 ± 2
1-[Fe^{III}(TPP)Cl]	stepwise	17 – 18	17 ± 3
2	–	11 – 12	16 ± 1
2-[Fe^{III}(TPP)Cl]	preformed	16 – 17	15 ± 1
2-[Fe^{III}(TPP)Cl]	stepwise	16 – 17	14 ± 1

imidazole.[5a] These results demonstrate not only the well-known diimidazolyl complex formation with [Fe^{III}(TPP)Cl], but also the strong tendency of the dipodal ligands **1** and **2** to undergo intramolecular reactions, to form complexes of 1:1 stochiometry (chelation effect).[5c]

The ^{1}H NMR spectra of the low-spin [Fe^{III}(TPP)Cl] complexes of ligands **1** and **2** showed a single set of signals, which indicated the formation of single complex species. Complete assignment of the proton signals was accomplished by comparison with literature values[6] and from 2D COSY NMR spectra recorded at $-30\,^{\circ}C$. The chemical shifts suggest an axial coordination of each imidazolyl residue to the iron porphyrin and a perpendicular orientation relative to each other.[7] Measurements between 295 K and 193 K revealed separate signals for the diastereotopic CH_2 protons in the chain of **1**-[Fe^{III}(TPP)Cl] and **2**-[Fe^{III}(TPP)Cl],[8] which is attributed to a slowing down of the ligand exchange process.[9] Nonequivalent pyrrolic proton signals,[10] which arise from an anisotropy of the ligand-bound porphyrin ring, strongly suggests there is restricted rotation of the metalloporphyrin around the Fe–N_{im} bonds (the "hinges") in the shorter **2**-[Fe^{III}(TPP)Cl], but not in the longer **1**-[Fe^{III}(TPP)Cl] complex. A representation of the **1**-[Fe^{III}(TPP)Cl] complex in solution, consistent with the experimental data and molecular modeling studies,[11] is shown in Figure 1 (top right).

Two methods were used to prepare metalloporphyrin monolayers of **1**-[Fe^{III}(TPP)Cl] and **2**-[Fe^{III}(TPP)Cl] on Au (1000 Å, evaporated on (111)Si,[12]): 1) One-step formation (Figure 1, right), where the preformed, characterized (see above) ligand – metalloporphyrin complex is assembled directly onto the gold surface; 2) stepwise formation (Figure 1, left), which is achieved by preparing the ligand monolayer followed by introduction of a metalloporphyrin capable of axial ligation to the imidazoyl groups. The possibility of interligand complexation in the stepwise method cannot be ruled out;[13] characterization of the complex in solution (as described above) strongly suggests that this configuration is unfavorable when a preformed complex is used.

The thickness of the monolayers were measured ellipsometrically[4a] (Table 2), and also calculated from a theoretical model.[14, 15] Good agreement between the measured and the theoretical monolayer thickness is obtained for **1**-[Fe^{III}(TPP)Cl]. The ellipsometry of the adsorbed ligand **2** suggests formation of a bilayer, which is attributed to ligand – ligand hydrogen bonding.[16] Successive treatment with an EtOH/H_2O solution (1/1; 25 min) resulted in the removal of the second layer (breaking of the hydrogen bonds), as evident from a change in the thickness of the monolayer to 9.4 ± 1 Å.[17] The bilayer appears to break upon introduction of [Fe^{III}(TPP)Cl] and form the complex monolayer and free excess ligand. In both cases (namely with both methods) and using the two ligands the binding of the porphyrin adds approximately 4 – 5 Å to the monolayer thickness, which is approximately equal to half the diameter of a porphyrin ring and consistent with a perpendicular orientation of the porphyrin.

Analysis of the systems by X-ray photoelectric spectroscopy (XPS) showed the expected elements on the surface (Table 2). Both complex monolayers (but not the ligand monolayers) showed the iron peak at 711 eV. Transmission spectroscopy in the visible region of preformed and stepwise-formed monolayers of **1**-[Fe^{III}(TPP)Cl] on thin gold films (approximately 25 Å on mica)[18] showed peaks at 424 and 554 nm, which is similar to those measured for the same complex in solution (our results) and for other [Fe^{III}(TPP)Im_2] complexes.[5a] The absorption peaks of the stepwise-formed **1**-[Fe^{III}(TPP)Cl] monolayer are broader and smaller than those of the preformed monolayer, which is in agreement with the voltammetric results (see below).

It is evident from steric considerations (Figure 1) that the binding of the disulfide group to the gold surface forces the porphyrin rings into a perpendicular orientation (hence isolation), even if a certain tilt exists. This conclusion is supported by 1) the 1:1 ligand:iron porphyrin stochiometry and the axial coordination of the imidazole to the porphyrin found in the complex in solution, 2) the thickness of the complex monolayer relative to that of the ligand monolayer, and 3) the existence of only bis-ligated species on the surface.

Cyclic voltammetry (CV) of **1**-[Fe^{III}(TPP)Cl] monolayers on gold (Figure 2) shows peaks that generally agree with previous measurements of porphyrinic systems in solution,[3c, 19] while CV of a monolayer of **1** shows no identifiable peaks in the measured range.[20] The peak – peak separation for the preformed complex monolayer is approximately 200 mV smaller than that of the monolayer formed stepwise, which indicates a more facile electron transfer for the former. The difference in peak height between the reduction and oxidation waves does not reflect chemical irreversibility, but rather a smearing of the oxidation wave, as evident from repetitive cycles (not shown). This is likely to indicate a certain distribution of structures in the reduced state.

Integration of the CV reduction peaks (Figure 2), as well as the absorbance intensity in the UV/Vis spectra (see above), indicate a considerably smaller amount of bound iron porphyrin in the monolayers formed stepwise, and shows

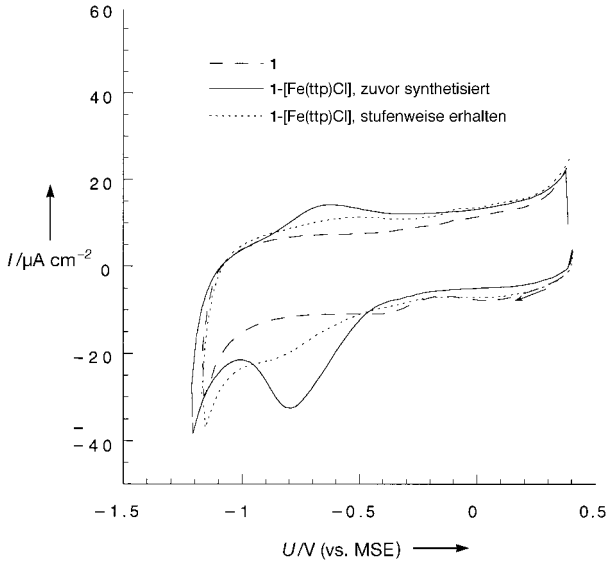

Figure 2. Cyclic voltammetry (first scan) of **1** and **1**-[Fe^{III}(TPP)Cl] monolayers on gold in aqueous 0.1 M Na_2SO_4 at 200 mV s^{-1} (using a Solartron 1286 potentiostat, reference electrode: Mercurous sulfate electrode (MSE; 0.400 V versus the standard calomel electrode)).

the advantage of the one-step procedure in obtaining stochiometric amounts of bound iron porphyrin. This advantage reflects the different nature of the two self-assembled monolayers. The stepwise method produces monolayers that satisfy the lower energy arrangement of the ligand molecules, and are only partially useful for iron porphyrin incorporation. Self-assembly of the preformed complex, on the other hand, allows the massive complex molecules to arrange optimally in the monolayer, by taking into account the necessity for intramolecular interactions. This also implies that the density of ligand molecules is higher in the monolayer formed stepwise, which accounts for the similar ellipsometric thickness measured for the two (Table 2) despite the different number of bound porphyrins. This difference in packing arrangements would also account for the difference, noted above, in voltammetric peak–peak separation between the preformed and stepwise-formed monolayers.

The systems presented here allow the anisotropic assembly of metalloporphyrins perpendicular to conducting surfaces while avoiding stacking of the porphyrin rings. These unique features may be of substantial importance, for example, in solar energy conversion systems where they may help to reduce lateral energy dissipation while retaining the possibility of electron transfer between the surface and the chromophore (as evident from the electrochemical results). Modifications of the present methodology, already in progress, will provide monolayers containing diamagnetic metalloporphyrins (for example, Mg^{2+} and Zn^{2+}) as well as multilayers containing metalloporphyrins in controllable relative orientations.

Experimental Section

Synthesis of **1** and **2**: *trans*-1,2-dithiane-4,5-diol (racemic mixture) was treated with acrylonitrile (2.2 equiv) and NaOH, and stirred overnight at room temperature. The mixture was then hydrolyzed for 3 h by refluxing with HCl to give the *trans*-1,2-dithiane dicarboxylic acid derivative (yield: 90%). The extended diacid was coupled at room temperature, through the acyl chloride, to 1-(3-aminopropyl)imidazole to give **1** (yield: 60%), or through the pentachlorophenolate to histamine, to give **2** (yield: ca. 30%). **1:** ^{1}H NMR (CD_3OD): $\delta = 7.72$ (s, 1H), 7.12 (s, 1H), 6.98 (s, 1H), 4.07 (t, 2H, $J = 6.2$ Hz), 3.90 (m, 2H), 3.40 (br, 1H), 3.21 (br, 3H), 2.85 (m, 1H), 2.48 (t, $J = 5.7$ Hz, 2H), 1.99 (quint., $J = 6.2$ Hz, 2H); IR ($CHCl_3$): $\tilde{\nu} = 1667$ cm^{-1}, 1108 cm^{-1}; MS (FAB): $m/z = 509$ [MH^+]. **2:** ^{1}H NMR (CD_3OD): $\delta = 7.58$ (s, 1H), 6.85 (s, 1H), 3.78 (m, 2H) 3.42 (t, $J = 7.2$ Hz, 2H), 3.24 (br, 1H), 3.14 (ABq, $^3J = 3.1$ Hz, Δ(AB) = 13 Hz, 1H), 2.75 (t, $J = 7.2$ Hz, 2H) 2.69 (m, 1H), 2.39 (t, $J = 6.2$ Hz, 2H); MS (FAB): $m/z = 482$ [M^+].

NMR spectra of the low-spin complexes: 20–30 mM; 1:1 mixtures of [Fe^{III}(TPP)Cl] with **1** or **2** in $CDCl_3$ or CD_2Cl_2/CD_3OD, respectively.

Monolayer assembly: a) Stepwise method: **1** or **2** were adsorbed onto evaporated gold (1–10 mM in $CHCl_3$ or DMF, overnight). The monolayers were then immersed in [Fe^{III}(TPP)Cl] solution (8–15 mM in $CHCl_3$, 1–3 min). b) Preformed method: **1**-[Fe^{III}(TPP)Cl] and **2**-[Fe^{III}(TPP)Cl] were adsorbed from 15–18 mM solution in $CHCl_3$ or DMF for 6 h. All monolayers were rinsed successively for 10–15 min in the adsorption solvents and in EtOH, and dried under a stream of purified nitrogen.

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[14] Theoretic monolayer thicknesses were calculated from a model where the complexes or free ligands are oriented perpendicularly with respect to the surface.
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[18] G. Kalyuzhny, A. Vaskevich, G. Ashkenasy, A. Shanzer, I. Rubinstein, unpublished results.
[19] P. O'Brien, D. A. Sweigart, *Inorg. Chem.* **1985**, *24*, 1405–1409.
[20] Gold exposed to a [Fe^{III}(TPP)Cl] solution under the same conditions showed no voltammetric peak or a very weak peak > 100 mV negative of that of the complex monolayer, which is attributed to physisorbed porphyrins.

$[(Ph)_2(NMe_2)C(OLi)\cdot THF]_2$: Crystal Structure of the Tetrahedral Intermediate Formed in the Reaction of *N,N*-Dimethylbenzamide and Phenyllithium**

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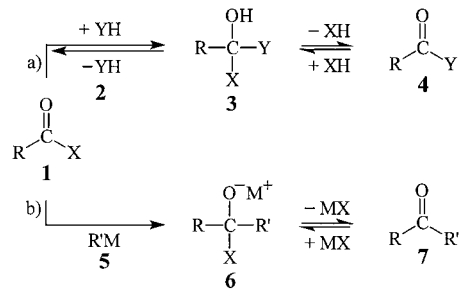
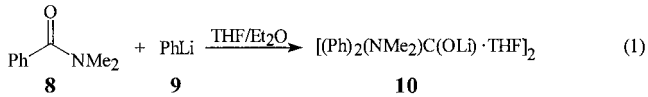
Dedicated to Professor Reiner Sustmann on the occasion of his 60th birthday

The tetrahedral intermediate RC(OH)XY (**3**) formed in reactions of carboxylic acid derivatives RC(O)X (**1**) with nucleophiles YH (**2**) to give RC(O)Y (**4**; Reaction a in Scheme 1) is of continued interest, for example, because of its significance for in vivo acylation rections.[1] Only recently, the solid-state structure of the (protonated) intramolecular amine adduct of a carboxylic acid was determined in a rather special case.[2]

Similarly, reactions of **1** with organometallic compounds R′M (**5**) proceed via a tetrahedral intermediate **6** (Reaction b in Scheme 1). In the case of X = Hal, SR, and OR, **6** undergoes a very fast 1,2-elimination of MX to give aldehyde or ketone **7**, which may react further with **5**. In the case of X = NR_2, **6** is more stable, a fact that has been utilized for the preparation of ketones **7** (**1** + **5** → **6**; **6** + H_3O^+ → **7**)[3] as well as for the protection of aldehydes and ketones (**7** + MNR_2 → **6**).[4] What is the structure of a compound of type **6**, and in particular what is the environment at the new tetrahedral carbon atom? The X-ray crystal structure of $[(Ph)_2(NMe_2)C(OLi)\cdot THF]_2$ (**10**),[5] which is prepared from *N,N*-dimethylbenzamide (**8**) and phenyllithium (**9**) and crystallized from tetrahydrofuran/diethyl ether [Eq. (1)], gives an answer to these questions (Figure 1).



Scheme 1. Reaction of carboxylic acid derivatives **1** with nucleophiles YH (**2**; a) and R′M (**5**; b). R = H, alkyl, aryl; X = Hal, SR, OR, NR_2; YH = R″SH, R″OH, R″NH_2; R″ = H, alkyl, aryl; R′ = alkyl, aryl; M = Li, MgX, etc.



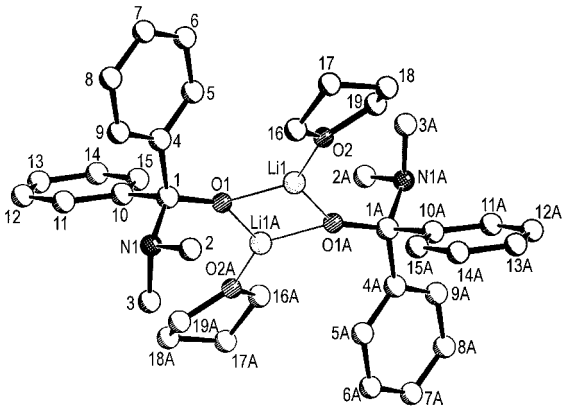


Figure 1. Crystal structure of **10**. Important bond lengths [pm] and bond angles [°]: C1–O1 137.1(2), C1–N1 150.0(3), C1–C4 154.8(3), C1–C10 154.9(3), Li1–N1 375.1(4), Li1–N1A 373.7(4); O1-C1-N1-C2 – 58.4(2), O1-C1-N1-C3 63.8(2), C4-C1-N1-C2 65.3(2), C10-C1-N1-C3 – 60.8(2).

In the dimeric structure the Li atoms Li1 and Li1A are bound to the anionic O atoms O1 and O1A and to the O atom of a THF molecule (O2 and O2A, respectively), leading to three-coordinate Li cations, which is rarely observed. The C1–O1 bond is 137.1(2) pm long, which corresponds to the C–O bond length in an α-alkoxyamine (137 pm).[6] In $(CH_3)_3C$–OLi a length of 139.2 pm has been determined for

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