Porphyrid Complexes with Highly Electronegative Metals – A New Chapter in Nucleophilic Substitution of Hydrogen?

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Abstract: The attempts of direct substitution of hydrogen in porphyrin macrocyclic systems, with carbanions of weak nucleophilicity, are described. Porphyrins, when converted into the corresponding metal chelates, were reacted with the above mentioned carbanions, and the coordinated central metal atom (e.g., Au(III), Sn(IV)), which reveals considerable electronegativity, played a role of activating group. It could be easily removed from the system after reaction. A number of attempts to substitute hydrogen by carbon nucleophiles led to various products (addition of nucleophile to porphyrin ring, ligands substitution at metal center, etc.). These investigations were successfully finalized for meso-tetraphenylporphyrin–dichlorotin(IV) complex. Further development of this idea may open a new chapter in the functionalization of porphyrins.

Keywords: Porphyrins, Gold and tin complexes, Nucleophilic substitution of hydrogen, Carbanions.

1. Introduction
The selective functionalization of porphyrins is intensively studied in recent years.1] Earlier, we published several examples of the reactions of weak nucleophiles (carbanions) with these compounds leading to substitution of hydrogen products, however, the macrocycle was activated by the strong electronwithdrawing groups, e.g. NO₂, which needs to be introduced to the porphyrin system before the reaction.1] We set up the hypothesis that the same role could be played by the central metal atom when porphyrins are converted into corresponding chelates. This approach has one considerable advantage. The metal can be easily removed (often with almost quantitative yield) from the system after the H-substitution reaction. This metal should reveal enough high electronegativity (e). The natural candidates for this purpose are metals of e higher than 2.0; e.g., Au (e = 2.54), Sb (2.05), W (2.36), Ge (2.01) (Pauling scale). So, their corresponding porphyrin complexes could be able to react even with weak carbanions. The solution of this problem may open a new chapter in the functionalization of porphyrins.

Herein, the studies on possibility of direct substitution of hydrogen in the porphyrin ring, activated by the highly electronegative central metal atom when porphyrins are converted into corresponding chelates, are described.

2. Results and discussion
2.1. Gold complexes. Electronegativity of gold is relatively high, e = 2.54. Thus, at the beginning, we tested 5,10,15,20-tetraphenylporphyrin–gold(III) chloride (meso-tetraphenylporphyrin–gold(III) chloride) (I) which can be easily prepared according to literature prescriptions.1) This porphyrinate was purified by column chromatography and the yield was even higher (76%) as compared to that described previously.1) However, its reaction with carbanion of CICH₂SO₂Tol, which usually allows nucleophilic substitution of hydrogen in electrophilic aromatic compounds according to vicarious nucleophilic substitution mechanism (VNS),1[ herein, in t-BuOK/THF system, led to a complicated mixture of several products. They were probably an effect of ligand-exchange processes. Some modifications of the procedure and the reaction conditions did not give better results (see Experimental). Next, we have undertaken some attempts to enhance the electrophilicity of the parent system by exchanging Cl⁻ ligand for CN⁻. However, in this case, CN⁻ instead of exchange chloride Cl⁻ anion entered immediately the addition to meso-carbon atom, thus giving phlorin moiety 3 (80%; Scheme 1). Similar reactions (with OH⁻) for gold(III) and for antimony(V) porphyrin complexes were observed by Segawa1[ and Knör.6]

We also tried to use another model, 2,3,7,8,12,13,17,18-octaethylporphyrin complex ([OEP-Au(III)]Cl,
4; having unsubstituted meso-positions). In this case, the synthesis of the substrate was somewhat troublesome. When the reaction was carried out in CHCl₃/ AcOH mixture (OEP + KAuCl₄ + AcONa, 19 h, reflux), unexpectedly the only product obtained (with very small yield; 7.7%) was the acetooxy-derivative 5 (Figure 1). It was probably formed via tandem chlorination / Cl⁻→AcO⁻ exchange processes (source of chloride: KAuCl₄). At higher temperature (130°C) in DMF/CHCl₃, after shortening the reaction time to 13 h, the chlorinated product 6 was isolated in poor yield (7.8%), along with a large amount of the starting octaethylporphyrin (63%). Its meso-Cl structure was elucidated by HR-MS and ¹H NMR measurements. Finally, in the reaction carried out in chloroform/methanol mixture (60°C, 20 h) both the above products were identified. In all the experiments the conversion rate was rather low and a lot of substrate OEP was recovered. In some reactions we also observed a pink, very polar spot on TLC which after longer period of time of refluxing disappeared.

Analysis of the reaction mixture (after 3 h of heating in CHCl₃/AcOH) allowed us to identify this new compound(s). Probably this is a mixture of gold complex chloride of octaethylporphyrin (4); on the basis of HR-MS (ESI): m/z = 729.3239 [(M(4)-Cl)⁺]; C₃₆H₃₆Cl₂Au and its derivative 7 with additional Cl tethered to CH₂CH₂ chain or introduced to the meso-position (m/z = 763.2869 [(M(7)-Cl)⁺]; C₃₆H₃₄Cl₃Au).

The attempts to obtain the desired complex 4 directly by the macrocyclization, in which from the beginning of the reaction an excess of KAuCl₄ was added to cause a template effect, also failed. Due to the above problems with the synthesis of the desired gold substrate the investigations were temporarily suspended. It is worth mentioning that Jamin and Iwamoto observed similar difficulties when trying complexation of etioporphyrin with KAuCl₄.[⁹]

2.2. Tin complexes: meso-tetraphenylporphyrin–dichlorotin(IV) and octaethylporphyrin–dichlorotin(IV) systems. We tried to verify the above concept using another relatively easily available porphyrin complexes (dichlorotin derivatives; ε₉₀ = 1.96): octaethylporphyrin–dichlorotin(IV) (8) and meso-tetraphenylporphyrin–dichlorotin(IV) (9). They were synthesized on the basis of two literature reports.[⁹] Nevertheless, some modifications were introduced (sulfolane as a solvent, 170–200°C, ca 1 h, 68–100%; see Experimental). Confirmation of their structures was not a trivial problem. In MS spectrum of product 8 (ESI(+), in MeOH) instead of molecular and pseudomolecular ions M⁺ or (M+H)⁺, we observed another ions, probably formed during the measurements (m/z = 665 and m/z = 679; see Figure 2). Their formation can be explained easily by the ligand-exchange and ligand-losing processes. This is rather characteristic in the chemistry of such labile chelates and we observed it earlier.[¹⁰] In MS-FD spectrum the only observed peaks also were originating from the fragmentation ions and multicharged ions. Thus, the structure cannot be confirmed definitively on the basis of these data.

Some verifications came from the ¹H NMR studies. The spectrum was in agreement with the structure.

**Figure 1**
The diagnostic singlet at δ = 10.48 ppm (4H), originating from meso-protons, and triplet/quartet pattern [2.04 ppm (24 H) and 4.21 ppm (16 H); 8×Et] confirm the structure of the expected porphyrinate. Additionally, the signal at δ = -3.73 ppm (characteristic for the inner NH-protons in substrate) disappeared, thus providing evidence for full conversion of octaethylporphyrin into complex 8.

![Figure 2](image)

The complex obtained 8 was reacted, in the presence of base, with CH(Br)SO₂Tol carbanion, and we expected nucleophilic substitution of hydrogen [4] in meso-position. It could be an exceptional example of direct substitution of hydrogen with a carbanion nucleophile in porphyrinoid system. However, the reaction failed to afford the desired product. When analyzing the post-reaction mixture by MS method (APPI–photospray(+) in AcOEt), we observed only the fragmentation ions as a result of ligand-exchange and ligand-losing process in the substrate (m/z = 683, OEPSnCl⁺, and m/z = 707, OEPSn(OAc)⁺). There were no ions originated from the substitution of hydrogen product. The outcome of the reaction with carbanion of para-chlorophenoxyacetanitriile (CH(CN)OC₆H₄Cl''), which is stronger nucleophile as compared to CH(Br)SO₂Tol, was similar (degradation of the reagents occurred).

Finally, in the reaction of 5,10,15,20-tetraphenylporphyrin–dichlorotin(IV) (9) with halomethyl para-tolyl sulphone carbanion (CH(Cl)SO₂Tol; t-BuOK/ DMSO, r.t.) we observed the formation of new product (TLC monitoring). One can suppose it was a VNS product, formed due to substitution of hydrogen at the β-position. Initially, we couldn’t confirm its molecular formula directly by MS method; however, we found in the spectrum (ESI(+) in CH₃OH) an ion peak m/z = 927 originating from the product 10 (see Scheme 2 and Experimental). This ion is a result of ligand-exchange/ligand-losing process which is possible during the MS measurement. We supported this hypothesis when the sample of product was dissolved and measured in ethanol. The formation of the analogous ion m/z = 941 was observed. It seems these ions are rather strong evidence for the structure of the desired product because such an easy spontaneous conversion of dichlorotin porphyrin complexes into dialkoxy- and diphenoxy-tin moieties was reported earlier by Arnold [11]. Similar observations were made in our previous studies [10].

Nevertheless, finally we also detected the molecular ion of the examined compound by MS-FD method (m/z = 966; C₅₂H₄₃N₃O₂SnClSn). Independently, we confirmed its structure by ¹H NMR. All the diagnostic signals were found in the spectrum: 2.21 (s, 3H, CH₃–Tol), 4.62 (s, 2H, CH₂), 6.89/7.18 (2×d, 4 H, J = 8.2 Hz, H–Tol), and 9.05-9.24 (m, 7H²).

![Scheme 2](image)

Decomplexation of the product obtained with lithium in ethylenediamine (reflux, 3 h) [12] leads to the free base porphyrin moiety substituted with CH₂SO₂Tol group at the β-position (11, m/z = 782, M⁺, C₅₂H₄₃N₃O₂S); and this is one more proof for the structure 10.

3. Conclusions
We reported herein the attempts of direct nucleophilic substitution of hydrogen in porphyrin systems, activated by the coordinated central metal atom (of increased electronegativity), when porphyrins are converted into the corresponding chelates. Complexes of Au(III) and Sn(IV), and their reactions with carbanions of weak nucleophilicity, were examined. These investigations were successfully finalized for meso-tetraphenylporphyrin–dichlorotin(IV) complex.

The above mentioned metal atom played a role of activating moiety, as well as a labile protective group...
for the inner NH-protons, and after reaction can be easily removed from the system, if needed. We believe that our concept involving complexation/de-complexation procedure and new type of activation for nucelophilic attack will receive future attention in the area of porphyrin skeleton functionalizations. Further development of this idea may also open a new chapter in nucelophilic substitution of hydrogen in aromatic and heteroaromatic compounds.

Experimental

**General.** $^1$H NMR spectra were recorded with a Varian MR-400 spectrometer operating at 400 MHz. Coupling constants $J$ are expressed in hertz [Hz]. Mass spectra were measured with a GCT Premier (Waters, FD-TOF) spectrometer (FD method), MARINER (PerSeptive Biosystems, ESI-TOF) spectrometer (ESI method), and 4000-QTRAP (Applied Biosystems) spectrometer (ESI–turbospray and APPI–photospray methods); $m/z$ intensity values for peaks are given as a % of relative intensity. UV-Vis spectra were measured with a Beckman DU-68, Metertech SP-8001, and UV-3600 Shimadzu spectrophotometers. TLC analysis was performed on aluminium foil plates pre-coated with silica gel (60 F-254, Merck AG). All the products were isolated by column chromatography (silica gel, 230-400 mesh; Merck AG); some compounds and fractions were isolated or rechromatographed on preparative TLC plates (silica gel, 60 F-254, 0.5 mm; Merck AG).

Molecular formulas of new compounds were confirmed by elemental analysis, HR-MS (ESI and FD), and by comparing the isotope molecular patterns (theoretical and experimental).

Porphyrinate 1 was obtained according to known procedure described in the literature [3] (modification: in AcO/HCl/HCl, 3:2). It was isolated by column chromatography (elucent: CHCl$_3$/MeOH, 1:1), yield, 76%; lit., [13] 70%.

Also octaethylporphyrin was obtained according to known procedure. [13] Octaethylporphyrin–dichlorotin(IV) complex (8) was prepared therefrom according to modified procedure described in the literature for similar compounds [6,8] (Octaethylporphyrin (50 mg, 0.094 mmol) and SnCl$_2$·2H$_2$O (31 mg, 0.137 mmol) in sulfone (4 mL) were heated (under argon) at 170°C in a round-bottomed light-shielded flask equipped with a reflux condenser over a period of 1.5 h. Then, the reaction mixture was cooled to room temperature and to this mixture CHCl$_3$ (30 mL) was added. The organic layer was washed with water (4×40 mL) and dried with anhydrous MgSO$_4$. After evaporating the solvent, the column chromatography was performed using gradient mixture as eluent (from CHCl$_3$ to CHCl$_3$/MeOH, 20:1) to give product 8; yield – 46 mg (68%).

Similarly, 5,10,15,20-tetraphenylporphyrin–dichlorotin(IV) (9) was obtained (reaction temp. 200°C, 1 h); yield – 100%, lit., [8] 85%.

**Data for substrates:**

(5,10,15,20-Tetraphenylporphyrinato)gold(III) chloride (1): Its $^1$H NMR and UV-Vis spectra were in agreement with those reported earlier in the literature [8a] MS (APPI–photospray (+)); $m/z$ (% rel. int.): 811 (16), 810 (56), 809 (100) [isotope M–Cl (m-TPP)Au$^+$/]; MS (APPI–photospray(–)); $m/z$ (% rel. int.): 343 (5), 341 (21), 339 (42), 337 (34) [isotope (AuCl)$_3$]; 271 (14), 269 (68), 267 (100) [isotope (AuCl)$_2$].

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(38), 765 (49), 764 (18), 763 (21) [isotope (M–Cl)]
737 (8), 736 (15), 735 (7), 734 (19), 733 (40), 732
(100), 731 (57), 730 (78), 729 (40), 728 (38) [isotope
(M–2×Cl)]
368.5 (1.0), 368 (2.1), 367.5 (2.1), 367
(4.2), 366.5 (7.5), 366 (15), 365.5 (10), 365
(12), 364.5 (7.4), 364 (7.8) [isotope (M–2×Cl)]
. The molecular formula was confirmed by comparing the
theoretical and experimental isotope patterns for the M
ion (C28H26N2SnCl2); it was found to be identical
within the experimental error limits. Other MS
investigations: MS (ESI, CH3OH); m/z (% rel. int.):
769 (5), 768 (8), 767 (15), 766 (12), 765 (26), 764
(54), 763 (100), 762 (57), 761 (70), 760 (32), 759
(27) [isotope m–TPPSn(OCH3)]
. MS (ESI–turbo
spray, CH3OH/CH2Cl2); m/z (% rel. int.): 769 (4), 768
(10), 767 (20), 766 (11), 765 (28), 764 (52), 763
(100), 762 (62), 761 (85), 760 (45), 759 (43) [isotope
m–TPPSn(OCH3)]
. MS (ESI–turbo-spray, (CH3)2CHOH/CH2Cl2); m/z (% rel. int.):
797 (3), 796
(9), 795 (17), 794 (9), 793 (27), 792 (52), 791
(100), 790 (59), 789 (74), 789 (40), 787 (39) [isotope
m–TPPSn(OCH3/CH2Cl2)]
. MS (APPI–photospray, AcOEt
/CH2Cl2); after treatment of 9 with H2O; m/z (% rel. int.):
796 (4), 795 (10), 794 (6), 793 (14), 792 (26), 791
(51), 790 (29), 789 (37), 788 (19), 787 (18) [isotope
m–TPPSn(OAc)]
. 770 (3), 769 (8), 768 (10), 767
(21), 766 (11), 765 (18), 764 (18), 763 (31) [isotope
m–TPPSnCl3, M–Cl]; 755 (3), 754 (8), 753 (19),
752 (9), 751 (26), 750 (50), 749 (100), 748 (57), 747
(71), 746 (37), 745 (40) [isotope (M+H)] of side product
formed via partial spontaneous hydrolysis of 9 followed by
dehydration; m–TPPSn(O=)
. Elemental anal.
calculated for C48H34N2SnCl4×2H2O (838.36):
C, 63.04; H, 3.85; N, 6.68. Found: C, 63.36; H, 4.40;
N, 5.96.

Reaction of 1 with carbanion of CICH2SO2Tol in
t–BuOK/THF system

Procedure A: In a round-bottomed flask t–BuOK (50
mg, 0.45 mmol) was stirred in anhydrous THF (7
mL; under argon) at room temperature for 6 hr. To
this solution a mixture of porphyrin–gold(III)
chloride (1; 50 mg, 0.059 mmol) and chloromethyl
para-tolyl sulphine (98 mg, 0.479 mmol) in THF (5
mL) was added dropwise via syringe. After 30 min of
stirring, the mixture was poured into 3% HCl
containing ice (10 mL) and extracted with CHCl3
(3×15 mL). The combined organic layers were
washed with water (3×50 mL) and dried with
anhydrous MgSO4. Several products were observed
(TLC monitoring). After evaporation of the solvent,
the column chromatography was performed using gradient mixture as eluent (from CHCl3 to
CHCl3/MeOH, 20:1). None of the defined products
were isolated.

Procedure B: In a round-bottomed flask chloromethyl
para-tolyl sulphine (87 mg, 0.425 mmol) was stirred in anhydrous THF (3 mL; under argon) at
room temperature for 2 hr. To this solution

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subjected to column chromatography (eluent: CHCl₃/n-hexane, 2:1); 3.4 mg of product 5 was isolated (7.7%), along with the recovery of 5.4 mg of octaethylporphyrin (13.5%).

Procedure B: In a round-bottomed flask, equipped with a reflux condenser, KAuCl₄ (37 mg, 0.098 mmol) and AcONa (46 mg, 0.56 mmol) were preheated to reflux (under argon) in DMF (4 mL) for ca 20 min. Then, octaethylporphyrin (40 mg, 0.075 mmol) dissolved in DMF–CHCl₃ mixture (24 mL; 1:2) was added and the reaction was continued at 130°C for the next 1.3 h. To this mixture (cooled to room temperature), CHCl₃ (40 mL) was added and it was washed with water (3×40 mL). Isolation of the product – as in Procedure A (eluent for chromatography – CHCl₃/n-hexane, 2:1; then CHCl₃); recovery of octaethylporphyrin, 25 mg (63%); product 6, 3.3 mg (7.8%).

Procedure C: As in Procedure A. Reagents: KAuCl₄ (40 mg, 0.106 mmol) and AcONa (46 mg, 0.56 mmol) in CHCl₃/MeOH (4 mL; 1:1) were heated to reflux for ca 5 min; octaethylporphyrin (40 mg, 0.075 mmol) dissolved in CHCl₃/MeOH (16 mL; 3:1); reaction time – 20 h (at 60°C). Recovery of octaethylporphyrin, 25.6 mg (64%); product 6, 3.9 mg (9.1%); product 5, 4.0 mg (9.0%).

When the reaction was carried out according to Procedure A and the time was shortened to 3 h (heating at reflux) a mixture of products 4 and 7 was isolated (by preparative TLC; eluent: CHCl₃, five times developed); yield below 5%.

5: M.p. > 300°C. ¹H NMR (CDCl₃, 400 MHz); δH [ppm]: 10.65 (s, 1H, H-meso), 10.12 (s, 2H, H-meso), 4.20–4.05 (m, 16H, 8×CH₂), 2.31 (s, 6O-COCH₃), 1.96–1.90 (m, 24H, 8×CH₃), -3.70 (broad s, 2H, 2×NH). UV-Vis spectrum was not recorded because this compound still was contaminated with small amounts of other by-products. MS (ESI); m/z (% rel. int.): 595 (11), 594 (43), 593 (100) [isotope (M+H)+]. MS (ESI): calculated for C₃₃H₃₈N₄O₂; [M(H)+] – 593.39, found – 593.40. The molecular formula was also confirmed by comparing the theoretical and experimental isotope patterns for the (M+H)+ ion (C₃₃H₃₈N₄O₂): it was found to be identical within the experimental error limits.

6: M.p. > 300°C. ¹H NMR (CDCl₃, 400 MHz); δH [ppm]: 10.09 (s, 2H, H-meso), 9.88 (s, 1H, H-meso), 4.22 (q, J = 7.5 Hz, 4H, 2×CH₂), 4.14–3.99 (m, 8 lines, 12H, 6×CH₂), 1.94–1.83 (m, 6 lines, 24H, 8×CH₃), UV-Vis (CHCl₃); λmax [nm] (log ε): 630 (3.00), 577 (3.64), 541.5 (3.63), 507 (4.07), 408.5 (5.15; Soret band). MS (ESI); m/z (% rel. int.): 1143 (0.7), 1142 (1.6), 1141 (3.3), 1140 (5.1), 1139 (7.8), 1138 (7.4), 1137 (8.2) [isotope (2×M+H)+]; 573 (4), 572 (15), 571 (39), 570 (44), 569 (100) [isotope (M+H)+]. HR-MS (ESI): calculated for C₃₉H₅₄N₄Cl [(M+H)+] – 569.3411, found – 569.3423. The molecular formula was also confirmed by comparing the theoretical and experimental isotope patterns for the (M+H)+ ion (C₃₉H₅₄N₄Cl); it was found to be identical within the experimental error limits.

Mixture of compounds 4 and 7; their structures were proposed on the basis of MS spectrum: MS (ESI, CH₃OH/CH₂Cl₂); m/z (% rel. int.): 766 (5), 765 (11), 764 (13), 763 (28) [compound 7; isotope (M–7–Cl)+]; 731 (10), 730 (46), 729 (100) [compound 4; isotope (M–4–Cl)+]. HR-MS (ESI); compound 7, calculated for C₈₆H₇₅N₃Cl[(M–7–Cl)+]–763.2842, found – 763.2869; compound 4, calculated for C₈₆H₇₅N₃Cl[(M–4–Cl)+]–729.3232, found – 729.3239.

Substitution of hydrogen in porphyrin systems with carbanions of halomethyl para-tolyl sulphones (XCH₂SO₂ Tol)
In a round-bottomed light-shielded flask r-BuOK (88 mg, 0.78 mmol, for 8: 41 mg, 0.37 mmol, for 9) was stirred under argon in anhydrous THF (16 mL, for 8) or in DMSO (3.5 mL, for 9) at room temperature. To this solution, a mixture of porphyrin (8: 57 mg, 0.079 mmol; 9: 41.1 mg, 0.051 mmol) and BrCH₂SO₂Tol (44 mg, 0.177 mmol; for 8) or CICH₂SO₂Tol (22.5 mg, 0.110 mmol; for 9) in THF (12 mL; for 8) or in DMSO (2.0 mL; for 9) was added dropwise via syringe (septum) over a period of ca 5 min. After 0.5–1.5 h of intense stirring (TLC monitoring; CHCl₃/MeOH, 15:1), the mixture was poured into 3% HCl containing ice (50 mL) and extracted with CHCl₃ (5×25 mL). The combined organic layers were washed with water (4×40 mL) and dried with anhydrous MgSO₄. After evaporating the solvent, the residue was analyzed by TLC and MS. In the mixture obtained from 8 none of the defined products were observed and ions originating from the substrate were identified only in MS spectrum [APPI–photospray(+) in AcOEt; m/z (% rel. int.): 715 (3.3), 714 (2.4), 713 (4.1), 712 (5.0), 711 (12), 710 (6.5), 709 (8.9), 708 (4.1), 707 (4.5) [isotope OEPSn(OAc)³]; 693 (6.7), 692 (7.3), 691 (18), 690 (14), 689 (45), 688 (46), 687 (100), 686 (52), 685 (72), 684 (30), 683 (33) [isotope OEPSnCl⁴⁺].

The crude mixture obtained from 9 was subjected to column chromatography using gradient mixture as eluent (CHCl₃/n-hexane, 2:1; CHCl₃); then CHCl₃/MeOH, from 20:1 to 5:1); 13 mg of the substrate was recovered (32%); then, 21.5 mg of product 10 was isolated (43.5%).

M.p. > 300°C. ¹H NMR (CDCl₃, 400 MHz); δH [ppm]: 9.24–9.05 (m, 7H, H₅-pyrrrole), 8.40–8.15 (m, 8H, H–Ph), 7.90–7.70 (m, 12H, H–Ph), 7.18 (d, J = 8.2 Hz, 2H of H–Tol), 6.89 (d, J = 8.2 Hz, 2H of H–Tol), 4.62 (s, 2H, CH₂), 2.21 (s, 3H, CH₃). UV-Vis spectrum was not recorded because this compound was contaminated with small amounts of side
products formed via spontaneous hydrolysis and subsequent dehydratation; see MS investigations below. MS (FD); m/z (% rel. int.): 976 (10), 975 (9), 974 (11), 973 (10), 972 (12), 971 (17), 970 (22), 969 (18), 968 (9), 967 (8), 966 (11) [isotope M⁺]; 939 (7), 938 (9), 937 (11), 936 (15), 935 (22), 934 (10), 933 (12), 932 (18), 931 (16) [isotope (M–Cl)]; 838 (18), 837 (30), 836 (32), 835 (80), 834 (100), 833 (49), 832 (80), 931 (42), 830 (57) [isotope (M–2+Cl–SO₂)⁺]; 781 (15), 780 (25), 779 (41), 778 (74), 777 (28), 776 (48) [isotope (M–Cl–SO₂Tol)⁺]; 749 (20), 748 (35), 747 (31), 746 (41), 745 (43), 744 (95), 743 (60), 742 (52), 741 (30), 740 (48) [isotope (M–Cl–HCl–SO₂Tol)⁺]. Other MS investigations: MS (ESI, CH₃OH); m/z (% rel. int.): 937 (11), 936 (15), 935 (22), 934 (20), 933 (39), 932 (63), 931 (100), 930 (57), 929 (63), 928 (32), 927 (22) [isotope (M–2+Cl+OCH₃)⁺]: C₅H₇NO₂SnSn. The molecular formula was confirmed by comparing the theoretical and experimental isotope patterns for the (M–2+Cl +OCH₃)⁺ ion (C₅H₇NO₂SnSn); it was found to be identical within the experimental error limits. MS (ESI, CH₃OH); m/z (% rel. int.): 951 (12), 950 (17), 949 (23), 948 (24), 947 (42), 946 (66), 945 (100), 944 (61), 943 (69), 942 (36), 941 (30) [isotope (M–Cl +OCH₃H⁺): C₅H₇NO₂SnSn]. MS (ESI–turbo-spray, CH₃CN/CHCl₃); when left for a longer period of time, compound 12 was formed via spontaneous hydrolysis and subsequent dehydratation; m/z (% rel. int.): 923 (6), 922 (11), 921 (21), 920 (14), 919 (36), 918 (56), 917 (100), 916 (87), 915 (99), 914 (49), 913 (43) [isotope (M+H)⁺ of 12; (TPP(SnO)CH₃SO₂Tol+H⁺)]. The molecular formula was confirmed by comparing the theoretical and experimental isotope patterns for the (M+H)⁺ ion (C₅H₇N₂O₂SnSn); it was found to be identical within the experimental error limits.

Decomplexation of VNS product 10

A crude sample of product 10 (6.4 mg) in ethylenediamine (4 mL) was preheated to reflux (under argon) in a round-bottomed flask equipped with a reflux condenser. After 1 h, 34 mg of lithium was added (as thin wires) and the reaction was continued at reflux for the next 3 h. Then, the post-reaction mixture was poured into water (30 mL) and extracted with CHCl₃ (3×20 mL). The combined organic layers were washed with water (3×30 mL) and dried with anhydrous MgSO₄. After evaporation of the solvent, the residue was analyzed by MS method. The molecular ion originating from the desired product 11 was observed. MS (APPI–photospray(+), AcOEt/CH₂Cl₂);

m/z (rel. int.), among other ions: 787 (2.3), 786 (2.0), 785 (4.2), 784 (3.9), 783 (7.4), 782 (6.0) [isotope M⁺ and (M+H)⁺ of 11; C₅H₇N₂O₂SnSn].
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[15] Three of naturally occurring isotopes of tin (\(^{115}\)Sn, 0.3%; \(^{117}\)Sn, 7.7%; \(^{119}\)Sn, 8.6%) are magnetically active, and the doublet is a consequence of tin-proton coupling constants of these isotopes to the β-pyrole protons.