

Salophan Complexes of Group IV Metals

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The coordination chemistry of tetradentate Salophan ligands with titanium and zirconium alkoxides is described for the first time. Three new Salophan ligand precursors featuring different phenolate substituents (*ortho*-Me, *ortho,para*-di-Cl, *ortho,para*-di-*t*Bu) were synthesized in addition to the known prototypical Salophan precursor, by a sequence of condensation and reduction. All ligand precursors were reacted with the metal alkoxides Ti(O*i*Pr)₄ and Zr(O*t*Bu)₄. The unsubstituted Salophan led to a complex product mixture for both titanium and zirconium. The methyl-substituted ligand led to a clean complex only with zirconium, and the other ligands gave well-defined coordination chemistry with both metals.

NMR analysis indicated that these Salophans acted as dianionic ligands, giving rise to hexa-coordinate complexes of C₂-symmetry. X-ray analysis of three complexes supported this view, and revealed that the ligands wrapping mode was *fac-fac* and that the orientation of the labile groups was *cis*. A partial hydrolysis of one of the titanium complexes led to a dinuclear bridging oxo complex in which the ligand wrapping mode had changed to *fac-mer*, as revealed from its crystal structure.

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Introduction

Tetradentate diamino-diphenolate [ONNO]-type ligands exhibit a versatile chemistry with many transition and main-group elements.^[1–4] Salan-type ligands bind to early transition metals almost exclusively in a *fac-fac* geometry, forming octahedral C₂-symmetrical complexes with the two labile groups in a *cis* geometry. This disposition is suitable for olefin polymerization catalysis.^[2,5] In contrast, Salen-type ligands exhibit mostly a *mer-mer* geometrical preference, leading to *trans* disposition of the labile groups.^[6] It would thus seem that the hybridization at the nitrogen atom, i.e. sp² or sp³, plays a major role on the [ONNO] ligand wrapping mode.^[7] In this regard, the coordination mode of Salan-type ligands, featuring an aromatic spacer between the two nitrogen donors (also known as Salophan ligands), is intriguing when compared with the common Salan ligands possessing an aliphatic spacer.

Lig¹H₂, the prototypical Salophan ligand that features no substituents on the phenolate rings, was studied by several research groups,^[8,9] and its coordination behavior was reported to be versatile. Atwood and co-workers have shown that, upon binding to group III alkyls (Al, Ga), this ligand normally acts as a tetra-anionic ligand, forming complexes of varying nuclearity.^[8a–8c] In most cases, the ligand was found to bind to the “central” Al in a “flat” fashion, forming the basis of a square-pyramidal complex. For

Zn, this ligand acted as a dianionic ligand, forming a dimeric pentacoordinate complex.^[8d] For Mo^{VI}, Lig¹H₂ may bind as a tetradentate dianionic ligand, wrapping around the metal in a *fac-fac* fashion forming octahedral complex, or as a tridentate tri-anionic ligand (one of the phenolates unbound and protonated), forming a *mer*-bis(homoleptic) complex.^[9] As part of our continuing interest in various [ONNO]-type ligands, we report herein on the preparation of new Salophan-type ligands, and describe our initial results concerning their chemistry with Group IV metals.

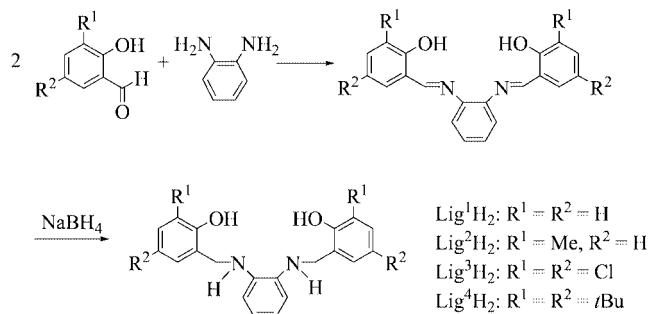
Results and Discussion

Two readily available complexes, Ti(O*i*Pr)₄ and Zr(O*t*Bu)₄, were used as metal precursors for alcoholysis reactions with the ligand precursors. All reactions were performed by adding an ethereal solution of the corresponding ligand to a stirred solution of the metal precursor at –30 °C, followed by warming to room temp. and stirring for an additional hour. At first, we explored the reactivity of the prototypical ligand, Lig¹H₂. The reaction between Lig¹H₂ and Ti(O*i*Pr)₄ led to the formation of a red material whose NMR spectra indicated a complex mixture featuring at least six different methyl groups. Under the same conditions, the reaction of Lig¹H₂ and Zr(O*t*Bu)₄ also led to a complex mixture. We therefore turned to substituted ligands.

For this purpose, we prepared three additional Salophan-type ligands, having varying steric and electronic influence. In comparison to Lig¹H₂, Lig²H₂ features electron-donating methyl groups at the *ortho* positions of the phenolate

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rings, Lig³H₂ features electron-withdrawing chloro groups at the *ortho*, *para* positions, and Lig⁴H₂ bears bulky electron-donating *t*Bu groups at the *ortho*, *para* positions. The ligands were prepared by a two-step route involving condensation between the corresponding 2-hydroxybenzaldehyde and 1,2-phenylenediamine, followed by reduction with sodium borohydride (Scheme 1). For Lig¹H₂ – Lig³H₂, this route is practical, and leads to the desired ligand precursors smoothly in high yields. For Lig⁴H₂, this route is not very effective, as the reduction of the Schiff-base intermediate is very slow, and leads to additional products. Fortunately, the solubility of Lig⁴H₂ in methanol is low, so it may be purified by methanol washings of the crude product, or by column chromatography.



Scheme 1. Synthesis of Salophan ligands Lig¹H₂ – Lig⁴H₂.

The reaction between Lig²H₂ bearing methyl substituents and Ti(O*i*Pr)₄ led to an initial off-white solid whose color changed within a few minutes to deep-red. The ¹H NMR spectrum of this product exhibited broad signals that may indicate some equilibrating species. Recrystallization of this product from cold ether yielded bright-yellow crystals (**2-Ti**), whose solid-state structure was consistent with all subsequent structures (*vide supra*). However, dissolving these bright-yellow crystals in deuteriobenzene led to a deep red color in seconds, and the spectrum was consistent with the spectrum of the crude product, containing only broad absorptions. In contrast, the initially-formed Zr complex of this ligand, **2-Zr**, did not change color either in the solid phase or in solution for prolonged periods of time, and its ¹H NMR spectrum featured sharp absorptions. Interestingly, Lig³H₂ that carries chloro groups, reacted cleanly with both titanium and zirconium to giving the well-defined **3-Ti** and **3-Zr**, respectively, albeit the smaller size of the Cl groups. The bulky Lig⁴H₂, carrying *t*Bu groups near the metal center, also presented a well-behaved reactivity with both metals, yielding the species **4-Ti** and **4-Zr** cleanly.

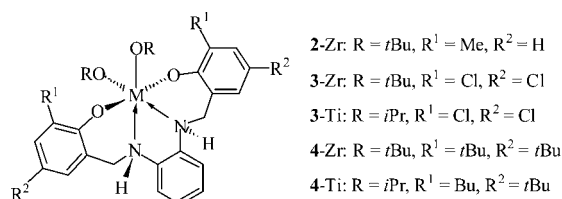


Figure 1. The C₂-symmetrical structure of Salophan-Group IV metal complexes.

Thus, relative to Lig²H₂, both the electron withdrawing ligand Lig³H₂ and the bulky ligand Lig⁴H₂ lead to well defined products. The stable Salophan complexes obtained in this work are outlined in Figure 1.

The ¹H and ¹³C NMR spectra support a C₂-symmetry of all these complexes as judged by the presence of two distinct aromatic doublets for the phenolate hydrogens, an AB system for the ligand methylene protons, and a single type of labile groups. The diastereotopic methyl groups of the isopropoxide ligands give rise to two peaks in both ¹H and ¹³C NMR spectra of the titanium complexes. According to the presence of NH signals in the ¹H NMR spectra and the number of labile groups, these ligands bind to the metal centers in a dianionic fashion. Interestingly, the ligand methylene protons present an additional splitting, seemingly from the NH proton, and this splitting is different for the diastereotopic CH₂ protons. In the sterically congested **4-Ti** complex, two types of splitting are clearly observed (1.2 Hz, 2.7 Hz), while in the more open **3-Ti** complex, only one type of splitting (2.1 Hz) could be observed. For the zirconium species, only one of the AB signals exhibits this additional splitting, and it is consistent throughout the series (3.0–4.0 Hz).

X-ray quality crystals of the complexes **3-Zr**, and **4-Ti**, were obtained upon recrystallization from pentane, and their crystal structures were solved, in addition to the structure of **2-Ti**, obtained upon recrystallization from ether (for the crystal structures see Figure 2, Figure 3 and Figure 4). In agreement with the NMR spectroscopic data, the Salophan ligands wrap around the Group IV metals in a *fac-fac* mode to afford non-crystallographic C₂-symmetrical complexes. As previously observed for the complexes of the Salophan series, the phenolate oxygen atoms are located mutually *trans* (160° for **2-Ti**, 156° for **3-Zr**, 160° for **4-Ti**), and the monodentate ligands are mutually *cis* (106° in **2-Ti**, 108° in **3-Zr**, 105° in **4-Ti**), and *trans* to the amine donors (159–166°). Thus, the exchange of the aliphatic spacer between

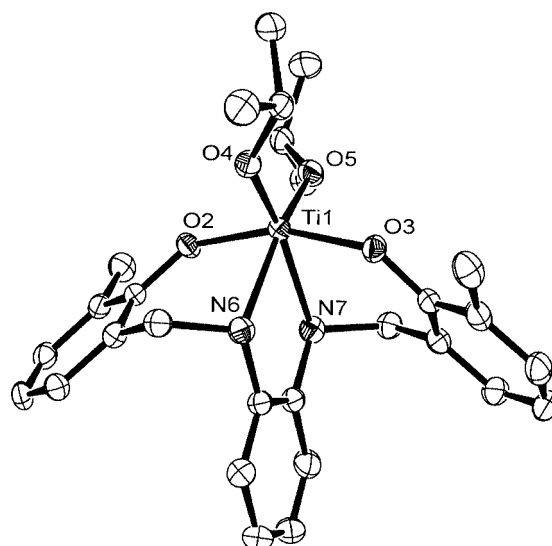


Figure 2. ORTEP representation (50% probability ellipsoids) of **2-Ti**; hydrogen atoms are omitted for clarity.

two amine donors by an aromatic one preserves the overall binding mode in this ligand family. Moreover, the N–M dative bonds for the potentially poorer σ -donor (aniline) are very close to the N–M dative bonds in the complexes featuring ethylene diamine backbone (2.31 Å for **4-Ti** vs. 2.29 Å for the analogous complex with the ethylene diamine backbone).^[2b] The M–OPh bond lengths are also comparable to those reported for Salan complexes, with a slight

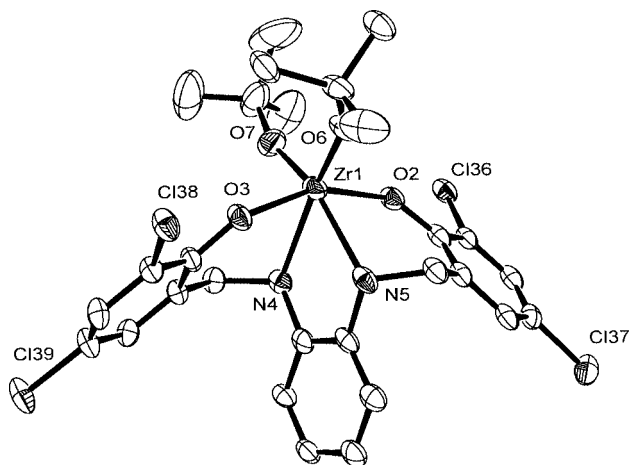


Figure 3. ORTEP representation (30% probability ellipsoids) of **3-Zr**. A second, chemically identical molecule, that is present in the asymmetric unit, crystallization solvent and the hydrogen atoms are omitted for clarity.

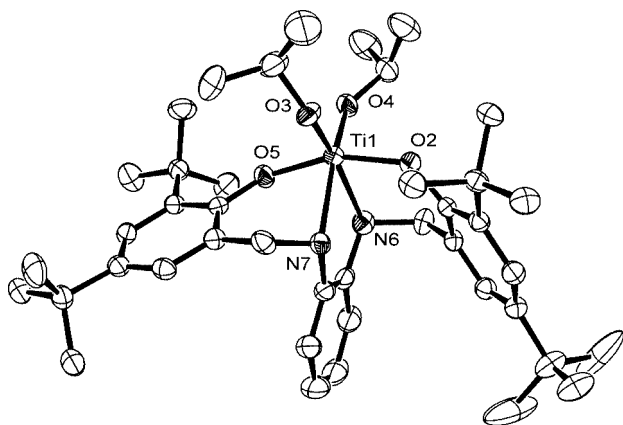
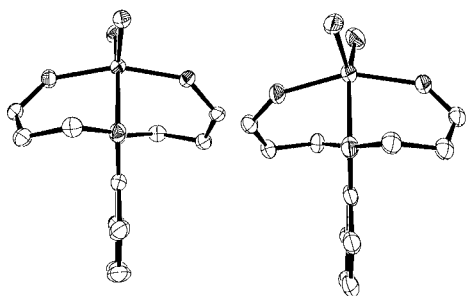


Figure 4. ORTEP representation (50% probability ellipsoids) of **4-Ti**; hydrogen atoms were omitted for clarity.



difference for Zr {2.05 Å for **3-Zr** vs. 2.01 Å for [Salan]-Zr(CH₂Ph)₂}^[2a] probably resulting from the bulkier monodentate ligands. Most notably, the metal is coplanar with the phenylene diamine unit for the sterically open **2-Ti** and **3-Zr**, while for the sterically congested **4-Ti**, the metal lies slightly outside the phenyl plane (see Figure 5).

We found that the titanium complexes are relatively unstable to hydrolysis. For example, the sterically congested complex **4-Ti** undergoes a slow decomposition when stored in a paraffin-sealed NMR tube outside the glovebox. The resulting main product, **4-Ti-a**, which is only slightly soluble in benzene, crystallizes out to give yellow crystals. The NMR spectrum of this compound is complicated, and shows a low symmetry of the ligand backbone, being composed of four *t*Bu peaks, two N–H signals, and four different methylene signals (coupled to two carbon atoms). In addition, the spectrum contains a single isopropoxide group. The X-ray structure determination disclosed a dinuclear structure with a [Ti₂O] μ -oxo core (see Figure 6). Each Ti center is of nearly octahedral geometry, being surrounded by a bridging oxo ligand (Ti1–O 1.848 Å, Ti2–O 1.834 Å), and the isopropoxide ligand, in addition to the [ONNO] donor set of the Salophan ligand. The Ti–OPh distances differ significantly, with the Ti–OPh bond length *trans* to the oxo ligand being longer (1.928 Å vs. 1.847 Å).

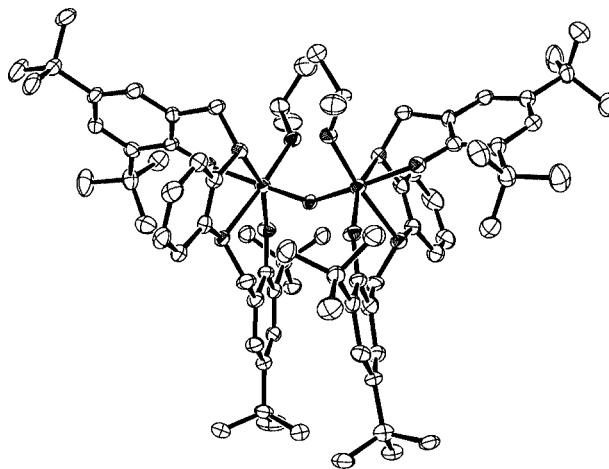


Figure 6. ORTEP representation of **4-Ti-a**, 50% probability; hydrogen atoms, and the crystallization solvent are omitted for clarity. One of the *t*Bu groups is disordered.

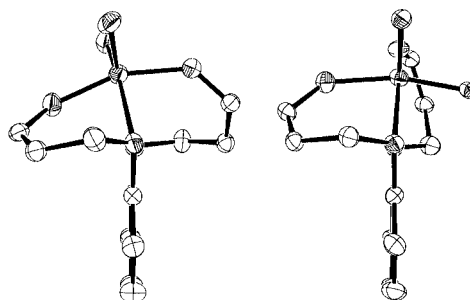


Figure 5. ORTEP representations of the cores of **2-Ti**, **3-Zr**, **4-Ti**, **4-Ti-a** (from left to right, respectively) along the plane of the phenylene ring, demonstrating the relative conformations of the phenylene diamine unit and the metal.

Most significantly, the ligand binds to the metal in a *fac-mer* mode for the first time. The Ti–N bond lengths are relatively different in this disposition: the Ti–N bond in the *mer* fragment is longer than in the *fac* fragment (2.275 and 2.278 Å for the former, and 2.211 and 2.222 Å for the latter), possibly indicating a stronger binding in the *fac* disposition. Finally, the metal is coplanar with the phenylene diamine unit in both parts of the molecule (Figure 5), as previously encountered in **2-Ti** and **3-Zr** complexes, and in contrast to its sterically congested precursor, **4-Ti**.

In conclusion, we have prepared a variety of new Salophan-type ligands, and their titanium and zirconium complexes. The coordination chemistry of these ligands with Group IV metals was found to depend on the phenolate substituents: The substituents-free Lig¹ led to complex mixtures, while the 2,4-dichloro- or di-*t*Bu-substituted ligands Lig³ or Lig⁴ led to a clean chemistry for both metals. The ligand bearing *ortho*-methyl groups Lig² formed a stable zirconium complex, and an unstable titanium complex. In all cases in which stable complexes were formed, they possessed C₂-symmetry on the NMR timescale, and their wrapping mode, being supported by X-ray structures, was found to be *fac-fac*, as previously found in Salan-Group IV complexes. The sterically congested di(isopropoxo) titanium complex **4-Ti** was found to undergo a facile (partial) hydrolysis, forming a μ -oxo product, in which the Salophan ligand coordinates to the metal in a *fac-mer* fashion. We are currently investigating the reactivity of these species, and exploring the chemistry of the newly prepared Salophan ligands with other early transition metals.

Experimental Section

Materials and Instrumentation: All syntheses of metal complexes were performed under dry nitrogen in a nitrogen-filled glovebox. Ether was purified by reflux and distillation under dry argon from

Na/benzophenone. Pentane was washed with HNO₃/H₂SO₄ prior to distillation from Na/benzophenone/tetraglyme. Ti(O*i*Pr)₄ and Zr(O*t*Bu)₄ were purchased from Aldrich Inc and used without purification. NMR spectroscopic data for the ligand precursors were recorded with a Bruker AC-200 spectrometer in CDCl₃ and referenced to TMS (δ = 0.00) in proton spectra, or to the chemical shift of CDCl₃ in carbon NMR spectroscopy. NMR spectroscopic data for the metal complexes were recorded with a Bruker AC-200 or Bruker Avance 400 spectrometers and referenced to protio impurities in [D₆]benzene (δ , 7.15), and to ¹³C chemical shift of benzene (δ , 128.70). Elemental analyses were performed by the microanalytical laboratory of the Hebrew University of Jerusalem. The metal complexes were analyzed within a few hours of being taken out of the freezer of the glovebox. The X-ray diffraction measurements were performed on a Nonius Kappa CCD diffractometer system, using Mo-K α (λ = 0.7107 Å radiation). The analyzed crystals were embedded within a drop of viscous oil and freeze-cooled to ca. 110 K. The structures were solved by a combination of direct methods and Fourier techniques using the SIR-92 software,^[10] and were refined by full-matrix least-squares with SHELXL-97.^[11] The crystal data are summarized in Table 1. The crystals of **3-Zr** and **4-Ti-a** contain partly disordered *t*Bu groups, and partly disordered solvent, thus affecting to some extent the precision of the structure determination.

Lig¹H₂: A solution of salicylaldehyde (4.60 g, 38 mmol) and 1,2-phenylenediamine (2.05 g, 19 mmol) in 60 mL of methanol was placed in a 100 mL round-bottomed flask equipped with a magnetic stir-bar and a reflux condenser. After several minutes, a yellow solution had formed, followed by formation of an orange precipitate (Salophen intermediate). The reaction mixture was allowed to stand for 30 min at room temp. and sodium borohydride (2.86 g, 5 equiv.) was added in small portions to the stirred heterogeneous mixture. The orange precipitate gradually disappeared, and a bright yellow transparent solution formed. The reaction mixture was poured into 100 mL of water, and allowed to stand for several hours. The resulting white solid was isolated by vacuum filtration, washed several times with water, and dried under vacuum at 50 °C for 2 h, yielding 4.99 g of Lig¹H₂ (82% yield). The ¹H/¹³C NMR spectra indicated its sufficient purity, being consistent with those previously described.^[8]

Table 1. Crystallographic experimental details.

	2-Ti	3-Zr	4-Ti	4-Ti-a
Empirical formula	C ₂₈ H ₃₆ N ₂ O ₄ Ti	C _{30.5} H ₃₈ Cl ₄ N ₂ O ₄ Zr	C ₄₂ H ₆₄ N ₂ O ₄ Ti	C ₄₅ H ₆₃ N ₂ O _{3.50} Ti
Formula mass	512.49	729.65	708.85	735.87
<i>a</i> [Å]	10.1360(2)	12.093(1)	9.8910(2)	14.2740(8)
<i>b</i> [Å]	18.9990(5)	17.124(1)	15.8450(3)	16.8810(8)
<i>c</i> [Å]	14.4670(3)	19.413(1)	26.8520(6)	19.2770(10)
α (°)	90.00	99.682(5)	90.00	89.727(3)
β (°)	108.9220(15)	93.196(4)	97.691(1)	102.663(3)
γ (°)	90.00	103.812(3)	90.00	109.904(3)
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1̄
<i>V</i> [Å ³]	2635.41(10)	3828.8(4)	4170.5 (2)	4248.9(4)
<i>D</i> _{calcd.} [g cm ⁻³]	1.292	1.266	1.464	1.150
μ [cm ⁻¹]	0.360	0.598	0.245	0.242
<i>Z</i>	4	4	4	2
No. of measd. reflns.	6263	13401	9865	18165
No. of reflns. [<i>I</i> > 2 σ (<i>I</i>)]	4717	7095	5384	6917
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0473	0.0906	0.0737	0.0770
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.1257	0.2425	0.1549	0.1551
GOF	1.033	1.005	0.992	0.935

Lig²H₂: A solution of 2-methylsalicylaldehyde (0.95 g, 7.1 mmol) and 1,2-phenylenediamine (0.38 g, 3.5 mmol) in 30 mL of methanol was placed in a 100 mL round-bottomed flask equipped with a magnetic stir-bar and a reflux condenser. The resulting bright yellow solution was heated to reflux for 2 h. Upon cooling to room temp. an orange crystalline solid had formed. The solid was collected by vacuum filtration, and identified by ¹H NMR as a Salophen intermediate. The orange intermediate product was suspended in 60 mL of methanol, and ca. 5 equiv. of sodium borohydride were added. The reaction mixture became entirely homogeneous and colorless. The solution was poured into 100 mL of water, and the resulting white solid was isolated by vacuum filtration, and dried under vacuum. The yield of Lig²H₂ was 0.49 g (40%). C₂₂H₂₄N₂O₂ (348.44): calcd. C 75.83, H 6.94, N 8.04; found C 75.81, H 6.92, N 8.18. ¹H NMR (200 MHz, CDCl₃): δ = 8.21 (s, 2 H, O–H), 7.09 (d, ³J_{H,H} = 7.6 Hz, 2 H), 7.04 (d, ³J_{H,H} = 7.6 Hz, 2 H), 6.94 (s, 4 H), 6.79 (t, ³J_{H,H} = 7.5 Hz, 2 H), 4.38 (d, ³J_{H,H} = 5.4 Hz, 4 H), 3.66 (t, ³J_{H,H} = 5.2 Hz, 2 H), 2.21 (s, 6 H) ppm. ¹³C NMR (50.29 MHz, CDCl₃): δ = 154.8 (C), 136.8 (C), 130.8 (CH), 126.9 (CH), 125.4 (C), 122.1 (C), 121.8 (CH), 119.9 (CH), 114.4 (CH), 48.2 (CH₂), 15.8 (CH₃) ppm.

Lig³H₂: 2,4-Dichlorosalicylaldehyde (4.92 g, 26 mmol) was dissolved in ca. 30 mL of methanol and added dropwise to a stirred suspension of 1,2-phenylenediamine (1.41 g, 13 mmol) in 20 mL of methanol. The reaction color changed immediately, and the deep-orange Salophen intermediate crystallized out. The reaction mixture was allowed to stand for 20 min. Sodium borohydride (3 equiv., 2.78 g) was added in small portions to the vigorously stirred heterogeneous mixture. The resulting homogeneous bright yellow solution was poured into 100 mL of water, and extracted with two 50 mL portions of dichloromethane. The combined (yellow) organic phase was dried with anhydrous magnesium sulfate, filtered, and the solvent was removed. The resulting yellow solid was dried under vacuum at 50 °C for 2 h, yielding 3.22 g of pure Lig³H₂ (54% yield). C₂₀H₁₆Cl₄N₂O₂·H₂O (476.18): calcd. C 50.45, H 3.81, N 5.88; found C 50.74, H 3.55, N 5.95. ¹H NMR (200 MHz, CDCl₃): δ = 7.28 (d, ⁴J_{H,H} = 2.5 Hz, 2 H), 7.14 (d, ⁴J_{H,H} = 2.4 Hz, 2 H), 6.90 (m, 2 H), 6.79 (m, 2 H), 4.37 (s, 4 H) ppm. ¹³C NMR (50.29 MHz, CDCl₃): δ = 150.0 (C), 136.5 (C), 128.4 (CH), 127.7 (CH), 126.6 (C), 125.2 (C), 121.6 (CH), 121.4 (C), 114.4 (CH), 46.4 (CH₂) ppm.

Lig⁴H₂: A homogeneous bright yellow solution of 3.98 g (17 mmol) of 2,4-di-*tert*-butylsalicylaldehyde and 0.89 g (8.5 mmol) of 1,2-phenylenediamine in 50 mL of methanol was heated to reflux in a 100 mL round-bottomed flask equipped with a magnetic stir-bar and a reflux condenser for 2 h, and then left at room temp. overnight. The orange solid that had formed was collected by vacuum filtration, and identified by ¹H NMR as a Salophen intermediate. The yield was 1.54 g (33%). The orange intermediate product was suspended in 60 mL of methanol, and ca. 10 equiv. of sodium borohydride were added, and the reaction mixture was stirred overnight. After hydrolysis, the bright-yellow solid was isolated by vacuum filtration. According to ¹H NMR, the solid contained at least two different products. The solid was washed several times with methanol, yielding the insoluble Lig⁴H₂. Alternatively, Lig⁴H₂ could be isolated by flash chromatography, using chloroform as an eluent; however, in this case the yield was lower. Drying under vacuum for 2 h at 100 °C, yielded 0.5 g of Lig⁴H₂ (34% relative to the corresponding Salophen). C₃₆H₅₂N₂O₂·0.5H₂O (553.82): calcd. C 78.07, H 9.65, N 5.06; found C 78.43, H 9.67, N 5.12. ¹H NMR (200 MHz, CDCl₃): δ = 7.98 (s, 2 H), 7.26 (d, ⁴J_{H,H} = 2.2 Hz, 2 H), 7.04 (d, ⁴J_{H,H} = 2.2 Hz, 2 H), 6.97 (s, 4 H), 4.35 (d, ³J_{H,H} = 5.9 Hz, 4 H), 3.57 (t, ³J_{H,H} = 5.9 Hz, 2 H), 1.37 (s, 18 H), 1.28 (s,

18 H) ppm. ¹³C NMR (50.29 MHz, CDCl₃): δ = 153.3 (C), 142.0 (C), 136.9 (C), 136.4 (C), 124.2 (CH), 124.0 (CH), 122.3 (C), 121.9 (CH), 114.6 (CH), 49.0 (CH₂), 35.1 (C), 34.4 (C), 31.8 (CH₃), 29.9 (CH₃) ppm.

2-Zr: 80 mg (0.17 mmol) of Lig²H₂ was treated with 67 mg (0.17 mmol) of Zr(OrBu)₄. The resulting white solid was washed with a small volume of pentane. The yield was 105 mg (0.15 mmol, 89%). C₃₀H₄₀N₂O₄Zr (583.87): calcd. C 61.71, H 6.91, N 4.80; found C 61.72, H 6.85, N 4.85. ¹H NMR (200 MHz, C₆D₆): δ = 7.00 (t, ³J_{H,H} = 4.6 Hz, 2 H), 6.54 (m, 2 H), 6.44 (d, ³J_{H,H} = 4.7 Hz, 2 H), 6.30 (m, 2 H), 4.69 (d, ²J_{H,H} = 11.9 Hz, 2 H), 3.58 (br. s, 2 H), 3.46 (dd, ²J_{1,H-H} = 12.2, ³J_{2,H-H} = 4.0 Hz, 2 H), 2.33 (s, 6 H), 1.51 (s, 18 H) ppm. ¹³C NMR (50.29 MHz, C₆D₆): δ = 161.3 (C), 141.3 (C), 131.3 (CH), 128.4 (CH), 127.3 (CH), 126.6 (C), 125.7 (CH), 122.1 (C), 116.8 (CH), 75.5 (C), 53.5 (CH₂), 33.3 (CH₃), 16.9 (CH₃) ppm.

3-Zr: 69 mg (0.15 mmol) of Lig³H₂ was treated with 58 mg (0.15 mmol) of Zr(OrBu)₄. The yield was 105 mg (0.15 mmol, 100%). X-ray quality crystals were obtained upon recrystallization from a minimal volume of pentane at –30 °C. C₂₈H₃₂N₂O₄Cl₄Zr (693.60): calcd. C 48.49, H 4.65, N 4.04; found C 48.61, H 4.79, N 3.97. ¹H NMR (200 MHz, C₆D₆): δ = 7.07 (d, ⁴J_{H,H} = 2.6 Hz, 2 H), 6.36 (m, 2 H), 6.29 (d, ⁴J_{H,H} = 2.6 Hz, 2 H), 6.02 (m, 2 H), 4.65 (d, ²J_{H,H} = 12.8 Hz, 2 H), 3.58 (br. s, 2 H), 3.10 (dd, ²J_{H,H} = 12.9, ³J_{H,H} = 3.5 Hz, 2 H), 1.57 (s, 18 H) ppm. ¹³C NMR (50.29 MHz, CDCl₃): δ = 156.9 (C), 139.8 (C), 129.7 (CH), 128.9 (CH), 128.2 (CH), 126.2 (CH), 124.9 (C), 123.7 (C), 120.9 (C), 76.8 (C), 52.9 (CH₂), 33.0 (CH₃) ppm.

4-Zr: Lig⁴H₂ (63 mg, 0.12 mmol) was treated with Zr(OrBu)₄ (53 mg, 0.13 mmol). The yield was 83 mg (0.11 mmol, 89%). C₄₄H₆₈N₂O₄Zr (780.25): calcd. C 67.73, H 8.78, N 3.59; found C 67.67, H 8.91, N 3.71. ¹H NMR (200 MHz, C₆D₆): δ = 7.30 (d, ⁴J_{H,H} = 2.5 Hz, 2 H), 6.46 (m, 4 H), 6.36 (m, 2 H), 4.94 (d, ²J_{H,H} = 12.3 Hz, 2 H), 3.73 (br. s, 2 H, N–H), 3.46 (dd, ²J_{H,H} = 12.3, ⁴J_{H,H} = 3.2 Hz, 2 H), 1.72 (s, 18 H), 1.55 (s, 18 H), 1.17 (s, 18 H) ppm. ¹³C NMR (50.29 MHz, C₆D₆): δ = 159.0 (C), 141.2 (C), 138.3 (C), 136.3 (C), 127.1 (CH), 126.4 (CH), 126.1 (CH), 123.4 (CH), 122.7 (C), 75.7 (C), 54.3 (CH₂), 35.5 (C), 34.1 (C), 33.5 (CH₃), 31.9 (CH₃), 30.1 (CH₃) ppm.

3-Ti: Lig³H₂ (45 mg, 0.10 mmol) was treated with Ti(OrPr)₄ (28 mg, 0.10 mmol). The yield was 60 mg (0.10 mmol, 100%). C₂₆H₂₈N₂O₄Cl₄Ti (622.19): calcd. C 50.19, H 4.54, N 4.50; found C 50.59, H 4.61, N 4.51. ¹H NMR (200 MHz, C₆D₆): δ = 7.10 (d, ⁴J_{H,H} = 2.6 Hz, 2 H), 6.39 (m, 2 H), 6.34 (d, ⁴J_{H,H} = 2.6 Hz, 2 H), 6.13 (m, 2 H), 5.29 (s, ³J_{H,H} = 6.1 Hz, 2 H), 4.66 (br. d, ²J_{H,H} = 12.9 Hz, 2 H), 3.78 (br. s, 2 H), 3.13 (dd, ²J_{1,H-H} = 13.2, ³J_{2,H-H} = 1.9 Hz, 2 H), 1.51 (d, ³J_{H,H} = 6.2 Hz, 6 H), 1.43 (d, ³J_{H,H} = 6.2 Hz, 6 H) ppm. ¹³C NMR (50.29 MHz, C₆D₆): δ = 158.4 (C), 141.0 (C), 130.1 (CH), 129.1 (CH), 129.0 (CH), 128.8 (C), 126.2 (CH), 125.9 (C), 123.5 (C), 122.0 (C), 79.9 (CH), 53.7 (CH₂), 26.9 (CH₃), 26.8 (CH₃) ppm.

4-Ti: Lig⁴H₂ (47 mg, 0.09 mmol) was treated with Ti(OrPr)₄ (24 mg, 0.09 mmol). The yield was 63 mg (0.09 mmol, 100%). Recrystallization from pentane (ca. 1 mL) afforded yellow-orange crystals of X-ray quality. C₄₄H₆₈N₂O₄Ti (708.84): calcd. C 71.17, H 9.10, N 3.95; found C 71.42, H 9.14, N 3.96. (400 MHz, C₆D₆): δ = 7.31 (d, ⁴J_{H,H} = 2.5 Hz, 2 H), 6.55 (d, ⁴J_{H,H} = 2.4 Hz, 2 H), 6.48 (s, 4 H), 5.03 (s, ³J_{H,H} = 6.1 Hz, 2 H), 4.79 (dd, ²J_{H,H} = 12.5, ³J_{H,H} = 1.2 Hz, 2 H), 4.00 (br. s, 2 H), 3.51 (dd, ²J_{H,H} = 12.6, ³J_{H,H}

= 2.8 Hz, 2 H), 1.74 (s, 18 H), 1.49 (d, $^3J_{\text{H,H}} = 6.0$ Hz, 6 H), 1.39 (d, $^3J = 6.1$ Hz, 6 H), 1.17 (s, 18 H) ppm. ^{13}C NMR (50.29 MHz, C_6D_6): $\delta = 160.1$ (C), 142.1 (C), 138.9 (C), 135.9 (C), 127.1 (CH), 125.6 (CH), 125.4 (CH), 123.1 (CH), 123.1 (C), 77.4 ($\text{CH}(\text{CH}_3)_2$), 54.3 (CH_2), 35.4 (C), 34.1 (C), 31.9 ($\text{CH}(\text{CH}_3)_3$), 30.2 ($\text{CH}(\text{CH}_3)_3$), 26.9 ($\text{CH}(\text{CH}_3)_2$), 26.5 ($\text{CH}(\text{CH}_3)_2$) ppm.

4-Ti-a: Lig⁴H₂ (84 mg, 0.15 mmol) was treated with Ti(OiPr)₄ (43 mg, 0.15 mmol). The solvent was removed, and the crude product was re-dissolved in deuteriobenzene and kept outside the glovebox in a paraffin-sealed capped vial. After two days, bright-yellow crystals had formed. The crystals were separated from the solution, washed with cold ether and dried in vacuo to give 23 mg of **4-Ti-a** (23% yield). ^1H NMR (400 MHz, C_6D_6): $\delta = 9.66$ (s, 1 H, N-H), 7.37 (d, $^4J_{\text{H,H}} = 2.4$ Hz, 1 H), 7.34 (d, $^3J_{\text{H,H}} = 7.84$ Hz, 1 H), 7.21 (d, $^4J_{\text{H,H}} = 2.4$ Hz, 1 H), 6.96 (t, $^3J_{\text{H,H}} = 7.8$ Hz, 1 H), 6.77 (d, $^4J_{\text{H,H}} = 2.4$ Hz, 2 H), 6.60 (t, $^3J_{\text{H,H}} = 7.8$ Hz, 1 H), 6.34 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 1 H), 5.30 (s, $^3J_{\text{H,H}} = 5.9$ Hz, 1 H, $(\text{CH}_3)_2\text{CH}$), 4.90 (d, $^2J_{\text{H,H}} = 12.5$ Hz, 1 H), 4.60 (t, $J_{\text{H,H}} = 13.0$ Hz, 1 H), 4.20 (dd, $^2J_{\text{H,H}} = 12.7$, $^3J_{\text{H,H}} = 2.2$ Hz, 1 H), 3.58 (d, $^3J_{\text{H,H}} = 13.2$ Hz, 1 H, N-H), 3.54 (d, $^2J_{\text{H,H}} = 13.4$ Hz, 1 H), 1.87 (d, $^3J_{\text{H,H}} = 6.0$ Hz, 3 H, $(\text{CH}_3)_2\text{CH}$), 1.42 (m, 12 H), 1.38 (s, 9 H), 1.34 (s, 9 H), 1.20 (s, 9 H) ppm. ^{13}C NMR (100.58 MHz, C_6D_6): $\delta = 160.2$, 159.6, 144.4, 142.8, 139.98, 138.7, 135.8, 135.5, 128.2, 128.0, 126.6, 125.9, 125.4, 124.8, 124.4, 123.9, 123.3, 123.3, 74.9, 55.9, 55.1, 35.4, 35.3, 34.4, 34.2, 32.1, 31.9, 30.2, 29.9, 27.8, 27.7 ppm.

CCDC-266239 to -266242 (for complexes **3-Zr**, **4-Ti**, **4-Ti-a**, and **2-Ti**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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