Soluble monometallic salen complexes derived from *O*-functionalised diamines as metalloligands for the synthesis of heterobimetallic complexes[†]

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O-Functionalised salen ligands were employed as bridging ligands in the synthesis of homo- and heterometallic salen complexes with early and late transition metals (H2salen: N,N'-bis(salicylidene)ethylenediamine, systematic name: 2,2'-{ethane-1,2-diylbis(nitrilomethylidine)}diphenol). A new type of O-functionalised salen ligand was synthesised, which contains alkyl groups to enhance the solubility in organic solvents as well as carboxyl groups to allow introduction of an early transition metal. Two new salen ligands derived from O-functionalised diamines were synthesised from 3,5-di-tert-butylsalicylaldehyde (bsal) and 3,4-diaminobenzoic acid (4cpn) or (R)-2,3-diaminopropionic acid (cen). By using the aryl diamines, a conjugated backbone is obtained, and the alkyl diamines can be used to introduce a chiral centre. The salen ligand derived from 3,4-diaminobenzoic acid was accessible only via a zinc(II)-mediated template reaction. Monometallic salen complexes could be obtained by template synthesis with nickel(II) and copper(II). The analogous chromium(III), manganese(III) and molybdenum(IV) salen complexes were synthesised directly from the salen ligands. The crystal structures of the molybdenum(IV) salen complex and a decomposition product thereof gave insight into the stability of this compound. Starting from (R)-2,3-diaminopropionic acid the corresponding nickel(II), chromium(III), manganese(III) and molybdenum(IV) salen complexes were obtained. Reactions of the conjugated nickel(II) salen complex with metallocene derivatives resulted in the formation of soluble di- and trinuclear heterobimetallic complexes, depending on the stoichiometry used. The compounds were characterised by NMR, IR and EPR spectroscopy, mass spectrometry and, for selected complexes, by X-ray crystallography. For selected mono- and bimetallic salen complexes the catalytic activity in the epoxidation of styrene was tested under different reaction conditions and with different oxidising agents. The highest values (up to 24%) for the conversion of styrene to styrene oxide were obtained with manganese(III) salen complexes.

1 Introduction

Monometallic salen complexes have been studied extensively after Kochi *et al.*¹ reported their highly chemoselective catalytic activity in epoxidation reactions. Further extensive studies were carried out by Jacobsen *et al.*² and Katsuki *et al.*,³ who reported independently the excellent performance of chiral manganese(III) complexes with a wide variety of salen ligands having various chiralities and bulky alkyl or aryl groups in the enantioselective catalytic oxidation of unfunctionalised olefins.⁴

Despite extensive work on tuning of asymmetric induction of salen ligands, hardly any attention has been paid to *O*functionalised salen complexes, *e.g.*, with hydroxyl or carboxyl substituents, or their activity in catalytic epoxidation.⁵ There is only one report on employing a carboxy-functionalised salen complex in the catalytic epoxidation of chromene.⁶ This is in contrast to the large number of existing studies on alkoxy-substituted salen complexes and early/late heterobimetallic compounds thereof,⁷ with special focus on their magnetic behaviour.⁸

We recently reported the synthesis of soluble monometallic salen complexes derived from *O*-functionalised salicylaldehydes⁹ and hydroxy-functionalised diamines¹⁰ as metalloligands for the synthesis of heterobimetallic complexes and immobilisation of some of these complexes on organo-modified mesoporous silica gel as well as their catalytic activity in the epoxidation of olefins.¹¹

Now we report the synthesis and characterisation of two new salen ligands derived from carboxy-functionalised diamines, $Na(H_2bsalcen)$ and $H_3bsal4cpn$,¹² and their mono- and hetero-bimetallic complexes.

2 Results and discussion

2.1 Salen ligands derived from carboxy-functionalised alkyl and aryl diamines

For comparison of the properties of salen complexes having a flexible alkyl diimine backbone with those having a conjugated aryl diimine backbone, different ligands were synthesised. For all ligands, 3,5-di-*tert*-butyl-salicylaldehyde (bsal) was used, which

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[†] Electronic supplementary information (ESI) available: Cyclic voltammogram of the complexes [Na{Cu(bsalcen)}](1b) and [Tp*₂La{Cu(bsalcen)}] (4b) in dichloromethane; and cyclic voltammograms of the complexes [Ni(Hbsal4cpn)] (2a) and [Tp*₂La{Ni(bsal4cpn)}] (5a) in dichloromethane and thf. CCDC reference numbers 736166–736176. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b920706f

results in enhanced solubility of the ligands in organic solvents due to its *tert*-butyl groups.

The synthesis of carboxy-functionalised salen ligands derived from alkyl diamines (see Scheme 1) was carried out as described for related ligands.¹³



Scheme 1 Synthesis of the salen ligand Na(H₂bsalcen).

This procedure could be easily employed for the synthesis of Na(H₂bsalcen) by addition of a stoichiometric amount of NaOH to enantiopure (*R*)-2,3-diaminopropionic acid mono-hydrochloride (cen). However, racemisation took place at some stage (as shown by X-ray crystallography on the hetero-bimetallic complexes [Tp*₂La{Ni(bsalcen)}]-n-hexane (**4a**) and [Tp*₂La{Cu(bsalcen)}]-n-hexane (**4b**); see Section 4). Racemisation of α -amino acids on formation of Schiff bases was already described by Grigg *et al.*¹⁴

A salen ligand derived from the carboxy-functionalised aryl diamine 3,4-diaminobenzoic acid was mentioned in the literature,¹⁵ and only the *in situ* synthesis of N,N'-bis(salicylidene)-3,4-diaminobenzoic acid from salicylaldehyde and 3,4-diaminobenzoic acid, which was used without further characterisation in the synthesis of the corresponding nickel(II) complex (characterised by elemental analysis only), was reported.¹⁶

Therefore, we tried to synthesise the carboxy-functionalised ligand H₃bsal4cpn employing the general procedure, *i.e.*, treating two equivalents of salicylaldehyde with one equivalent of diamine in methanol. The reaction mixture was heated to reflux for 2 h and then stirred for 18 h at room temperature. However, the yield of the isolated yellow solid was only 23%. The ¹H NMR spectrum of the solid in methanol showed the formation of the "half-salen" ligand, whereas the ¹H NMR spectrum of the supernatant solution showed only unchanged salicylaldehyde (see Scheme 2). An explanation for the incomplete reaction is formation of zwitterions in which only the unprotonated amino group will react with the aldehyde to form the half-salen ligand.



Scheme 2 Reaction of 3,5-di-*tert*-butylsalicylaldehyde with 3,4-diaminobenzoic acid.

Attempts to prepare the salen ligand H_3 bsal4cpn in boiling toluene with increased reaction time, use of dry thf and five equivalents of Na_2SO_4 as drying agent, or addition of two equivalents of NaOH in methanol, only resulted in formation of the half-salen ligand and unreacted salicylaldehyde (Scheme 2).

The salen ligand H₃bsal4cpn could finally be obtained in a template synthesis using the weakly coordinated zinc(II) cation, which prefers tetrahedral coordination and thus forms a kinetically labile Zn salen complex from which the metal cation is readily eliminated, e.g., in methanol. It is also known that zinc(II) compounds can activate starting materials by coordination.¹⁷ Using this approach and heating to reflux a mixture of two equivalents of salicylaldehyde, one equivalent of 3,4-diaminobenzoic acid (4cpn) and two equivalents [ZnCl₂(thf)₂] in thf for 1 h resulted in a dark green solution. Removal of thf and addition of methanol gave the salen ligand H₃bsal4cpn as a nearly insoluble yellow solid (Scheme 3). In the FAB mass spectrum the molecular ion peak is observed at m/z = 585.4, and in the IR spectrum vO-H (3425 cm⁻¹) and vC=O (1690 cm⁻¹) bands indicate the presence of a COOH group. H₃bsal4cpn is soluble in thf and dmso, but only slightly soluble in methanol and ethanol.



Scheme 3 Synthesis of the salen ligand H₃bsal4cpn with [ZnCl₂(thf)₂].

Attempts to obtain the ligand H_3 bsal4cpn with catalytic amounts (10 mol%) of $[ZnCl_2(thf)_2]$ or $ZnCl_2 \cdot 4H_2O$ were not successful.

2.2 Monometallic (d-block) and heterometallic (d-block/s-block) salen complexes derived from carboxy-functionalised alkyl- and aryl diamines

The complexes $[M{Na(bsalcen)}]$ (M = Ni, 1a; Cu, 1b) were prepared from the salen ligand Na(H₂bsalcen) and the appropriate transition metal chloride in methanol. NaOH or NaOCH₃ was used as deprotonating agent. These complexes were characterised by ¹H NMR (1a), ¹³C NMR (1a), EPR (1b) and IR spectroscopy, elemental analysis and mass spectrometry.

The synthesis of the corresponding Mn, Cr and Mo complexes $[M{Na(bsalcen)}]$ (M = MnCl, 1c; CrCl, 1d; MoCl₂, 1e) was performed in thf or toluene using Na(H₂bsalcen) and the water-free metal chlorides in the presence of two equivalents of Et₃N (Scheme 4).



Scheme 4 Synthesis of monometallic complexes $[M{Na(bsalcen)}] (M = Ni, L = H_2O, m = 2, n = 6, base = 2 NaOH, 1a; M = Cu, L = H_2O, m = 2, n = 0, base = 2 NaOCH_3, 1b; M = MnCl, L = thf, m = 1, n = 2, base = 2 Et_3N, air, 1c; M = CrCl, L = thf, m = 2, n = 3, base = 2 Et_3N, 1d and M = MoCl_2, L = CH_3CN, m = 2, n = 2, base = 2 Et_3N, 1e).$

The solubility of the complexes in toluene facilitates separation from insoluble ammonium chloride. However, complete separation was difficult, as was apparent from the elemental analysis and ESI MS of the chromium(III) and molybdenum(IV) complexes, in

 Table 1
 Selected IR vibrations (vib.) of Na(H2bsalcen) and complexes derived therefrom

Compound	vib. C=N/cm ⁻¹	vib. M-Cl/cm ⁻¹	further vib. in CsI/cm ⁻¹
$\label{eq:linear} \begin{array}{l} Na(H_2bsalcen) \\ [MnCl{Na(bsalcen)}] \mbox{ (lc)} \\ [CrCl{Na(bsalcen)}] \mbox{ (ld)} \\ [MoCl_2{Na(bsalcen)}] \mbox{ (le)} \end{array}$	1629 (s) 1611 (s) 1610 (s) 1618 (s)		646 (w), 539 (m), 488 (w), 454 (w), 278 (w) 644 (w), 563 (m), 491 (w), 473 (w), 270 (w) 639 (w), 547 (m), 510 (w), 494 (w), 279 (w) 644 (w), 560 (m), 483 (w), 465 (w), 278 (w)

which Et_3N adducts were detected. The complexes, **1c**, **1d**, and **1e** were characterised by IR spectroscopy, mass spectrometry and elemental analysis, and their magnetic moments were determined.

The IR spectra of $Na(H_2bsalcen)$ and salen complexes derived therefrom have characteristic C=N vibrations and, where appropriate, M–Cl vibrations (Table 1).

In the complexes the C=N vibration is shifted by *ca.* 20 cm⁻¹ to lower wavenumbers compared to Na(H₂bsalcen), which is attributable to the lower C=N bond order due to coordination to the metal atom. The M–Cl vibrations are expected between 300 and 450 cm⁻¹.¹⁸ Only one M–Cl valence vibration is expected and observed for the square-pyramidal chromium(III) **1d** (397 cm⁻¹) and manganese(III) complexes **1c** (391 cm⁻¹), whereas the slightly distorted octahedral molybdenum(IV) complex **1e** with two *trans* chloro ligands exhibits two absorptions, for the symmetric and, at higher wavenumbers, the antisymmetric vibration, at 392 and 319 cm⁻¹ which are in the range observed for [MoCl₂(salen)] (309 cm⁻¹),¹⁹ and dimeric MoCl₅ (418 to 345 cm⁻¹).²⁰ The Cr–Cl vibration for chromium(III) complex **1d** is in the range observed for CrOCl₃ (404 cm⁻¹).²¹

The synthesis of metal salen complexes with the salen ligand containing a carboxy-functionalised aryl diimine backbone, H_3 bsal4cpn, was achieved *via* two routes. Firstly, monometallic complexes [Ni(Hbsal4cpn)] (**2a**) and [Cu(Hbsal4cpn)] (**2b**) were obtained by template synthesis starting from 3,4-diaminobenzoic acid, 3,5-di-*tert*-butylsalicylaldehyde and hydrated nickel(II) chloride or copper(II) chloride (Scheme 5).



Scheme 5 Synthesis of monometallic complexes [NHEt₃][M(bsal4cpn)] (with M = Ni, n = 6, **2a**; M = Cu, n = 0, **2b**).

Secondly, monometallic complexes [MnCl(Hbsal4cpn)] (2c), [CrCl(Hbsal4cpn)] (2d), [Fe(bsal4cpn)] (2e) and [MoCl₂(Hbsal4cpn)] (2f) could be obtained starting from the salen ligand H₃bsal4cpn and the appropriate metal chloride complex (Mn, Cr, Mo) (Scheme 6) or Fe(OAc)₂. In order to avoid formation of NHEt₃ salts (as was observed for the Mn complex), no amine (Fe, Cr) or nBu_3N (Mo, the ammonium salt of which is very soluble in thf, while the Mo complex is not) was employed for the synthesis of the chromium(III) complex 2d (obtained in 98% yield) and molybdenum(IV) complex 2f (65% yield).

The iron(III) complex **2e** was isolated as a zwitterion (positive charge at the Fe atom and negative charge at the carboxyl group).



Scheme 6 Synthesis of monometallic complexes [M(Xbsal4cpn)] (M = MnCl, X = [NHEt₃], L = thf, m = 1, n = 2, oxidation by air, 2c; M = CrCl, X = H, L = thf, m = 2, n = 3, 2d and M = MoCl₂, X = H, L = CH₃CN, m = 2, n = 2, 2f)

Presumably, this complex forms an oligomeric structure in the solid state.

All monometallic complexes were characterised by IR spectroscopy and mass spectrometry. The nickel complex was additionally characterised by ¹H NMR and ¹³C NMR spectroscopy.

2.3 Heterobimetallic (d-block/d-block, d-block/f-block) salen complexes derived from carboxy-functionalised alkyl or aryl diamines

Starting from the monometallic complexes or the heterometallic sodium salts described in Section 2.2., heterobimetallic complexes with early transition metals and lanthanoids were synthesised. It was necessary to find co-ligands which were able to stabilise the coordination sphere of the second metal and which allowed the preparation of discrete dinuclear or trinuclear complexes. In view of the catalytic oxidation reactions the co-ligands should also be stable against oxidation. These requirements were achieved by use of cyclopentadienyl (Cp) and hydridotrispyrazolyl (Tp) ligands and their derivatives.

2.3.1 Titanium- and zirconium-containing heterobimetallic salen complexes. Two equivalents of the nickel(II) complex **2a** reacted with one equivalent of the early transition metal metallocene derivatives $[Cp_{2}^{R}M'(CH_{3})_{2}]$ (M' = Ti, Zr; $Cp^{R} = Cp$ ($C_{5}H_{5}$) or Cp° ($C_{5}EtMe_{4}$)) *via* methane formation to give the symmetrical heterotrinuclear complexes $[Cp_{2}Zr{Ni(bsal4cpn)}_{2}]$ (**3a**) and $[Cp^{\circ}_{2}Ti{Ni(bsal4cpn)}_{2}]$ (**3b**) (Scheme 7).

The heterobimetallic complexes were characterised by ¹H NMR spectroscopy, IR spectroscopy and elemental analysis. The 1:1 reaction of $[Cp_{2}^{R}M'(CH_{3})_{2}]$ with the nickel(II) complex **2a** led, however, to an inseparable mixture of trinuclear and binuclear complexes and unconverted starting material.

2.3.2 Lanthanoid-containing heterobimetallic salen complexes. Heterobimetallic Ni/Ln and Cu/Ln complexes could easily be obtained by salt elimination. Thus, the monometallic nickel(II) (1a, 2a) and copper(II) complexes (1b, 2b) were treated with a stoichiometric amount of NaOH followed by reaction with [LnTp*₂(OTf)] to give the heterobimetallic lanthanoid complexes



4a, 4b with an alkyl backbone as well as the aryl derivatives 5a, 5b (La) and **6a**, **6b** (Nd) in addition to NaOTf (Scheme 8).

M'

CpR

COO

This procedure could not be applied in the synthesis of complexes containing Fe and Cr which form stable betaines. Thus, for the preparation of heterobimetallic complexes with Fe and Cr the monometallic betaine complexes [M(bsal4cpn)] were converted to the carboxylic acids with a solution of HCl/diethyl ether and then treated with [LaTp*2(pz*)]. Formation of the heterobimetallic complexes is accompanied by the generation of pz*H, which then coordinates as a neutral axial ligand in the complex $[Tp_{2}La{CrCl(pz^{*}H)(bsal4cpn)}]$ (5c), as indicated by an N-H absorption in the IR spectrum at 3293 cm⁻¹ and the elemental analysis. On the other hand, the IR spectrum and elemental analysis of the complex $[Tp_2La{FeCl(bsal4cpn)}]$ (5d) indicated no coordination of pz*H. Thus, the Fe atom presumably has a square-pyramidal coordination sphere, as was observed for similar complexes.22,23

In the synthesis of the heterobimetallic Cr/La complex $[Tp_{2}La{CrCl(pz^{*}H)(bsal4cpn)}]$ (5c) a few crystals of $[Tp_{2}La(Cr{pz^{H}}_{2}{b(H)sal4cpn})]$ (5f) were also obtained (see

molecular structure, Section 2.4.4), in which one of the two C=Nbonds was reduced to a C-N single bond. The synthesis of this complex could not be reproduced nor could the reducing agent be unambiguously determined. Addition of hydride and enolate to the imine bond of an aluminium(III) salophen complex was also observed by Portalone, Rissanen, et al.²⁴ We assume that Tp*, which contains a hydridic B-H group, could be responsible for the reduction, because reducing agents like NaBH4 are well known for the reduction of Schiff bases.25

2.3.3. ¹H **NMR** investigation of the complexes $[Na{Ni(bsal4cpn)}]$ (2a') and $[Tp*_2Ln{Ni(bsal4cpn)}]$ (Ln = La, 5a; Ln = Nd, 6a). In order to investigate the stability of the lanthanoid-containing heterobimetallic complexes in solution, the mono- and heterobimetallic complexes were analysed by ¹H NMR spectroscopy in different solvents. First, the spectra were measured in the less polar solvents C_6D_6 and CD_2Cl_2 . Solutions of the nickel complex 2a' showed very broad signals. This broadening is ascribed to the associative dynamic behaviour of carboxyl groups and was not diminished by cooling the solutions. Accordingly, sharp signals were observed for the monometallic complex in $[D_8]$ thf. On the other hand, coordination of the carboxyl group to the lanthanoid cation also eliminates this associative dynamic behaviour, resulting in sharp proton resonances. In Table 2 selected ¹H NMR signals of aromatic H atoms of the nickel complex 2a' and the heterometallic La- or Nd-containing complexes 5a and 6a are summarised.

The differences between analogous signals of the complexes $[Na{Ni(bsal4cpn)}]$ (2a) and $[Tp*_2La{Ni(bsal4cpn)}]$ (5a) are rather small. Due to the paramagnetism of Nd^{III}, the ¹H NMR signals of [Tp*2Nd{Ni(bsal4cpn)}] (6a) are shifted strongly downfield. The highest downfield shift is observed for H atoms 10 and 12, which are located in the position ortho to the COO group. This observation confirms stable coordination of the carboxyl group to the lanthanoid cation.

2.3.4. Molecular structure of $[(Tp*_2La{Fe(bsal4cpn)})_2(\mu-O)]$ (5e). It is well known that the formation of dimeric oxo-bridged



Scheme 8 Synthesis of lanthanoid-containing heterobimetallic salen complexes 4a, 4b, 5a, 5b, 5c and 5d

Table 2Selected 1 HNMRchemicalshiftsofthecomplexes[X{Ni(bsal4cpn)}](X = Na, 2a'; Tp*2La, 5a; Tp*2Nd, 6a, in [D_8]thf)^a



^{*a*} The sodium salt of 2a (= 2a') was employed.

iron complexes is responsible for the continuous deactivation during the catalytic oxidation.¹ The introduction of a bulky substituent in the diimine backbone was assumed to avoid the formation of the oxo-bridged dimer and thus maintain the catalytic activity of the Fe complex **2e**. Oyaizu *et al.* have already shown that additional phenyl groups in the diimine backbone reduce the formation of oxo-bridged dimers.²³ However, addition of one equivalent of NaOH to [Fe(bsal4cpn)] (**2e**) followed by two equivalents of [LaTp*₂(OTf)] gave [(Tp*₂La{Fe(bsal4cpn)})₂(μ -O)] (**5e**).

The oxo-bridged dimer crystallises with 3.5 toluene molecules. The Fe atoms have square-pyramidal coordination spheres and are located about 55 pm and 53 pm above the N₂O₂ plane (Fig. 1). The Fe1–O9–Fe2 angle of 155.9(2)° is rather small compared to the analogous angle of 176.5(2)° in the oxo-bridged dimer which contains a sterically less hindered 1,2-phenylenediimine backbone. The Fe(1, 2)–O(1, 2, 5, 6) and Fe(1, 2)–O9 bond lengths are in the



Fig. 1 ORTEP of the molecular structure of $[(Tp^*_2La{Fe(bsal4cpn)})_2-(\mu-O)]$ (5e). H atoms are omitted for clarity. The size of the ellipsoids relates to a probability of 50% (metal atoms) or 5% (other atoms).

2.4 Molecular structures of mono- and heterobimetallic salen complexes derived from carboxy-functionalised aryl and alkyl diamines

2.4.1. Molecular structure of the monometallic complexes [Ni(Hbsal4cpn)] (2a), [CrCl(CH₃CN)(Hbsal4cpn)] (2d'), [CrCl(pz*H)(Hbsal4cpn)] (2d'') and [MoCl₂(Hbsal4cpn)] (2f). In the solid state, all complexes form dimers by intermolecular hydrogen bonding between the carboxyl groups (Fig. 2–4), a feature which is usually observed for carboxylic acids. The intermolecular O3 \cdots O4 distances are about 260 pm and comparable to those of similar compounds.²⁷



Fig. 2 ORTEP of the monomeric unit of [Ni(Hbsal4cpn)] (**2a**). In the solid state, **2a** forms hydrogen-bonded dimers. H atoms (other than H1O4) are omitted for clarity. The size of the ellipsoids relates to a probability of 50%.

While chromium(III) and molybdenum(IV) prefer an octahedral coordination sphere, nickel(II) is coordinated in a square-planar fashion. Remarkably, the organic ligand is not planar, despite its conjugated backbone. Salen complexes with a conjugated ligand cannot compensate ring strain by formation of λ or δ conformations of the five-membered rings as in non-conjugated salen complexes. Comparison of the MN₂O₂ planes (see Fig. 2-4) reveals almost no strain in the nickel and chromium complex and high strain in the Mo complex. The dihedral angle between the salicylidene rings and the MoN₂O₂ plane in the Mo complex is approximately 30° and thus about six times larger than in the nickel and chromium complexes ($< 5^{\circ}$) and more than twice as large as in a non-conjugated hexacoordinate manganese(III) salen complex.²⁸ The distortion in the molybdenum complex 2f is also obvious from the small O-Mo-N bond angles of 159.0(2) and $159.1(2)^{\circ}$ as compared to 172 to 176° in the nickel and chromium complexes. This clearly indicates that the distortion is not due to steric interaction of adjacent tert-butyl groups but due to the size of the central atom. The size of the molybdenum atom causes a drastic expansion of the N2O2 coordination sphere, which is also



Fig. 3 ORTEP of the molecular structures of $[CrCl(CH_3CN)-(Hbsal4cpn)]\cdot 6CH_3CN (2d') and <math>[CrCl(pz^*H)(Hbsal4cpn)]\cdot 1,4-dioxane (2d''). The 1,4-dioxane molecule, the CH_3CN molecules and the H atoms (excepted O3H and N4H) are omitted for clarity. The size of the ellipsoids relates to a probability of 50%.$

reflected in the O1 \cdots O2 distance of about 320 pm, as opposed to only about 250 and 280 pm in the nickel and chromium complexes, respectively.

2.4.2. Molecular structure of a decomposition product 2f' of [MoCl₂(Hbsal4cpn)]. During the NMR spectroscopic measurements on the diamagnetic molybdenum(IV) salen complex 2f in moist C₆D₆ only broad signals were observed and, furthermore, red needles formed in the NMR tube, which were shown to be a decomposition product by X-ray crystallography. The asymmetric unit contains two independent molecules which form a dimer *via* (presumably) oxo bridges, four C₆D₆ molecules and one [*n*Bu₃NH]Cl (Fig. 5). Although refinement was only possible to an R_1 value of 10.1%, a closer look at the obtained product is valuable, as it was formed in an unusual manner and offers new insights into the stability of such salen complexes.

The molybdenum atom is coordinated in a distorted octahedral fashion by one chloro ligand, one oxygen and one nitrogen atom of a rearranged salen ligand and three oxygen atoms, two of which bridge two molybdenum centres. The intramolecular Mo–O bond lengths of the oxygen atoms O7, O8, O9 and O10 are 164.7(8) and 170.3(8) pm which is typical for terminal Mo–O double bonds.²⁹



Fig. 4 ORTEP of [MoCl₂(Hbsal4cpn)] (**2f**). The molecules form dimers *via* intermolecular COOH hydrogen bonds (acetonitrile molecules are omitted for clarity; ellipsoid probability: 50%).



Fig. 5 ORTEP of the dimeric structure of the decomposition product 2f' of [MoCl₂(Hbsal4cpn)] (2f). The hydrogen atoms and the C₆D₆ and [*n*Bu₃NH]Cl molecules are omitted for clarity. The size of the ellipsoids relates to a probability of 40%.

The Mo–O bond lengths of the bridging oxygen atoms Mo1–O8 and Mo2–O9 are only slightly larger than Mo1–O7 and Mo2–O10, by 3.5 or 5.6 pm, whereas the intermolecular Mo–O distances are much longer (253.8 and 255.3 pm). Molybdenum was, therefore, apparently oxidised from the original molybdenum(IV) salen complex **2f** to the formal oxidation state +6.

Besides the change in the oxidation state of molybdenum, the second benzylidene ring is missing and a new heterocycle was formed. Apparently, the coordinated salen ligand was hydrolysed, 3,5-di-*tert*-butylsalicylaldehyde was eliminated and rearrangement of the ligand resulted in the formation of an imidazole ring, according to the proposed mechanism shown in Scheme 9.

The assignment of the position of the C=N double bond in the imidazole ring is not directly possible, as the distances C37–N4 (135(1) pm) and C37–N3 (137(1) pm) are nearly identical,



Scheme 9 Proposed mechanism for the formation of the decomposition product 2f' of [MoCl₂(Hbsal4cpn)] (2f).

but it can be derived from a similar molecular structure from Behrens *et al.*³⁰ for formation of an imidazole ring starting from Schiff bases. Behrens *et al.* and Döring *et al.*³¹ describe oxidative formation of an imidazole ring using catalytic amounts of copper(II).

Two further arguments support the proposed mechanism:

1) During the reaction of [MoCl₂(Hbsal4cpn)] (**2f**) with one equivalent of water in toluene in air a red solid was formed. Efforts to crystallise the solid by different crystallisation techniques resulted, however, only in oils.

2) In the ¹H NMR spectra of the supernatant solution of the obtained decomposition product as well as in the solution obtained in 1), the proposed hydrolysis product 3,5-di-*tert*-butylsalicylaldehyde could be identified.

Other possible "destruction" mechanisms could be anticipated, whereby both imine groups are cleaved and one aldehyde is expelled from the coordination sphere of the Mo complex. Reorganisation of coordinated aldehyde and diamine on the Mo complex could also lead to the imidazole ring and then to the observed complex. However, this should result in different isomers, whereby after imidazole formation the carboxyl group is either in *para* or in *meta* position to the N atom coordinating at Mo, which was not observed in the crystal structure of **2f**'. Further experiments using different ratios of aldehyde and diamine (with or without oxygen atmosphere) did not produce the decomposition product.

The formation of the decomposition product **2f**' illustrates the reactivity of the hydrogen atom at the imine carbon atom. Attempts to use 2-hydroxy-4-methoxybenzophenone instead of salicylaldehyde in the synthesis of the salen ligand (to replace the hydrogen atom at the imine carbon atom with an aryl substituent) resulted, however, in inseparable product mixtures which indicates that ketones have a distinctly lower reactivity.

2.4.3. Molecular structures of the heterometallic complexes $[Tp_2La{Ni(bsal4cpn)}]$ (5a), $[Tp_2La{Cu(bsal4cpn)}]$ (5b), $[Tp_2La{Ni(bsalcen)}]$ (4a), and $[Tp_2La{Cu(bsalcen)}]$ (4b). The molecular structures of the heterobimetallic complexes 5a and 5b are shown in Fig. 6.

The Ni and Cu atoms are coordinated in a square-planar fashion by the N_2O_2 coordination sphere of the bsal4cpn ligand. The M–N and M–O (M = Ni, Cu) bond lengths are in the expected



Fig. 6 ORTEP of the molecular structures of $[Tp_2La{Ni(bsal4cpn)}]$. 1,4-dioxane-0.5n-hexane (**5a**) and $[Tp_2La{Cu(bsal4cpn)}]$.n-hexane (**5b**). The n-hexane molecules and the H atoms are omitted for clarity. The size of the ellipsoids relates to a probability of 50%.

range for salen complexes.³² The Ni–N and Ni–O bond lengths are nearly identical to those in the monometallic Ni complex **2a**. The distances between the two transition metal atoms within the

heterobimetallic complexes are about 933 pm (d(Ni ··· La)) and 937 pm (d(Cu ··· La)). The La–O3 and La–O4 bond lengths of the complexes differ between 251.8(2) and 248.7(3) pm (**5b**) and 248.4(7) and 255.7(7) pm (**5a**). This is due to the steric interaction between the bulky Tp* ligands and the metallosalen ligand. The complex [LaTp*₂(O₂NO)],³³ for instance, has two nearly identical La–O bond lengths of 258.4(1) pm and 258.6(1) pm. The La–N bond lengths for the **5a** and **5b** are in the range of 258.5(9) to 277.5(8) and 258.9(3) to 275.6(4) pm, respectively, and are thus slightly longer than the La–N bonds of the starting material [LaTp*₂(OTf)(CH₃CN)] (254.0(5) pm to 270.8(5) pm).³³ The reason is the stronger electron-donating effect of the carboxyl group in the heterobimetallic complexes.

The complexes **4a** and **4b** crystallise as racemic mixtures of the (S, δ) and (R, λ) enantiomers with one n-hexane molecule in the asymmetric unit. Only the (S, δ) enantiomer of nickel(II) complex **4a** and the (R, λ) enantiomer of copper(II) complex **4b** are depicted in Fig. 7.



Fig. 7 ORTEP of the molecular structures of $[Tp*_2La{Ni(bsalcen)}]$ n-hexane (4a) and $[Tp*_2La{Cu(bsalcen)}]$ -n-hexane (4b). The n-hexane molecules and the H atoms are omitted for clarity. The size of the ellipsoids relates to a probability of 50%.

The M–N and M–O (M = Ni, Cu) bond lengths are in the expected range for salen complexes.³² The difference between the La–O3 (**4b**: 263.7(2) pm, **4a**: 263.7(3) pm) and La–O4 (**4b**: 253.4(2) pm, **4a**: 250.8(3) pm) bond lengths is larger than in the heterobimetallic complexes **5a** and **5b**. This can be explained by the shorter metal-metal distances of about 593.1(8) pm (d(Ni ··· La)) and 607.4(7) pm (d(Cu ··· La)) and the resulting increased steric repulsion between the bulky Tp* ligands and the metallosalen ligand. For steric reasons, the COO ligand would be expected to occupy an equatorial position, but the COO groups are located in the sterically unfavourable axial position in both complexes. Because of this conformation the distance between the atoms C35H and O1 is rather short, *e.g.*, C35···O1 325.7(4) pm (**4b**) and 352.48(7) pm (**4a**), respectively, and the C35–H bond is directed towards O1, indicating a weak hydrogen bond.³⁴

2.4.4. Molecular structure of [Tp*2La(Cr{pz*H}2-{b(H)sal4cpn})] (5f). The chromium atom in the heterobimetallic complex 5f is octahedrally coordinated (Fig. 8). Two pz*H molecules occupy the axial position and form Cr-N(3,5) bonds with an average bond length of 211.4 pm. This bond length is comparable to that of the monometallic chromium(III) complex 2d" (212.7(2) pm). The 3,5-dimethylpyrazole rings are fixed by N6H ··· O2 and N4H ··· O4 hydrogen bonds, similar to the monometallic complex. The N6...O2 and N4...O4 distances are 259(1) pm and 264(1) pm, respectively.



Fig. 8 ORTEP of the molecular structure of $[Tp_2La(Cr{b(H)sal4cpn})]$ (5f). The n-hexane molecules, the H atoms and the *t*-butyl groups are omitted for clarity. The size of the ellipsoids relates to a probability of 50%.

One of the C=N imine bonds was reduced to a C–N single bond, as revealed by the N2–C30–C16 bond angle of $112.1(7)^{\circ}$ and the C30–N2 bond length of 145.7(7) pm. Accordingly, the Cr–N bond lengths in the equatorial plane differ by about 10 pm (d(Cr–N2) = 192.9(4) pm and d(Cr–N1) = 202.2(4) pm).

2.5 Cyclovoltammetric experiments

In accordance with our previous work⁹ we investigated the electrochemical properties of the mono- and heterobimetallic salen complexes. Besides many cyclovoltammetric measurements of

heterobimetallic complexes,³⁵ wherein the two metals are bridged by donor atoms, there exist only a few examples of cyclovoltammetric investigations of heterobimetallic complexes which contain two transition metals located at least two bonds apart.^{36,37} Weaker interactions between the transition metal atoms are expected in the latter, which represent the type of complexes in our studies, but the influence of the early transition metal on the redox potential of the late transition metal coordinated by the N₂O₂ coordination sphere is an important aspect with regard to the application of these complexes, *e.g.*, in catalytic oxidation reactions. For this reason the behaviour of the complexes was studied, especially under oxidative conditions.

A representative selection of mono- and heterobimetallic complexes was chosen for the cyclovoltammetric experiments. For the ligand H₃bsal4cpn, the monometallic complex [Ni(Hbsal4cpn)] (**2a**) and the heterobimetallic complex [Tp*₂La{Ni(bsal4cpn)}] (**5a**) were chosen. In case of the ligand Na(H₂bsalcen), the complexes [Na{Cu(bsalcen)}] (**1b**) and [Tp*₂La{Cu(bsalcen)}] (**4b**) were studied (see Fig. SI 1, ESI[†]).

The copper(II) complex 1b first undergoes an irreversible oxidation at $E_p = 0.66$ V (vs. SCE). Two quasireversible redox signals appear at $E_{1/2} = 0.90$ V and $E_{1/2} = 1.15$ V (vs. SCE), which were assigned to Cu^{II}/Cu^{III} and $Cu^{III}L/Cu^{III}L^+$ (L = salen ligand) by comparison with similar complexes.³⁸ The analogous quasireversible redox signals in the heterobimetallic complex 4b appear at $E_{\rm 1/2}$ = 0.85 V and $E_{\rm 1/2}$ = 1.15 V (vs. SCE). The irreversible signal has vanished in the heterobimetallic complex, which indicates the oxidation of the carboxy group in the monometallic complex 1b but not in the heterobimetallic complex 4b. It is well known that carboxylates undergo Kolbe electrolysis, which includes decarboxylation. Most likely the coordination of the carboxyl group to the $[LaTp_2^*]^+$ fragment prevents this reaction. A comparison of redox potentials of 1b and 4b is not reasonable because of the Kolbe electrolysis of the monometallic complex.

The cyclovoltammogram of the mononuclear nickel(II) complex 2a in dichloromethane (see Fig. SI 2, ESI[†]) shows two quasireversible signals at $E_{1/2} = 1.10$ V and $E_{1/2} = 1.39$ V (vs. SCE) which were assigned to Ni^{II}/Ni^{III} and $Ni^{III}L/Ni^{III}L^+$ (L = salen ligand), respectively. The analogous signals of the heterobimetallic complex 5a appear at $E_{1/2} = 1.09$ V and $E_{1/2} = 1.44$ V (vs. SCE) (see Fig. SI 2, ESI[†]). The difference between equivalent redox potentials of the mono- and heterobimetallic complexes is rather small and only significant in the case of E_{1/2}(Ni^{III}L/Ni^{III}L⁺). The redox potential $E_{1/2}(Ni^{III}L/Ni^{III}L^{+})$ of the heterobimetallic complex 5a is 50 mV higher than that of the monometallic equivalent 2a, which indicates a small electron-withdrawing effect caused by the early transition metal. To confirm this electronwithdrawing effect, another cyclic voltammetric measurement in the negative potential range was performed. As dichloromethane is unsuitable in the negative potential range, thf was used as solvent (see Fig. SI 3, ESI^{\dagger}). The E_{1/2}(Ni^I/Ni^{II}) values of the monoand heterobimetallic complex were determined to be -1.66 and -1.55 V (vs. SCE), respectively. The difference of 110 mV proves an electron-withdrawing effect of the early transition metal. The fact that this electron-withdrawing effect has a bigger influence on $E_{1/2}(Ni^{II}/Ni^{II})$ than on $E_{1/2}(Ni^{II}/Ni^{III})$ and $E_{1/2}(Ni^{III}L/Ni^{III}L^{+})$ was already observed in electrochemical investigations of Ni/Ru heterobimetallic salen complexes.³⁷

 Table 3
 Results of catalytic oxidation experiments with monometallic and heterobimetallic salen complexes

Complex	Oxidant	Reaction Time/h	Conversion [%]	Yield styrene oxide [%]
2c	mcpba/nmo	0.75 (15)	13.5 (24.4)	13.5 (24.4)
2a ^b	tbhp	18	11.5	2.0
2b ^b	tbhp	21	0	0
1a	tbhp	18	11.2	2.4
1b	tbhp	18	33.6	2.0
5b	tbhp	21	0.8	0.3
4a	tbhp	18	2.4	1.0
4b	tbhp	18	19.6	5.6
2d	phIO	18	23.2	9.2
5c	phIO	18	6.4	3.3
$2e^{a}$	phIO	1 (18)	3.7 (11.5)	3.0 (9.0)
5d	phIO	18	5.2	5.0

Conditions: CH₂Cl₂, 20 °C, complex : oxidant : styrene, 0.04 : 2 : 1, n_{complex} = 3×10^{-5} mol. Oxidants: mcpba/nmo = *meta*-chloroperoxybenzoic acid/N-methylmorpholine *N*-oxide, tbhp = *tert*-butylhydroperoxide, phIO = iodosobenzene,^{*a*} n_{complex} = 6×10^{-5} mol, ^{*b*} Na-salt employed.

2.6 Catalytic investigations

Selected monometallic and heterobimetallic complexes were tested in the homogeneous catalytic epoxidation of styrene. *meta*-Chloroperoxybenzoic acid/*N*-methylmorpholine *N*-oxide (mcpba/nmo), iodosobenzene (phIO) and *tert*-butyl hydroperox-ide (tbhp) were used as oxidants, depending on the transition metal involved (Table 3).

The sodium salts of the complexes 2a and 2d were tested because of their better solubility in CH_2Cl_2 .

Catalytic epoxidation reactions of olefins with Cu- and Nicontaining salen complexes were studied previously by Decinti *et al.*, Kochi *et al.* and Burrows *et al.*,³⁹ who observed a low activity of these complexes. Similarly, we achieved moderate conversions with the mono- and heterobimetallic Ni- and Cu-containing salen complexes. The maximum conversion of 33.6% was observed for the monometallic complex **1b** but with a very low styrene oxide yield of 2%.

Surprisingly the Mn, Cr and Fe complexes showed low catalytic activity in the oxidation of styrene. The maximum conversion of 24% after 15 h was obtained with the manganese(III) complex **2c**.

Extended reaction times with mcpba/nmo and phIO as oxidant did not result in a proportional increase of the conversion, while the opposite was observed for tbhp. This indicates that the complexes likely decompose in the presence of the oxidants mcpba/nmo and phIO whereas they are stable in the presence of tbhp. This is also indicated by brightening of the reaction solutions or suspensions after addition of mcpba/nmo and phIO within the stated reaction time.

Table 3 reveals that the heterobimetallic complexes always have a lower conversion rate than their monometallic analogues. However, these lower conversion rates were accompanied by higher selectivity with respect to styrene oxide. We assume that steric hindrance of the early transition metal complex fragment influences the reactivity by hampering approach to the catalytically active centre (transition metal).

3 Conclusions

Several monometallic salen complexes derived from *O*-functionalised diamines were prepared and used as metalloligands in the synthesis of heterobimetallic complexes. Monometallic salen complexes could be obtained *via* template synthesis from nickel(II) and copper(II). The analogous chromium(III), manganese(III) and molybdenum(IV) salen complexes were synthesised directly from the salen ligands. Reactions of the conjugated nickel(II) salen complex **2a** with metallocene derivatives gave soluble di- and trinuclear heterobimetallic complexes depending on the stoichiometry used. Cyclovoltammetric experiments on **2a**, **5a**, **1b** and **4b** showed the electron-withdrawing influence of the Tp*₂La fragment. The catalytic activity in the epoxidation of styrene was low for all tested complexes. The highest values (up to 24%) for the conversion of styrene to styrene oxide were obtained with manganese(III) salen complexes.

4 Experimental

All manipulations were carried out with standard high-vacuum and dry-nitrogen techniques. NMR spectra: Avance DRX 400 (Bruker), standards: ¹H NMR (400 MHz): TMS, ¹³C NMR (100.6 MHz): TMS. The IR spectra were recorded as KBr pellets on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer in the range 400-4000 cm⁻¹. The FAB mass spectra were obtained on an MAT-8030 VG ZAB-HSQ (Finnigan). The ESI mass spectra were recorded on an FT-ICR-MS device type Apex II (Bruker-Daltonics). For air- and water-sensitive samples atmospheric pressure photo-ionisation (APPI) was used as ionisation technique; the samples were dissolved in toluene-methanol and evaporated in vacuo. EPR spectra were recorded at 9.4 GHz (X band) using an ESP 300E spectrometer (Bruker). Magnetic moments were determined with the magnetic balances MK1 and MK2 (Johnson-Matthey) and corrected for the diamagnetic increments. Elemental analysis was performed on a VARIO EL (Heraeus). Melting points were determined in sealed capillaries and are uncorrected.

Cyclic voltammetry was carried out under N₂ atmosphere in dry, O₂-free dichloromethane with a three-electrode cell at room temperature (20 ± 2 °C). A platinum working electrode (diameter 2 mm, Metrohm), a platinum-plate counter-electrode (Meinsberg) and a Ag/AgCl reference electrode (filled with LiCl-saturated ethanol solution, Metrohm) in combination with a salt bridge, which was freshly filled with the supporting electrolyte before all measurements were made. A 0.1 M solution of [*n*Bu₄N]BF₄ in dry, O₂-free dichloromethane was used as supporting electrolyte. The analyte concentration was 3 mM and the scan rate 0.1 V s⁻¹. The cyclovoltammograms were recorded with a PAR 273A (Princeton Applied Research, now Ametek) potentiostat and analysed with "PowerCV". The system Fc/Fc⁺ was used as external standard. All redox potentials are referenced to SCE and were recalculated based on the system Fc/Fc⁺.⁴⁰

The reagents employed in the synthesis of Schiff base ligands and their complexes were used as received. 3,4-Diaminobenzoic acid and (R)-2,3-diaminopropionic acid monohydrochloride were purchased from Merck, NiCl₂·6H₂O, CuCl₂ and nBu_3N from Fluka and Fe(OAc)₂ from Aldrich. 3,5-Di-*tert*-butylsalicylaldehyde⁴¹ was synthesised by following literature procedures. [MnCl₂(thf)₂], [CrCl₃(thf)₃] and $[MoCl_4(CH_3CN)_2]$,^{42,43} $[Cp_2Zr(CH_3)_2]$ and $[Cp_2^{\circ}Ti(CH_3)_2]$,^{42,44} $[ZnCl_2(thf)_2]$,⁴⁵ $[LaTp_2^{*}(OTf)]$ and $[NdTp_2^{*}(OTf)]^{46}$ were synthesised according to literature procedures. $[LaTp_2^{*}(pz^*)]$ was already obtained as a by-product by Carpentier *et al.*⁴⁷ A new and improved synthesis was developed for this compound.

Improved synthesis of [LaTp*2(pz*)]

A solution of Na(pz*) in thf (2.17 mL of a 0.809 M solution, 1.76 mmol) was added *via* syringe at room temperature to a solution of [LaTp*₂(OTf)] (1.55 g, 1.76 mmol) in thf (30 mL). The solvent was removed *in vacuo* after stirring for 14 h. The retained solid was suspended in toluene (10 mL) and the suspension filtered. Subsequently, the filtrate was reduced in volume until a white solid precipitated. This solid was redissolved by warming the suspension. Storage at -35 °C overnight gave a white crystalline solid, which was isolated by cold filtration and dried in vacuo. The yield can be increased by layering the filtrate with n-hexane (twice the volume) and storing the solution for 15 h at room temperature and then for about 15 h at -35 °C. The resulting white precipitate was separated by filtration and dried in vacuo. The two crops of crystalline solid were combined.

Yield of $[LaTp_{2}(pz^{*})]$: 0.84 g (58%). ¹H NMR ($[D_{6}]$ benzene): $\delta_{\rm H}$ 6.04 (1H, s, $H_{pz^{*}}$), 5.62 (6H, s, $H_{Tp^{*}}$), 2.23 (18H, s, $H_{Tp^{*}}$), 1.97 (6H, s, $H_{pz^{*}}$), 1.79 (18H, s, $H_{Tp^{*}}$). IR (KBr): 3119 (w), 2927 (m), 2551 (w), 2525 (w), 1545 (s), 1517 (m), 1489 (m), 1441 (s), 1417 (s), 1380 (m), 1362 (s), 1342 (s), 1205 (s), 1076 (s), 1068 (s), 1031 (s), 981 (m), 832 (m), 809 (s), 778 (s), 697 (m), 650 (s), 460 (w), 430 (w) cm⁻¹.

Synthesis of Na(H₂bsalcen)

A solution of 3,5-di-tert-butylsalicylaldehyde (1.67 g, 7.12 mmol) in methanol (25 mL) was added via dropping funnel over 20 min at room temperature to a stirred suspension of (R)-2,3diaminopropionic acid mono-hydrochloride (0.50 g, 3.56 mmol) and sodium hydroxide (0.28 g, 7.12 mmol) in methanol (15 mL). The resulting yellow reaction mixture was heated to reflux for 20 min. The supernatant was filtered off from the bright yellow solid (impurities) via a filter cannula. From the yellow solution the solvent was evaporated *in vacuo* giving Na(H₂bsalcen). Yield: 1.97 g (98%), mp 192–195 °C. Found: C, 70.04; H, 7.99; N, 4.88%. C₃₃H₄₇N₂O₄Na requires C, 70.94; H, 8.48; N, 5.01%. IR (KBr): 3406 (w), 2958 (s), 1695 (sh), 1629 (s), 1527 (m), 1470 (s), 1441 (s), 1361 (m), 1251 (s), 1173 (m), 1113 (m), 1025 (m), 877 (m), 828 (m), 803 (m), 646 (w), 529 (w) cm⁻¹. IR (CsI): 646 (w), 539 (m), 488 (w), 454 (w), 278 (w) cm⁻¹.¹H NMR ([D_6]dmso): δ_H 14.47 (1H, s, C(2)OH), 14.07 (1H, s, C(2')OH), 8.52 (1H, s, C(7)H=N), 8.41 $(1H, s, C(7')H=N), 7.25 (1H, d, {}^{4}J_{HH} = 2.4 Hz, C(6)H), 7.50 (1H, d)$ d, ${}^{4}J_{HH} = 2.0$ Hz, C(6')H), 7.19 (1H, d, ${}^{4}J_{HH} = 2.4$ Hz, C(4)H), 7.15 (1H, d, ${}^{4}J_{HH} = 2.0$ Hz, C(4')H), 4.16 (1H, dd, ${}^{2}J_{HH} = 12.2$ Hz, ${}^{3}J_{\rm HH} = 3.6$ Hz, C(8)H₂), 4.00 (1H, dd, ${}^{3}J_{\rm HH} = 8.4$ Hz, ${}^{3}J_{\rm HH} =$ 3.6 Hz, C(9)*H*), 3.89 (1H, dd, ${}^{2}J_{HH} = 12.2$ Hz, ${}^{3}J_{HH} = 8.4$ Hz, $C(8)H_2$, 1.36 (9H, s, $C(3)C(CH_3)_3$), 1.34 (9H, s, $C(3')C(CH_3)_3$), 1.23 (18H, s, C(5)C(CH₃)₃ + C(5')C(CH₃)₃). 13 C NMR ([D₆]dmso): $\delta_{\rm C}$ 172.8 (s, C(9)COONa), 169.0 (d, ${}^{1}J_{\rm CH} = 125$ Hz, C(7)H=N), 167.7 (d, ${}^{1}J_{CH} = 126$ Hz, C(7')H=N), 160.5 (s, C(2)OH), 159.4 (s, C(2')OH), 140.6 (s, C(1)), 140.0 (s, C(1')), 137.2 (s, C(3)),

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137.0 (s, *C*(3')), 127.3 (d, ${}^{1}J_{CH} = 163$ Hz, *C*(4)H + *C*(4')H + *C*(6)H + *C*(6')H), 119.6 (s, *C*(5) + *C*(5')), 73.9 (d, ${}^{1}J_{CH} = 132$ Hz, *C*(9)H), 63.3 (t, ${}^{1}J_{CH} = 141$ Hz, *C*(8)H₂), 36.0 (s, *C*(3)*C*(CH₃)₃ + C(3')*C*(CH₃)₃), 35.2 (s, C(5)*C*(CH₃)₃ + C(5')*C*(CH₃)₃), 32.7 (q, ${}^{1}J_{CH} = 130$ Hz, C(3)*C*(CH₃)₃ + C(3')*C*(CH₃)₃), 30.7 (q, ${}^{1}J_{CH} = 124$ Hz, C(5)*C*(CH₃)₃ + C(5')*C*(CH₃)₃). FAB MS: *m*/*z* 625.3 ([M + 3 Na – 2 H]⁺, 18.6%), 603.3 ([M + 2 Na – H]⁺, 71.0%), 581.3 ([M + Na]⁺, 100.0%).

Synthesis of H₃bsal4cpn

A solution of 3,5-di-*tert*-butylsalicylaldehyde (4.68 g, 0.02 mol) in thf (40 mL) was added *via* dropping funnel over 20 min to a suspension of 3,4-diaminobenzoic acid (1.52 g, 0.01 mol) in thf (50 mL). Subsequently a solution of $[\text{ZnCl}_2(\text{thf})_2]$ (2.80 g, 0.01 mol) in thf (25 mL) was added over 10 min. The resulting yellow-green reaction mixture was heated to reflux for 45 min and the solvent was evaporated in vacuo. The resulting solid was suspended in methanol (25 mL) and stirred for 15 min. After filtering off the supernatant *via* a filter cannula the remaining yellow solid was washed two times with methanol (25 mL) and dried in vacuo.

Yield of H₃bsal4cpn: 5.27 g (90%), mp 231–233 °C. IR (KBr): 3425 (w), 2988 (s), 1690 (m), 1616 (s), 1575 (s), 1438 (m), 1362 (m), 1252 (m), 1172 (s), 1132 (w), 1026 (w), 771 (m) cm^{-1} . ¹H NMR ([D_6]dmso): δ_H 13.58 (1H, s, C(2)OH), 13.50 (1H, s, C(2')OH), 9.05 (1H, s, C(7)H=N), 8.99 (1H, s, C(7')H=N), 8.03 (1H, s, C(12)H), 7.95 (1H, d, ${}^{3}J_{HH} = 8.0$ Hz, C(9)H), 7.58 (1H, d, ${}^{3}J_{\rm HH} = 8.0$ Hz, C(10)H), 7.57 (1H, s, C(6)H), 7.50 (1H, s, C(6')H), 7.43 (1H, s, C(4)H), 7.41 (1H, s, C(4')H), 1.38 (18H, s, $C(3)C(CH_3)_3 + C(3')C(CH_3)_3), 1.30 (18H, s, C(5)C(CH_3)_3 +$ $C(5')C(CH_3)_3$). (The COOH proton could not be identified regardless the usage of $[D_6]$ dmso.) ¹³C{¹H} NMR ($[D_8]$ thf): $\delta_{\rm C}$ 167.6 (C(7)H=N), 167.0 (C(11)COOH), 166.8 (C(7')H=N), 159.8 (C(2)OH), 159.6 (C(2')OH), 147.6 (C(8)), 143.6 (C(13)), 141.2 (C(1)), 141.1 (C(1')), 137.7 (C(3)), 137.5 (C(3')), 130.8 (C(11)COOH), 129.6 (C(10)H), 129.1 (C(12)H), 128.8 (C(9)H), 128.5 (C(4)H), 128.4 (C(4')H), 121.7 (C(6)H), 120.7 (C(6')H), 119.8 (C(5)), 119.7 (C(5')), 33.4 ($C(3)C(CH_3)_3 + C(3')C(CH_3)_3$), 32.5 $(C(5)C(CH_3)_3 + C(5')C(CH_3)_3)$, 28.9 $(C(3)C(CH_3)_3 + C(5')C(CH_3)_3)$ $C(3')C(CH_3)_3$, 27.1 ($C(5)C(CH_3)_3 + C(5')C(CH_3)_3$). FAB MS: m/z 585.4 ([M + H]⁺, 58.9%), 376.2 ([M-C₁₅H₂₂O₂ + H₂O + H]⁺, 51.5%), 219.3 ([M-C₁₅H₂₂O₂-C₇H₈N₂O₂-CH₃ + 2H₂O]⁺, 100.0%).

Synthesis of [Ni{Na(bsalcen)}] (1a)

A solution of NaOH (0.04 g, 1.08 mmol) in methanol (10 mL) and NiCl₂·6H₂O (0.13 g, 0.54 mmol) dissolved in methanol (10 mL) was added *via* dropping funnel at room temperature over 15 min to a solution of Na(H₂bsalcen) (0.30 g, 0.54 mmol) in methanol (10 mL). After heating the resulting red-brown suspension to reflux for 1 h the supernatant solution was filtered off *via* a filter cannula from the bright red solid. The solvent was evaporated from the dark red filtrate and the remaining solid was dried in vacuo.

Yield of **1a**: 0.28 g (84%), red solid, mp 284–289 °C. Found: C, 63.80; H, 7.09; N, 4.13; O, 10.80%. C₃₃H₄₅N₂O₄NaNi requires C, 64.40; H, 7.37; N, 4.55; O, 10.40%. ¹H NMR ([D_6]dmso): $\delta_{\rm H}$ 7.75 (1H, s, C(7)H=N), 7.60 (1H, s, C(7)H=N), 7.15 (2H, s, C(6)H + C(6')H), 7.03 (2H, s, C(4)H + C(4')H), 3.66 (1H, d, ³ $J_{\rm HH}$ = 12.0 Hz, C(8) H_2), 3.54 (1H, t, ³ $J_{\rm HH}$ = 12.0 Hz, C(9)H), 3.45 (1H, d, ${}^{3}J_{HH} = 12.0$ Hz, C(8) H_{2}), 1.32 (9H, s, C(3)C(CH₃)₃), 1.31 (9H, s, C(3')C(CH₃)₃), 1.23 (9H, s, C(5)C(CH₃)₃), 1.21 (9H, s, C(5')C(CH₃)₃). ${}^{13}C{}^{1}H{}$ NMR ([D_{6}]dmso): δ_{C} 164.3 (s, C(10)OONa), 163.0 (s, C(7)H=N + C(7')H=N), 161.7 (s, C(2)O), 161.5 (s, C(2')O), 138.9 (s, C(1)), 138.7 (s, C(1')), 135.1 (s, C(3)), 135.0 (s, C(3')), 127.6 (s, C(4)H), 127.4 (s, C(4')H), 127.1 (s, C(6)H), 126.8 (s, C(6')H), 120.5 (s, C(5)), 120.4 (s, C(5')), 69.3 (s, C(9)H), 62.8 (s, C(8)H₂), 35.8 (s, C(3)C(CH₃)₃ + C(3')C(CH₃)₃), 34.0 (s, C(5)C(CH₃)₃ + C(5')C(CH₃)₃), 31.9 (s, C(3)C(CH₃)₃ + C(3')C(CH₃)₃), 30.1 (s, C(5)C(CH₃)₃ + C(5')C(CH₃)₃). FAB MS: m/z 637.2 ([M + Na]⁺, 100.0%), 615.3 ([M + H]⁺, 24.1%), 593.3 ([M⁺-Na + H]⁺, 19.8%).

Synthesis of [Cu{Na(bsalcen)}] (1b)

A solution of NaOCH₃ (0.097 g, 1.79 mmol) in methanol (10 mL) was quickly added at room temperature to a solution of Na(H₂bsalcen) (0.50 g, 0.9 mmol) in methanol (20 mL). After stirring the yellow solution for 10 min CuCl₂ (0.12 g, 0.9 mmol) dissolved in methanol (10 mL) was added at room temperature. The dark-green suspension was heated to reflux for 30 min. Subsequently, the solvent was removed *in vacuo* and the retained green solid was suspended in thf (15 mL). After filtration the solvent of the filtrate was removed *in vacuo* and the resulting green solid was washed with diethyl ether (5 mL) and dried in vacuo.

Yield of **1b**: 0.32 g (58%), mp 262 °C. Found: C, 63.08; H, 7.13; N, 4.63%. C₃₃H₄₅N₂O₄NaCu requires C, 63.90; H, 7.31; N, 4.51%. IR (KBr): 2957 (s), 1614 (sh), 1596 (s), 1536 (s), 1464 (sh), 1430 (s), 1410 (s), 1387 (m), 1362 (m), 1321 (m), 1273 (m), 1256 (m), 1236 (w), 1200 (w), 1172 (m), 1025 (w), 842 (w), 538 (w) cm⁻¹. ESI MS neg. (methanol): *m*/*z* 596.3 ([M–Na]⁻, 100%). EPR (thf): $a_0^{Cu} = 87.9 \times 10^{-4}$ cm⁻¹, $g_0 = 2.102$ (at 293 K); $g_{\parallel} = 2.205$, $g_{\perp} = 2.051$, $A_{\parallel}^{Cu} = 203.7 \times 10^{-4}$ cm⁻¹, $A_{\perp}^{Cu} = 33.7 \times 10^{-4}$ cm⁻¹ (at 130 K); a_0^{Cu} , $A_i^{Cu} = \pm 1.0 \times 10^{-4}$ cm⁻¹, $g_i = \pm 0.001$.

Synthesis of [MnCl{Na(bsalcen)}] (1c)

Solid $[MnCl_2(thf)_2]$ (0.21 g, 0.79 mmol) was added at room temperature over 15 min to a solution of Na(H₂bsalcen) (0.46 g, 0.79 mmol) in thf (25 mL) and Et₃N (0.22 mL, 0.16 g, 1.6 mmol). The resulting light brown suspension was heated to reflux for 1 h. Afterwards, air was bubbled through the dark brown solution through an inlet for 1 h and then the solution was heated to reflux again for 2 h. The solvent was evaporated from the resulting dark brown solution and the remaining dark brown solid was suspended in toluene (10 mL). After stirring at room temperature the formed ammonium chloride was filtered off *via* a filter cannula and a dark brown solid was obtained after removing the solvent in vacuo.

Yield of **1c**: 0.46 g (90%), mp 220–223 °C. Found: C, 61.73; H, 7.43; N, 4.67%. $C_{33}H_{45}N_2O_4NaMnCl$ requires C, 61.25; H, 7.01; N, 4.33%. IR (KBr): 3047 (sh), 2960 (s), 1611 (s), 1536 (s), 1463 (m), 1435 (s), 1390 (s), 1307 (m), 1254 (s), 1176 (s), 1098 (m), 1026 (m), 842 (m), 751 (m), 563 (m) cm⁻¹. IR (CsI): 644 (w), 563 (m), 491 (w), 473 (w), 391 (m), 270 (w) cm⁻¹. FAB MS: *m*/*z* 589.1 ([M–Cl–Na + H]⁺, 62.9%), 544.1 ([M–Cl–COO–Na]⁺, 89.4%).

Synthesis of [CrCl{Na(bsalcen)}] (1d)

 $[CrCl_3(thf)_3]$ (0.44 g, 1.16 mmol) was suspended in toluene (10 mL), added to a solution of Na(H₂bsalcen) (0.65 g, 1.16 mmol)

in toluene (20 mL) and Et₃N (0.32 mL, 0.24 g, 2.32 mmol) and stirred at room temperature for 1 h. After heating the suspension to reflux for 30 min the reaction mixture was reduced to approx. 20 mL and kept afterwards for 4 h at -18 °C. The precipitated ammonium chloride was filtered off at 0 °C *via* a filter cannula. The solvent was evaporated from the dark brown filtrate and the remaining dark brown solid was dried in vacuo.

Yield of **1d**: 0.73 g (98%), mp 338–340 °C. Found: C, 61.40; H, 8.20; N, 4.24%. $C_{33}H_{45}N_2O_4NaCrCl C$, 61.53; H, 7.04; N, 4.35%. IR (KBr): 3047 (sh), 2958 (s), 2711 (w), 2486 (w), 1610 (s), 1532 (s), 1459 (s), 1411 (s), 1387 (s), 1323 (m), 1257 (s), 1170 (s), 1134 (s), 1026 (m), 814 (m), 746 (m), 545 (m) cm⁻¹. IR (CsI): 639 (w), 547 (m), 510 (w), 494 (w), 397 (m), 279 (w) cm⁻¹. FAB MS: *m/z* 586.2 ([M–Cl]⁺, 100.0%).

Synthesis of [MoCl₂{Na(bsalcen)}] (1e)

A suspension of $[MoCl_4(CH_3CN)_2]$ (0.20 g, 0.63 mmol) in toluene (10 mL) was added at room temperature over 10 min to a solution of Na(H₂bsalcen) (0.35 g, 0.63 mmol) in toluene (15 mL) and Et₃N (0.18 mL, 0.13 g, 1.26 mmol). The resulting black brown suspension was heated to reflux for 90 min. The formed ammonium chloride was filtered off *via* a filter cannula and a black solid was obtained after removing the solvent in vacuo. Black crystals suitable for X-ray analysis could be obtained from an acetonitrile solution of **1e** at room temperature.

Yield of **1e**: 0.33 g (72%), mp 290–295 °C. Found: C, 54.50; H, 7.27; N, 4.36%. C₃₃H₄₅N₂O₄NaMoCl₂ requires C, 54.78; H, 6.27; N, 3.87%. IR (KBr): 3017 (sh), 2961 (s), 1618 (m), 1603 (m), 1537 (m), 1463 (m), 1362 (m), 1261 (s), 1246 (s), 1098 (m), 1025 (m), 805 (s), 560 (m) cm⁻¹. IR (CsI): 644 (w), 560 (m), 491 (w), 483 (w), 465 (w), 392 (m), 319 (w), 278 (w) cm⁻¹. ESI MS (toluene–CH₃CN): m/z 749.37 ([M–2 Cl + O + Et₃NH]⁺, 62.9%). Magnetic moment: 2.51 BM (calc. 2.83 BM (spin only)).

Template synthesis of [Ni(Hbsal4cpn)] (2a) and [Cu(Hbsal4cpn)] (2b)

General method: A solution of 3,4-diaminobenzoic acid (0.76 g, 5 mmol) in methanol (70 mL) and the corresponding hydrated metal chloride (5 mmol) dissolved in methanol (40 mL) was added *via* dropping funnel at room temperature over 10 min to a solution of 3,5-di-*tert*-butylsalicylaldehyde (2.34 g, 10 mmol) in methanol (70 mL). After refluxing the resulting brown suspension for 1 h and reducing the volume to 30 mL, the reaction mixture was left overnight and a red solid precipitated, which was washed three times with methanol (10 mL) and dried in vacuo. Red crystals suitable for X-ray analysis were obtained from 1,4-dioxane.

Yield of **2a**: 1.82 g (57%), red solid, mp 380 °C. Found: C, 64.60; H, 7.44; N, 3.69%. C₃₇H₄₆N₂O₄Ni + 2 H₂O + CH₃OH requires C, 64.33; H, 7.67; N, 3.95%. IR (KBr): 3422 (m), 3054 (m), 2959 (s), 1688 (m), 1618 (s), 1579 (s), 1526 (s), 1463 (m), 1426 (s), 1386 (s), 1359 (s), 1260 (m), 1200 (s), 1180 (s), 1130 (m), 1026 (m), 788 (m), 541 (m) cm⁻¹. ¹H NMR ([D_6]dmso): $\delta_{\rm H}$ 13.24 (1H, s, C(11)COOH), 8.98 (1H, s, C(7)H=N), 8.91 (1H, s, C(7')H=N), 8.72 (1H, s, C(12)H), 8.27 (1H, d, ³J_{HH} = 8.8 Hz, C(9)H), 7.84 (1H, d, ³J_{HH} = 8.8 Hz, C(10)H), 7.62 (1H, d, ⁴J_{HH} = 2.4 Hz, C(6)H), 7.48 (1H, d, ⁴J_{HH} = 1.9 Hz, C(6')H), 7.37 (1H, d, ⁴J_{HH} = 2.4 Hz, C(4)H), 7.37 (1H, d, ⁴J_{HH} =

1.9 Hz, C(4')*H*), 1.40 (18H, s, C(3)C(*CH*₃)₃ + C(3')C(*CH*₃)₃), 1.29 (18H, s, C(5)C(*CH*₃)₃ + C(5')C(*CH*₃)₃). ¹³C{¹H} NMR ([*D*₈]thf): $\delta_{\rm C}$ 167.1 (*C*(7)H=N), 164.4 (C(11)COOH), 163.7 (*C*(7')H=N), 158.2 (*C*(2)O), 157.9 (*C*(2')O), 146.4 (*C*(8)), 142.9 (*C*(13)), 139.9 (*C*(1)), 139.1 (*C*(1')), 136.8 (*C*(3)), 136.6 (*C*(3')), 130.7 (*C*(11)COOH), 130.3 (*C*(10)H), 129.4 (*C*(12)H), 128.7 (*C*(9)H), 128.3 (*C*(4)H), 128.0 (*C*(4')H), 120.3 (*C*(6)H + *C*(6')H), 117.3 (*C*(5)), 116.2 (*C*(5')), 35.9 (C(3)*C*(*CH*₃)₃ + C(3')*C*(*CH*₃)₃), 34.2 (C(5)*C*(*CH*₃)₃ + C(5')*C*(*CH*₃)₃), 31.6 (*C*(3)*C*(*CH*₃)₃), 42.2 (*C*(5)*C*(*CH*₃)₃ + C(5')*C*(*CH*₃)₃), 31.6 (*C*(3)*C*(*CH*₃)₃). ESI MS (*CH*₃OH/isopropanol): *m*/*z* 639.274 ([M – H]⁻, 100.0%).

Yield of **2b**: 1.42 g (44%), red solid, mp 325 °C (decomp.). Found: C, 68.30; H, 7.49; N, 4.63%. C₃₇H₄₆N₂O₄Cu requires C, 68.76; H, 7.17; N, 4.33%. IR (KBr): 3428 (m), 2959 (sh), 1690 (m), 1618 (s), 1597 (s), 1578 (s), 1523 (s), 1427 (s), 1358 (s), 1256 (s), 1198 (s), 1175 (s), 1129 (m), 1025 (w), 792 (m), 766 (w), 533 (m) cm⁻¹. ESI MS (isopropanol): m/z 644.262 ([M – H]⁻, 100.0%). EPR (thf): $a_0^{Cu} = 85.2 \times 10^{-4}$ cm⁻¹, $g_0 = 2.106$ (at 293 K); $g_{\parallel} = 2.217$, $g_{\perp} = 2.050$, $A_{\parallel}^{Cu} = 202.7 \times 10^{-4}$ cm⁻¹, $A_{\perp}^{Cu} = 30.8 \times 10^{-4}$ cm⁻¹ (at 130 K); a_0^{Cu} , $A_i^{Cu} = \pm 1.0 \times 10^{-4}$ cm⁻¹, $g_i = \pm 0.001$.

Synthesis of [NHEt₃][MnCl(bsal4cpn)] (2c)

Solid $[MnCl_2(thf)_2]$ (0.16 g, 0.6 mmol) was added at room temperature over 5 min to a solution of H₃bsal4cpn (0.35 g, 0.6 mmol) in thf (35 mL). The resulting light brown suspension was stirred for 1 h at room temperature and heated to reflux afterwards for 20 min. Et₃N (0.17 mL, 0.12 g, 1.2 mmol) was added *via* pipette to the reaction mixture, and then air was bubbled through the dark brown solution *via* an inlet for 45 min. The resulting dark brown solution was reduced to dryness and the remaining dark brown solid was suspended in toluene (10 mL). After stirring for 2 h at room temperature the formed light brown solid was left to settle over night. The supernatant solution was filtered off *via* a filter cannula and a dark brown solid was retained after removing the solvent in vacuo.

Yield of **2c**: 0.25 g (63%), mp 242–245 °C. Found: C, 68.90; H, 7.14%. $C_{37}H_{46}N_2O_4MnCl$ requires C, 66.02; H, 6.89%. IR (KBr): 3430 (m), 2960 (m), 1670 (sh), 1610 (s), 1577 (s), 1463 (s), 1389 (s), 1361 (s), 1313 (s), 1255 (s), 1198 (s), 1180 (s), 1097 (s), 1027 (s), 807 (s), 781 (s), 545 (m) cm⁻¹. ESI MS (thf/CH₃CN): *m/z* 774.380 ([M + NHEt₃]⁺, 100.0%), 637.280 ([M–Cl]⁺, 25.9%).

Synthesis of [CrCl(Hbsal4cpn)] (2d)

A solution of $[CrCl_3(thf)_3]$ (0.19 g, 0.5 mmol) in toluene (25 mL) was added *via* dropping funnel at room temperature within 15 min to a solution of H₃bsal4cpn (0.29 g, 0.5 mmol) in toluene (20 mL). After heating the suspension to reflux for 15 min and reducing the resulting dark red mixture to dryness, the solid was washed two times with diethyl ether (10 mL) and dried in vacuo. Red crystals suitable for X-ray analysis were obtained either from acetonitrile ([CrCl(CH₃CN)(Hbsal4cpn)], **2d**') or on addition of pz*H in 1,4-dioxane/n-hexane ([CrCl(pz*H)(Hbsal4cpn)], **2d**'').

Yield of **2d**: 0.33 g (98%), dark red solid, mp 350 °C. Found: C, 65.20; H, 7.83; N, 4.23%. $C_{37}H_{46}N_2O_4CrCl$ requires C, 66.31; H, 6.92; N, 4.18%. IR (KBr): 3385 (w), 3051 (sh), 2959 (s), 1715 (sh), 1612 (s), 1576 (s), 1526 (s), 1461 (sh), 1362 (s), 1328 (sh), 1259 (s), 1198 (s), 1172 (s), 1099 (s), 1023 (s), 872 (m), 804 (s), 730 (m) cm⁻¹.

FAB MS: *m*/*z* 669.2 ([M]⁺, 10.0%), 634.3 ([M–Cl]⁺, 100.0), 619.3 ([M–Cl–CH₃]⁺, 69.0%), 585.3 ([M–Cr–Cl–3 H]⁺, 38.0%). Magnetic moment: 3.60 BM (calc. 3.87 BM (spin only)).

Synthesis of [Fe(bsal4cpn)] (2e)

Solid Fe(OAc)₂ (0.12 g, 0.68 mmol) was added at room temperature to a solution of H₃bsal4cpn (0.4 g, 0.68 mmol) in thf/methanol (25 mL/25 mL). The resulting dark brown suspension was heated to reflux for 45 min in air. After cooling the solution to room temperature, the solvent was removed in vacuo. The retained solid was suspended in methanol (10 mL) and then filtered. The dark brown solid was washed with diethyl ether (10 mL) and dried for 15 h *in vacuo* at 100 °C.

Yield of **2e**: 0.37 g (85%), mp > 300 °C. Found: C, 69.27; H, 7.26%. C₃₇H₄₅N₂O₄Fe requires C, 69.70; H, 7.11%. IR (KBr): 2958 (s), 1663 (m), 1609 (s), 1579 (s), 1551 (m), 1531 (s), 1463 (m), 1426 (s), 1388 (m), 1377 (m), 1361 (s), 1312 (m), 1272 (m), 1253 (s), 1238 (m), 1198 (m), 1176 (m), 1132 (m), 1099 (w), 870 (w), 842 (m), 822 (w), 783 (w), 774 (w), 749 (w), 543 (m) cm⁻¹. ESI MS (methanol-acetonitrile/thf): *m/z* 1293.6 ([2M + 2H + OH]⁺, 100.0%), 1275.6 ([2M + H]⁺, 32.1%), 710.3 ([M + H + thf]⁺, 47.1%). Magnetic moment: 5.99 BM (calc. 5.90 BM (d⁵ high spin, spin only)).

Synthesis of [MoCl₂(Hbsal4cpn)] (2f)

 nBu_3N (1.81 mL, 1.41 g, 7.6 mmol) was added *via* pipette to a solution of H₃bsal4cpn (2.20 g, 3.8 mmol) in thf (30 mL). Then solid [MoCl₄(CH₃CN)₂] (1.21 g, 3.8 mmol) was added at room temperature over 15 min to the orange solution. After refluxing the suspension for 50 min and reducing the resulting black-brown solution to half its volume, the supernatant dark brown solution was filtered off *via* a filter cannula. The remaining black solid was washed two times with thf (10 mL) and dried in vacuo. Black crystals suitable for X-ray analysis were obtained from acetonitrile at room temperature.

Yield of **2f**: 1.85 g (65%), mp 222 °C. Found: C, 59.70; H, 7.14%. $C_{37}H_{46}N_2O_4MoCl_2$ requires C, 59.28; H, 6.18%. IR (KBr): 3415 (w), 3043 (sh), 2961 (s), 1715 (m), 1602 (m), 1573 (s), 1530 (s), 1463 (m), 1363 (m), 1261 (s), 1184 (m), 1099 (s), 1027 (m), 803 (s), 770 (s), 705 (m) cm⁻¹. FAB MS: m/z 750.1 ([M]⁺, 90.0%), 715.2 ([M–Cl]⁺, 76.0%), 696.2 ([M–Cl–OH–2 H]⁺, 100.0%), 585.3 ([M– Mo–2 Cl–2 H]⁺, 60.0). Magnetic moment: 2.85 BM (calc. 2.83 BM (spin only)).

Synthesis of [Cp₂Zr{Ni(bsal4cpn)}₂] (3a)

In a round-bottom Schlenk flask **2a** (0.7 g, 1.1 mmol) was dried *in vacuo* for 30 min and afterwards suspended in toluene (25 mL). A solution of $[Cp_2Zr(CH_3)_2]$ (0.137 g, 0.55 mmol) in toluene (50 mL) was added *via* a Schlenk flask with a cone inlet at room temperature over 10 min. After the addition, slight gas evolution was observed. The reaction mixture was heated to reflux for 30 min and then stirred at room temperature for 10 h. A small amount of precipitate was filtered off *via* a filter cannula. After removing the solvent *in vacuo* from the red filtrate a dark red solid was obtained.

Yield of **3a**: 0.73 g (88%), mp 360 °C (decomp.). IR (KBr): 3047 (sh), 2957 (m), 1720 (w), 1646 (w), 1577 (s), 1524 (s), 1424 (s), 1358 (m), 1259 (s), 1179 (s), 1100 (s), 1022 (m), 810 (s), 730 (m) cm⁻¹. ¹H NMR ([D_8]toluene): $\delta_{\rm H}$ 8.62 (2H, s, C(7)H=N), 8.17 (2H, d,

³ $J_{\text{HH}} = 8.8 \text{ Hz}, C(9)H$, 8.03 (2H, s, C(7')H=N), 7.69 (2H, s, C(12)H), 7.65 (2H, s, C(6)H), 7.60 (2H, s, C(6')H), 7.08 (2H, d, ³ $J_{\text{HH}} = 8.8 \text{ Hz}, C(10)H$), 7.02 (2H, s, C(4)H), 6.84 (2H, s, C(4')H), 6.20 (10H, s, (C₅ H_5)₂), 1.73 (36H, s, C(3)C(C H_3)₃ + C(3')C(C H_3)₃), 1.41 (18H, s, C(5)C(C H_3)₃), 1.29 (18H, s, C(5')C(C H_3)₃). FAB MS: m/z 1498.5 ([M]⁺, 0.7%), 640.3 ([M–Ni(Hbsal4cpn)–Zr(C₅ H_5)₂ + H]⁺, 100.0%).

Synthesis of $[Cp^{\circ}_{2}Ti{Ni(bsal4cpn)}_{2}]$ (3b)

In a round-bottom Schlenk flask **2a** (0.48 g, 0.74 mmol) was dried *in vacuo* for 30 min and then suspended in toluene (40 mL). A solution of $[Cp^{\circ}_{2}Ti(CH_{3})_{2}]$ (0.14 g, 0.37 mmol) in toluene (50 mL) was added *via* dropping funnel at room temperature over 15 min. After addition, slight gas evolution was observed. The reaction mixture was stirred at room temperature for 14 h. A small amount of precipitate was filtered off *via* a filter cannula. After removing the solvent *in vacuo* from the red filtrate, a dark red solid was obtained.

Yield of **3b**: 0.46 g (76%), mp 400 °C (decomp.). Found: C, 69.29; H, 8.15; N, 3.25%. C₉₆H₁₂₄N₄O₈Ni₂Ti requires C, 70.86; H, 7.68; N, 3.44%. IR (KBr): 3349 (m), 3255 (m), 2960 (s), 2869 (m), 1610 (sh), 1580br, 1424br, 1383br, 1261 (m), 1198 (m), 1179 (m), 1024br, 786 (m), 729 (w), 666 (m), 622 (m), 495 (s) cm⁻¹. ¹H NMR ([*D*₆]dmso): $\delta_{\rm H}$ 7.62 (4H, s, C(7)*H*=N + C(7')*H*=N), 7.44 (8H, br, C(6)*H*, C(6')*H*, C(4)*H* + C(4')*H*), 6.87 (2H, d, ³*J*_{HH} = 8.0 Hz, C(10)*H*), 6.76 (2H, d, ³*J*_{HH} = 8.0 Hz, C(9)*H*), 6.42 (2H, s, C(12)*H*), 3.65 (4H, s, (C₅(CH₂CH₃)(CH₃)₄)₂), 1.68 (6H, s, (C₅(CH₂CH₃)(CH₃)₄)₂), 1.66 (6H, s, (C₅(CH₂CH₃)(CH₃)₄)₂), 1.59 (6H, s, C(5)C(CH₂CH₃)(CH₃)₄)₂), 1.36 (6H, s, (C₅(CH₂CH₃)(CH₃)₄)₂), 1.31 (36H, s, C(3)C(CH₃)₃ + C(3')C-(CH₃)₃), 1.19 (36H, s, C(5)C(CH₃)₃ + C(5')C(CH₃)₃), 1.04 (6H, s, (C₅(CH₂CH₃)(CH₃)₄)₂).

Synthesis of [Tp*₂La{Ni(bsalcen)}] (4a)

A solution of $[LaTp*_2(OTf)]$ (0.20 g, 0.23 mmol) in toluene (10 mL) was added over 5 min at 0 °C to a suspension of **1a** (0.14 g, 0.23 mmol) in toluene (10 mL). The suspension was stirred for 2 h at 0 °C and then filtered. The solvent was removed *in vacuo* and the retained brown solid was washed with a small amount of diethyl ether. The resulting compound was dried in vacuo. Red crystals suitable for X-ray analysis were obtained from n-hexane.

Yield of 4a: 0.18 g (60%), mp 250-255 °C. Found: C, 57.46; H, 6.58; N, 14.53%. C₆₃H₈₉B₂N₁₄O₄LaNi requires C, 57.08; H, 6.77; N, 14.79%. IR (KBr): 2958 (s), 2555 (w), 2513 (w), 1615 (s), 1573 (s), 1543 (s), 1437 (s), 1416 (s), 1360 (s), 1325 (s), 1259 (s), 1203 (s), 1176 (s), 1099 (s), 1070 (s), 1035 (s), 982 (m), 869 (m), 807 (s), 784 (s), 697 (m), 637 (m) cm⁻¹. ¹H NMR ([D_6]benzene): δ_H 7.60 (1H, d, ${}^{4}J_{\rm HH} = 2.0$ Hz, $H_{\rm arom.}$), 7.52 (1H, d, ${}^{4}J_{\rm HH} = 2$ Hz, $H_{\rm arom.}$), 7.16 (1H, s, *H*C=N), 6.69 (1H, d, ${}^{4}J_{HH} = 2.0$ Hz, $H_{arom.}$), 6.62 (1H, d, ${}^{4}J_{HH} =$ 2.0 Hz, $H_{\text{arom.}}$), 6.53 (1H, s, HC=N), 5.72 (6H, s, $H_{\text{Tp}*}$), 4.76 (2H, br, BH_{Tp^*}), 3.06 (1H, d, ${}^{2}J_{HH} = 14$ Hz, H_2C_2), 2.82 (1H, d, ${}^{3}J_{HH} =$ 6 Hz, *H*CCOO), 2.70 (1H, dd, ${}^{2}J_{HH} = 14$ Hz, ${}^{3}J_{HH} = 6$ Hz, H_{2} C), 2.11 (18H, s, H_{Tp^*}), 2.10 (18H, s, H_{Tp^*}), 1.83 (9H, s, H_{tBu}), 1.78 (9H, s, H_{tBu}), 1.41 (9H, s, H_{tBu}), 1.25 (9H, s, H_{tBu}). ¹³C{¹H} NMR $([D_8]$ benzene): δ_C 181.1 (COO), 165.6 (C=N), 162.1 (C=N), 150.4 (C_{Tp^*}) , 145.7 (C_{Tp^*}) , 163.6, 163.2, 140.7, 140.6, 135.4, 135.2, 129.0, 128.6, 126.8, 126.5, 120.7, 120.5 (C_{arom}), 106.8 (C_{Tp*}), 71.1 (CH₂),

59.3 (CCO	O), 36.4 (C_{tBu}), 36.3 (C_{tBu}), 34.1 (C_{t1}	_{Bu}), 33.9 (C_{tBu}), 31.8
$(C_{tBu}), 31.6$	$(C_{tBu}), 30.29$	$(C_{tBu}), 30.27$	$(C_{tBu}), 13.3$	$8(C_{Tp^*}), 1$	$3.2(C_{Tp^*}).$

Synthesis of [Tp*2La{Cu(bsalcen)}] (4b)

A solution of $[LaTp*_2(OTf)]$ (0.20 g, 0.22 mmol) in thf (5 mL) was added at room temperature to a solution of **1b** (0.14 g, 0.22 mmol) in thf (15 mL). The resulting suspension was stirred for 6 h at room temperature. Afterwards, the solvent was removed in vacuo, the retained solid suspended in toluene (10 mL) und the resulting suspension filtered. The volume of the filtrate was reduced to 1-2 mL in vacuo. Subsequently, the green solution was covered with a layer of n-hexane (8 mL). Brown crystals suitable for X-ray analysis formed overnight.

Yield of **4b**: 0.14 g (50%), mp 235 °C. Found: C, 57.69; H, 6.49; N, 14.82%. $C_{63}H_{89}B_2N_{14}O_4LaCu$ requires C, 57.87; H, 6.74; N, 14.74%. IR (KBr): 2958 (s), 2553 (w), 2523 (w), 1615 (s), 1568 (m), 1442 (s), 1528 (s), 1439 (s), 1415 (s), 1389 (s), 1361 (s), 1325 (m), 1271 (m), 1256 (m), 1233 (w), 1202 (s), 1168 (s), 1070 (m), 1036 (m), 981 (m), 864 (w), 832 (w), 807 (m), 789 (m), 778 (m), 746 (w), 729 (w), 696 (w), 646 (m), 534 (w), 463 (w) cm⁻¹. Magnetic moment: 1.68 BM (calc. 1.73 BM (spin only)). EPR (thf): $a_0^{Cu} = 87.9 \times 10^{-4} \text{ cm}^{-1}$, $B_0 = 2.101$ (at 293 K); $g_{\parallel} = 2.203$, $g_{\perp} = 2.051$, $A_{\parallel}^{Cu} = 205.7 \times 10^{-4} \text{ cm}^{-1}$, $A_{\perp}^{Cu} = 32.9 \times 10^{-4} \text{ cm}^{-1}$ (at 130 K); a_0^{Cu} , $A_i^{Cu} = \pm 1.0 \times 10^{-4} \text{ cm}^{-1}$, $g_i = \pm 0.001$.

Synthesis of [Tp*2La{Ni(bsal4cpn)}] (5a)

A solution of NaOH (14 mg, 0.36 mmol) in methanol (1.5 mL) was added at room temperature to a suspension of 2a (0.23 g, 0.36 mmol) in methanol (10 mL). After stirring for 1 h the solvent was removed in vacuo. The retained red solid was suspended in toluene/thf(15 mL/5 mL) and the suspension filtered. The solvent of the filtrate was removed in vacuo. The resulting red solid was dried, weighed and then suspended in toluene (10 mL). A solution of [LaTp*₂(OTf)] (0.33 g, 0.37 mmol) in toluene (10 mL) was added. The suspension was stirred for 3 h at room temperature and then filtered. The solvent was removed *in vacuo* and the retained red solid washed with n-hexane (5 mL) and dried in vacuo. Red crystals suitable for X-ray analysis were obtained by diffusion of n-hexane vapour into a solution of the product in 1,4-dioxane.

Yield of 5a: 0.26 g (54%), mp 240 °C. Found: C, 58.78; H, 6.36; N, 14.67%. C₆₇H₈₉B₂N₁₄O₄LaNi requires C, 58.58; H, 6.53; N, 14.28%. IR (KBr): 2957 (s), 2553 (w), 2523 (w), 1616 (m), 1605 (m), 1579 (s), 1544 (s), 1524 (s), 1417 (s), 1402 (s), 1384 (s), 1361 (s), 1263 (m), 1200 (s), 1180 (s), 1131 (m), 1099 (w), 1069 (m), 1033 (m), 981 (w), 846 (w), 830 (m), 809 (m), 787 (s), 778 (s), 697 (w), 649 (m), 541 (w), 465 (w), 437 (w) cm⁻¹. ¹H NMR ([D_6]benzene): $\delta_{\rm H}$ 8.36 (1H, s, $H_{\rm arom.}$), 7.81 (1H, d, ${}^{3}J_{\rm HH}$ = 8.8 Hz, $H_{\rm arom.}$), 7.65 $(1H, d, {}^{4}J_{HH} = 2.4 \text{ Hz}, H_{arom.}), 7.62 (1H, s, HC=N), 7.58 (1H, d, d)$ ${}^{4}J_{\rm HH} = 2.4$ Hz, $H_{\rm arom.}$), 7.47 (1H, s, HC=N), 6.94 (1H, d, ${}^{4}J_{\rm HH} =$ 2.0 Hz, $H_{\text{arom.}}$), 6.66 (1H, d, ${}^{3}J_{\text{HH}} = 8.8$ Hz, $H_{\text{arom.}}$), 6.39 (1H, d, ${}^{4}J_{\rm HH} = 2.0$ Hz, $H_{\rm arom.}$), 5.64 (6H, s, $H_{\rm Tp^*}$), 4.89 (2H, br, $BH_{\rm Tp^*}$), 2.16 (18H, s, H_{Tp*}), 2.06 (18H, s, H_{Tp*}), 1.77 (9H, s, H_{tBu}), 1.75 (9H, s, H_{tBu}), 1.38 (9H, s, H_{tBu}), 1.28 (9H, s, H_{tBu}). ¹³C{¹H} NMR $([D_8]$ benzene): $\delta_C 180.4 (COO), 154.8 (C=N), 154.7 (C=N), 150.1$ $(C_{\text{Tp}*})$, 145.4 $(C_{\text{Tp}*})$, 166.2, 165.5, 145.8, 142.9, 141.5, 140.8, 136.9, 136.4, 133.9, 130.9, 130.6, 127.6, 127.1, 127.9, 120.2, 120.1, 115.8,

114.1, 106.6 ($C_{\text{Tp}*}$), 2 × 36.4 (C_{tBu}), 2 × 34.1 (C_{tBu}), 2 × 31.5 (C_{tBu}), 2 × 30.2 (C_{tBu}), 13.5 ($C_{\text{Tp}*}$), 13.4 ($C_{\text{Tp}*}$).

Synthesis of [Tp*2La{Cu(bsal4cpn)}] (5b)

The synthesis of **5b** was carried out according to the synthesis of **5a**. Brown crystals suitable for X-ray analysis were obtained from n-hexane.

Yield of **5b**: 0.28 g (65%), brown solid, mp 230 °C. Found: C, 57.91; H, 6.15; N, 14.29%. $C_{67}H_{89}B_2N_{14}O_4LaCu$ requires C, 58.37; H, 6.51; N, 14.22%. IR (KBr): 2957 (s), 2556 (w), 2523 (w), 1612 (sh), 1604 (s), 1579 (s), 1645 (s), 1523 (s), 1463 (s), 1427 (s), 1385 (s), 1360 (s), 1259 (s), 1198 (s), 1174 (s), 1131 (m), 1068 (m), 1031 (m), 981 (w), 829 (m), 809 (s), 791 (m), 779 (m), 695 (w), 649 (m), 534 (w), 459 (w) cm⁻¹. Magnetic moment: 1.89 BM (calc. 1.73 BM (spin only)). EPR (thf): $a_0^{Cu} = 88.2 \times 10^{-4}$ cm⁻¹, $g_0 = 2.104$ (at 293 K); $g_{\parallel} = 2.214$, $g_{\perp} = 2.049$, $A_{\parallel}^{Cu} = 201.4 \times 10^{-4}$ cm⁻¹, $A_{\perp}^{Cu} = 35.7 \times 10^{-4}$ cm⁻¹ (at 130 K); $(a_0^{Cu}, A_i^{Cu} = \pm 1.0 \times 10^{-4}$ cm⁻¹, $g_i = \pm 0.001$).

Synthesis of [Tp*2Nd{Ni(bsal4cpn)}] (6a)

The synthesis of **6a** was carried out according to the synthesis of **5a**.

Yield of **6a**: 0.36 g (73%), red solid, mp 290 °C. Found: C, 58.35; H, 6.50; N, 14.35%. C₆₇H₈₉B₂N₁₄O₄NdNi requires C, 58.35; H, 6.50; N, 14.28%. IR (KBr): 2957 (s), 2557 (w), 2524 (w), 1616 (m), 1605 (m), 1579 (s), 1545 (s), 1525 (s), 1417 (s), 1360 (s), 1263 (m), 1200 (s), 1179 (s), 1068 (m), 1033 (s), 831 (m), 809 (m), 788 (m), 778 (m), 648 (w) cm⁻¹. ¹H NMR ([*D*₈]thf): $\delta_{\rm H}$ 21.61 (1H, *H*_{arom}), 20.56 (1H, *H*_{arom}), 12.50 (1H, *H*_{arom}), 12.66 (1H, *H*C=N), 11.00 (1H, *H*C=N), 8.90 (1H, *H*_{arom}), 8.50 (1H, *H*_{arom}), 8.00 (1H, *H*_{arom}), 7.89 (1H, *H*_{arom}), 2.04 (9H, *H*_{*t*Bu}), 2.01 (9H, *H*_{*t*Bu}), 1.85 (9H, *H*_{*t*Bu}), 1.68 (9H, *H*_{*t*Bu}). ¹³C{¹H} NMR ([*D*₈]thf): $\delta_{\rm C}$ 193.3, 167.3, 166.5, 160.2 (*C*=N), 158.9 (*C*=N), 151.9, 150.8, 144.2, 143.9, 142.0, 141.5, 138.1, 137.8, 131.8, 131.4, 129.1, 129.7, 122.9, 122.6, 37.2 (*C*_{*t*Bu}), 35.2 (*C*_{*t*Bu}), 32.1 (*C*_{*t*Bu}), 30.9 (*C*_{*t*Bu}), 15.0 (*C*T_{p*}). CH_{Tp*} not observed. Magnetic moment: 4.02 BM (calc. 3.62 BM).

Synthesis of [Tp*₂Nd{Cu(bsal4cpn)}] (6b)

The synthesis of **6b** was carried out according to the synthesis of **5a**.

Yield of **6b**: 0.58 g (66%), brown solid, mp 237 °C. Found: C, 57.49; H, 6.87; N, 13.64%. $C_{67}H_{89}B_2N_{14}O_4NdCu$ requires C, 58.15; H, 6.48; N, 14.17%. IR (KBr): 2958 (s), 2554 (w), 2524 (w), 1615 (sh), 1604 (s), 1580 (s), 1545 (s), 1523 (s), 1427 (s), 1385 (s), 1361 (s), 1259 (m), 1199 (s), 1174 (s), 1131 (m), 1099 (w), 1068 (m), 1032 (m), 982 (w), 830 (m), 809 (m), 792 (m), 779 (m), 648 (m) cm⁻¹. Magnetic moment: 4.01 BM (calc. 3.92 BM). EPR (thf): $a_0^{Cu} = 88.2 \times 10^{-4}$ cm⁻¹, $g_0 = 2.105$ (at 293 K); $g_{\parallel} = 2.214$, $g_{\perp} = 2.049$, $A_{\parallel}^{Cu} = 203.1 \times 10^{-4}$ cm⁻¹, $A_{\perp}^{Cu} = 35.7 \times 10^{-4}$ cm⁻¹ (at 130 K); $(a_0^{Cu}, A_i^{Cu} = \pm 1.0 \times 10^{-4}$ cm⁻¹, $g_i = \pm 0.001$).

Synthesis of [Tp*2La{CrCl(pz*H)(bsal4cpn)}] (5c)

Solid $[LaTp_2^*(pz^*)]$ (0.26 g, 0.31 mmol) was added at room temperature to a solution of **2d** (0.22 g, 0.31 mmol) in thf (10 mL). The resulting red solution was stirred for 18 h at room temperature. Subsequently the solvent was removed *in vacuo* and the retained solid suspended in n-hexane (10 mL). The suspension was stirred

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Table 4 Crystallographic data and structure refinement for complexes 2a, 2d', 2d'', 2f, 2f', 4a, 4b, 5a, 5b, 5e, and 5f

	1		1								
	[Ni(Hbsal4cpn)]. 1,4-dioxane (2a-1,4-dioxane)	[CrCl(CH ₃ CN)- (Hbsal4cpn)]. 6acetonitrile <i>a</i> (2d ⁴ 6acetonitrile)	[CrCl(pz*H)- (Hbsal4cpn)]-1,4- dioxane (2d "-1,4-dioxane)	[MoCl ₂ (Hbsal4cpn)]- 4acetonitrile (2f 4acetonitrile)	Decomp. product of [MoCl ₂ (Hbsal- 4cpn]]: 2f'	[Tp*2La{Ni- (bsalcen)}]. n-hexane (4a · n-hexane)	[Tp*2La{Cu- (bsalcen)}]- n-hexane (4b n-hexane)	[Tp*2La{Ni- (bsal4cpn)}]. 1,4-dioxane- 0.5n-hexane (5a-1,4-dioxane- 0.5n-hexane)	[Tp*2La{Cu- (bsal4cpn)}]. n-hexane (5b-n-hexane)	[(Tp * ₂ La{Fe- (bsal4cpn)}) ₂ - (μ-O)]- 3.5toluene (5 e-3.5toluene)	$\label{eq:constraints} \begin{split} & [Tp^*_2La(Cr- \\ \{pz^*H\}_2\{b(H)-saldepn\})] \\ & saldepn\})]. \\ & 2n-hexane \\ & b(\mathbf{5f}, 2n-hexane) \end{split}$
Formula	C45H67N3NiO8	C ₅₁ H ₆₇ ClCrN ₉ O ₄	C46 He2 CICrN 4 O6	C45H58Cl2-	C ₈₀ H ₁₀₂ Cl ₃ Mo ₂ -	C60 H103B2-	C ₆₀ H103B2-	C74H104B2-	C ₇₃ H ₁₀₃ B,Cu-	C158 5 H206 B4-	C ₈₀ H ₁₃₄ B ₂ -
	0			MoN ₆ O ₄	N5O10	LaN ₁₄ NiO ₄	CuLaN ₁₄ O ₄	LaN ₁₄ NiO ₆	LaN ₁₄ O ₄	Fe2LaN2809	CrLaN ₁₈ O ₄
f.w. [g mol ⁻¹]	817.68	957.59	854.45	913.81	1591.90	1411.89	1416.72	1504.95	1464.76	3080.27	1732.67
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	C2/c	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a/pm	1747.6(1)	1551.2(1)	952.5(2)	1512.9(2)	1820.0(6)	1765.4(4)	1445.18(8)	2342.8(1)	1656.0(2)	1928.9(1)	1683.4(1)
b/pm	1490.9(1)	1675.1(1)	1581.2(3)	1650.8(3)	2150.9(7)	1723.6(4)	1665.3(2)	3633.8(1)	2266.7(2)	2400.6(1)	1734.4(1)
c/pm	1913.0(1)	2145.5(2)	1753.9(3)	2058.5(3)	2077.8(7)	2378.7(6)	1723.6(2)	2103.3(1)	2181.3(2)	3693.8(2)	2014.8(1)
α (°)	90	90	66.03(2)	90	90	90	108.151(9)	90	90	90	68.716(1)
β ()	115.318(6)	101.405(1)	79.98(2)	106.592(3)	92.341(7)	96.492(4)	109.351(7)	112.113(3)	107.794(9)	101.821(1)	66.965(1)
γ (°) 32	90	90 (11)	76.19(2)	90	90	90	95.541(7)	90	90 5 20 200	90 5 - 15 (2)	67.794(1)
$\int_{c} \operatorname{mu} dA$	4.5054(5)	5.4647(7)	2.3352(7)	4.927(1)	8.13(1)	7.19(1)	3.6254(6)	16.589(1)	7.796(1)	16.742(2)	4.8496(5)
N	4	4	2	4	4	4	2	8	4	4	2
$\rho_{\rm c}/{\rm g~cm^{-3}}$	1.205	1.164	1.215	1.232	1.301	1.304	1.298	1.205	1.248	1.222	1.187
μ/mm^{-1}	0.482	0.307	0.351	0.419	0.465	0.904	0.930	0.789	0.867	0.731	0.601
F(000)	1752	2036	910	1912	3328	2968	1486	6312	3068	6444	1834
Crystal size/mm	$0.30 \times 0.20 \times 0.10$	$0.40 \times 0.40 \times 0.30$	$0.30 \times 0.20 \times 0.10$	$0.30 \times 0.30 \times 0.30$	$0.40 \times 0.10 \times 0.05$	$0.30 \times 0.20 \times 0.10$	$0.30 \times 0.28 \times 0.20$	$0.38 \times 0.06 \times 0.04$	$0.21 \times 0.20 \times 0.05$	$0.30 \times 0.30 \times 0.30$	$0.30 \times 0.20 \times 0.10$
θ range for data	2.49 to 25.96	1.81 to 26.81	2.55 to 30.51	1.93 to 26.37	1.47 to 23.25	1.81 to 28.30	2.53 to 30.51	3.07 to 23.25	2.05 to 26.03	1.56 to 26.46	1.49 to 23.30
ounceuou [] no of refins collected	30196	3 5900	68185	26767	348.50	75513	105164	37286	57213	83550	21299
no of inden reflux R	8271 0.0895	11401 0.0306	14196 0.0449	10009 0.0755	11649 0155	17722 0.066	21995 0 0273	11844 0 1052	14483 0 0829	29634 0.0665	13764 0.0466
restraints/ parameters	0/519	87/632	0/545	0/514	147/806	10/875	23/873	16/870	9/888	228/1794	1/979
goodness-of-fit on F^2	0.563	1.060	1.032	1.164	1.003	1.077	1.035	1.041	0.663	1.000	0.944
$R[I > 2\sigma(I)]$	$R_1 = 0.0362$	$R_1 = 0.0572$	$R_1 = 0.0475$	$R_1 = 0.0797$	$R_{\rm l} = 0.1010$	$R_1 = 0.0692$	$R_1 = 0.0330$	$R_1 = 0.0955$	$R_1 = 0.0366$	$R_1 = 0.0653$	$R_1 = 0.0576$
	$wR_2 = 0.0615$	$wR_2 = 0.1593$	$wR_2 = 0.1218$	$wR_2 = 0.1608$	$wR_2 = 0.2305$	$wR_2 = 0.1235$	$wR_2 = 0.0779$	$wR_2 = 0.2144$	$wR_2 = 0.0666$	$wR_2 = 0.1504$	$wR_2 = 0.1291$
R (all data)	$R_1 = 0.1233$	$R_1 = 0.0854$	$R_1 = 0.0811$	$R_1 = 0.1384$	$R_1 = 0.2075$	$R_1 = 0.1093$	$R_1 = 0.0448$	$R_1 = 0.1495$	$R_1 = 0.0927$	$R_1 = 0.1303$	$R_1 = 0.0941$
	$wR_2 = 0.0710$	$wR_2 = 0.1716$	$wR_2 = 0.1392$	$wR_2 = 0.1895$	$wR_2 = 0.2853$	$wR_2 = 0.1362$	$wR_2 = 0.0847$	$wR_2 = 0.2386$	$wR_2 = 0.0747$	$wR_2 = 0.1729$	$wR_2 = 0.1403$
Largest diff peak and hole [e/10 ⁶ nm ³]	0.276 and -0.229	0.399 and -0.325	0.656 and -0.622	1.133 and -0.990	1.677 and -1.126	1.185 and -0.651	2.031 and -1.257	3.991 and -0.914	0.515 and -0.271	0.789 and -0.519	0.766 and -0.600
CCDC number	736166	736167	736176	736168	736169	736173	736174	736171	736172	736170	736175
" Two acetonitrile n	nolecules were rei	moved by SOUE	EZE ^b Two mole	cules n-hexane were	e removed by SC	UEEZE					

for 10 min and then filtered. The collected red solid was dried in vacuo.

Yield of **5c**: 0.21 g (45%), mp > 300 °C. Found: C, 55.89; H, 6.85; N, 14.92%. $C_{67}H_{89}B_2N_{14}O_4LaCrCl\cdot C_5H_8N_2$ requires C, 57.70; H, 6.53; N, 14.96%. IR (KBr): 3404 (w), 3293 (w), 2958 (s), 2553 (w), 2524 (w), 1610 (s), 1579 (s), 1543 (s), 1526 (s), 1417 (s), 1379 (s), 1362 (s), 1274 (m), 1256 (m), 1197 (s), 1172 (s), 1134 (m), 1097 (m), 1070 (m), 1035 (s), 982 (m), 872 (w), 829 (m), 809 (m), 783 (s), 748 (w), 697 (w), 650 (m), 540 (m), 464 (w), 431 (w) cm⁻¹. Magnetic moment: 4.11 BM (calc. 3.92 BM (spin only)).

Synthesis of $[Tp*_2La{FeCl(bsal4cpn)}]$ (5d)

HCl/diethyl ether (0.15 mL of 2 M solution, 0.30 mmol) was added at room temperature to a stirred solution of **2e** (0.19 g, 0.30 mmol) in thf (10 mL). The solution was stirred for 10 min. Subsequently the solvent was removed in vacuo. The retained solid was dissolved in thf (15 mL) and was then treated with a solution of $[LaTp*_2(pz*)]$ (0.24 g, 0.3 mmol) in thf (6 mL). The solution was stirred for 14 h at room temperature and then the solvent was removed in vacuo. The resulting brown solid was dissolved in hot n-hexane (10 mL). A microcrystalline brown solid precipitated overnight and was dried in vacuo.

Yield of **5d**: 0.21 g (50%), mp > 300 °C. Found: C, 57.18; H, 6.82; N, 14.01%. $C_{67}H_{89}B_2N_{14}O_4LaFeCl$ requires C, 57.21; H, 6.38; N, 14.01%. IR (KBr): 2958 (s), 2553 (w), 2521 (w), 1608 (s), 1579 (s), 1543 (s), 1530 (s), 1424 (s), 1377 (s), 1361 (s), 1274 (m), 1255 (s), 1199 (s), 1177 (s), 1134 (m), 1119 (w), 1099 (w), 1068 (m), 1032 (s), 981 (m), 870 (m), 830 (s), 810 (s), 780 (s), 748 (m), 730 (w), 697 (m), 665 (w), 649 (m), 542 (m), 492 (w), 461 (w), 426w cm⁻¹. Magnetic moment: 5.07 BM (calc. 5.92 BM (spin only)).

Synthesis of $[(Tp*_2La{Fe(bsal4cpn)})_2(\mu-O)]$ (5e)

NaOH in methanol (1 mL of a 1.02 M solution, 1.07 mmol) was added at room temperature to a suspension of 2e (0.68 g, 1.07 mmol) in methanol (10 mL). During the addition the solid dissolved and the colour changed from green to dark brown. The solution was stirred for 1 h and separated from a small amount of solid by filtration. The solvent of the filtrate was removed in vacuo. Subsequently, the orange-brown solid was dissolved in toluene (20 mL) and treated with a solution of $[LaTp*_2(OTf)]$ (0.94 g, 1.07 mmol) in toluene (20 mL). The brown suspension was stirred for 16 h at room temperature and then filtered. The solvent of the filtrate was removed in vacuo, the retained orange solid was washed with n-hexane and dried in vacuo. Crystals were obtained by dissolving the solid in toluene (10 mL) and vapour-phase diffusion of n-hexane into this solution after three weeks.

Yield of **5e**: 0.59 g (41%), mp > 300 °C. Found: C, 59.40; H, 6.92; N, 13.99%. $C_{134}H_{178}B_4N_{28}O_9La_2Fe_2\cdot C_7H_8$ requires C, 59.42; H, 6.58; N, 13.76%. IR (KBr): 2958 (s), 2556 (w), 2524 (w), 1610 (s), 1600 (sh), 1579 (s), 1544 (s), 1527 (s), 1423 (s), 1387 (s), 1361 (s), 1258 (m), 1198 (s), 1175 (s), 1069 (m), 1034 (m), 868 (m), 829 (m), 809 (m), 780 (m), 649 (m), 537 (m) cm⁻¹. Magnetic moment: 3.01 BM (calc. 8.37 BM (spin only)).

X-ray crystallography

The data for 2d'·6CH₃CN, 2f·4CH₃CN, the decomp. product 2f', 4a·n-hexane, 5e·3.5toluene and 5f·2n-hexane were collected

on a Siemens CCD diffractometer (SMART)⁴⁸ in ω scan mode. Data reduction with SAINT,⁴⁹ including the program SADABS⁵⁰ for empirical absorption correction. The data for **2a**·1,4-dioxane, **5a**·1,4-dioxane·0.5n-hexane and **5b**·n-hexane were collected on a Stoe IPDS imaging plate diffractometer, ϕ scan mode, numerical absorption correction with XRED,⁵¹ and the data for **4b**·n-hexane and **2d**["]·1,4-dioxane on an Xcalibur-S diffractometer (Oxford Diffraction), ω and ϕ scan mode. Data reduction with CrysAlis Pro,⁵² including the program SCALE3 ABSPACK⁵³ for empirical absorption correction. Used radiation: Mo-K α (λ = 71.073 pm). The structures were solved by direct methods and the refinement of all non-hydrogen atoms was performed with SHELX97.⁵⁴ Details are summarised in Table 4. Structure figures were generated with DIAMOND-3.⁵⁵

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