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A dianionic C_3-symmetric scorpionate: synthesis and coordination chemistry†

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Introducing charges into ligand systems fine-tunes their electronic properties and influences the solubility of their metal complexes. Herein, we present a synthesis of a dianionic, C_3-symmetric ligand combining three anionic N-donors tethered to a positively charged phosphonium center. The tris-skatylmethylphosphonium (TSMP) ligand, isolated in the form of its dipotassium salt $TSMPK_2$, is the first dianionic homoscorpionate capable of metal exchange. The potassium cations in $TSMPK_2$ are exchangeable for other metals, which results in rich coordination chemistry. Thus, the ligand displays a bridging $\mu^2{:}\kappa^2{:}\kappa^1$ coordination mode with trigonal planar Cu(I) centers in the tetrameric complex $[(TSMP)Cu]_4^{4-}$. The κ^3 mode is accessed upon addition of 1 equiv. of $P(OEt)_3$ per Cu(I) to yield the tetrahedral monomeric complex $[(TSMP)CuP(OEt)_3]^-$. Both Fe(II) and Ni(II) in pyridine give octahedral high-spin κ^3 complexes with composition $(TSMP)M(Py)_3$ (M = Fe, Ni). Displacement of three pyridine ligands in $(TSMP)Fe(Py)_3$ for a second equivalent of TSMP gives a high-spin pseudotetrahedral 2 : 1 complex $[(TSMP)_2Fe]^{2-}$ with the ligands in κ^2 coordination mode. The reduction in coordination number is likely due to electrostatic repulsion of the negatively-charged indolides as well as their weaker π-accepting character as compared to pyridine.

Introduction

The term "scorpionate" was introduced by Trofimenko[1] and refers to tripodal tridentate ligand systems that are able to coordinate to a metal with two identical donor moieties, similarly to the pincers of a scorpion. The third donor moiety rotates forward akin to a scorpion stinger to attack the metal in a *fac* manner. If it is identical to the first two, a C_3-symmetric homoscorpionate complex forms; otherwise, coordination results into a heteroscorpionate complex.

Most scorpionates are six-electron donors, which makes them isoelectronic to another common ligand, cyclopentadienyl (Cp). A considerable amount of research was done to compare these two systems.[1,2] It is important to point out, however, that while they are isoelectronic, they are not isolobal,[3] therefore the extent of such a comparison is limited. Additionally, in some situations, scorpionates are capable of displaying a κ^2 coordination mode freeing the third arm for binding to another metal center,[1] which sets them apart from Cp ligands.

The first generation of homoscorpionates involved trispyrazolylborates[1] and proved to be highly versatile spectator ligands. By modifying the nature, number and position of substituents of the pyrazolyl rings, a wide range of ligands was prepared enabling both electronic and steric properties of a coordinated metal to be fine-tuned. Such systems have found applications in biomimetics,[4] catalysis,[5] material science[6] and production of radiopharmaceuticals.[7] Following this success, the definition of scorpionates has been extended to tripodal tridentate systems with other donor groups and bridging atoms. Among the employed donors are imidazole,[8] pyridine,[9] triazole,[10] indole,[11] methimazole,[12] oxazoline,[13] N-heterocyclic carbenes[14] and others, and even acyclic donor groups.[15] Variation of the bridging atom allowed to further tune electronics and charge of the scorpionate ligands, thus influencing coordination behavior and solubility of their complexes. Reported systems include CH/COH,[9] CH_3/C_6H_5-Si,[16] N,[9a] P,[8,9,17] $[R–P]^+$,[18] P=O,[9b,19] As,[9a] As=O,[9b] $[CH_3$-Al$]^-$,[20] $[CH_3$-Ga$]^-$,[21] C^-,[22] Si-,[23] Ge^-, Sn^-,[24] Pb^-.[20]

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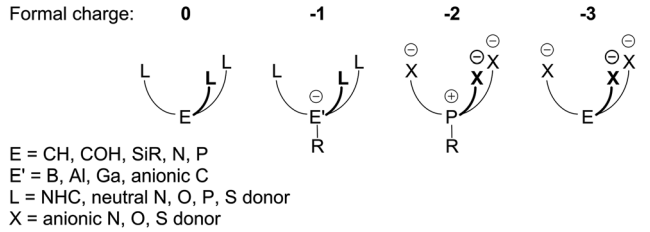


Chart 1 C_3-Symmetric scorpionates with distinct formal charges.

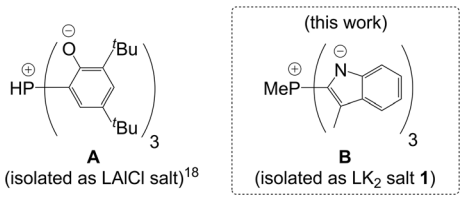


Chart 2 Dianionic C_3-symmetric scorpionates.

A more general way to classify the existing C_3-symmetric scorpionates is by formal charge, which is a combined property of the donor moieties and the bridging atom. Thus, one can differentiate neutral, mono-, di- and trianionic homoscorpionates (Chart 1). Whereas there is a plethora of known neutral[8,9,14,16,17] and monoanionic[1,10,12,13,20–22,24] homoscorpionates as well as some trianionic examples,[11] dianionic ligands are rare with only one reported precedent[18] (**A** in Chart 2). The latter was isolated as a LAlCl complex, and its LAlMe complex could be methylated at phosphorus to afford a methylphosphonium derivative. However strong Al–O bonds would likely preclude the possibility of a subsequent metal exchange and make broader exploration of its coordination chemistry difficult.

Herein, we present the synthesis of a C_3-symmetric dianionic ligand **B** (Chart 2), isolated as its dipotassium salt **1**, which fills the aforementioned gap in the assortment of charged scorpionates available for complexation. Taking advantage of the fact that potassium cations are easily exchangeable for other metal ions, we further delve into its coordination chemistry with Cu(I), Fe(II) and Ni(II) salts.

Results and discussion

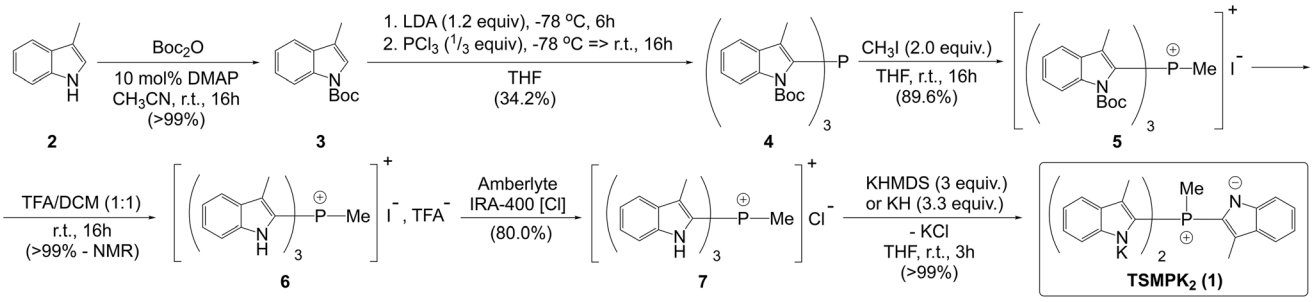
Ligand synthesis

The dipotassium salt of tris-(2-skatyl)methylphosphonium (**1**), further abbreviated as $TSMPK_2$, was synthesized as depicted in Scheme 1. In the first step, skatole (**2**) was treated with di-*tert*-butyl dicarbonate (Boc_2O) in the presence of 4-dimethylaminopyridine (DMAP) to yield the corresponding *N*-Boc derivative (**3**). The second position of the indole ring was subsequently lithiated with lithium diisopropylamide (LDA) using *N*-Boc as a directing group. Without isolation, the lithium salt was quenched with a third of an equivalent of PCl_3 to yield tris-2-(*N*-Boc-skatyl)phosphine (**4**). The phosphine was then methylated by treatment with an excess (2.0 equiv.) of methyl iodide to form the corresponding methylphosphonium iodide (**5**). Attempted methylation with an equimolar amount of methyl iodide instead resulted in the incomplete methylation and partial deprotection of the *N*-Boc-skatole subunits. It is worth pointing out that tris-2-(*N*-Boc-skatyl)methylphosphonium iodide (**5**) exists in DCM-d_2 solution as a *ca.* 1.00 : 0.15 mixture of interexchanging tris-*exo* and bis-*exo*-mono-*endo* rotamers (see ESI section S4.1†).[25]

Complete deprotection of the isolated methylphosphonium iodide **5** can be achieved in a 1 : 1 mixture of dichloromethane and trifluoroacetic acid (TFA). The product, **6**, was subjected to ion exchange using the chloride form of the anion exchange resin Amberlite® IRA-400, affording a white crystalline solid of tris-(2-skatyl)methylphosphonium chloride (**7**).

Deprotonation of tris-indole **7** with either KHMDS or KH gives the $TSMPK_2$ salt (**1**). A highly pure material (>99% according to NMR) was isolated by crystallization from acetonitrile/diethyl ether. X-ray crystal structure determination confirmed the expected molecular structure with a K : P ratio of 2 : 1 (Fig. 1).

The K^+ cations are involved in an extensive network of cation–N and cation–π interactions (η^1 to η^6). The K–N distances vary between 2.723(4) and 3.425(4) Å, and the K–C distances between 2.995(4) and 3.510(4) Å. With such a large variation of distances it is not possible to derive a clearly defined coordination number. Overall, K^+ coordination leads to the formation of one-dimensional chains in the [110] direction, which are stacked upon each other in *c*-direction. This stacking



Scheme 1 Synthesis of $TSMPK_2$ salt **1**. Unless otherwise stated, parentheses underneath reaction arrows indicate isolated yields.

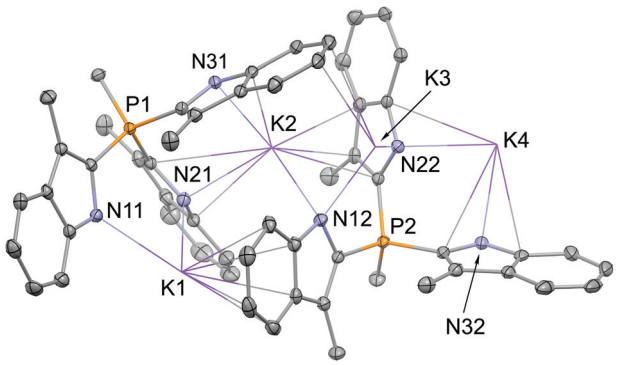


Fig. 1 Asymmetric unit of the $TSMPK_2$ (**1**) crystal. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms and acetonitrile solvent molecules are omitted for clarity. Potassium atoms are shown in a wireframe style.

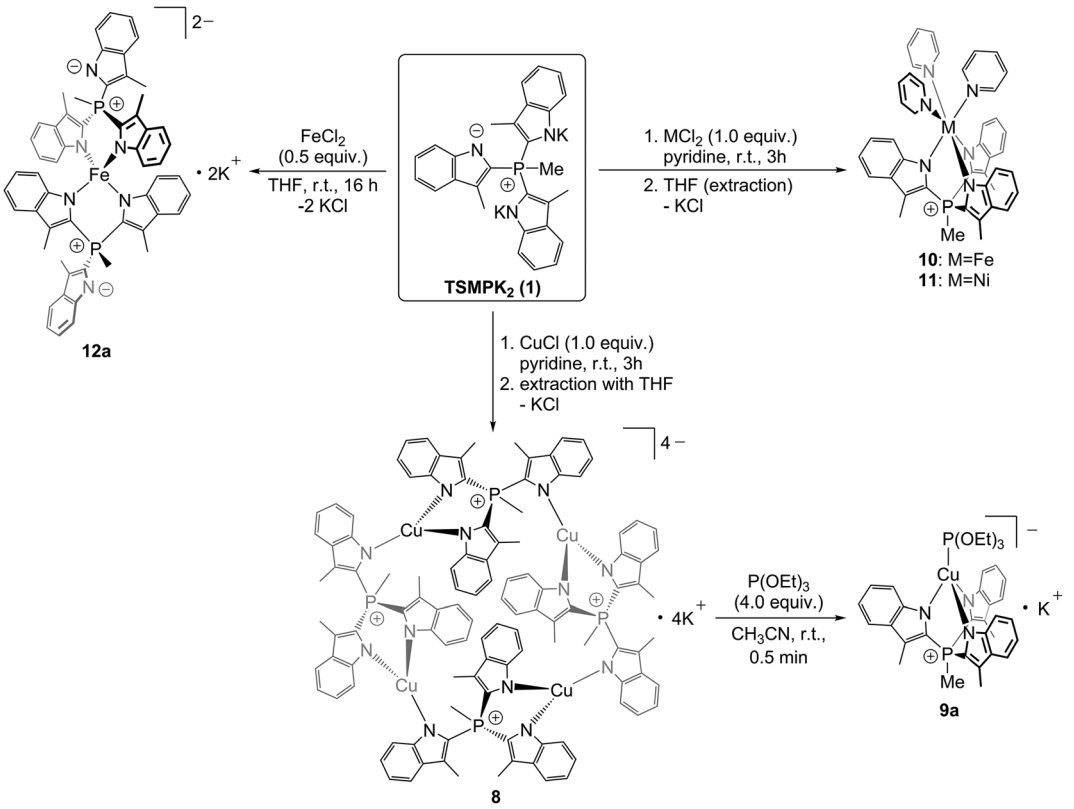
is interrupted by the inclusion of acetonitrile solvent molecules between every second layer (see ESI section S3†).

The existence of a free alkaline trianionic-monocationic phosphonium salt is, to our knowledge, unprecedented. Quaternary phosphonium salts are generally incompatible with basic counterions and convert either into ylides,[26] phosphoranes[27,28] or form charge-transfer complexes followed by complex decomposition manifolds.[29] The exceptions, however, feature electronically stabilized bulky anions (*e.g.* diphenylamide[30] and 2,4,6-trimethylphenolate[31]). We speculate that the stability of **1** is due to the above reasons as well: the anionic indolide nitrogen atoms lose a lot of their nucleophilicity due to being involved in an aromatic π-system, and the phosphonium center is too encumbered to accommodate a fourth indolide in its vicinity. Additionally, the latter would experience electrostatic repulsion from other anionic indolides already present in a molecule.

Coordination chemistry of TSMP

In order to study the ligation behaviour of the novel TSMP platform, we undertook a series of metal exchange reactions with salt **1**. It shows rich coordination chemistry with a number of first-row transition metal salts (Scheme 2).

Reacting equimolar amounts of $TSMPK_2$ salt **1** with cuprous chloride in pyridine led to an orange-red solution, from which yellow crystalline compound **8** was isolated upon freeing from solvent *in vacuo* and extraction with THF. NMR spectroscopy in acetonitrile-d_3 reveals one predominant species, albeit an oligomer. To elaborate, the ^{31}P NMR spectrum (Fig. 2) shows a single quartet consistent with $^2J_{P,H}$ coupling with a methyl group. In the ^1H NMR spectrum (Fig. 2), there are two singlets in a 2 : 1 ratio corresponding to aromatic methyl groups $CH_3{}^{Ar}{}_A$ and $CH_3{}^{Ar}{}_B$. Moreover, multiplets in the aromatic region are present in the same ratio and, according to magnitude gCOSY (see ESI section S4.2†), constitute two distinct spin systems. This implies 2 : 1 inequivalence of indo-



Scheme 2 Coordination behavior of the TSMP ligand platform.

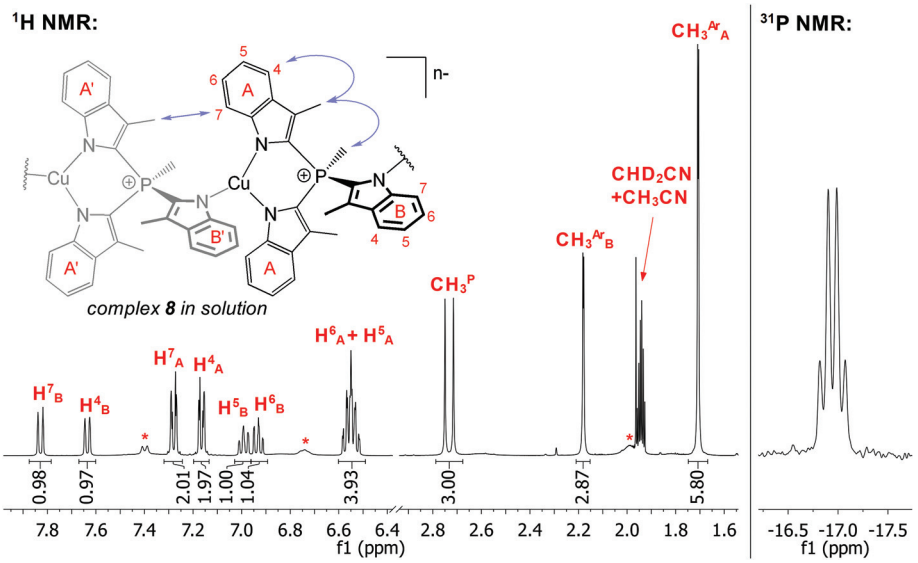


Fig. 2 ^{1}H (400 MHz) and ^{31}P NMR (162 MHz) spectra of **8** in acetonitrile-d_3. Lilac arrows in the structural formula indicate diagnostic NOESY correlations discussed in the text. Only one of two equivalent CH_3^P–$CH_3^{Ar}{}_A$ correlations is shown.

lide units in the complex. A NOESY spectrum (see ESI section S4.2†) shows a correlation between the phosphonium methyl group CH_3^P and two aromatic $CH_3^{Ar}{}_A$ (mapped out in Fig. 2) but not $CH_3^{Ar}{}_B$, from which it follows that $CH_3^{Ar}{}_B$ is pointing away from the phosphonium methyl group. Lastly, $H^4{}_A$ and $H^7{}_A$ have comparable correlation intensities with $CH_3^{Ar}{}_A$. Since NOE rapidly decays with distance, and $H^7{}_A$ is clearly further away from $CH_3^{Ar}{}_A$ than $H^4{}_A$, it can only be the case if there is an equivalent methyl group in the vicinity of $H^7{}_A$, *i.e.* if the complex is oligomerized. Based on this reasoning, in Fig. 2 we suggest an oligomeric structure of the complex **8** in solution.

It is worth mentioning that the NOESY spectrum also features multiple exchange peaks between indolide groups **A** and **B**, which means that these positions exchange on the mixing timescale. This could either be due to reversible dissociation of the oligomer to smaller units or to an intramolecular exchange process. Furthermore, the asterisk-labeled aromatic peaks in the spectrum show exchange with some of the assigned signals, which suggests that they may belong to a minor unassigned form of **8** in solution. However, the number and intensity of the peaks do not allow to deduce molecular connectivity.

While the degree of oligomerization in solution is unclear, our NMR assignment is consistent with the X-ray structure of a crystal grown from pyridine/hexane. Complex **8** crystallizes as a cyclic {[(TSMP)Cu]K}$_4$ tetramer (Fig. 3) with distorted trigonal planar CuN_3 centers and Cu–N distances ranging within 1.926(3)–2.007(3) Å (see ESI section S3†). The TSMP ligand adopts a $\mu^2{:}\kappa^2{:}\kappa^1$ coordination mode, which has been previously observed for other Cu(I) complexes with scorpionate ligands.[32] The unit cell contains two independent tetrameric molecules, both being located on exact, crystallographic inversion centers. K^+ ions in the proximity of indolide moieties show clear cation–π interactions. Their environment is saturated by coordinated pyridine molecules. The two independent {[(TSMP)Cu]K}$_4$ molecules differ in the number of K^+-coordinated pyridines: 14 pyridine molecules for the first tetramer, and 12 for the second. There are also significant differences between the two independent molecules in the coordination mode of K^+ to the indolide moieties (see ESI section S3†). The content of the crystallographic unit cell is completed by six non-coordinated pyridine molecules.

The oligomeric structure of {[(TSMP)Cu]K}$_4$ (**8**) in solution can be broken down upon addition of one equivalent of $P(OEt)_3$ per equivalent of copper. The ^{1}H NMR spectrum immediately simplifies to a single aromatic methyl peak, four aromatic multiplets, a methylphosphonium doublet and an ethyl group of triethylphosphite (see ESI section S4.3†), signifying the formation of the C_3-symmetric structure [(TSMP)CuP(OEt)$_3$]K (**9a**). Furthermore, NOE spectra (see ESI section S4.4†) do not show a correlation analogous to $H^4{}_A$–$H^7{}_A$ in **8** (Fig. 2), which points at a monomeric structure of **9a** in solution. This assignment is, again, consistent with an X-ray crystal structure determination of the 18-crown-6 adduct **9b** crystallized from acetonitrile/benzene/ether (Fig. 3). With the exception of 18-crown-6 peaks, solution NMR spectra of **9a** and **9b** are identical. The complex features a distorted tethahedral CuN_3P center (angle variance[33] of 244.58 deg^2) with N^Cu^N angles varying from 92.38(8) to 95.06(7)°. The Cu–P bond length is 2.1201(2) Å, as expected for Cu(I),[34] and Cu–N distances lie within 2.0622(19)–2.0759(19) Å (see ESI section S3†), similarly to those in tetranuclear **8**. The $[(TSMP)CuP(OEt)_3]^-$ anion has approximate C_3 symmetry with the $P(OEt)_3$ ligand in an approximately staggered conformation with respect to the scorpionate [O^P^Cu^N 41.79(11)°]. The geometry of **9b** closely resembles that of the neutral tris(pyrazolyl)methanide

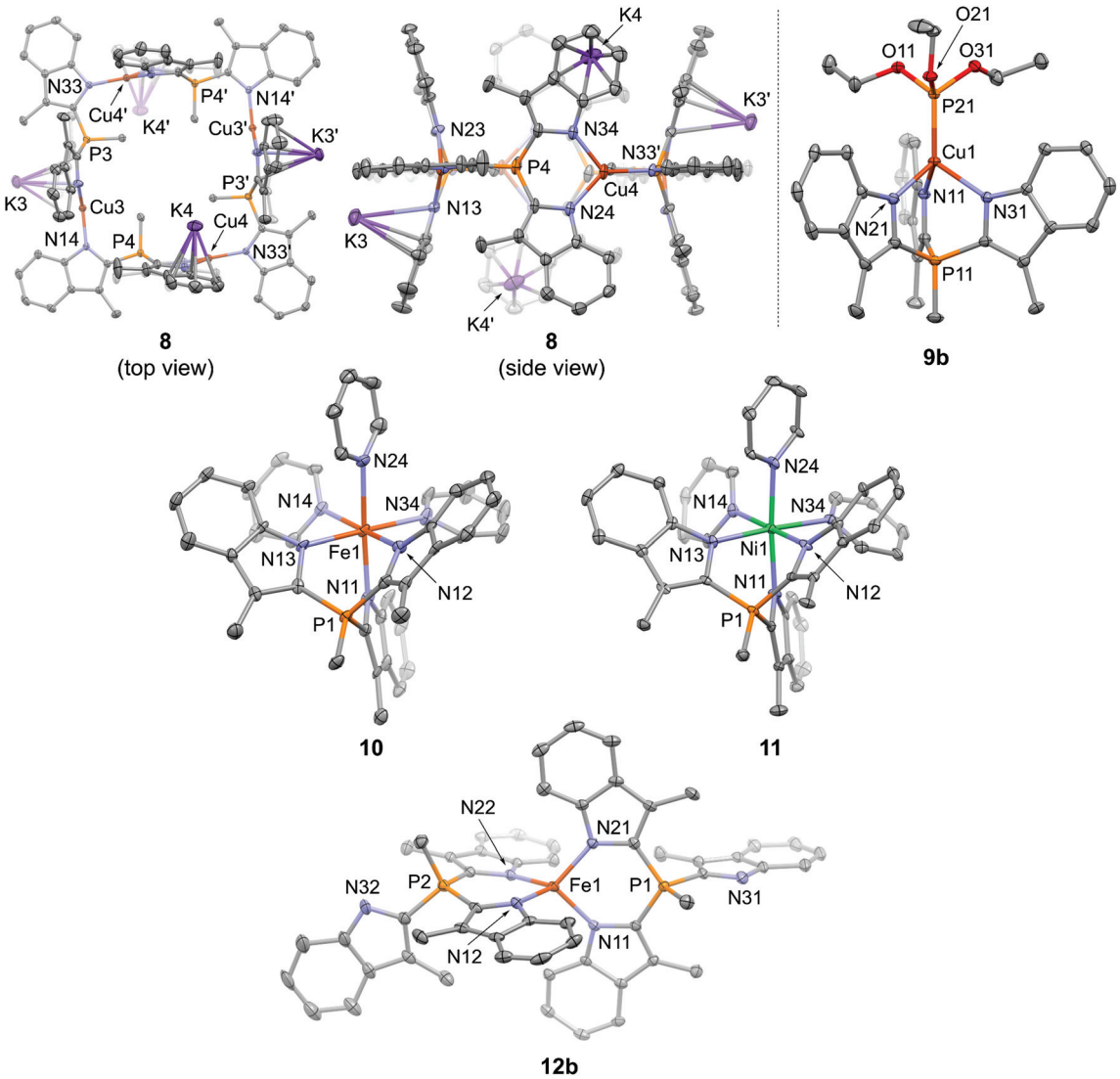


Fig. 3 Molecular structure of **8**, **9b**, **10**, **11** and **12b** according to X-ray crystal structure determination. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms, some counterions and non-coordinated solvent molecules are omitted for clarity. The asymmetric unit of **8** contains two independent molecular fragments that make up two independent molecules; only one full molecule is shown. Symmetry code: ii: 1 – *x*, 1 – *y*, 1 – *z*. The asymmetric units of **10** and **11** contain two independent molecules, only one of which is shown. Selected bond distances and angles are provided in the ESI section S3.†

analogue {[C(3,5-Me_2pz)$_3$]CuP(OMe)$_3$}, which features Cu–N bonds in the range 2.047(2)–2.102(2) Å and a Cu–P bond length of 2.122(2) Å.[34b]

Reactions of equimolar amounts of $TSMPK_2$ (**1**) with either $FeCl_2$ or $NiCl_2$·dme adduct in pyridine give, correspondingly, bright-yellow or olive-brown solutions. Subsequent evaporation of solvent and extraction with THF yield yellow (TSMP)Fe(Py)$_3$ (**10**) and green (TSMP)Ni(Py)$_3$ (**11**) complexes. All attempts to form related complexes with $CoCl_2$ under the same conditions led to intractable mixtures of products.

According to ^{1}H NMR of **10** and **11** in pyridine-d_5, these compounds are paramagnetic, and the number of lines with their integral intensity correspond to three-fold symmetric metallabicyclo[2.2.2]octane topology. Remarkably, in both spectra, the spacing between the pyridine peaks deviates from the normal values by up to 0.3 ppm with α-pyridine hydrogens being most affected. This difference is likely due to a hyperfine shift induced in pyridine hydrogens upon labile coordination to the metal centers. X-ray structure determination of crystals grown from pyridine/hexane reveals isostructural octahedral complexes that feature one TSMP and three pyridine ligands (**10** and **11**, respectively, in Fig. 3). Importantly, the FeN_6 core in **10** has much shorter bonds with TSMP nitrogens than pyridine nitrogens, *viz.* 2.158(6)–2.201(6) Å *vs.* 2.261(7)–2.351(6) Å (see ESI section S3†). In fact, the latter are even longer on average than Fe–N distances in the $[FePy_6]^{2+}$ solvate: 2.22(3)–2.29(3) Å.[35] This is consistent with rather weak bonding and the observed lability of pyridine ligands in solution. The NiN_6

core in **11** shows a similar situation: the Ni–N distances for the TSMP nitrogen atoms are within 2.115(7)–2.148(7) Å, whereas the corresponding values for pyridine nitrogens are 2.163(8)–2.241(8) Å (see ESI section S3†). The long metal–ligand bond lengths in **10** and **11** indicate high-spin electronic states.[36] This assignment is also supported by the effective solution magnetic moments measured by Evans method in pyridine-d_5: 5.19μ_B for Fe(II) complex **10** and 2.82μ_B for Ni(II) complex **11**, whereas the spin-only expectation values for S = 2 and S = 1 metal centers, respectively, are 4.90 and 2.82μ_B.

Interestingly, replacement of three pyridine ligands in **10** with another equivalent of TSMP gives a highly air-sensitive bright-yellow tetracoordinate complex $[(TSMP)_2Fe]K_2$, **12a** (Scheme 2). The complex can be crystallized from acetonitrile/toluene/ether as the tetrakis(benzo-15-crown-5) adduct **12b** (Fig. 3). The NMR spectra of **12a** and **12b** in solution are identical with the exception of benzo-15-crown-5 peaks. Compound **12b** in the crystal features a pseudo-tetrahedral FeN_4 core where each TSMP ligand coordinates with two arms while the third remains uncoordinated (κ^2 mode). The N^Fe^N angles vary from 96.35(13)° to 119.68(13)° (see ESI section S3†). The angle variance[33] of 111.29 deg^2 is, consequently, rather large. The distortion is mainly caused by the chelate effect: the dihedral angle between the N11–Fe1–N21 and the N12–Fe1–N22 planes is 85.2(2)° and deviates only slightly from perfect 90°. The Fe–N distances of 2.017(3)–2.028(3) Å indicate a high-spin electronic state of the Fe(II) center. A comparison with structurally related high-spin complexes[37] shows similar bonding distances of >2.0 Å. Solution effective magnetic moment measurement by Evans method in pyridine-d_5 gives 5.17μ_B, which is close to the spin-only expectation value of 4.90μ_B for an S = 2 metal center. The tetrahedral geometry of **12a** contrasts with the common octahedral geometry of neutral and dicationic pyrazolate-based bis(scorpionate) Fe(II) complexes[38] and of the tris-pyridine complex **10**. We speculate that the reduction in coordination number is due to electrostatic repulsion of the negatively-charged indolides as well as their weaker π-accepting properties as compared to pyridine or pyrazolate ligands.

Conclusions

A dianionic C_3-symmetric tris-skatylmethylphosphonium (TSMP) ligand platform can be synthesized in the form of dipotassium salt $TSMPK_2$ (**1**). This system is the first dianionic homoscorpionate capable of metal exchange and fills a gap in the assortment of charged scorpionates. Despite a possibility of recombination between negatively charged indolides and a positively charged phosphonium atom, salt **1** is stable both in the solid state and solution, which is likely due to a combination of electronic and steric factors.

The potassium cations in $TSMPK_2$ (**1**) are exchangeable for other metals, demonstrating the versatility of TSMP as a ligand for transition metals. The expected scorpionate κ^3 binding mode is observed in octahedral, high spin complexes (TSMP)$M(Py)_3$ (**10**: M = Fe; **11**: M = Ni) as well as in the tetrahedral complex $[(TSMP)CuP(OEt)_3]^-$ (**9**). In addition, the bridging μ^2:κ^2:κ^1 mode is preferred with Cu(I) in the absence of a co-ligand, affording the tetrameric complex $\{[(TSMP)Cu]K\}_4$ (**8**). Finally, the bidentate κ^2 mode is observed in the tetracoordinate 2 : 1 Fe(II) complex $[(TSMP)_2Fe]^{2-}$, which displays a high-spin ground state.

The rich coordination chemistry of the dianionic homoscorpionate ligand invites further investigations. Amongst other, it has a potential to electronically stabilize high-valent metal states due to its electron-rich character, but additional derivatization might be required for kinetic stabilization. Studies in these directions are currently ongoing in our laboratories.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

1 The following review and references therein: S. Trofimenko, *Chem. Rev.*, 1993, **93**, 943–980.
2 (*a*) S. Trofimenko, *Scorpionates*, Imperial College Press, London, 1999; pp. 1–25; (*b*) C. Pettinari and C. Santini, *Comprehensive Coordination Chemistry II: From Biology to Nanotechnology. Volume 1: Fundamentals: Ligands, Complexes, Synthesis, Purification, and Structure*, ed. A. B. P. Lever and J. A. McCleverty, T. J. Meyer, Elsevier Pergamon, Amsterdam, Boston, 2004, pp. 159–210; (*c*) D. M. Tellers, S. J. Skoog, R. G. Bergman, T. B. Gunnoe and W. D. Harman, *Organometallics*, 2000, **19**, 2428–2432.
3 C. Janiak, *Coord. Chem. Rev.*, 1997, **163**, 107–216.
4 The following reviews and references therein: (*a*) C. Santini, M. Pellei, G. G. Lobbia and G. Papini, *Mini-Rev. Org. Chem.*, 2010, **7**, 84–124; (*b*) M. Pellei and C. Santini, *Biomimetic Based Applications*, ed. A. George, InTech, 2011.
5 (*a*) The following review and references therein: C. Slugovc, R. Schmid and K. Kirchner, *Coord. Chem. Rev.*, 1999, **185–186**, 109–126; (*b*) M. M. Díaz-Requejo, T. R. Belderraín, S. Trofimenko and P. J. Pérez, *J. Am. Chem. Soc.*, 2001, **123**, 3167–3168; (*c*) M. M. Díaz-Requejo, T. R. Belderraín and P. J. Pérez, *Chem. Commun.*, 2000, **19**, 1853–1854; (*d*) M. E. Morilla, M. M. Díaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenko and P. J. Pérez, *Chem.*

Commun., 2002, **24**, 2998–2999; (*e*) S. Milione, C. Montefusco, T. Cuenca and A. Grassi, *Chem. Commun.*, 2003, **10**, 1176–1177; (*f*) H. V. R. Dias and J. Wu, *Angew. Chem., Int. Ed.*, 2007, **46**, 7814–7816.

6 For example: (*a*) R. M. Silva, C. Gwengo, S. V. Lindeman, M. D. Smith and J. R. Gardinier, *Inorg. Chem.*, 2006, **45**, 10998–11007; (*b*) B. Zhai, W.-Z. Shen, X.-Y. Chen, H.-B. Song, W. Shi and P. Cheng, *Inorg. Chem. Commun.*, 2006, **9**, 1293–1296; (*c*) J. A. McCleverty and M. D. Ward, *Acc. Chem. Res.*, 1998, **31**, 842–851; (*d*) C. Janiak, T. G. Scharmann, P. Albrecht, F. Marlow and R. Macdonald, *J. Am. Chem. Soc.*, 1996, **118**, 6307–6308.

7 The following review and references therein: P. Martini, M. Pasquali, A. Boschi, L. Uccelli, M. Giganti and A. Duatti, *Molecules*, 2018, **23**, 2039.

8 For example: (*a*) C. G. J. Tazelaar, E. Nicolas, T. van Dijk, D. L. J. Broere, M. Cardol, M. Lutz, D. Gudat, J. C. Slootweg and K. Lammertsma, *Dalton Trans.*, 2016, **45**, 2237–2249; (*b*) M. M. Bittner, S. V. Lindeman, C. V. Popescu and A. T. Fiedler, *Inorg. Chem.*, 2014, **53**, 4047–4061; (*c*) A. A. Fischer, J. R. Miller, R. J. Jodts, D. M. Ekanayake, S. V. Lindeman, T. C. Brunold and A. T. Fiedler, *Inorg. Chem.*, 2019, **58**, 16487–16499; (*d*) A. A. Fischer, N. Stracey, S. V. Lindeman, T. C. Brunold and A. T. Fiedler, *Inorg. Chem.*, 2016, **55**, 11839–11853.

9 For example: (*a*) L. F. Szczepura, L. M. Witham and K. J. Takeuchi, *Coord. Chem. Rev.*, 1998, **174**, 5–32; (*b*) T. Gneuß, M. J. Leitl, L. H. Finger, N. Rau, H. Yersin and J. Sundermeyer, *Dalton Trans.*, 2015, **44**, 8506–8520.

10 The following review and references therein: E. T. Papish, N. A. Dixon and M. Kumar, *Molecular Design in Inorganic Biochemistry. Structure and Bonding*, ed. D. Rabinovich, Springer, Berlin, Heidelberg, 2013, vol. 160, pp. 115–150.

11 For example: (*a*) G. T. Sazama and T. A. Betley, *Inorg. Chem.*, 2010, **49**, 2512–2524; (*b*) T. S. Barnard and M. R. Mason, *Organometallics*, 2001, **20**, 206–214.

12 For example: (*a*) M. Garner, J. Reglinski, I. Cassidy, M. D. Spicer and A. R. Kennedy, *Chem. Commun.*, 1996, **355**, 1975–1976; (*b*) J. Reglinski, M. Garner, I. D. Cassidy, P. A. Slavin, M. D. Spicer and D. R. Armstrong, *J. Chem. Soc., Dalton Trans.*, 1999, **13**, 2119–2126.

13 For example: J. F. Dunne, J. Su, A. Ellern and A. D. Sadow, *Organometallics*, 2008, **27**, 2399–2401.

14 For example: X. Hu, Y. Tang, P. Gantzel and K. Meyer, *Organometallics*, 2003, **22**, 612–614.

15 For example: (*a*) A. L. Sargent, E. P. Titus, C. G. Riordan, A. L. Rheingold and P. Ge, *Inorg. Chem.*, 1996, **35**, 7095–7101; (*b*) I. R. Shapiro, D. M. Jenkins, J. C. Thomas, M. W. Day and J. C. Peters, *Chem. Commun.*, 2001, 2152–2153.

16 For example: (*a*) E. E. Pullen, A. L. Rheingold and D. Rabinovich, *Inorg. Chem. Commun.*, 1999, **2**, 194–196; (*b*) W. C. Blackwell III, D. Bunich, T. E. Concolino, A. L. Rheingold and D. Rabinovich, *Inorg. Chem. Commun.*, 2000, **3**, 325–327; (*c*) F. Neumeyer, M. I. Lipschutz and T. D. Tilley, *Eur. J. Inorg. Chem.*, 2013, **2013**, 6075–6078.

17 T. N. Sorrell, W. E. Allen and P. S. White, *Inorg. Chem.*, 1995, **34**, 952–960.

18 W.-J. Su and L.-C. Liang, *Inorg. Chem.*, 2018, **57**, 553–556.

19 V. S. Joshi, V. K. Kale, K. M. Sathe, A. Sarkar, S. S. Tavale and C. G. Suresh, *Organometallics*, 1991, **10**, 2898–2902.

20 The following review and references therein: H. R. Simmonds and D. S. Wright, *Chem. Commun.*, 2012, **48**, 8617–8624.

21 A. Frazer, B. Piggott, M. Harman, M. Mazid and M. B. Hursthouse, *Polyhedron*, 1992, **11**, 3013–3017.

22 The following review and references therein: I. Kuzu, I. Krummenacher, J. Meyer, F. Armbruster and F. Breher, *Dalton Trans.*, 2008, **35**, 5836–5865.

23 F. Armbruster, I. Fernández and F. Breher, *Dalton Trans.*, 2009, **29**, 5612–5626.

24 A. Steiner and D. Stalke, *Inorg. Chem.*, 1995, **34**, 4846–4853.

25 E. Martin-Mothes, E. Puig, L. Vendier, C. Bijani, M. Grellier and S. Bontemps, *Dalton Trans.*, 2018, **47**, 10139–10146.

26 G. Wittig and U. Schöllkopf, *Chem. Ber.*, 1954, **87**, 1318–1330.

27 G. Wittig and M. Rieber, *Justus Liebigs Ann. Chem.*, 1949, **562**, 187–192.

28 (*a*) H. Schmidbaur and H. Stühler, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 145–146; (*b*) H. Schmidbaur, W. Buchner and F. H. Koehler, *J. Am. Chem. Soc.*, 1974, **96**, 6208–6210.

29 N. A. A. Nesmeyanov, O. A. Rebrova, V. V. Mikul'shina, P. V. Petrovsky, V. I. Robas and O. A. Reutov, *J. Organomet. Chem.*, 1976, **110**, 49–57.

30 M. G. Davidson and S. Lamb, *Polyhedron*, 1997, **16**, 4393–4395.

31 M. G. Davidson, *J. Chem. Soc., Chem. Commun.*, 1995, **9**, 919–920.

32 (*a*) E. Haldón, M. Delgado-Rebollo, A. Prieto, E. Álvarez, C. Maya, M. C. Nicasio and P. J. Pérez, *Inorg. Chem.*, 2014, **53**, 4192–4201; (*b*) S. M. Carrier, C. E. Ruggiero, R. P. Houser and W. B. Tolman, *Inorg. Chem.*, 1993, **32**, 4889–4899.

33 K. Robinson, G. V. Gibbs and P. H. Ribbe, *Science*, 1971, **172**, 567–570.

34 (*a*) R. Mothes, T. Rüffer, Y. Shen, A. Jakob, B. Walfort, H. Petzold, S. E. Schulz, R. Ecke, T. Gessner and H. Lang, *Dalton Trans.*, 2010, **39**, 11235; (*b*) I. Krummenacher, H. Rüegger and F. Breher, *Dalton Trans.*, 2006, 1073–1081.

35 R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, 1966, **88**, 4847–4855.

36 (*a*) J. D. Oliver, D. F. Mullica, B. B. Hutchinson and W. O. Milligan, *Inorg. Chem.*, 1980, **19**, 165–169; (*b*) A. Michaud, F.-G. Fontaine and D. Zargarian, *Inorg. Chim. Acta*, 2006, **359**, 2592–2598; (*c*) R. Wanke, M. F. C. Guedes Da Silva, S. Lancianesi, T. F. S. Silva, L. M. D. R. S. Martins, C. Pettinari and A. J. L. Pombeiro, *Inorg. Chem.*, 2010, **49**, 7941–7952.

37 (*a*) W. D. Morris, P. T. Wolczanski, J. Sutter, K. Meyer, T. R. Cundari and E. B. Lobkovsky, *Inorg. Chem.*, 2014, **53**, 7467–7484; (*b*) A. Panda, M. Stender, R. J. Wright, M. M. Olmstead, P. Klavins and P. P. Power, *Inorg. Chem.*, 2002, **41**, 3909–3916; (*c*) D. M. Granum, P. J. Riedel,

J. A. Crawford, T. K. Mahle, C. M. Wyss, A. K. Begej, N. Arulsamy, B. S. Pierce and M. P. Mehn, *Dalton Trans.*, 2011, **40**, 5881–5890; (*d*) J. R. Hagadorn and J. Arnold, *Inorg. Chem.*, 1997, **36**, 132–133; (*e*) B. Vendemiati, G. Prini, A. Meetsma, B. Hessen, J. H. Teuben and O. Traverso, *Eur. J. Inorg. Chem.*, 2001, **2001**, 707–711; (*f*) C. A. Nijhuis, E. Jellema, T. J. J. Sciarone, A. Meetsma, P. H. M. Budzelaar and B. Hessen, *Eur. J. Inorg. Chem.*, 2005, **2005**, 2089–2099; (*g*) L. Zhang, L. Xiang, Y. Yu and L. Deng, *Inorg. Chem.*, 2013, **52**, 5906–5913; (*h*) F. Liu, X. Qiao, M. Wang, M. Zhou, H. Tong, D. Guo and D. Liu, *Polyhedron*, 2013, **52**, 639–644.

38 (*a*) J. P. Jesson, S. Trofimenko and D. R. Eaton, *J. Am. Chem. Soc.*, 1967, **89**, 3148–3158; (*b*) C. Janiak, S. Temizdemir, S. Dechert, W. Deck, F. Girgsdies, J. Heinze, M. J. Kolm, T. G. Scharmann and O. M. Zipffel, *Eur. J. Inorg. Chem.*, 2000, 1229–1241; (*c*) D. L. Reger, J. R. Gardinier, W. R. Gemmill, M. D. Smith, A. M. Shahin, G. J. Long, L. Rebbouh and F. Grandjean, *J. Am. Chem. Soc.*, 2005, **127**, 2303–2316; (*d*) B. Moubaraki, B. A. Leita, G. J. Halder, S. R. Batten, P. Jensen, J. P. Smith, J. D. Cashion, C. J. Kepert, J.-F. Létard and K. S. Murray, *Dalton Trans.*, 2007, 4413–4426.