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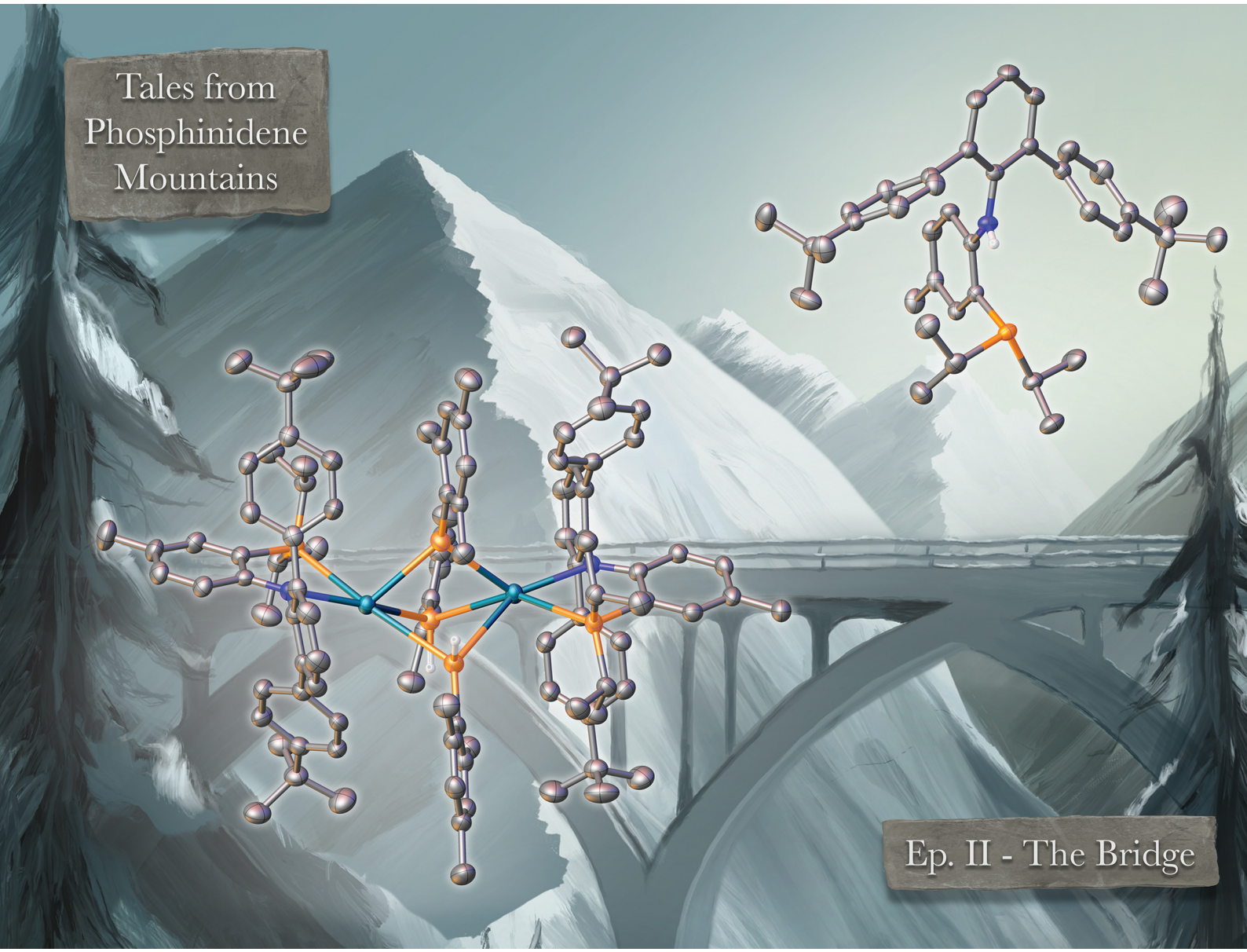

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A bridging bis-phosphanido-phosphinidene complex of lanthanum supported by a sterically encumbering PN ligand†

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Synthesis of a bulky anilidophosphine ligand (short PN^{Terph}) and its lanthanum complexes 1 and 3 is reported. When exposed to KPHMes, both complexes form the first example of a bis-phosphanido-phosphinidene complex 2. This complex undergoes Phospha-Wittig type reactions and its reactivity towards strong bases is further investigated.

Although metal–ligand multiple bonds (MLMB) are ubiquitous in (early) transition metal chemistry,[1] their isolation in f-block chemistry is associated with severe challenges.[2] Due to strong charge polarisation and postulated low covalency, resulting from the energy mismatch and low spatial overlap between the respective frontier orbitals,[3] these species tend to be very reactive and hard to handle/isolate.

Nevertheless, in the last decade, a considerable number of examples with lanthanide and rare earth MLMB have emerged in the literature. These examples mostly focused on the use of group 15 and 16 elements (O, N). They included the facile isolation of various Ce^{IV}=O[4,5] and Ce^{IV}=N(Aryl)[4,6] bonds as well as a nucleophilic Ce^{IV} carbene complex.[7] While these "initial" systems mostly focus on the use of Ce^{IV},[8] which allows a higher covalent character of the MLMB, the Anwander group recently reported various strategies to isolate Ln^{III} imido complexes (Ln = Ce, Nd, Sm, Dy, Ho, Lu).[9–11] While their approaches eased the accessibility of imido complexes across the lanthanide series,[9–11] for heavier group 15 elements, especially phosphorus, examples of MLMBs, especially terminal MLMBs, are still rare.[12] Asides from a number of (multimetallic) Sc^{III} phosphinidene complexes (*e.g.* Fig. 1 G)[13] and two phosphinophosphinidene complexes,[14] to date only six bridged phosphinidene complexes are known, which have been reported by Kiplinger (Fig. 1 A),[15] Chen (Fig. 1 B–D),[16,17] Layfield (Fig. 1 E)[18] and Zhang (Fig. 1 F).[19] In addition to the examples of Sc^{III} phosphinidene complexes, the Anwander group recently reported the isolation of a terminal yttrium phosphinidene complex (Fig. 1 H).[20]

We recently started to investigate the potential of anilidophosphine ligands to stabilize a variety of highly reactive lanthanide complexes starting from the halide complex **I** (Fig. 1).[21] In this context, we found that the framework is capable of stabilizing an elusive η^3 coordinated [SCP]$^-$ anion in complex **J**[22] and a phosphanido complex **K**.[21,23] Notably, deprotonation of the phosphanido ligand in **K** gave access to a C–H activated complex **L**, which was computationally and experimentally confirmed to form *via* a transient phosphinidene.[24] Here, we aim to construct a novel anilidophosphine ligand to stabilize a putative terminal lanthanum phosphinidene complex by avoiding the presence of vulnerable C–H protons and offering severe steric protection, to tame the reactivity of such a species.

Synthesis of the new PN ligand **HPN^{Terph}** is achieved by a modified synthetic route (Scheme 1, top), which includes α-bromination of *o*-toluidine to yield 2-bromo-toluidine **M** followed by Buchwald-Hartwig amination reaction using 4,4″-di-*tert*-butyl-2′-iodo-1,1′:3′,1″-terphenyl **N** and subsequent bromide-lithium exchange on **O** followed by nucleophilic substitution on chlorodiisopropylphosphine. This procedure gives access to **HPN^{Terph}** in 23% yield over all steps on a 5 g scale. Formation of the anilidophosphine was unambiguously determined by ^{31}P NMR spectroscopy showing a singlet at −17.3 ppm (Fig. S9, ESI†) and by X-ray diffraction analysis of single crystals grown from concentrated diethyl ether solution (Fig. S77, ESI†). **HPN^{Terph}** can be further converted to the corresponding lithium and potassium salts **LiPN^{Terph}** and **KPN^{Terph}** by deprotonation of the protonated ligand with BuLi or KHMDS. Formation of the corresponding salts is clearly indicated by the shift of the ^{31}P{^{1}H} NMR resonance from −17.3 ppm in **HPN^{Terph}** to −10.3 ppm in **LiPN^{Terph}** (Fig. S15, ESI†) and −12.2 ppm in **KPN^{Terph}** (Fig. S24, ESI†). Additionally, the ^{7}Li NMR of **LiPN^{Terph}** shows a resonance at −0.63 ppm unambiguously proving the presence of a lithium ion (Fig. S18, ESI†). Unambiguous proof for the formation of **KPN^{Terph}** was also given by X-ray diffraction analysis of single

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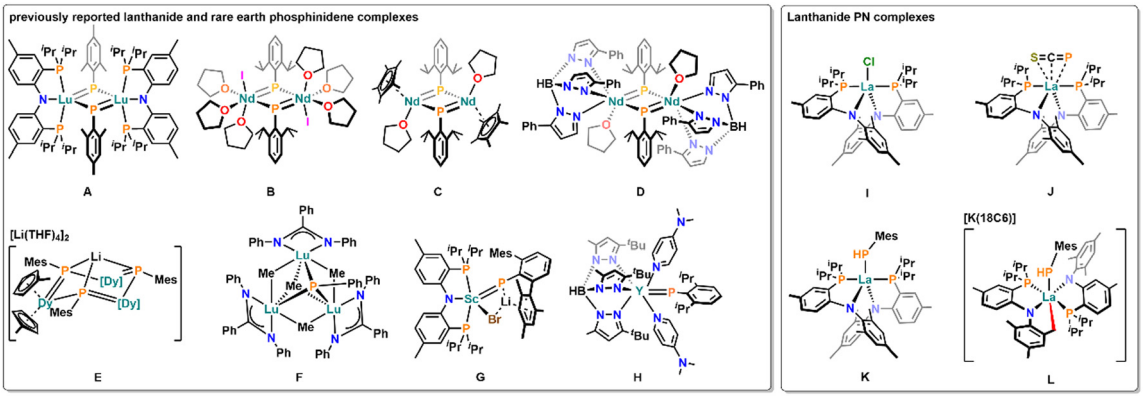
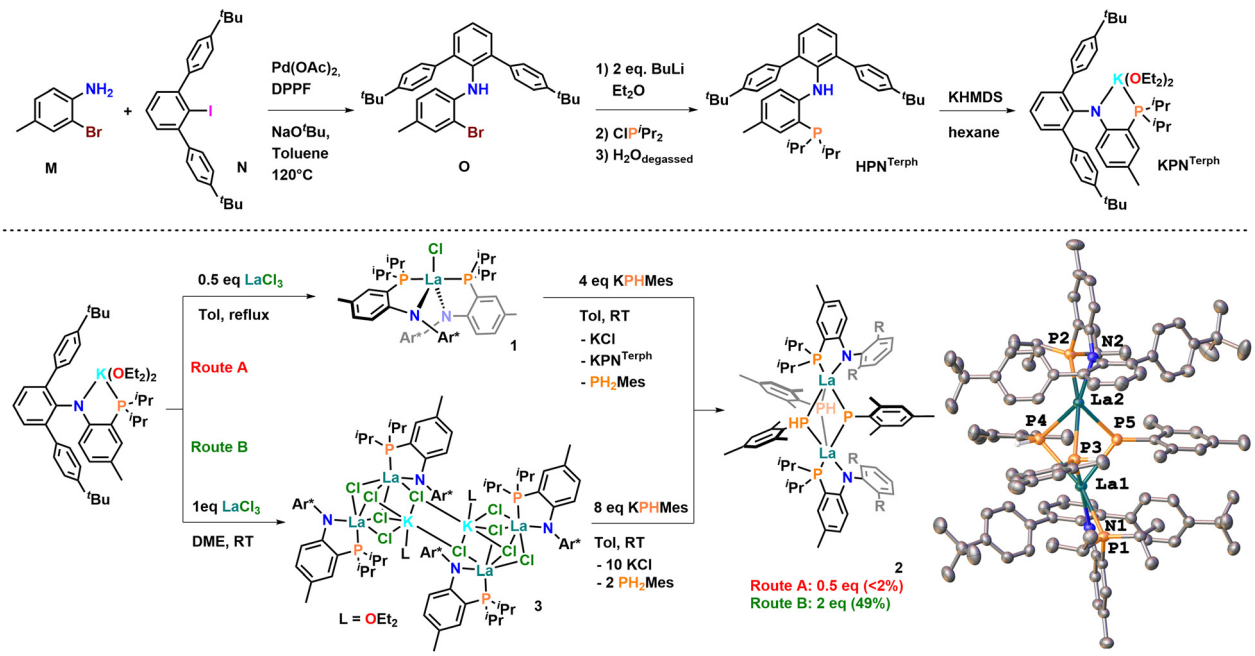


Fig. 1 Previously reported bridging (A–D), clustered (E, F) and the only terminal phosphinidene complexes (G, H) of the rare earth metals so far (left). Previous lanthanum complexes (I–L) reported by our group, stabilized by monoanionic bidentate anilidophosphine ligand $\mathbf{PN^{Mes}}$ (right).



Scheme 1 Top: Synthesis of bulky $\mathbf{HPN^{Terph}}$ and $\mathbf{KPN^{Terph}}$ following a three/four step synthetic protocol. Bottom: Synthesis of mono and bis-PN complexes **1** and **3** and subsequent transformation to bis-phosphanido-phosphinidene complex **2** combined with the molecular structures of the phosphanido-phosphinidene complex **2**. Ellipsoids are shown at a probability level of 50% and hydrogen atoms (except for the protons at P3 and P4) are omitted for clarity.

crystals grown form diethyl ether at room temperature (Fig. S78, ESI†). The structure reveals a monomeric potassium salt, in which the coordination sphere of the potassium ion K1 is completed by two additional ether ligands, forming a distorted tetrahedral environment around K1 (τ_4' = 0.72). The K1–P1 and K1–N1 are 3.3347(6) and 2.6923(13) Å and are comparable to previously reported potassium PN salts.[21] Complexation reactions with lanthanum were initially conducted in boiling toluene using a 2 : 1 stoichiometry $\mathbf{KPN^{Terph}}$ *vs.* $LaCl_3(THF)$. ^1H and $^{31}P\{^1H\}$ NMR spectroscopy revealed the formation of a single species after reaction with a $^{31}P\{^1H\}$ NMR resonance at 0.36 ppm confirming successful salt metathesis reaction, yielding the anticipated bis-$\mathbf{PN^{Terph}}$ complex **1**. Structural characterisation of **1** reveals a pentacoordinate lanthanum center in a distorted square pyramidal coordination environment (τ_5 = 0.17, Fig. 3). The La1–N and La1–P distances are 2.436(3) and 3.2117(11) Å on average and are comparable to the previously reported complex **I**.[21] Analysis of the steric bulk of the co-ligands along the La–Cl bond reveals that the $\mathbf{PN^{Terph}}$ ligand is sterically much more demanding compared to the $\mathbf{PN^{Mes}}$ ligand. Calculation of the $\%V_{buried}$ resulted in a value of 69.9% for **1** compared to 47.5% for **I** (Fig. 2 and Table S3, ESI†).[25]

Given this steric protection along with the absence of vulnerable protons, we assumed this system to be able to stabilize a desired terminal phosphinidene complex. Thus, we next attempted the salt metathesis reaction with one equivalent

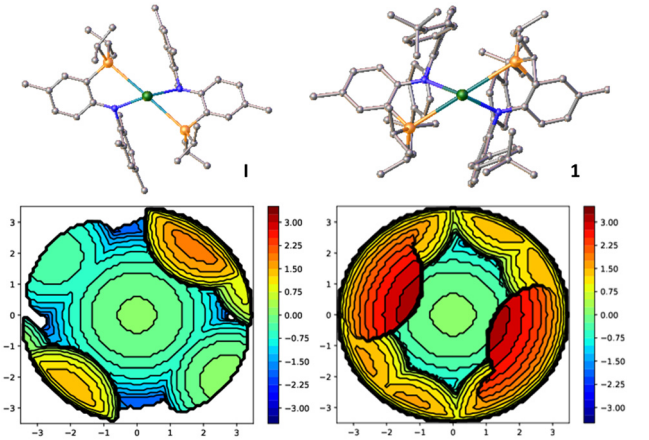


Fig. 2 Comparison between the $\%V_{buried}$ along La-Cl bond between complex **I** (left) and complex **1** (right), showing the steric protection offered by the 1,3-terphenyl substituents. Further information can be found in the ESI† Table S3.

KPHMes targeting the putative phosphanido complex **(PN^{Terph})$_2$-La(PHMes)**, analogous to complex **K**. However, analysis of the material after reaction revealed a very messy reaction with no clean species being formed. After numerous attempts of crystallisation, we found the formation of complex **2** in single crystalline quantity (>2%). X-ray diffraction analysis revealed two lanthanum centers, each supported by one **PN^{Terph}** ligand (suggesting the loss of 1 eq., of **KPN^{Terph}** during the reaction), being bridged by one phosphinidene and two phosphanido ligands (Scheme 1). The assignment of a phosphanido-phosphinidene complex is evident by X-ray diffraction analysis revealing four long La–P distances between 3.0268(11)–3.1130(10) Å for the bridging phosphanido ligands (P3 and P4), while the phosphinidene bridge (P5) displays La–P distances at 2.8471(11) and 2.8207(10) Å, clearly proving the phosphinidene character. The latter are substantially longer compared to Kiplinger's example using lutetium (2.5973(15)–2.6724(14) Å in **A**, Fig. 1)[15] or to Chen's examples on neodymium (2.7314(15)/2.7769(16) Å in **B**;[16] 2.7827(10)/2.7456(11) Å in **C**,[17] 2.7808(16)/2.7911(15) Å in **D**,[17] Fig. 1), as well as to the terminal yttrium phosphinidene complex recently reported by Anwander and co-workers (2.4855(7) Å, complex **H**, Fig. 1),[20] which is in line with the larger radius of La(III). However, since the formation of the phosphinidene complex **2** through the elimination of one equivalent of **PN^{Terph}** is far from being atom efficient, we targeted a mono-PN ligated complex **3**. While for **PN^{Mes}**, the synthesis of mono-PN complexes was not feasible by salt metathesis but only through protonolysis over 17 days using La(HMDS)$_3$, with the novel **KPN^{Terph}** ligand salt metathesis with $LaCl_3(THF)_{1.2}$ is easily achieved in DME and gives access to complex **3** in good yields of 76%. Formation of the complex is evident by $^{31}P\{^1H\}$ NMR spectroscopy showing a singlet at 8.96 ppm (compare complex **1** at 0.36 ppm, *vide supra*). Unambiguous proof for the formation of a mono-PN complex **3** was delivered again by X-ray diffraction analysis, which displayed the formation of an unexpected, tetranuclear *-ate* complex, in which two lanthanum ions are bridged by three chloride ligands, while the fourth chloride ligand is linking these units to a potassium ion, bridging the two dinuclear lanthanum units to give the tetranuclear scaffold. The bond distances between the PN ligands and the lanthanum ion are 3.1113(13) Å for La1–P1 and 2.409(4) Å for La1–N1 and are substantially shorter compared to the bis-PN^{Terph} complex **1** but similar to the phosphinidene complex **2**. This is in line with the enhanced steric pressure that is present in complex **1** with two bulky **PN^{Terph}** ligands coordinated to the lanthanum ion. Indeed, and as anticipated, the reaction between complex **3** and eight equivalents of **KPHMes** gives clean access to the phosphanido-phosphinidene complex **2** in moderate yields of 49%. In line with the results from X-ray diffraction analysis, the ^1H NMR spectrum shows six resonances in the CH_3-mesityl region which corresponds to the presence of three inequivalent mesityl groups. Surprisingly no $^1J_{PH}$ coupling was detected in C_6D_6 at room temperature. Similarly, the $^{31}P\{^1H\}$ NMR spectrum in C_6D_6 at room temperature showed only very broad resonances for the mesityl phosphines between −50 to −65 ppm and a sharp signal at 13.7 ppm corresponding to the PN ligand (Fig. S38, ESI†). Strikingly a very broad resonance was visible at 333.8 ppm. Given the fact that Kiplinger's lutetium phosphinidene complex **A** (Fig. 1) showed a phosphinidene resonance at 186.8 ppm in its $^{31}P\{^1H\}$ NMR,[15] the resonance at 333.8 ppm in **2** is strongly indicative of a phosphinidene complex. Cooling a sample of the product in toluene-d_8 to 288 K, these signals in the $^{31}P\{^1H\}$ NMR become more defined (Fig. S40, ESI†) and the resonances from the mesitylphosphanido ligands appear at −50.3, −53.1 and −64.1 ppm. Further cooling of the sample to 233 K results in further splitting of these resonances, which we attribute to the formation of *syn*/*anti* isomers with respect to the PN orientation (Fig. S48, ESI†). Overall, three multiplets at −49.5 ($^1J_{PH}$ = 256 Hz; $^2J_{PP}$ = 45 Hz, *syn*), −53.0 ($^1J_{PH}$ = 230 Hz; $^2J_{PP}$ = 51 Hz, *anti*) and −69.5 ppm ($^1J_{PH}$ = 260 Hz, *anti*) appear (Fig. S48, ESI†), revealing the expected $^1J_{PH}$ couplings for a phosphanido ligand. In addition, the phosphinidene resonance and the PN resonance split into two signals at 333.5/334.0 ppm (*anti*/*syn*) and 15.0/12.9 ppm (*syn*/*anti*). This interpretation is in line with the observation from the VT ^1H NMR spectrum, which also reveals characteristic $^1J_{PH}$ couplings after cooling. Overall, the results from NMR spectroscopy clearly speak for the presence of the phosphanido-phosphinidene complex **2** in solution as well.

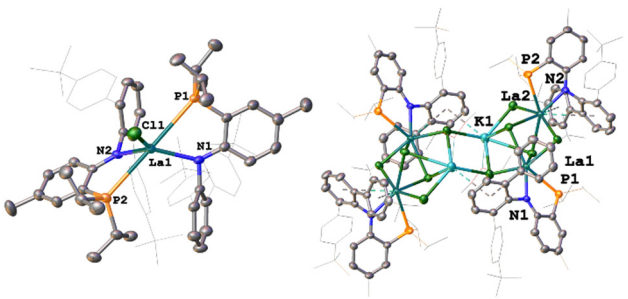


Fig. 3 Molecular structures of the lanthanum complexes **1** and **3**. All ellipsoids are shown at a probability level of 50% and hydrogen atoms are omitted while the terphenyl groups are reduced for better visibility.

Given the fact, that Kiplinger's bis-μ-phosphinidene complex **A** only forms at 80 °C, we investigated the thermal

stability of complex **2** to see if the formation of a similar bis-μ-phosphinidene complex would be feasible. While the complex is stable in solution for days at room temperature, at 333 K (60 °C) the formation of **HPN^{Terph}** is observed after 24 h, which continues to form at temperatures up to 373 K (100 °C) (Fig. S50, ESI†). Additionally, all attempts to deprotonate the remaining phosphanido ligands using strong bases such as $LiCH_2TMS$, KHMDS or KBn in the presence and absence of alkali metal scavengers (12C4, 18C6 or 222-Crypt) to make bis- or tris-μ-phosphinidene complexes have failed so far, giving only access to complicated reaction mixtures from which no defined material could be crystallized (Fig. S58, ESI†). However, complex **2** cleanly engages in Phospha-Wittig-type reactions, transferring the mesitylphosphinidene ligand to benzophenone giving access to the corresponding (diphenylmethylene)-(mesityl)phosphane (Fig. S60, ESI†). Considering the La complex, ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy reveals the formation of multiple products in this reaction, and no crystals could be obtained to determine the fate of the lanthanum fragment.

In conclusion we have presented the synthesis of a novel, highly bulky **PN^{Terph}** ligand and its coordination towards lanthanum(III) giving access to highly encumbered bis-PN complex **1** or hitherto inaccessible mono-PN complex **3** *via* simple salt metathesis protocols. The reaction of **1** and **3** with four/eight equivalents of **KPHMes** gives access to an unprecedented phosphanido-phosphinidene complex **2**, which is the first bridging phosphinidene complex of lanthanum and shows Phospha-Wittig type reactivity. The study gives important insights into stability and variability of PN ligands in lanthanide chemistry and delivers important results on the way to the first terminal phosphinidene complex of the (early) lanthanides.

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Conflicts of interest

There are no conflicts to declare.

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