Yttrium and scandium complexes of a bulky bis(phosphinimine)carbazole ligand

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A R T I C L E   I N F O

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Dedicated to Prof. T. Don Tilley on the occasion of his 60th birthday.

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A B S T R A C T

The synthesis and reactivity of a bulky bis(phosphinimine)carbazole pincer ligand (HL) bearing mesityl N-aryl groups is described. Reaction of HL with Y(CH₂SiMe₃)₃(THF)₂ afforded a doubly cyclometalated organoyttrium complex, whereby the ligand was k⁴N, k²C coordinated to the metal via three nitrogen atoms and two ortho-metalated P-phenyl rings. Deprotonation of (HL) with nBuLi liberated a monomeric and thermally stable lithium salt of the ligand (LLi). Salt metathesis reactions of LLi with ScCl₃(THF)₃ and YCl₃(THF)₅.₅ generated the corresponding rare earth dichloro complexes, which were found to be monomeric and Lewis-base free.

1. Introduction

The incorporation of phosphinimine functionalities into ancillary ligands for supporting main group [1], early [2] and late [3] transition metal, actinide [4], and rare earth [5] complexes has been the subject of increased attention in recent years. These phosphinimine complexes have been applied in a variety of catalytic transformations including hydrosilation [5h–k], as well as the polymerization of olefins [2c,5q,r] and lactones [1f,g,5a–e]. Of particular interest to us is the use of phosphinimine ligands in the fundamental study of structure and reactivity of rare earth complexes; notable examples include the use of phosphinimine ligands in the development of rare earth complexes that exhibit metal–ligand multiple bonds. For example, bis(phosphinimine)methane ligands have been used to pave the development of rare earth carbone complexes [6]. In addition, the synthesis of terminal scandium imido complexes supported by a cyclopentadienylphosphinimine ligand [7] and more recently, a phosphazene ligand have been described [8]. These reports have largely fueled our interest in the design and complexation of new phosphinimine pincer ligands that can be used in stabilizing rare earth metal ions, with the intent of developing a platform for obtaining unique bonding modes and reaction behavior. Herein, we report the synthesis, characterization and rare earth complexation of a bulky bis(phosphinimine)carbazole ligand bearing two mesityl N-aryl substituents. Insight gained from the fundamental studies of these complexes, including their reaction behavior is described.

2. Results and discussion

2.1. Ligand synthesis

We have previously reported the synthesis of a variety of bis(phosphinimine)carbazole pincers whereby the phosphinimine functionality was comprised of two phenyl rings attached to phosphorus, and an aryl group (phenyl, para-isopropylphenyl or pyrimidine) bound to nitrogen (ligands 1–3, Chart 1) or a dioxaphospholane ring, and a para-isopropylphenyl moiety at the nitrogen atom (ligand 4, Chart 1) [9]. Although these ligands possess a moderate degree of steric bulk, ancillary ligands that impose very high degrees of steric protection can sometimes permit the isolation of low-coordinate species that are not accessible when less bulky ligands are utilized [10]. In addition, sterically demanding complexes of the lanthanides have been instrumental in the development of sterically induced reduction (SIR) chemistry by Evans [11]. For these reasons, we were inclined to synthesize a more sterically encompassing bis(phosphinimine)carbazole pincer bearing two N-mesityl rings, with the intention of developing a
ligand that imparts a larger degree of steric protection to a coordinated metal than our previously reported derivatives 1–4.

Using a protocol similar to that previously described [9], our new bulky bis(phosphinimine) pincer was prepared via the Staudinger reaction of 1,8-diphenylphosphino)-3,6-dimethylcarbazole 5 with two equivalents of mesityl azide. The synthesis of reagent 5 has been previously reported by us [9a]; however, during this study an alternate route to the same precursor was discovered and is discussed below.

For this modified preparation, the compound 1,8-dibromo-3,6-dimethylcarbazole 6 was reacted with one equivalent of n-butyllithium followed by trimethylsilyl chloride to afford 1,8-dibromo-3,6-dimethyl-9N-trimethylsilylcarbazole in situ. Subsequently, a lithium halogen exchange reaction was performed by addition of tert-butyllithium. The resultant lithiated species was then quenched with an excess of chlorodiphenylphosphine to afford the compound 1,8,9N-tris(diphenylphosphino)-3,6-dimethylcarbazole 7 (Scheme 1). The formation of 7 via this route is unsurprising as the reaction of a chlorophosphine with a silylamine is facile and proceeds to form an aminophosphine with concomitant loss of chlorosilane. A similar approach is utilized in the preparation of dichalcogenomimidodiphosphinates [(E = PR2)2NH, E = O, S, Se], whereby a chlorophosphine (PR2 = R = Ph, Pr) is reacted with hexamethyldisilazane to generate a (PR2)2NH product, which is then oxidized to the corresponding dichalcogenomidophosphinate [12]. Triphosphine 7 can be readily prepared in good yield and purity via this method. The 31P{1H} NMR spectrum of 7 (chloroform-d) exhibits a triplet at δ 53.3 (1P, 1PP = 69.5 Hz) and a doublet at δ −17.2 (2P, 1PP = 69.5 Hz) indicating coupling between the 1,8-carbazole phosphines and the N-bound phosphine. The 1H and 31C{1H} NMR spectra corroborated the expected structure of 7 and suggest C2v symmetry in solution.

Single crystals of 7 were obtained from a concentrated toluene solution at −35 °C and the solid-state structure was determined by X-ray crystallography. The compound crystallized in the orthorhombic space group Pna21 with one molecule of toluene in the asymmetric unit. The molecular structure is depicted in Fig. 1 as a thermal ellipsoid plot and selected metrical parameters are listed in Table 1.

The C–P bond lengths in 7 are unexceptional (average C–P = 1.836 Å, range = 1.818(2)–1.846(3) Å). The N–P bond distance of 1.742(2) Å also falls within the normal range. In the compound, P1 resides within the plane defined by the carbazole backbone; however, P2 sits below the same plane by 0.918 Å and P3 lies above by 0.611 Å. This twisting of the diphenylphosphino moieties in and out of the carbazole plane is likely due to steric crowding.

Compound 7 can be reacted with [Et3NH]I in refluxing methylene chloride under an inert atmosphere to cleave the P–N bond and liberate the known compound 1,8-bis(diphenylphosphino)-3,6-dimethylcarbazole 5 (Scheme 1). Following recrystallization from hot toluene, we found that samples of 5 prepared by this method were consistently contaminated with the reaction byproduct PPPh2 and required column chromatography for purification. Due to the oxophilic nature of compound 5, rigorous exclusion of oxygen was required as the diphosphine rapidly oxidizes to the phosphine oxide under atmospheric oxygen at ambient temperature. For this reason, we prefer our previously reported synthesis of 5, which allows for the quick and effective removal of reaction byproducts to afford pure product 5 without the need for column chromatography.

As mentioned previously, the final step of the ligand synthesis involves a Staudinger reaction of diphosphine 5 with an aryl azide to generate the phosphinimine functionality. To this end, reaction of 5 with two equivalents of mesityl azide in toluene at ambient temperature afforded proteo ligand HL (8) in 68% yield after recrystallization (Scheme 2). The compound exhibits a single resonance in its 31P{1H} NMR spectrum at δ −6.5 (benzene-d6) and its 1H and 31C{1H} NMR spectra indicate C2v symmetry in solution. The proton NMR spectrum (benzene-d6) has a broad NH peak at δ 12.18, an expectedly complicated aromatic region and three methyl resonances at δ 2.26, 2.22 and 1.95 corresponding to the

![Diagram](image-url)
p-mesityl, 3,6-carbazole and o-mesityl methyl signals, respectively. The high frequency of the NH resonance signifies that the group is likely involved in a hydrogen bonding interaction. Single crystals of 8 suitable for an X-ray diffraction experiment were grown from a concentrated toluene solution at 35°C. The ligand crystallized in the space group P2$_1$2$_1$2$_1$ with two crystallographically independent molecules in the asymmetric unit; both structures are depicted in Fig. 2 as thermal ellipsoid plots.

The solid-state structure of 8 corroborated its identity, as previously suggested by multinuclear NMR spectroscopy. In each independent molecular unit of the structure, one phosphinimine nitrogen donor interacts with the carbazole N–H through a hydrogen bond (d(N$_2$–N1/C1/C1/C1/N3) = 2.805(4) Å, d(N$_2$B–N1B/C1/C1/C1/N1B) = 2.835(4) Å). The phosphinimine groups are rotated periplanar to the aromatic carbazole backbone with N1–P1–C1–C2 and N3–P2–C8–C7 torsion angles of $154.4(3)^\circ$ and $173.4(3)^\circ$ in one molecule, and $153.2(3)^\circ$ and $165.5(3)^\circ$ in the other. Finally, the phosphinimine P–N bond lengths (ranging from 1.549(3) to 1.560(3) Å) correlate well with others in the literature and are indicative of significant P=N double bond character [9,13]. A survey of selected metrical parameters from both independent molecules of 8 (Table 2) indicated a high degree of agreement between the two structures.

<table>
<thead>
<tr>
<th>Bond Distance/Å</th>
<th>Angle/°</th>
<th>Torsion Angle/°</th>
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<tr>
<td>P1–N1</td>
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</tr>
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<td>N1B–P1B–C1B–C2B</td>
</tr>
<tr>
<td>N3–P2–C8–C7</td>
<td>−173.4(3)</td>
<td>N3B–P2B–C8B–C7B</td>
</tr>
</tbody>
</table>

Table 2

Selected bond distances/Å, angles/° and torsion angles/° for the crystallographically independent molecules of compound 8.

Fig. 1. Thermal ellipsoid plot (50% probability) of 7. Hydrogen atoms and toluene solvent molecule are omitted for clarity.

Scheme 2. Synthesis of mesityl substituted bis(phosphinimine) ligand 8.

In an effort to access an organolanthanide complex of the bis(phosphinimine) ligand via alkane elimination, proteo ligand 8 was reacted with one equivalent of the rare earth precursor Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ at ambient temperature. When the reaction was followed in situ by NMR spectroscopy in benzene-$d_6$ solution, the $^{31}$P($^1$H) NMR spectrum revealed the formation of a doublet at $\delta$ 24.1 ($^2$J$_{PY}$ = 6.2 Hz) and unreacted proteo ligand at $\delta$ 6.5 with relative integrations of 20:80 after 1 h. Continued reaction at ambient temperature over the course of 24 h resulted in complete conversion to product. The doublet at $\delta$ 24.1, resulting from coupling between $^{89}$Y (100% abundant, I = $1/2$) and the phosphorus nuclei of the ancillary ligand, is indicative of ligand coordination to yttrium. Analysis of the product by $^1$H and $^{13}$C($^1$H) NMR spectroscopy revealed that the expected dialkyl yttrium complex had not been isolated, but rather, a doubly cyclometalated product. The complex consisted of the ligand bound to the yttrium center in a $\eta^5$ mode through its three nitrogen atoms and two ortho-metalated P-phenyl rings. The $^1$H and $^{13}$C($^1$H) NMR spectra suggested a molecule with C$_2$-symmetry; accordingly, the numerous signals in the aromatic regions corresponded to inequivalent phenyl rings bound to phosphorus. A particularly diagnostic signal in the $^{13}$C($^1$H) NMR spectrum was the metalated carbon directly bonded to yttrium. This ipso carbon was highly deshielded and resonated as a doublet of doublets at $\delta$ 198.1 (dd, $^1$J$_{CP}$ = 42.5 Hz, $^2$J$_{CP}$ = 38.8 Hz). It was also found that the $^1$H and $^{13}$C($^1$H) NMR spectra of the...
product were consistent with a complex that possessed mesityl rings incapable of free rotation on the NMR timescale at ambient temperature. Thus, it is reasonable to conclude that the complex is extremely sterically crowded.

It is likely that formation of the observed yttrium complex occurred as outlined in Scheme 3, in a manner similar to that previously documented for organolutetium complexes of the related bis(phosphinimine)carbazole pincer ligands 1 and 2 [9a]. Presumably, reaction of 8 with Y(CH2SiMe3)3(THF)2 liberated the dialkyl yttrium complex 9 as a highly reactive species with loss of one equivalent of tetramethylsilane. Subsequently, 9 likely rapidly decomposed by two sequential intramolecular cyclometalative alkane elimination reactions to afford doubly cyclometalated product 10. Due to the fact that proto ligand 8 reacted slowly with Y(CH2SiMe3)3(THF)2, attempts to conduct this reaction at low temperatures (i.e. –35 °C) in an effort to observe putative dialkyl complex 9 prior to cyclometalation, were hampered by extremely slow reaction rates. The apparent relative rates of formation and decomposition contrast the alkane elimination reactivity of our previously reported less bulky bis(phosphinimine)carbazole derivatives 1-4; all of these ligands underwent rapid reaction (<10 min) with the organolutetium reagent Lu(CH2SiMe3)3(THF)2 at ambient temperature to afford dialkyl complexes of generic form Lu(CH2SiMe3)3. The retarded rate of formation of complex 9 is a testament to the high degree of steric bulk imparted by the mesityl-substituted ancillary ligand.

Due to the fact that the ancillary ligand in putative complex 9 forms two six-membered chelate rings with yttrium, its subsequent double cyclometalation reactivity is facilitated by this tightly enforced pincer chelation geometry. Specifically, the ortho carbon atoms on the P-phenyl rings are situated with appropriate distance and angle to the metal centre that they can readily undergo C–H bond activation. This can be contrasted with an analogous bis(phosphinimine)pyrrole NNN pincer ligand, which we have previously documented [13a,c], whereby upon tridentate coordination with a metal, the ligand forms two five-membered chelate rings. The more open chelation geometry enforced by the analogous bis(phosphinimine)pyrrole framework has been demonstrated to aid in reducing the propensity for rare earth dialkyl complexes to undergo ligand cyclometalative reactivity.

Complex 10 can be obtained as a pure microcrystalline solid in reasonable yield (69%) after recrystallization. Unfortunately, single crystals suitable for an X-ray diffraction experiment could not be isolated despite repeated attempts. Consequently, the solid-state structure of 10 was not determined. In light of the fact that the dialkyl yttrium complex of the carbazole pincer ligand was thermally unstable and only spectroscopic data could be obtained for its decomposition product, the alkane elimination reactivity of 8 with organorare earth reagents was not investigated further.

2.3. Synthesis and characterization of LLnCl2 (Ln = Sc, Y)

Reaction of 8 with one equiv of n-butyllithium resulted in facile and quantitative conversion to the expected lithiated derivative 11, (L-κ2N)Li, with loss of butane (Scheme 4). Compound 11 exhibited a 31P{1H} NMR resonance at δ 11.0 (benzene-d6), which was 17.5 ppm downfield from that observed for the proteo ligand. In general, the chemical shift of the 31P{1H} phosphinimine resonance was found to be highly sensitive to the coordination environment of the ligand with a downfield shift being indicative of strong σ-donation from the phosphinimine functionalities to a metal center. Like the proto derivative, the 1H and 13C{1H} NMR spectra of 11 were suggestive of C2v, symmetry in solution.

X-ray quality single crystals of 11 were readily obtained from a concentrated toluene solution at ~35 °C and its molecular structure was determined. Compound 11 crystallized in the space group P1 with one disordered molecule of toluene in the asymmetric unit. The solid-state structure of 11 is depicted in Fig. 3 as a thermal ellipsoid plot and selected metrical parameters are listed in Table 3.

Compound 11 exhibits a pseudotrigonal planar lithium cation that is coordinated by the three nitrogen atoms. Notably, the ligand has sufficient steric bulk to saturate the coordination sphere of the cation; as such, lithio derivative 11 is both monomeric and solvent-free. In the solid state, the complex exhibits three N–Li contacts that are similar to one another (N1–Li1 = 2.008(5) Å, N3–Li1 = 2.011(5) Å, N2–Li1 = 1.945(5) Å) and short P–N bonds (P1–N1 = 1.585(2) Å, P2–N3 = 1.570(2) Å). The P–N bonds are slightly elongated relative to those of proto ligand 8, but remain consistent with double bond character. In the ligand, there is rotation.

![Scheme 3. Synthesis and decomposition of organoyttrium complex 9.](image)

![Scheme 4. Synthesis of complexes 11–13.](image)
Table 3

<table>
<thead>
<tr>
<th></th>
<th>11</th>
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<td>2.000(5)</td>
<td>2.223(3)</td>
<td>2.356(2)</td>
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<td>2.188(4)</td>
<td>2.317(2)</td>
</tr>
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<td>–129.4(3)</td>
<td>170.0(3)</td>
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* M corresponds to the atom Li1 for compound 11, Sc1 for compound 12 and Y1 for compound 13.

of the pincer phosphinimine groups out of the plane defined by the carbazole backbone (N1–P1–C1–C2 and N3–P2–C8–C7 torsion angles of 134.6(2)° and –129.4(3)°, respectively). As a result of this twisting, the lithium cation sits below the plane of the aromatic backbone by 0.771 Å. An interesting feature in the solid-state structure of 11 is a π-stacking interaction between the mesityl aromatic rings wherein they exhibit near parallel alignment with a centroid–centroid distance of 4.156 Å.

Lithio ligand 11 was found to be thermally robust. A solution of 11 in benzene–d₆ was heated to 140 °C for 48 h in a J-Young NMR tube with no sign of decomposition. Such thermal stability is a desirable feature because salt metathesis reactions involving bulky ligands with rare earth metal halides often require forcing conditions [14].

Lithio ligand 11 reacts readily with rare earth metal chlorides to afford the corresponding dichloride complexes (Scheme 4). For example, reaction of 11 with the THF adducts of scandium or yttrium trichloride (ScCl₃(THF)₃ or YCl₃(THF)₅) in toluene solution at 60 °C gave the anticipated base-free group 3 dichloride complexes (L–κ-³N)LnCl₂ [Ln = Sc, 12; Y, 13] in good yield. The NMR spectral properties of 12 and 13 are quite similar, with the exception of ⁸⁹Y coupling observed in spectra of 13. Complex 12 exhibits a single resonance in its ³¹P{¹H} NMR spectrum at δ 26.4 while a doublet at δ 25.2 (Jₚₓₓ = 2.3 Hz) is evident in the spectrum of 13.

Recrystallization of complexes 12 and 13 from concentrated toluene solutions at –35 °C generated high quality yellow crystals suitable for X-ray diffraction experiments. The two complexes are isostructural and crystallized in the rhombohedral space group R3 (#148). Complex 13 is depicted in Fig. 4 as a thermal ellipsoid plot. The similar geometries of 12 and 13 are reflected in the highly comparable metrical parameters listed in Table 3.

In the solid state, complexes 12 and 13 are THF-free, monomeric and adopt a distorted square pyramidal geometry at the metal center defined by coordination of two chloride ligands and the κ³ bond pincer ligand. The nitrogen atoms of the ancillary ligand (N1, N2 and N3) and one chloride (Cl2) make up the base of the pyramid while Cl1 occupies the apical site. The bond angles around the base of the pyramid are close to 90° (N2–Sc1–N1 = 85.3(1)°, N2–Sc1–N3 = 84.5(1)°, N1–Sc1–Cl2 = 88.7(1)°, N3–Sc1–Cl2 = 92.9(1)°). As expected, the Y–Cl bond lengths (2.532(1) and 2.570(1) Å) are slightly longer than the Sc–Cl distances (2.392(1) and 2.434(1) Å). The phosphinimine P–N contacts in 12 and 13 (ranging
from 1.608(2) to 1.619(4) Å are longer than those in 8 and 11 (ranging from 1.549(3) to 1.585(2) Å); this elongation is indicative of strong electron donation of the phosphinimine functionality to the scandium and yttrium metal centers, which is also reflected in the downfield chemical shift of the $^{31}$P($^1$H) NMR resonances (vide supra).

A space-filling diagram of 13, depicted in Fig. 5, illustrates the substantial steric shielding that the bulky ligand provides the metal center. In the diagram, the metal is largely obscured by the chloride ligands; however, coordination of the nitrogen donor atoms to the metal is evident. The combination of phenyl and mesityl groups on the ancillary ligand provides a sterically crowded coordination pocket for the metal, essentially sandwiching the chloride ligands in place. In light of the solid state structure of complex 13, it seems probable that the instability of the fleeting dialkyl complex (L-$\kappa^2$N)(CH$_2$SiMe$_3$)$_2$ 9 (which contained two sterically demanding –CH$_2$SiMe$_3$ ligands), and its resultant cyclo-metallative C–H bond activation chemistry, is due to steric pressure imparted by the ancillary ligand [15].

3. Conclusions

The design and synthesis of a new mesityl-substituted bis(phosphinimine)carbazole pincer ligand (HL, 8) has been demonstrated and its ability to coordinate rare earth metals was demonstrated. It was found that the presence of bulky mesityl rings afforded a sterically demanding coordination pocket for rare earth metals and as such, ligand coordination via alkane elimination proved to be slow. Furthermore, the high degree of steric pressure inflicted by the ligand caused a dialkyl yttrium complex to be highly susceptible to a cyclometallative C–H bond activation process resulting in a doubly ortho-metalated derivative. Ligand 8 proved to be suitable for salt metathesis reactivity; the deprotonated compound reacted readily with the THF adducts of rare earth trichlorides to afford dichloride complexes of the ligand in high yield. The developed complexes acted as useful models to study the reactivity patterns of the ancillary ligand and its ability to support rare earth metal complexes.

4. Experimental

4.1. General

All reactions were carried out under an argon atmosphere with the rigorous exclusion of oxygen and water using standard glovebox (Mbraun) or high vacuum line techniques. The solvents diethyl ether, pentane, heptane and toluene were dried and purified using the rigorous exclusion of oxygen and water using standard glovebox (Mbraun) or high vacuum line techniques. The solvents diethyl ether, pentane, heptane and toluene were dried and purified using the rigorous exclusion of oxygen and water using standard glovebox (Mbraun) or high vacuum line techniques. The solvents diethyl ether, pentane, heptane and toluene were dried and purified using the rigorous exclusion of oxygen and water using standard glovebox (Mbraun) or high vacuum line techniques.

4.2. Synthesis of compounds

4.2.1. 1,8,9N-Tris(diphenylphosphino)-3,6-dimethylcarbazole (7)

A hexane solution (1.6 M) of n-Buli (0.38 mL, 0.608 mmol) was added dropwise to a solution of 1,8-dibromo-3,6-dimethylcarbazole (0.210 g, 0.595 mmol) in diethyl ether at 0 °C. The yellow reaction mixture was stirred for 1 h, following which, an aliquot of trimethylsilyl chloride (83 μL, 0.652 mmol) was added by syringe. The solution was warmed to ambient temperature and stirred for 1 h to give a cloudy yellow mixture. The flask was cooled to −78 °C and a pentane solution (1.7 M) of t-Buli (1.5 mL, 2.55 mmol) was added dropwise via syringe. The solution was stirred at −78 °C for 1 h, followed by 3 h at ambient temperature and over this time, acquired a very cloudy yellow appearance with the formation of a thick precipitate. The flask was cooled back to −78 °C and chlorodiphenylphosphine (3.2 mL, 1.78 mmol) was slowly added to generate an intense orange-red colored solution. The reaction mixture was allowed to slowly warm to ambient temperature as it stirred overnight for 12.5 h and over this time acquired a cloudy yellow appearance. The solution was filtered through a fine porosity frit to remove insoluble byproducts and the filtrate was then washed with diethyl ether (2 × 20 mL) until the washings were colorless. All volatile components were removed from the clear, dark yellow filtrate under reduced pressure to afford a yellow residue. The residue was washed with heptane (25 mL), collected on a fine porosity frit and dried thoroughly under reduced pressure. Yield: 0.224 g (50.4%).

4.2.2. HL (8)

Toluene (40 mL) was added to a flask charged with 1,8-bis(diphenylphosphino)-3,6-dimethyl-9H-carbazole (1.324 g, 2.35 mmol) to give a yellow solution. An aliquot of mesityl azide (0.798 g, 4.95 mmol) was added via syringe at ambient temperature. Upon addition, a reaction was evident by the evolution of nitrogen gas. The reaction mixture was stirred for 22 h under an argon atmosphere and the solvent was removed under vacuum to afford a yellow solid. In a glovebox, the residue was reconstituted in hot toluene (5 mL), allowed to slowly cool to ambient temperature and then left at −35 °C to crystallize. The mother liquor was decanted to allow for collection of pale yellow crystals of 8, which were washed with pentane (5 × 1 mL) and dried thoroughly under reduced pressure. Yield: 1.33 g (68.1%).
2.22 (s, 6H, Cz CH3), 1.95 (d, JF2 = 1.6 Hz, 12H, mesityl Cz). 13C [1H] NMR (benzene-d6): δ 145.3 (d, JCP = 3.2 Hz, aromatic ipso-C), 141.2 (d, JCP = 3.4 Hz, aromatic ipso-C), 132.8 (s, aromatic ipso-C), 132.5 (d, JCP = 9.6 Hz, aromatic CH), 131.5 (s, aromatic ipso-C), 131.2 (d, JCP = 2.6 Hz, aromatic CH), 129.9 (d, JCP = 8.8 Hz, aromatic CH), 128.9 (d, JCP = 3.8 Hz, aromatic CH), 128.6 (d, JCP = 12.0 Hz, aromatic CH), 127.6 (s, aromatic ipso-C), 127.4 (d, JCP = 4.1 Hz, aromatic ipso-C), 124.0 (d, JCP = 2.2 Hz, aromatic CH), 123.9 (d, JCP = 8.4 Hz, aromatic ipso-C), 117.1 (d, JCP = 106.2 Hz, aromatic ipso-C), 21.4 (s, CH3), 21.0 (ov s, CH3), 21.0 (ov s, CH3). 31P [1H] NMR (benzene-d6): δ −6.5. Anal. Calc. (%) for Cs6H5N3P2C: C, 81.04; H, 6.44; N, 5.06. Found: C, 81.24; H, 6.30; N, 4.73.

4.2.3. (L-κN,NκC)Y(THF) (10)

In a glovebox, toluene (2 mL) was added to a 25 mL Erlenmeyer flask charged with 8 (0.134 g, 0.161 mmol) and Y(CH3SiMe3)2(THF)2 (0.0795 g, 0.161 mmol) to give a clear yellow solution. The reaction mixture was stirred at ambient temperature for 17.5 h and gradually acquired a red color. The solution was filtered through a bed of Celite and the Celite was washed with a further 2 mL of toluene. The clear red filtrate was concentrated to a small volume under vacuum and then left at −35 °C to crystallize. The mother liquor was decanted off, leaving a yellow microcrystalline solid that was washed with cold pentane and dried under reduced pressure. Yield: 0.110 g (69.4%). 1H NMR (benzene-d6): δ 7.77 (br ov m, 6H, 4.5-Cz C + phenyl CH), 7.71 (dd, JCP = 7.6 Hz, JCP = 8.7 Hz, 2H, phenyl CH), 7.56 (d, JCP = 6.7 Hz, 2H, phenyl CH), 7.38 (dd, JCP = 14.2 Hz, JCP = 1.3 Hz, 2H, 2,7-Cz-C), 7.18 (m, obscured by solvent, 2H, phenyl CH), 7.11–6.90 (ov m, 8H, phenyl CH), 6.72 (s, 2H, mesityl m-CH), 6.63 (s, 2H, mesityl m-CH), 4.32 (m, 2H, OCH2CH3), 3.48 (m, 2H, OCH2CH3), 2.32 (s, 6H, CH3C), 2.10 (s, 6H, mesityl CH3), 1.97 (s, 6H, mesityl CH3), 1.74 (s, 6H, mesityl CH3), 1.22 (m, 4H, OCH2CH3). 13C [1H] NMR (benzene-d6): δ 191.8 (dd, JCP = 42.5 Hz, JCP = 38.8 Hz, C-C), 150.6 (d, JCP = 4.9 Hz, aromatic ipso-C), 144.2 (d, JCP = 8.0 Hz, aromatic ipso-C), 143.9 (d, JCP = 123.4 Hz, aromatic ipso-C), 139.1 (d, JCP = 25.9 Hz, aromatic CH), 137.7 (d, JCP = 5.6 Hz, aromatic ipso-C), 134.8 (d, JCP = 5.8 Hz, aromatic ipso-C), 134.3 (d, JCP = 8.6 Hz, phenyl CH), 132.2 (d, JCP = 2.0 Hz, phenyl CH), 131.4 (d, JCP = 3.9 Hz, aromatic ipso-C), 129.7 (s, Mes-CH), 129.6 (d, JCP = 2.9 Hz, phenyl CH), 128.2 (s, mesityl m-CH), 128.1 (d, JCP = 6.2 Hz, phenyl CH), 127.4 (d, JCP = 3.5 Hz, phenyl CH), 127.3 (d, JCP = 10.0 Hz, Cz 2,7-CH), 126.6 (d, JCP = 9.2 Hz, aromatic ipso-C), 125.9 (d, JCP = 0.8 Hz, aromatic ipso-C), 124.8 (d, JCP = 14.5 Hz, phenyl CH), 124.2 (d, JCP = 12.0 Hz, aromatic ipso-C), 123.8 (d, JCP = 1.5 Hz, Cz 4,5-CH), 118.1 (d, JCP = 94.0 Hz, aromatic ipso-C), 71.8 (s, OCH3CH3), 25.9 (s, OCH2CH3), 21.5 (s, Cz CH3), 21.0 (s, Mes CH3), 20.4 (s, Mes CH3), 20.3 (d, JCP = 1.2 Hz, Mes CH3). 31P [1H] NMR (benzene-d6): δ 24.1 (d, JCP = 6.2 Hz). Anal. Calc. (%) for Cs6H5N3P2Sc: C, 71.19; H, 5.55; N, 4.45. Found: C, 67.82; H, 6.39; N, 4.32.

4.2.4. (L-κN,NκC)Li (11)

A hexane solution of n-BuLi (15.2 mL, 24.4 mmol) was added dropwise over 10 min to a vigorously stirred solution of 8 (10.2 g, 24.4 mmol) in heptane (200 mL) at −78 °C. The cloudy white suspension was stirred at −78 °C for 2.5 h and then allowed to gradually warm to 0 °C where it was stirred for a further 40 min with the formation of a clear yellow solution and the evolution of butane gas. The reaction mixture was allowed to warm to ambient temperature where it was stirred for 1 h to ensure complete reaction. The solvent was removed in vacuo leaving pure lithiated ligand as an orange solid in nearly quantitative yield (10.2 g, 98.3%). 1H NMR (benzene-d6): δ 8.28 (s, 2H, Cz 4,5-CH), 7.42 (m, 20H, phenyl CH), 6.80 (d, JCP = 15.0 Hz, 2H, Cz 2,7-CH), 6.49 (s, 4H, mesityl CH2), 2.41 (s, 6H, CH3), 2.10 (s, 6H, CH3), 1.48 (s, 12H, CH3). 13C NMR (chloroform-d): δ 127.7 (s, aromatic ipso-C), 138.7 (d, JCP = 8.4 Hz, aromatic ipso-C), 134.9 (d, JCP = 6.5 Hz, aromatic ipso-C), 134.0 (d, JCP = 9.5 Hz, aromatic CH), 133.4 (d, JCP = 4.0 Hz, aromatic ipso-C), 132.5 (s, aromatic CH), 132.0 (d, JCP = 11.1 Hz, aromatic CH), 129.4 (s, aromatic CH), 128.3 (d, JCP = 12.0 Hz, aromatic CH), 128.0 (d, JCP = 96.1 Hz, aromatic ipso-C), 126.4 (d, JCP = 8.8 Hz, aromatic ipso-C), 125.7 (d, JCP = 12.6 Hz, aromatic ipso-C), 125.2 (s, aromatic CH), 109.3 (d, JCP = 107.7 Hz, aromatic ipso-C), 21.2 (s, CH3), 20.8 (s, CH3), 20.0 (s, CH3). 31P [1H] NMR (benzene-d6): δ 25.2 (d, JCP = 2.3 Hz). Anal. Calc. (%) for Cs6H5ClNYLi: C, 68.02; H, 5.30; N, 4.25. Found: C, 65.60; H, 5.28; N, 4.24.
Lorentz polarization were performed using SAINT-Plus software. The structure of tropically. Some geometric and displacement restraints were treated toluene solvent molecule was disordered over two positions (C1c, 54%/C1d, 46%) and held isotropic.

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<th>Compound</th>
<th>Formula</th>
<th>Volume (Å³)</th>
<th>Density (g cm⁻³)</th>
<th>Crystal system</th>
<th>α (Å)</th>
<th>β (Å)</th>
<th>γ (Å)</th>
<th>μ (mm⁻¹)</th>
<th>Δρ_max (e Å⁻³)</th>
<th>Δρ_min (e Å⁻³)</th>
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<td>C₆H₅N₃P₃C₇H₈</td>
<td>4592.4(4)</td>
<td>1.215</td>
<td>orthorhombic</td>
<td>17.4632(10)</td>
<td>23.0658(13)</td>
<td>35.411(6)</td>
<td>0.16</td>
<td>0.427</td>
<td>0.943</td>
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<tr>
<td>8</td>
<td>C₅₆H₅₃N₃P₂</td>
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<td>1.186</td>
<td>orthorhombic</td>
<td>13.760(2)</td>
<td>18.851(3)</td>
<td>30.642(3)</td>
<td>0.12</td>
<td>0.396</td>
<td>1.153</td>
</tr>
<tr>
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<td>C₅₆H₅₂LiN₃P₂C₇H₈</td>
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<td>1.200</td>
<td>orthorhombic</td>
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<td>14.183(3)</td>
<td>24.063(3)</td>
<td>0.18</td>
<td>0.432</td>
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</tr>
<tr>
<td>12</td>
<td>C₅₆H₅₃Cl₁₂N₃P₂Sc₂C₇H₈</td>
<td>10369.4</td>
<td>1.064</td>
<td>orthorhombic</td>
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<td>23.6675(10)</td>
<td>23.7063(8)</td>
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<td>23.7063(8)</td>
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</table>

A. The structure contained two toluene molecules in the asymmetric unit, one of which was severely disordered. In addition, a void existed in the unit cell that contained highly disordered and unidentifiable solvent. The electron density associated with the disordered solvent regions was removed from the reflection file using the SQUEEZE subroutine of PLATON [26].

### 4.3. X-ray crystallography

#### 4.3.1. General crystallographic details for 7, 8, 11, 12 and 13

Recrystallization of compounds 7, 8, 11, 12 and 13 from concentrated toluene solutions at −35 °C afforded single crystals suitable for X-ray diffraction. Crystals were coated in dry Paratone oil under an argon atmosphere and mounted onto a glass fiber. Data were collected at −100 °C using a Bruker SMART APEX II diffractometer (Mo Kα radiation, λ = 0.71073 Å) outfitted with a CCD area-detector and a KRYO-FLEX liquid nitrogen vapor cooling device. A data collection strategy using ω and φ scans at 0.5° steps yielded full hemispherical data with excellent intensity statistics. Unit cell parameters were determined and refined on all observed reflections using APEX2 software [22]. Data reduction and correction for Lorentz polarization were performed using SAINT-Plus software [23]. Absorption corrections were applied using SAINT [24]. The structures were solved by direct methods and refined by the least squares method on F² using the SHELXTL software suite [25]. All non-hydrogen atoms were refined anisotropically, except for a certain case of disorder in 8 (discussed vide infra). Hydrogen atom positions were calculated and isotropically refined as riding models to their parent atoms. Details of the data collection and refinement are given in Table 4. Special considerations were required in the refinement of disordered moieties in the structures of 8, 11, 12 and 13. In the structure of 8, a toluene solvent molecule was disordered over two positions (C1c, 54%/C1d, 46%) and held isotropic. The disordered phenyl ring of this solvent was constrained to a regular hexagon with C–C bond lengths of 1.39 Å. In the refinement of 11, a toluene solvent molecule was disordered over two positions (C1s, 73%/C1r, 27%) and both components were modeled anisotropically. Some geometric and displacement restraints were applied in order to reasonably bound distances and angles. The structures of 12 and 13 both contained a severely disordered toluene molecule in the asymmetric unit, for which no suitable model could be found. Additionally, a solvent channel existed in both unit cells of 12 and 13 that contained highly disordered solvent. The electron density associated with the disordered regions was removed using the SQUEEZE subroutine of PLATON [26].

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#### Appendix A. Supplementary materials

CCDC 998409 contains the supplementary crystallographic data for compounds 7, 8, 11, 12 and 13, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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