Inorganica Chimica Acta xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

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

Kevin R.D. Johnson, Paul G. Hayes *

Department of Chemistry and Biochemistry, University of Lethbridge, 4401 University Drive, Lethbridge, AB T1K 3M4, Canada

ARTICLE INFO

Article history:
Received 29 April 2014
Accepted 30 May 2014
Available online xxxx

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

Keywords:
Ligand design
Rare earth
Scandium
Yttrium
Phosphinimine
Cyclometalation

ABSTRACT

The synthesis and reactivity of a bulky bis(phosphinimine)carbazole pincer ligand (H**L**) bearing mesityl *N*-aryl groups is described. Reaction of H**L** with $Y(CH_2SiMe_3)_3(THF)_2$ afforded a doubly cyclometalated organoyttrium complex, whereby the ligand was κ^3N, κ^2C coordinated to the metal via three nitrogen atoms and two *ortho*-metalated P-phenyl rings. Deprotonation of (H**L**) with ^{n}BuLi liberated a monomeric and thermally stable lithium salt of the ligand (**L**Li). Salt metathesis reactions of **L**Li with $ScCl_3(THF)_3$ and $YCl_3(THF)_{3.5}$ 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 hydroamination [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 for 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 carbene complexes [6]. In addition, the synthesis of terminal scandium imido complexes supported by a cyclopentadienyl-phosphinimine 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

* Corresponding author. Tel.: +1 403 329 2313; fax: +1 403 329 2057.
E-mail address: p.hayes@uleth.ca (P.G. Hayes).

http://dx.doi.org/10.1016/j.ica.2014.05.045
0020-1693/

Table 1
Selected bond distances/Å and angles/° for **7**.

P1–C1	1.845(2)	P1–C21	1.842(2)
P1–C15	1.836(2)	N1–P2	1.742(2)
P2–C33	1.818(2)	P2–C27	1.831(2)
P3–C8	1.844(2)	P3–C39	1.829(3)
P3–C45	1.846(3)	P1···P2	3.673(1)
P3···P2	3.111(1)		
C15–P1–C21	102.7(1)	C21–P1–C1	102.1(1)
C15–P1–C1	99.0(1)	C27–P2–N1	103.7(1)
C33–P2–N1	105.9(1)	C27–P2–C33	106.8(1)
C39–P3–C45	101.2(1)	C45–P3–C8	100.7(1)
C39–P3–C8	105.3(1)		

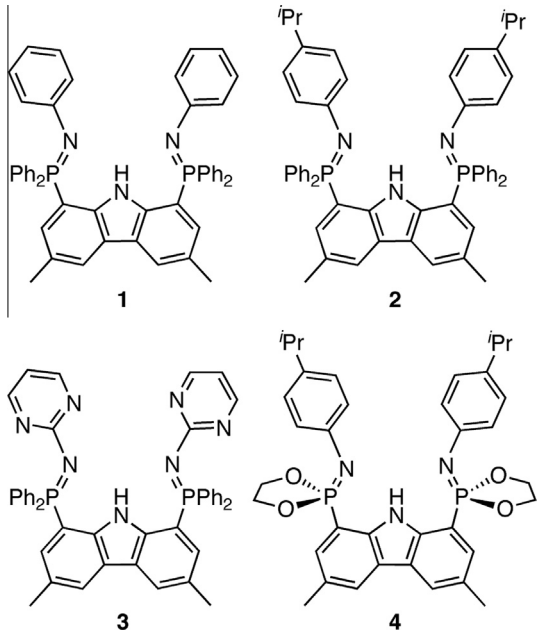


Chart 1. Bis(phosphinimine)carbazole proteo ligands **1**–**4**.

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-bis(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.

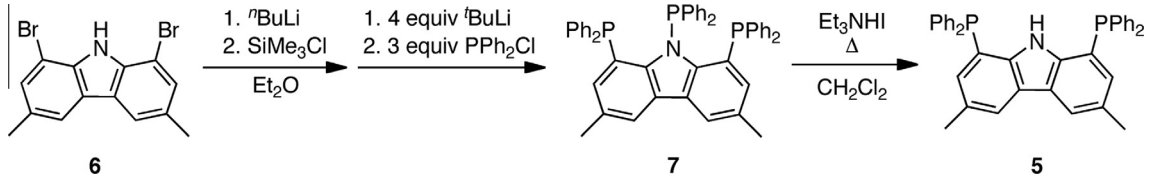
For this modified preparation, the compound 1,8-dibromo-3,6-dimethylcarbazole **6** was reacted with one equivalent of *n*-butyllithium followed by trimethylsilyl chloride to afford 1,8-dibromo-3,6-dimethyl-9*N*-trimethylsilylcarbazole *in situ*. Subsequently, a lithium halogen exchange reaction was performed by addition of *tert*-butyllithium. The resultant lithiated species was then quenched with an excess of chlorodiphenylphosphine to afford the compound 1,8,9*N*-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 silylamide is facile and proceeds to form an aminophosphine with concomitant loss of chlorosilane. A similar approach is utilized in the preparation of dichalcogenoimidodiphosphinates ($(E = PR_2)_2NH$, E = O, S, Se), whereby a chlorophosphine (PR_2Cl, R = Ph, ^{i}Pr) is reacted with hexamethyldisilazane to generate a $(PR_2)_2NH$ product, which is then oxidized to the corresponding dichalcogenoimidodiphosphinate [12]. Triphosphine **7** can be readily prepared in good yield and purity via this method. The $^{31}P\{^1H\}$ NMR spectrum of **7** (chloroform-*d*) exhibits a triplet at δ 53.3 (1P, J_{PP} = 69.5 Hz) and a doublet at δ −17.2 (2P, J_{PP} = 69.5 Hz) indicating coupling between the 1,8-carbazole phosphines and the *N*-bound phosphine. The ^1H and $^{13}C\{^1H\}$ NMR spectra corroborated the expected structure of **7** and suggest C_{2v} 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 $Pna2_1$ (#33) 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 $[Et_3NH]I$ 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 $IPPh_2$ and required column chromatography for purification. Due to the oxophillic 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 H**L** (**8**) in 68% yield after recrystallization (Scheme 2). The compound exhibits a single resonance in its $^{31}P\{^1H\}$ NMR spectrum at δ −6.5 (benzene-d_6) and its ^1H and $^{13}C\{^1H\}$ NMR spectra indicate C_{2v} symmetry in solution. The proton NMR spectrum (benzene-d_6) 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



Scheme 1. Synthesis of 1,8,9*N*-tris(diphenylphosphino)-3,6-dimethylcarbazole **7** and its reactivity to give **5**.

Please cite this article in press as: K.R.D. Johnson, P.G. Hayes, Inorg. Chim. Acta (2014), http://dx.doi.org/10.1016/j.ica.2014.05.045

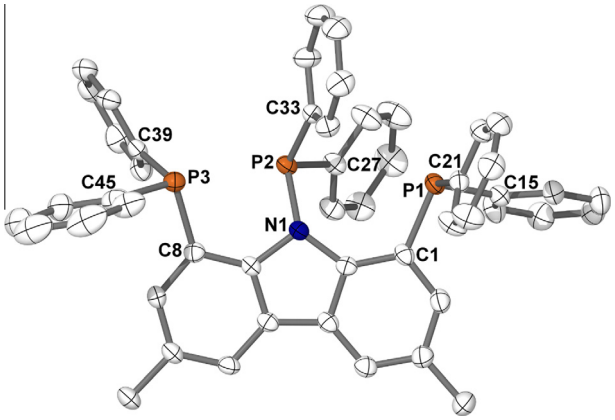
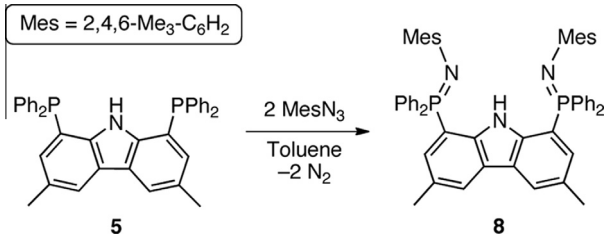


Fig. 1. Thermal ellipsoid plot (50% probability) of **7**. Hydrogen atoms and toluene solvent molecule are omitted for clarity.

Table 2
Selected bond distances/Å, angles/° and torsion angles/° for the crystallographically independent molecules of compound **8**.

P1–N1	1.549(3)	P1B–N1B	1.551(3)
P2–N3	1.560(3)	P2B–N3B	1.551(3)
N2···N3	2.805(4)	N2B···N1B	2.835(4)
N1–P1–C1	111.7(2)	N1B–P1B–C1B	110.3(2)
N3–P2–C8	110.1(2)	N3B–P2B–C8B	112.5(2)
N1–P1–C1–C2	−154.4(3)	N1B–P1B–C1B–C2B	165.5(3)
N3–P2–C8–C7	−173.4(3)	N3B–P2B–C8B–C7B	153.2(3)



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

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 $P\bar{1}$ 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(N2···N3) = 2.805(4) Å, d(N2B···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–C9 torsion angles of −154.4(3)° and −173.4(3)° in one molecule, and 153.2(3)° and 165.5(3)° 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.

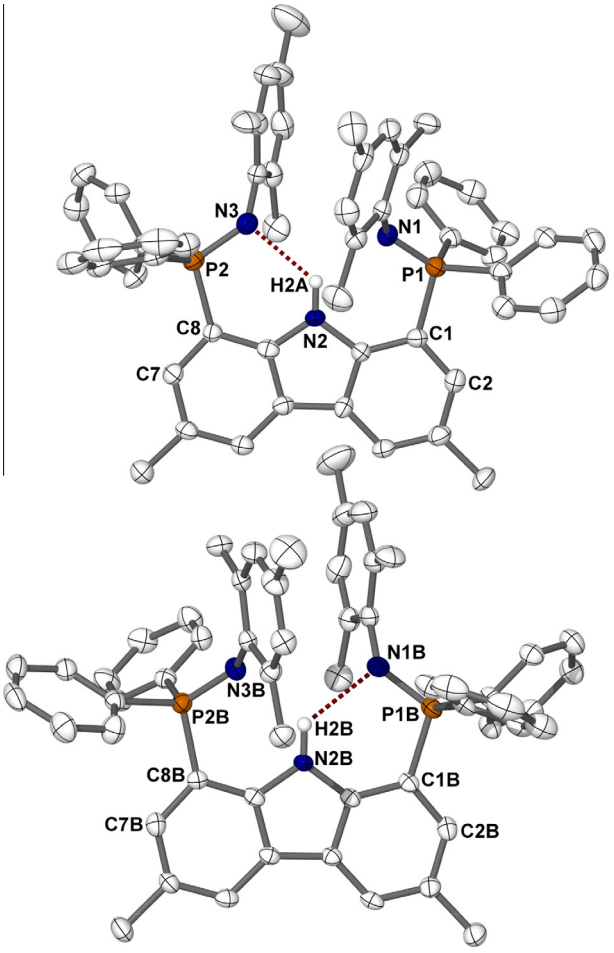


Fig. 2. Thermal ellipsoid plots (50% probability) depicting two crystallographically independent molecules of H**L** (**8**). Hydrogen atoms (except H2A and H2B) and toluene solvent molecules are omitted for clarity.

2.2. Protonolysis reactivity

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 $Y(CH_2SiMe_3)_3(THF)_2$ at ambient temperature. When the reaction was followed *in situ* by NMR spectroscopy in benzene-d_6 solution, the $^{31}P\{^1H\}$ NMR spectrum revealed the formation of a doublet at δ 24.1 ($^2J_{PY}$ = 6.2 Hz) and unreacted proteo ligand at δ −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 δ 24.1, resulting from coupling between ^{89}Y (100% abundant, I = ½) and the phosphorus nuclei of the ancillary ligand, is indicative of ligand coordination to yttrium.

Analysis of the product by ^1H and $^{13}C\{^1H\}$ 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 κ^5 mode through its three nitrogen atoms and two *ortho*-metalated *P*-phenyl rings. The ^1H and $^{13}C\{^1H\}$ 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 $^{13}C\{^1H\}$ NMR spectrum was the metalated carbon directly bonded to yttrium. This *ipso* carbon was highly deshielded and resonated as a doublet of doublets at δ 198.1 (dd, $^1J_{CY}$ = 42.5 Hz, $^2J_{CP}$ = 38.8 Hz). It was also found that the ^1H and $^{13}C\{^1H\}$ 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 $Y(CH_2SiMe_3)_3(THF)_2$ 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 proteo ligand **8** reacted slowly with $Y(CH_2SiMe_3)_3(THF)_2$, 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 $Lu(CH_2SiMe_3)_3(THF)_2$ at ambient temperature to afford dialkyl complexes of generic form $LLu(CH_2SiMe_3)_2$. 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.

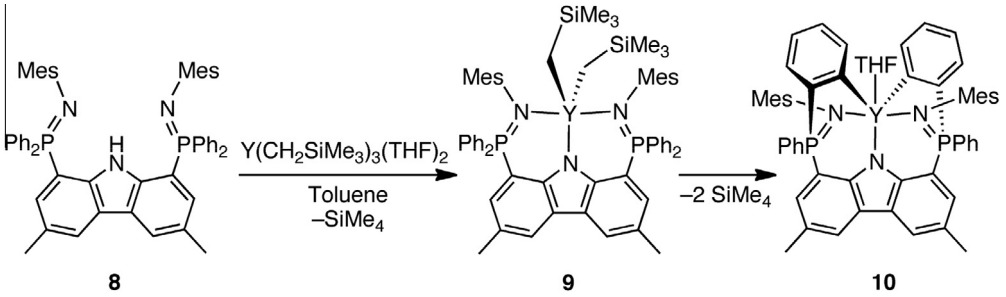
Complex **10** can be obtained as a pure microcrystalline solid in reasonable yield (69%) after recrystallization. Unfortunately, single crystals suitable for an X-ray diffraction experiment could not be isolated despite repeated attempts. Consequently, the solid-state structure of **10** was not determined. 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 $LLnCl_2$ (Ln = Sc, Y)

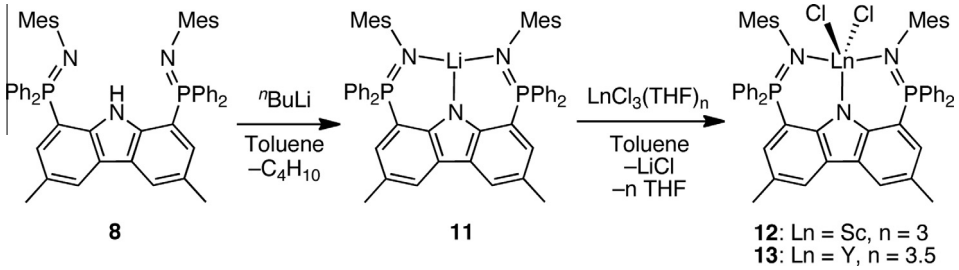
Reaction of **8** with one equiv of *n*-butyllithium resulted in facile and quantitative conversion to the expected lithiated derivative **11**, (**L**-κ^3N)Li, with loss of butane (Scheme 4). Compound **11** exhibited a $^{31}P\{^1H\}$ NMR resonance at δ 11.0 (benzene-d_6), which was 17.5 ppm downfield from that observed for the proteo ligand. In general, the chemical shift of the $^{31}P\{^1H\}$ 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 proteo derivative, the ^1H and $^{13}C\{^1H\}$ NMR spectra of **11** were suggestive of C_{2v} 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 $P\bar{1}$ 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 proteo ligand **8**, but remain consistent with double bond character. In the ligand, there is rotation



Scheme 3. Synthesis and decomposition of organoyttrium complex **9**.



Scheme 4. Synthesis of complexes **11**–**13**.

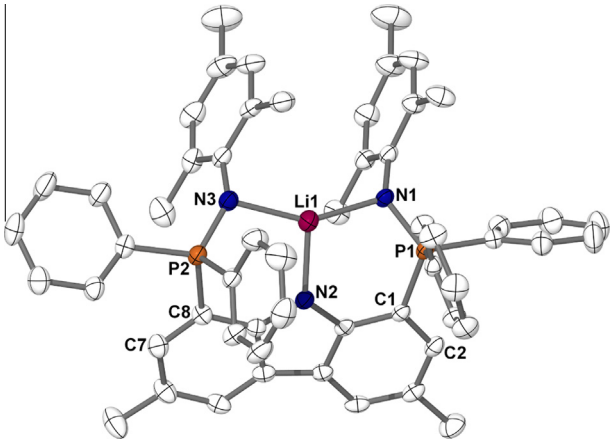


Fig. 3. Thermal ellipsoid plot (50% probability) of (**L**-κ^3N)Li (**11**). Hydrogen atoms and toluene solvent molecule are omitted for clarity.

Table 3
Selected bond distances/Å, angles/° and torsion angles/° for compounds **11**, **12** and **13**.

	11	**12**	**13**
P1–N1	1.585(2)	1.619(4)	1.608(2)
P2–N3	1.570(2)	1.619(4)	1.615(2)
N1–M[a]	2.008(5)	2.221(3)	2.356(2)
N3–M[a]	2.011(5)	2.188(4)	2.317(2)
N2–M[a]	1.945(5)	2.200(4)	2.358(2)
Cl1–M[a]	–	2.392(1)	2.532(1)
Cl2–M[a]	–	2.434(1)	2.570(1)
P1–N1–M[a]	108.6(2)	121.0(2)	121.8(1)
P2–N3–M[a]	107.7(2)	126.1(2)	126.3(1)
N2–M–N1[a]	104.1(2)	85.3(1)	82.41(7)
N2–M–N3[a]	103.6(2)	84.5(1)	81.92(8)
N1–M–Cl2[a]	–	88.7(1)	90.06(6)
N3–M–Cl2[a]	–	92.9(1)	95.93(6)
N2–M–Cl1[a]	–	96.9(1)	96.82(5)
Cl2–M–Cl1[a]	–	98.44(5)	99.82(3)
N1–M–Cl1[a]	–	111.3(1)	113.38(5)
Cl1–M–N3[a]	–	101.1(1)	100.52(6)
N1–P1–C1–C2	134.6(2)	−139.1(4)	−137.6(2)
N3–P2–C8–C7	−129.4(3)	170.0(3)	168.0(2)

[a] 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-d_6 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 ($ScCl_3(THF)_3$ or $YCl_3(THF)_{3.5}$) in toluene solution at 60 °C gave the anticipated base-free group 3 dichloride complexes (**L**-κ^3N)$LnCl_2$ (Ln = Sc, **12**; Y, **13**) in good yield. The NMR spectral properties of **12** and **13** are quite similar, with the exception of ^{89}Y coupling observed in spectra of **13**. Complex **12** exhibits

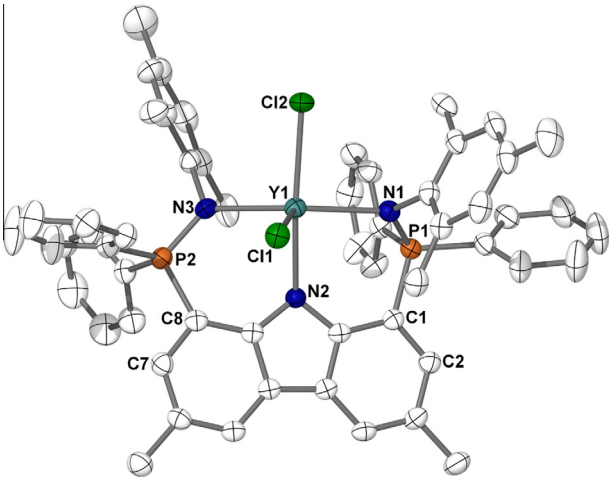


Fig. 4. Thermal ellipsoid plot (50% probability) of **13** (**L**-κ^3N)YCl_2 with hydrogen atoms and solvent molecules of crystallization omitted for clarity. The solid-state structure of (**L**-κ^3N)$ScCl_2$ (**12**) is isostructural to that of **13**.

a single resonance in its $^{31}P\{^1H\}$ NMR spectrum at δ 26.4 while a doublet at δ 25.2 ($^2J_{PY}$ = 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 $R\bar{3}$ (#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 κ^3 bound 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)°, **12**; N2–Y1–N1 = 82.41(7)°, N2–Y1–N3 = 81.92(8)°, N1–Y1–Cl2 = 90.06(6)°, N3–Y1–Cl2 = 95.93(6)°, **13**), and the apical atom (Cl1) is situated close to perpendicular to this base (average perpendicular angle = 101.9°, **12**; 102.6°, **13**). 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

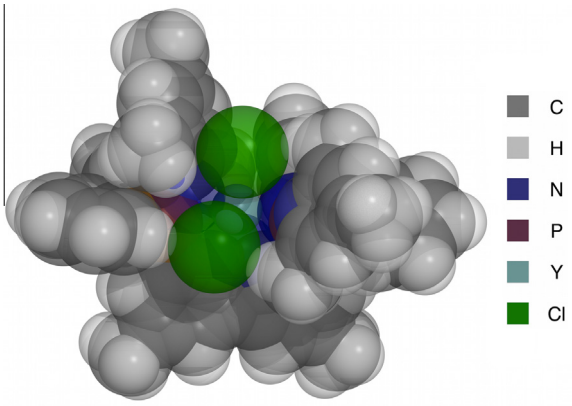


Fig. 5. Space-filling diagram of **13** (**L**-κ^3N)YCl_2 with atoms drawn at their respective van der Waals radii.

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**-κ^3N)Y(CH_2SiMe_3)$_2$ **9** (which contained two sterically demanding –CH_2SiMe_3 ligands), and its resultant cyclometalative 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 (H**L**, **8**) has been described 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 cyclometalative 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 a solvent purification system (MBraun) and distilled under vacuum prior to use from sodium benzophenone ketyl (diethyl ether) or "titanocene" indicator (pentane, heptane and toluene). Deuterated solvents were dried over sodium benzophenone ketyl (benzene-d_6) or CaH_2 (chloroform-*d*), degassed via three freeze–pump–thaw cycles, distilled under vacuum, and stored over 4 Å molecular sieves under an argon atmosphere. Samples for NMR spectroscopy were recorded on a 300 MHz Bruker Avance II (ultrashield) spectrometer (^{1}H 300.13 MHz, $^{13}C\{^{1}H\}$ 75.47 MHz, $^{31}P\{^{1}H\}$ 121.49 MHz) and referenced relative to either $SiMe_4$ through the residual solvent resonance(s) for ^{1}H and $^{13}C\{^{1}H\}$, or to external 85% H_3PO_4 for $^{31}P\{^{1}H\}$. All NMR spectra were recorded at ambient temperature (25 °C) unless specified otherwise. Elemental analyses were performed using an Elementar Americas Vario MicroCube instrument. Despite repeated attempts, several of the rare earth complexes consistently gave values that were low in carbon. Such problems are well known for rare earth complexes and are generally accepted to be the result of the formation of inert carbides [16]. The reagents $ScCl_3(THF)_3$ [17], $YCl_3(THF)_{3.5}$ [18], $Y(CH_2SiMe_3)_3(THF)_2$ [19], 1,8-dibromo-3,6-dimethylcarbazole [20], 1,8-bis(diphenylphosphino)-3,6-dimethyl-9H-carbazole [9a] and mesityl azide [21] were prepared according to literature procedures. All other reagents were obtained from commercial sources and used as received.

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 at 0 °C for 1 h, following which, an aliquot of trimethylsilyl chloride (83 μL, 0.652 mmol) was added by microsyringe. 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 frit 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 vacuum. Yield: 0.224 g (50.4%). ^{1}H NMR (chloroform-*d*): δ 7.96 (s, 2H, Cz 4,5-C*H*), 7.42–7.28 (ov m, 10H, aromatic C*H*), 7.24–7.10 (ov m, 12H, aromatic C*H*), 6.96–6.90 (ov m, 10H, aromatic C*H*), 2.43 (s, 6H, CH_3). $^{13}C\{^{1}H\}$ NMR (chloroform-*d*): δ 139.2 (d, J_{CP} = 5.9 Hz, aromatic *ipso*-*C*), 139.0 (d, J_{CP} = 5.9 Hz, aromatic *ipso*-*C*), 137.0 (dd, J_{CP} = 6.9 Hz, J_{CP} = 6.9 Hz, aromatic *ipso*-*C*), 136.8 (dd, J_{CP} = 6.9 Hz, J_{CP} = 6.9 Hz, aromatic *ipso*-*C*), 136.6 (s, aromatic *C*H), 133.2 (d, J_{CP} = 18.7 Hz, aromatic *C*H), 131.2 (s, aromatic *ipso*-*C*), 130.5 (dt, J_{CP} = 18.7 Hz, J_{CP} = 3.1 Hz, aromatic *C*H), 127.8 (s, aromatic *C*H), 127.7 (s, aromatic *C*H), 127.7 (d, J_{CP} = 26.1 Hz, aromatic *C*H), 127.3 (s, aromatic *C*H), 122.6 (dd, J_{CP} = 20.1 Hz, J_{CP} = 3.1 Hz, aromatic *ipso*-*C*), 121.0 (s, Cz, 4,5-*C*H), 21.2 (s, *C*H_3). $^{31}P\{^{1}H\}$ NMR (chloroform-*d*): δ 53.3 (t, J_{PP} = 69.5 Hz, 1P), 17.2 (d, J_{PP} = 69.5 Hz, 2P). *Anal. Calc.* (%) for $C_{50}H_{40}NP_3$: 80.31; H, 5.39; N, 1.87. Found: C, 80.36; H, 6.14; N, 1.83.

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%). ^{1}H NMR (benzene-d_6): δ 12.18 (s, 1H, N*H*), 7.78 (m, 10H, phenyl C*H* + Cz 4,5-C*H*), 7.29 (d, $^{3}J_{HP}$ = 13.9 Hz, 2H, Cz 2,7-C*H*), 6.95–6.85 (m, 12H, aromatic C*H*), 6.81 (s, 4H, mesityl C*H*), 2.27 (d, J_{HP} = 2.6 Hz, 6H, mesityl CH_3),

2.22 (s, 6H, Cz CH_3), 1.95 (d, J_{HP} = 1.6 Hz, 12H, mesityl CH_3). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 145.3 (d, J_{CP} = 3.2 Hz, aromatic *ipso*-*C*), 141.2 (d, J_{CP} = 3.4 Hz, aromatic *ipso*-*C*), 132.8 (s, aromatic *ipso*-*C*), 132.5 (d, J_{CP} = 9.6 Hz, aromatic *C*H), 131.5 (s, aromatic *ipso*-*C*), 131.2 (d, J_{CP} = 2.6 Hz, aromatic *C*H), 129.9 (d, J_{CP} = 8.8 Hz, aromatic *C*H), 128.9 (d, J_{CP} = 3.8 Hz, aromatic *C*H), 128.6 (d, J_{CP} = 12.0 Hz, aromatic *C*H), 127.6 (s, aromatic *ipso*-*C*), 127.4 (d, J_{CP} = 4.1 Hz, aromatic *ipso*-*C*), 124.0 (d, J_{CP} = 2.2 Hz, aromatic *C*H), 123.9 (d, J_{CP} = 8.4 Hz, aromatic *ipso*-*C*), 117.1 (d, J_{CP} = 106.2 Hz, aromatic *ipso*-*C*), 21.4 (s, CH_3), 21.0 (ov s, CH_3), 21.0 (ov s, CH_3). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ −6.5. *Anal. Calc.* (%) for $C_{56}H_{53}N_3P_2$: C, 81.04; H, 6.44; N, 5.06. Found: C, 81.24; H, 6.30; N, 4.73.

4.2.3. (**L**-κ^3*N*,κ^2*C*)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 $Y(CH_2SiMe_3)_3(THF)_2$ (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 1 mL 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-d_6): δ 7.77 (br ov m, 6H, 4,5-Cz C*H* + phenyl C*H*), 7.71 (dd, $^3J_{HP}$ = 7.6 Hz, $^3J_{HH}$ = 8.7 Hz, 2H, phenyl C*H*), 7.56 (d, $^3J_{HH}$ = 6.7 Hz, 2H, phenyl C*H*), 7.38 (dd, $^3J_{HP}$ = 14.2 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, 2,7-Cz C*H*), 7.18 (m, obscured by solvent, 2H, phenyl C*H*), 7.11–6.90 (ov m, 8H, phenyl C*H*), 6.72 (s, 2H, mesityl *m*-C*H*), 6.65 (s, 2H, mesityl *m*-C*H*), 4.23 (m, 2H, OCH_2-CH$_2$), 3.88 (m, 2H, OCH_2CH$_2$), 2.32 (s, 6H, Cz CH_3), 2.10 (s, 6H, mesityl CH_3), 1.97 (s, 6H, mesityl CH_3), 1.74 (s, 6H, mesityl CH_3), 1.22 (m, 4H, OCH$_2$CH_2). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 198.1 (dd, $^1J_{CY}$ = 42.5 Hz, $^2J_{CP}$ = 38.8 Hz, *C*–Y), 150.6 (d, J_{CP} = 4.9 Hz, aromatic *ipso*-*C*), 142.3 (d, J_{CP} = 8.0 Hz, aromatic *ipso*-*C*), 139.9 (d, J_{CP} = 123.4 Hz, aromatic *ipso*-*C*), 139.1 (d, J_{CP} = 25.9 Hz, phenyl *C*H), 137.7 (d, J_{CP} = 5.6 Hz, aromatic *ipso*-*C*), 134.8 (d, J_{CP} = 5.8 Hz, aromatic *ipso*-*C*), 134.3 (d, J_{CP} = 8.6 Hz, phenyl *C*H), 132.2 (d, J_{CP} = 2.0 Hz, phenyl *C*H), 131.4 (d, J_{CP} = 3.9 Hz, aromatic *ipso*-*C*), 129.7 (s, Mes *m*-*C*H), 129.6 (d, J_{CP} = 2.9 Hz, phenyl *C*H), 128.2 (s, mesityl *m*-*C*H), 128.1 (d, J_{CP} = 6.2 Hz, phenyl *C*H), 127.4 (d, J_{CP} = 3.5 Hz, phenyl *C*H), 127.3 (d, J_{CP} = 10.0 Hz, Cz 2,7-*C*H), 126.6 (d, J_{CP} = 9.2 Hz, aromatic *ipso*-*C*), 125.9 (d, J_{CP} = 0.8 Hz, aromatic *ipso*-*C*), 124.8 (d, J_{CP} = 14.5 Hz, phenyl *C*H), 124.2 (d, J_{CP} = 12.0 Hz, aromatic *ipso*-*C*), 123.8 (d, J_{CP} = 1.5 Hz, Cz 4,5-CH), 118.1 (d, J_{CP} = 94.0 Hz, aromatic *ipso*-*C*), 71.8 (s, OCH$_2$CH$_2$), 25.9 (s, OCH$_2$-CH$_2$), 21.5 (s, Cz CH_3), 21.0 (s, Mes CH_3), 20.4 (s, Mes CH_3), 20.3 (d, J_{CP} = 1.2 Hz, Mes CH_3). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 24.1 (d, $^2J_{PY}$ = 6.2 Hz). *Anal. Calc.* (%) for $C_{60}H_{58}N_3OP_2Y$: C, 72.94; H, 5.92; N, 4.25. Found: C, 67.82; H, 6.39; N, 4.32.

4.2.4. (**L**-κ^3*N*)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-d_6): δ 8.19 (s, 2H, Cz 4,5-C*H*), 7.64 (m, 8H, phenyl C*H*), 7.13 (d, partially obscured by solvent, 2H, Cz 2,7-C*H*), 6.97–6.81 (ov m, 12H, phenyl C*H*), 6.63 (s, 4H, mesityl C*H*), 2.42 (s, 6H, CH_3), 2.15 (s, 6H, CH_3), 2.01 (s, 12H, CH_3). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 153.7 (d, J_{CP} = 4.2 Hz, aromatic *ipso*-*C*), 144.1 (d, J_{CP} = 7.1 Hz, aromatic *ipso*-*C*), 133.9 (d, J_{CP} = 7.4 Hz, aromatic *ipso*-*C*), 132.7 (d, J_{CP} = 9.3 Hz, aromatic *C*H), 132.7 (s, aromatic *ipso*-*C*), 131.4 (d, J_{CP} = 2.9 Hz, aromatic *C*H), 129.4 (d, J_{CP} = 2.6 Hz, aromatic *C*H), 129.3 (d, J_{CP} = 4.0 Hz, aromatic *ipso*-*C*), 128.6 (s, obscured by solvent, aromatic *C*H), 128.4 (s, obscured by solvent, aromatic *C*H), 127.2 (s, aromatic *ipso*-*C*), 125.4 (d, J_{CP} = 3.3 Hz, aromatic *C*H), 122.4 (d, J_{CP} = 12.6 Hz, aromatic *ipso*-*C*), 115.2 (d, J_{CP} = 99.3 Hz, aromatic *ipso*-*C*), 21.9 (s, CH_3), 21.0 (s, CH_3), 20.9 (s, CH_3). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 11.0. *Anal. Calc.* (%) for $C_{56}H_{52}LiN_3P_2$: C, 80.46; H, 6.27; N, 5.03. Found: C, 80.39; H, 6.76; N, 4.26.

4.2.5. (**L**-κ^3*N*)$ScCl_2$ (**12**)

Toluene (25 mL) was added to a bomb charged with **11** (0.389 g, 0.466 mmol) and $ScCl_3(THF)_3$ (0.183 g, 0.499 mmol) to give an orange suspension. The reaction mixture was heated to 100 °C for 17 h resulting in a light orange solution with a white precipitate. The solution was brought into a glovebox where it was filtered through a fine porosity frit to remove LiCl. The filtrate was concentrated under reduced pressure and left at −35 °C to crystallize. Yellow crystals of **12** were collected by filtration, washed with pentane and dried under vacuum. Yield: 0.367 g (83.3%). ^1H NMR (chloroform-*d*): δ 8.17 (s, 2H, Cz 4,5-C*H*), 7.47 (m, 20H, phenyl C*H*), 6.85 (d, $^3J_{HP}$ = 15.2 Hz, 2H, Cz 2,7-C*H*), 6.55 (s, 4H, mesityl C*H*), 2.44 (s, 6H, CH_3), 2.05 (s, 6H, CH_3), 1.53 (s, 12H, CH_3). ^{13}C NMR (chloroform-*d*): δ 151.0 (d, J_{CP} = 4.1 Hz, aromatic *ipso*-*C*), 141.4 (d, J_{CP} = 9.1 Hz, aromatic *ipso*-*C*), 137.0 (d, J_{CP} = 6.0 Hz, aromatic *ipso*-*C*), 134.4 (d, J_{CP} = 9.7 Hz, aromatic *C*H), 133.2 (d, J_{CP} = 4.2 Hz, aromatic *ipso*-*C*), 132.4 (d, J_{CP} = 2.6 Hz, aromatic *C*H), 131.2 (d, J_{CP} = 10.5 Hz, aromatic *C*H), 129.2 (d, J_{CP} = 3.5 Hz, aromatic *C*H), 128.1 (d, J_{CP} = 12.1 Hz, aromatic *C*H), 127.8 (d, J_{CP} = 96.2 Hz, aromatic *ipso*-*C*), 126.2 (d, J_{CP} = 13.1 Hz, aromatic *ipso*-*C*), 125.8 (d, J_{CP} = 9.0 Hz, aromatic *ipso*-*C*), 125.0 (s, aromatic *C*H), 109.3 (d, J_{CP} = 106.5 Hz, aromatic *ipso*-*C*), 21.3 (s, CH_3), 20.8 (s, CH_3), 20.3 (s, CH_3). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 26.4. *Anal. Calc.* (%) for $C_{56}H_{52}Cl_2N_3P_2Sc$: C, 71.19; H, 5.55; N, 4.45. Found: C, 69.21; H, 5.59; N, 4.32.

4.2.6. (**L**-κ^3*N*)YCl_2 (**13**)

Toluene (50 mL) was added to a bomb charged with **11** (0.401 g, 0.481 mmol) and $YCl_3(THF)_{3.5}$ (0.226 g, 0.504 mmol) to give a red-orange suspension. The reaction mixture was heated to 60 °C for 95 h resulting in a light orange solution with a white precipitate. The solution was brought into a glovebox where it was filtered through a fine porosity frit to remove LiCl. The filtrate was concentrated under reduced pressure and left at −35 °C to crystallize. Yellow crystals of **13** were collected by filtration, washed with pentane and dried under vacuum. Yield: 0.343 g (72.1%). ^1H NMR (chloroform-*d*): δ 8.26 (s, 2H, Cz 4,5-C*H*), 7.42 (m, 20H, phenyl C*H*), 6.80 (d, $^3J_{HP}$ = 15.0 Hz, 2H, Cz 2,7-C*H*), 6.49 (s, 4H, mesityl C*H*), 2.41 (s, 6H, CH_3), 2.10 (s, 6H, CH_3), 1.48 (s, 12H, CH_3). ^{13}C NMR (chloroform-*d*): δ 151.1 (s, aromatic *ipso*-*C*), 138.7 (d, J_{CP} = 8.4 Hz, aromatic *ipso*-*C*), 136.9 (d, J_{CP} = 6.5 Hz, aromatic *ipso*-*C*), 134.0 (d, J_{CP} = 9.5 Hz, aromatic *C*H), 133.4 (d, J_{CP} = 4.0 Hz, aromatic *ipso*-*C*), 132.5 (s, aromatic *C*H), 132.0 (d, J_{CP} = 11.1 Hz, aromatic *C*H), 129.4 (s, aromatic *C*H), 128.3 (d, J_{CP} = 12.0 Hz, aromatic *C*H), 128.0 (d, J_{CP} = 96.1 Hz, aromatic *ipso*-*C*), 126.4 (d, J_{CP} = 8.8 Hz, aromatic *ipso*-*C*), 125.7 (d, J_{CP} = 12.6 Hz, aromatic *ipso*-*C*), 125.2 (s, aromatic *C*H), 109.3 (d, J_{CP} = 107.7 Hz, aromatic *ipso*-*C*), 21.2 (s, CH_3), 20.8 (s, CH_3), 20.0 (s, CH_3). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 25.2 (d, $^2J_{PY}$ = 2.3 Hz). *Anal. Calc.* (%) for $C_{56}H_{52}Cl_2N_3P_2Y$: C, 68.02; H, 5.30; N, 4.25. Found: C, 65.60; H, 5.28; N, 4.24.

Table 4
Summary of crystallography data collection and structure refinement for compounds **7**, **8**, **11**, **12** and **13**.

	7	**8**	**11**	**12**[a]	**13**[a]
Formula	$C_{50}H_{40}NP_3 \cdot C_7H_8$	$C_{56}H_{53}N_3P_2 \cdot C_7H_8$	$C_{56}H_{52}LiN_3P_2 \cdot C_7H_8$	$C_{56}H_{52}Cl_2N_3P_2Sc \cdot 2C_7H_8$	$C_{56}H_{52}Cl_2N_3P_2Y \cdot 2C_7H_8$
Formula weight (g mol^{-1})	839.87	922.09	928.02	1036.94	1080.89
Crystal system	orthorhombic	triclinic	triclinic	rhombohedral	rhombohedral
Space group	$Pna2_1$	$P\bar{1}$	$P\bar{1}$	$R\bar{3}$	$R\bar{3}$
a (Å)	17.4632(10)	13.702(2)	13.695(3)	23.6675(10)	23.7063(8)
b (Å)	23.0658(13)	18.851(3)	14.183(3)	23.6675(10)	23.7063(8)
c (Å)	11.4011(6)	20.642(3)	14.978(3)	23.6675(10)	23.7063(8)
α (°)	90	81.694(2)	113.836(2)	107.38	107.28
β (°)	90	79.290(2)	102.657(2)	107.38	107.28
γ (°)	90	83.504(2)	92.431(2)	107.38	107.28
Volume (Å^3)	4592.4(4)	5163.5(13)	2568.4(8)	10923.1(8)	11008.1(6)
Z	4	4	2	6	6
D_{calc} (g cm^{-3})	1.215	1.186	1.200	0.946	0.978
μ (mm^{-1})	0.169	0.127	0.128	0.250	0.943
Crystal size (mm^3)	0.29 × 0.19 × 0.17	0.24 × 0.12 × 0.07	0.40 × 0.22 × 0.19	0.32 × 0.23 × 0.07	0.39 × 0.35 × 0.23
θ range (°)	1.77–27.10	1.52–27.10	1.59–26.45	1.68–27.10	1.85–27.10
N	50663	74246	27644	122009	123788
N_{ind}	10146	22697	10519	16076	16199
Data/restraints/parameters	10146/1/553	22697/0/1213	10519/232/684	16076/44/637	16199/0/649
Goodness-of-fit (GoF) on F^2	1.036	0.973	1.003	0.876	1.074
R_1 ($I > 2\sigma(I)$)[b]	0.0433	0.0753	0.0592	0.0728	0.0479
wR_2 ($I > 2\sigma(I)$)[c]	0.1067	0.1360	0.1449	0.1646	0.1455
R_1 (all data)[b]	0.0559	0.1915	0.1065	0.2047	0.0738
wR_2 (all data)[c]	0.1149	0.1754	0.1706	0.2012	0.1561
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e Å^{-3})	0.427 and −0.282	1.064 and −0.396	1.153 and −0.432	0.887 and −0.495	0.547 and −0.411

[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.
[b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

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 SADABS [24]. The structures were solved by direct methods and refined by the least squares method on F^2 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 obtain reasonable bond 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].

Acknowledgements

This research was financially supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada and the Canada Foundation for Innovation (CFI). Prof. Jun Okuda and RWTH Aachen University are thanked for hosting PGH during the preparation of this manuscript.

Appendix A. Supplementary materials

CCDC 998405–998409 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.

References

[1] (a) C.M. Ong, P. McKarns, D.W. Stephan, Organometallics 18 (1999) 4197;
(b) T.K. Panda, A. Zulys, M.T. Gamer, P.W. Roesky, J. Organomet. Chem. 690 (2005) 5078;
(c) G.C. Welch, W.E. Piers, M. Parvez, R. McDonald, Organometallics 23 (2004) 1811;
(d) A.J. Wooles, M. Gregson, O.J. Cooper, A. Middleton-Gear, D.P. Mills, W. Lewis, A.J. Blake, S.T. Liddle, Organometallics 30 (2011) 5314;
(e) R.P. Kamalesh Babu, K. Aparna, R. McDonald, R.G. Cavell, Organometallics 20 (2001) 1451;
(f) H. Xie, Z. Mou, B. Liu, P. Li, W. Rong, S. Li, D. Cui, Organometallics 33 (2014) 722;
(g) C.A. Wheaton, P.G. Hayes, Comments Inorg. Chem. 32 (2011) 127.
[2] (a) O. Alhomaidan, C. Beddie, G. Bai, D.W. Stephan, Dalton Trans. (2009) 1991;
(b) R.P. Kamalesh Babu, R. Mcdonald, R.G. Cavell, Chem. Commun. (2000) 481;
(c) A. Ramos, D.W. Stephan, Dalton Trans. 39 (2010) 1328;
(d) M.J. Sarsfield, M. Said, M. Thornton-Pett, L.A. Gerrard, M. Bochmann, J. Chem. Soc., Dalton Trans. (2001) 822;

(e) R.G. Cavell, R.P. Kamalesh Babu, A. Kasani, R. McDonald, J. Am. Chem. Soc. 121 (1999) 5805;
(f) R.P. Kamalesh Babu, R. McDonald, R.G. Cavell, Organometallics 19 (2000) 3462.
[3] (a) C.C. Brown, C. Glotzbach, D.W. Stephan, Dalton Trans. 39 (2010) 9626;
(b) R. Cariou, T.W. Graham, F. Dahcheh, D.W. Stephan, Dalton Trans. 40 (2011) 5419;
(c) J.D. Masuda, P. Wei, D.W. Stephan, Dalton Trans. (2003) 3500.
[4] (a) O.J. Cooper, J. McMaster, W. Lewis, A.J. Blake, S.T. Liddle, Dalton Trans. 39 (2010) 5074;
(b) G. Ma, M.J. Ferguson, R. McDonald, R.G. Cavell, Inorg. Chem. 50 (2011) 6500.
[5] (a) A. Buchard, R.H. Platel, A. Auffrant, X.F. Le Goff, P. Le Floch, C.K. Williams, Organometallics 29 (2010) 2892;
(b) T.-P.-A. Cao, A. Buchard, X.F. Le Goff, A. Auffrant, C.K. Williams, Inorg. Chem. 51 (2012) 2157;
(c) M.T. Gamer, M. Rastätter, P.W. Roesky, A. Steffens, M. Glanz, Chem. Eur. J. 11 (2005) 3165;
(d) C. Bakewell, T.-P.-A. Cao, X.F. Le Goff, N.J. Long, A. Auffrant, C.K. Williams, Organometallics 32 (2013) 1475;
(e) M.T. Gamer, P.W. Roesky, I. Palard, M. Le Hellaye, S.M. Guillaume, Organometallics 26 (2007) 651;
(f) M.T. Gamer, P.W. Roesky, J. Organomet. Chem. 647 (2002) 123;
(g) M.T. Gamer, S. Dehnen, P.W. Roesky, Organometallics 20 (2001) 4230;
(h) T.K. Panda, A. Zulys, M.T. Gamer, P.W. Roesky, Organometallics 24 (2005) 2197;
(i) M. Rastätter, A. Zulys, P.W. Roesky, Chem. Commun. (2006) 874;
(j) M. Rastätter, A. Zulys, P.W. Roesky, Chem.-Eur. J. 13 (2007) 3606;
(k) A. Zulys, T.K. Panda, M.T. Gamer, P.W. Roesky, Chem. Commun. (2004) 2584;
(l) M. Wiecko, P.W. Roesky, V.V. Burlakov, A. Spannenberg, Eur. J. Inorg. Chem. (2007) 876;
(m) M. Wiecko, P.W. Roesky, Organometallics 28 (2009) 1266;
(n) K.D. Conroy, W.E. Piers, M. Parvez, J. Organomet. Chem. 693 (2008) 834;
(o) M.S. Hill, P.B. Hitchcock, Dalton Trans. (2003) 4570;
(p) D. Li, S. Li, D. Cui, X. Zhang, J. Organomet. Chem. 695 (2010) 2781;
(q) D. Li, S. Li, D. Cui, X. Zhang, A.A. Trifonov, Dalton Trans. 40 (2011) 2151;
(r) W. Rong, D. Liu, H. Zuo, Y. Pan, Z. Jian, S. Li, D. Cui, Organometallics 32 (2013) 1166;
(s) B. Liu, X. Liu, D. Cui, L. Liu, Organometallics 28 (2009) 1453;
(t) B. Liu, D. Cui, J. Ma, X. Chen, X. Jing, Chem.-Eur. J. 13 (2007) 834.
[6] (a) K. Aparna, M. Ferguson, R.G. Cavell, J. Am. Chem. Soc. 122 (2000) 726;
(b) A. Buchard, A. Auffrant, L. Ricard, X.F. Le Goff, R.H. Platel, C.K. Williams, P. Le Floch, Dalton Trans. (2009) 10219;
(c) S.T. Liddle, J. McMaster, J.C. Green, P.L. Arnold, Chem. Commun. (2008) 1747;
(d) D.P. Mills, O.J. Cooper, J. McMaster, W. Lewis, S.T. Liddle, Dalton Trans. (2009) 4547;
(e) D.P. Mills, A.J. Wooles, J. McMaster, W. Lewis, A.J. Blake, S.T. Liddle, Organometallics 28 (2009) 6771;
(f) A.J. Wooles, O.J. Cooper, J. McMaster, W. Lewis, A.J. Blake, S.T. Liddle, Organometallics 29 (2010) 2315;
(g) M. Gregson, E. Lu, J. McMaster, W. Lewis, A.J. Blake, S.T. Liddle, Angew. Chem., Int. Ed. 52 (2013) 13016;
R.G. Cavell, R.P. Kamalesh Babu, J. Organomet. Chem. 617–618 (2001) 158;
(i) D.P. Mills, L. Soutar, W. Lewis, A.J. Blake, S.T. Liddle, J. Am. Chem. Soc. 132 (2010) 14379;
(j) S.T. Liddle, D.P. Mills, A.J. Wooles, Chem. Soc. Rev. 40 (2011) 2164;
(k) T. Cantat, N. Mézailles, A. Auffrant, P. Le Floch, Dalton Trans. (2008) 1957;
(l) D.J. Mindiola, J. Scott, Nat. Chem. 3 (2011) 15.
[7] Z. Jian, W. Rong, Z. Mou, Y. Pan, H. Xie, D. Cui, Chem. Commun. 48 (2012) 7516.
[8] W. Rong, J. Cheng, Z. Mou, H. Xie, D. Cui, Organometallics 32 (2013) 5523.
[9] (a) K.R.D. Johnson, P.G. Hayes, Organometallics 28 (2009) 6352;
(b) K.R.D. Johnson, P.G. Hayes, Organometallics 32 (2013) 4046;
(c) K.R.D. Johnson, P.G. Hayes, Dalton Trans. 43 (2014) 2448.
[10] For example, see: (a) S. Nagendran, H.W. Roesky, Organometallics 27 (2008) 457;
(b) H.W. Roesky, S.S. Kumar, Chem. Commun. (2005) 4027;
(c) G.B. Deacon, C.M. Forsyth, F. Jaroschik, P.C. Junk, D.L. Kay, T. Maschmeyer, A.F. Masters, J. Wang, L.D. Field, Organometallics 27 (2008) 4772;
(d) G. Meyer, Angew. Chem., Int. Ed. 47 (2008) 4962;
(e) C. Ruspic, J.R. Moss, M. Schürmann, S. Harder, Angew. Chem., Int. Ed. 47 (2008) 2121;
(f) P.P. Power, Chem. Rev. 112 (2012) 3482;
(g) P.P. Power, J. Organomet. Chem. 689 (2004) 3904;
(h) P.P. Power, Organometallics 26 (2007) 4362;
(i) A.M. Bryan, G.J. Long, F. Grandjean, P.P. Power, Inorg. Chem. 53 (2014) 2692;
(j) J.N. Boynton, J.-D. Guo, J.C. Fettinger, C.E. Melton, S. Nagase, P.P. Power, J. Am. Chem. Soc. 135 (2013) 10720;
(k) T. Nguyen, A.D. Sutton, M. Brynda, J.C. Fettinger, G.J. Long, P.P. Power, Science 310 (2005) 844;
(l) M. Yoshifuji, J. Organomet. Chem. 611 (2000) 210.
[11] W.J. Evans, Inorg. Chem. 46 (2007) 3435.
[12] C. Silvestru, J.E. Drake, Coord. Chem. Rev. 223 (2001) 117.
[13] (a) K.R.D. Johnson, M.A. Hannon, J.S. Ritch, P.G. Hayes, Dalton Trans. 41 (2012) 7873;
(b) K.R.D. Johnson, P.G. Hayes, Organometallics 30 (2011) 58;
(c) M.T. Zamora, K.R.D. Johnson, M.M. Hänninen, P.G. Hayes, Dalton Trans. 43 (2014) 10739.
[14] (a) P.G. Hayes, W.E. Piers, L.W.M. Lee, L.K. Knight, M. Parvez, M.R.J. Elsegood, W. Clegg, Organometallics 20 (2001) 2533;
(b) K.R.D. Johnson, A.P. Côté, P.G. Hayes, J. Organomet. Chem. 695 (2010) 2747.
[15] (a) K.R.D. Johnson, P.G. Hayes, Chem. Soc. Rev. 42 (2013) 1947;
(b) M.I. Bruce, Angew. Chem., Int. Ed. 16 (1977) 73.
[16] (a) M. Konkol, M. Kondracka, P. Voth, T.P. Spaniol, J. Okuda, Organometallics 27 (2008) 3774;
(b) S. Bambirra, M.J.R. Brandsma, E.A.C. Brussee, A. Meetsma, B. Hessen, J.H. Teuben, Organometallics 19 (2000) 3197;
(c) J.P. Mitchell, S. Hajela, S.K. Brookhart, K.I. Hardcastle, L.M. Henling, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 1045.
[17] P.G. Hayes, W.E. Piers, Inorg. Synth. 35 (2010) 20.
[18] P. Sobota, J. Utko, S. Szafert, Inorg. Chem. 33 (1994) 5203.
[19] K.C. Hultzsch, P. Voth, K. Beckerle, T.P. Spaniol, J. Okuda, Organometallics 19 (2000) 228.
[20] G.J.P. Britovsek, V.C. Gibson, O.D. Hoarau, S.K. Spitzmesser, A.J.P. White, D.J. Williams, Inorg. Chem. 42 (2003) 3454.
[21] S. Murata, S. Abe, H. Tomioka, J. Org. Chem. 62 (1997) 3055.
[22] APEX2, version 2010.7-0; Data Collection and Refinement Program, Bruker AXS, Madison, WI, 2010.
[23] SAINT-Plus, version 7.68A, Data Reduction and Correction Program, Bruker AXS, Madison, WI, 2009.
[24] G.M. Sheldrick, SADABS, version 2008/1; Program for Empirical Absorption Correction, Bruker AXS, Madison, WI, 2008.
[25] G.M. Sheldrick, SHELXTL, version 6.19; Structure Determination Software Suite, Bruker AXS, Madison, WI, 2003.
[26] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7.

Please cite this article in press as: K.R.D. Johnson, P.G. Hayes, Inorg. Chim. Acta (2014), http://dx.doi.org/10.1016/j.ica.2014.05.045