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

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

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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

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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)		

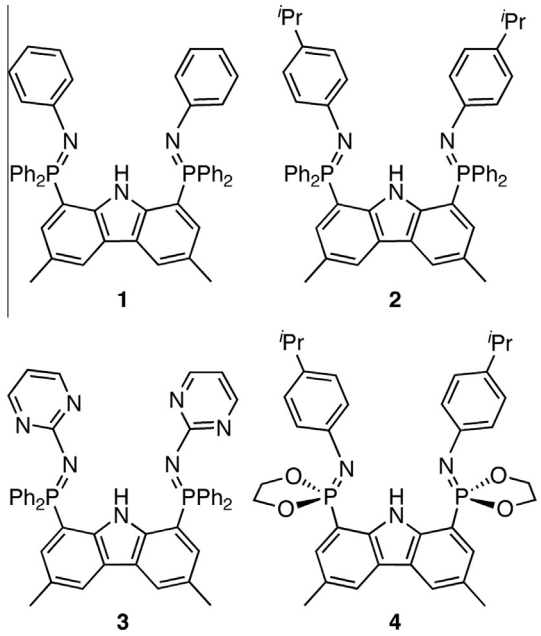


Chart 1. Bis(phosphinimine)carbazole proteo ligands **1**–**4**.

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.

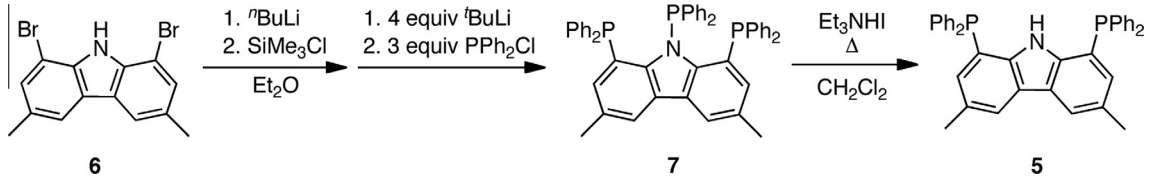
For this modified preparation, the compound 1,8-dibromo-3,6-dimethylcarbazole **6** was reacted with one equivalent of *n*-butyllithium followed by trimethylsilyl chloride to afford 1,8-dibromo-3,6-dimethyl-9*N*-trimethylsilylcarbazole *in situ*. Subsequently, a lithium halogen exchange reaction was 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**.

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