# Bulky aryl functionalized carbazolyl ligands: amido alternatives to the 2,6-diarylphenyl ligand class? $\ddagger \$ \$$

Natalie D. Coombs,<sup>*a,b*</sup> Andreas Stasch,<sup>*b,c*</sup> Andrew Cowley,<sup>*a*</sup> Amber L. Thompson<sup>*a*</sup> and Simon Aldridge<sup>\**a*</sup>

Received 30th October 2007, Accepted 26th November 2007 First published as an Advance Article on the web 11th December 2007 DOI: 10.1039/b716674e

Sterically encumbered amido ligands based on a 1,8-diarylcarbazol-9-yl backbone have been investigated as electronically distinct alternatives to the widely-used terphenyl ligand class in the stabilization of low-coordinate metal complexes, and structurally characterized for the first time. While 1,8-diphenylcarbazol-9-yl derivatives are readily available, facile rotation about the  $C_{ipso}-C_{ipso}$  bonds leads to structurally characterized main group derivatives {*e.g.* [(1,8-Ph<sub>2</sub>-3,6-Me<sub>2</sub>C<sub>12</sub>H<sub>4</sub>N)K]<sub>2</sub>} in which the coordination geometry at the metal centre is augmented by secondary metal–arene interactions. By contrast, the extra bulk inherent in the corresponding 1,8-dimesityl ligand results in essentially perpendicular alignments of the arene and carbazole planes, and a substituent-enforced sterically that the 1,8-dimesitylcarbazol-9-yl framework offers greater steric protection at the metal centre than does the corresponding 2,6-dimesitylphenyl ligand.

## 1. Introduction

Carbon donor ligands offering the possibility for extremely high steric loading at a metal centre have been exploited to great effect in recent years in the stabilization of electronically unsaturated complexes.<sup>1,2</sup> Such species have been of interest not only from a fundamental structure/bonding perspective (e.g. unusual multiple bonding or very low coordination numbers),<sup>3,4</sup> but also from the viewpoint of applied reactivity (e.g. in the activation of dihydrogen).5 Thus, in recent years 2,6-diarylphenyl ligands (I, Scheme 1), which were pioneered for main group metal systems,<sup>3</sup> have been further exploited in the synthesis of landmark multiply-bonded transition metal compounds.<sup>4</sup> In view of the key steric shielding in such complexes provided by the flanking aryl substituents, and with a view to extending the range of bulky ligands available to the synthetic chemist, we have targeted 1,8-diarylcarbazol-9-yl ligands (II) as alternative systems of potential interest. Such an approach would allow for the exploitation, for example, of the differing electronic properties of amido (vs. aryl) ligands. To date, a number of metal complexes containing the parent, unsubstituted carbazol-9-yl ligand have been reported, including homoleptic derivatives of both main group and transition metals.<sup>6</sup> Moreover, systems



**Scheme 1** The sterically encumbered 2,6-diarylphenyl (I) and 1,8-diarylcarbazol-9-yl (II) ligand families examined in the current study.

featuring additional N-donor substituents tethered to the 1- and 8-positions have also been examined in the context of transition metal catalyst design.<sup>7</sup>

However, given the versatility and widespread application of 2,6-diarylphenyl ligand systems (I), we were surprised to find that the structural characteristics of the potentially analogous 1,8-diarylcarbazol-9-yl derivatives have yet to be investigated. With this in mind, and with a view to comparing the size and angular extent of the sterically protected cavities generated by these two ligand families, we have synthesized and structurally characterized a number of species containing ligands of type II. Given that complexes of empirical composition 2,6-(2,4,6- $R_3C_6H_2$ )C<sub>6</sub>H<sub>3</sub>GaCl<sub>2</sub> have been structurally characterized (for R = Me, 'Pr),<sup>8</sup> and are known to exhibit different degrees of aggregation dependent on the steric bulk of R, we targeted analogous type II dichlorogallium complexes as comparative structural probes. It should be noted that target monomeric threecoordinate amido(dihalo)gallanes are as yet unknown, despite a range of interesting further chemistry for which they might serve as useful starting materials.

<sup>&</sup>lt;sup>a</sup>Inorganic Chemistry, University of Oxford, South Parks Road, Oxford, UK OX1 3QR. E-mail: simon.aldridge@chem.ox.ac.uk; Fax: +44 (0)1865 272690; Tel: +44 (0)1865 285201

<sup>&</sup>lt;sup>b</sup>School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, UK CF10 3TB

<sup>&</sup>lt;sup>c</sup>School of Chemistry, Monash University, PO Box 23, Victoria, 3800, Australia

<sup>†</sup> Dedicated to Professor Ken Wade on the occasion of his 75th birthday.

<sup>&</sup>lt;sup>‡</sup> The HTML version of this article has been enhanced with colour images. § CCDC reference numbers 665746–665748. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b716674e

<sup>¶</sup> Electronic supplementary information (ESI) available: Details of all three crystal structures and details of the synthesis of (1,8-diphenyl-3,6-dimethylcarbazol-9-yl)potassium dimer. See DOI: 10.1039/b716674e

### 2. Experimental

#### General

Manipulations involving air-sensitive compounds were carried out under a nitrogen or argon atmosphere using standard Schlenk line or dry box techniques. Hexanes and toluene were pre-dried over sodium wire and purged with nitrogen prior to distillation from potassium (hexanes) or sodium (toluene). Benzene-d<sub>6</sub> and chloroform-d (both Goss) were degassed and dried over potassium (benzene-d<sub>6</sub>) or molecular sieves (chloroform-d) prior to use. Ethanol,  $Pd(PPh_3)_4$ ,  $GaCl_3$ ,  $MesB(OH)_2$  (Mes = mesityl, 2,4,6- $Me_3C_6H_2$ -) and "BuLi (1.6 M solution in hexanes) were used as received; 1,8-dibromo-3,6-dimethylcarbazole and (1,8-diphenyl-3,6-dimethylcarbazol-9-yl)lithium (2a) were prepared by minor modification of literature methods.9 NMR spectra were measured on a Bruker AM-400 or Jeol Eclipse 300 Plus FT-NMR spectrometer; residual protons of solvent were used for reference for <sup>1</sup>H and <sup>13</sup>C NMR spectra. Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, University of Wales Swansea and by the departmental service. Perfluorotributylamine was used as the standard for high-resolution EI mass spectra. Abbreviations: s = singlet, m = multiplet.

#### Crystallographic method

Data for compounds **1b**, **3b** and (1,8-dimesityl-3,6-dimethylcarbazol-9-yl)potassium dimer (see Table 1) were collected on an Enraf Nonius Kappa CCD diffractometer equipped with a MoK $\alpha$  radiation source ( $\lambda = 0.71073$  Å). Data collection and cell refinement were carried out using DENZO, and structure solution and refinement (by full-matrix least-squares) using SIR-92, SHELXS-97 and SHELXL-97, respectively; empirical absorption corrections were carried out using SORTAV.<sup>10</sup> For **1b**, the hexanes solvent is disordered on an inversion centre and was modelled as a quarter molecule of n-hexane and a quarter molecule of cyclohexane in the asymmetric unit. The solvent carbon atoms were refined isotropically.

#### Syntheses

Synthesis of (1,8-diphenyl-3,6-dimethylcarbazol-9-yl)gallium dichloride (3a). To a suspension of (1,8-diphenyl-3,6-dimethylcarbazol-9-yl)lithium (2a, 0.825 g, 2.33 mmol) in hexanes (25 cm<sup>3</sup>) at -15 °C was added dropwise a solution of GaCl<sub>3</sub> (0.411 g, 2.33 mmol) also in hexanes (15 cm<sup>3</sup>). The reaction mixture was allowed to warm slowly to 20 °C and was stirred for a further 12 h, with the formation of a pale yellow solution and orange precipitate. Isolation of the precipitate by filtration and extraction into toluene (10 cm<sup>3</sup>) followed by layering with hexanes (30 cm<sup>3</sup>) led to the isolation of 3a as orange crystals at -30 °C. Isolated yield: 0.146 g, 13%. <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta_H$  2.34 (s, 6H, CH<sub>3</sub> of carbazol-9-yl), 6.89 (overlapping s, 4H, carbazol-9-yl and phenyl CH), 7.01 (m, 4H, phenyl CH), 7.26 (m, 4H, phenyl CH), 7.76 (s, 2H, carbazol-9-yl CH). <sup>13</sup>C NMR (76 MHz, C<sub>6</sub>D<sub>6</sub>): δ<sub>C</sub> 20.0 (CH<sub>3</sub>), 119.2 (aromatic CH), 124.8 (aromatic CH), 125.8 (quaternary aromatic carbon), 126.1 (aromatic CH), 127.8

Table 1 Crystallographic data for 1b, 3b and (1,8-dimesityl-3,6-dimethylcarbazol-9-yl)potassium dimer

	$1b \cdot \frac{1}{8} (C_6 H_{12}) \cdot \frac{1}{8} (C_6 H_{14})$	3b	$[(1,8\text{-}Ph_2\text{-}3,6\text{-}Me_2C_{12}H_4N)K]_2$
Empirical formula	C <sub>33.5</sub> H <sub>36.25</sub> N	$C_{32}H_{32}Cl_2GaN$	$C_{52}H_{40}K_2N_2$
Formula weight	452.89	571.24	771.06
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group Unit cell dimensions:	<i>P</i> -1	$P2_{1}/c$	$P2_1/n$
a/Å	7.939(2)	17.611(1)	11.050(5)
b/Å	13.589(3)	7.962(1)	11.472(5)
c/Å	25.682(5)	20.376(1)	16.097(5)
$a/^{\circ}$	78.42(3)	90	90
$\beta/^{\circ}$	81.45(3)	104.70(1)	105.146(5)
y/°	86.56(3)	90	90
Volume/Å <sup>3</sup>	2683.0(9)	2763.4(1)	1969.7(14)
Z, Density (calc.)/Mg $m^{-3}$	4, 1.121	4, 1.373	2, 1.300
Absorption coefficient/mm <sup>-1</sup>	0.064	1.211	0.280
F(000)	977	1184	808
Crystal size/mm <sup>3</sup>	$0.30 \times 0.15 \times 0.10$	$0.24 \times 0.24 \times 0.20$	$0.12 \times 0.10 \times 0.10$
Theta range for data colln./°	2.97 to 25.00	5.0 to 27.5	3.13 to 27.00
Index ranges:			
h	-9 to 9	-22 to 22	-14 to 14
k	-15 to 16	0 to 10	-14 to 14
l	-30 to 30	0 to 26	-20 to 20
Reflections collected	14902	29657	8311
Independent reflections, $R_{int}$	9075 (0.0416)	6730 (0.048)	4287 (0.0408)
Completeness to theta max. (%)	96.0	99.1	99.7
Max. and min. transmission	0.998, 0.665	0.78, 0.75	0.868, 0.778
Data/restraints/parameters	9075/4/636	3990/0/325	4287/0/255
Goodness-of-fit on $F^2$	1.018	1.084	1.034
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0874	R1 = 0.0459	R1 = 0.0498
	wR2 = 0.2172	wR2 = 0.0535	wR2 = 0.1065
<i>R</i> indices (all data)	R1 = 0.1178	R1 = 0.0779	R1 = 0.0801
٩	wR2 = 0.2372	wR2 = 0.0773	wR2 = 0.1178
Largest diff. pk and hole/e $Å^{-3}$	1.451, -0.309	0.77, -1.26	0.220, -0.303

(quaternary aromatic carbon), 128.1 (quaternary aromatic carbon), 128.6 (aromatic CH), 135.0 (aromatic CH), 141.1 (quaternary aromatic carbon), 144.1 (quaternary aromatic carbon). EI-MS (m/z): 485.0 {5%, [M]<sup>+</sup>}, 347.3 {100%, [M–GaCl<sub>2</sub>]<sup>+</sup>}: exact mass: calc. for [M]<sup>+</sup> 485.0223, meas. 485.0222. Microanalysis: calc. C 64.11, H 4.14, N 2.88; meas. C 64.58, H 4.44, N 2.55.

Synthesis of 1,8-dimesityl-3,6-dimethylcarbazole (1b). To a solution of 1.8-dibromo-3.6-dimethylcarbazole (3.184 g, 9.32 mmol) and  $Pd(PPh_3)_4$  (1.068 g, 0.96 mmol) in toluene (420 cm<sup>3</sup>) was added a solution of mesitylboronic acid (21.024 g, 128.35 mmol) in ethanol (100 cm<sup>3</sup>), followed by an aqueous solution of 1M Na<sub>2</sub>CO<sub>3</sub> (92.4 cm<sup>3</sup>, 92.4 mmol). After degassing (argon) the reaction mixture was stirred at 80 °C for 18 h, filtered while hot, and the filtrate washed with 1M NaOH ( $2 \times 180 \text{ cm}^3$ ) and water  $(2 \times 180 \text{ cm}^3)$ . After drying over MgSO<sub>4</sub> and filtration, the volatiles were removed in vacuo yielding a dark brown solid which was recrystallised from hot ethanol yielding 1 as a beige solid. Crystals suitable for X-ray diffraction were obtained by cooling an ethanol/hexanes solution to -30 °C. Isolated yield: 1.655 g, 43%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  1.87 (s, 12H, ortho-CH3 of Mes), 2.25 (s, 6H, para-CH3 of Mes), 2.51 (s, 6H, CH3 of carbazol-9-yl), 6.85 (s, 2H, aromatic CH of carbazol-9-yl), 6.88 (s, 4H, aromatic CH of Mes), 7.05 (s, 1H, NH of carbazol-9-yl), 7.78 (s, 2H, aromatic CH of carbazol-9-yl). <sup>13</sup>C NMR (76 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  19.2 (ortho-CH<sub>3</sub> of Mes), 20.0 (para-CH<sub>3</sub> of Mes), 20.4 (carbazol-9-yl CH<sub>3</sub>), 117.7 (quaternary aromatic carbon), 122.2 (quaternary aromatic carbon) 122.6 (quaternary aromatic carbon), 127.0 (quaternary aromatic carbon), 127.4 (aromatic CH), 127.7 (quaternary aromatic carbon), 133.6 (quaternary aromatic carbon), 135.3 (quaternary aromatic carbon), 135.5 (quaternary aromatic carbon), 136.0 (aromatic CH). EI-MS (m/z): 431.3 {100%, [M]<sup>+</sup>}; exact mass: calc for [M]<sup>+</sup> 431.2608, meas. 431.2610. Reproducible microanalysis was impossible to obtain for 1b, presumably due to the presence of hexanes in the lattice of crystalline samples.

Synthesis of (1,8-dimesityl-3,6-dimethylcarbazol-9-yl)gallium dichloride (3b). To a solution of 1,8-dimesityl-3,6-dimethylcarbazole (1.211 g, 2.81 mmol) in hexane (100 cm<sup>3</sup>) was added <sup>n</sup>BuLi (2.08 cm<sup>3</sup> of a 1.6 M solution in hexanes, 3.33 mmol) and the reaction mixture stirred at 20 °C for 3 h, after which the solution was concentrated in vacuo ca. 15 cm<sup>3</sup>. The resulting precipitate was isolated by filtration and dried in vacuo yielding an off-white powder (0.905 g, 74%) of (1,8-dimesityl-3,6-dimethylcarbazol-9yl)lithium (2b) which was used in the subsequent step without further purification. To a suspension of 2b (0.700 g, 1.60 mmol) in hexanes (20 cm<sup>3</sup>) was added a solution of GaCl<sub>3</sub> (0.282 g, 1.60 mmol) also in hexanes (30 cm<sup>3</sup>) at -30 °C. The reaction was warmed slowly to 20 °C and stirred for 12 h. The resulting grey precipitate was isolated by filtration, extracted into toluene (15 cm<sup>3</sup>), and filtered. Hexanes (50 cm<sup>3</sup>) were added to the concentrated toluene solution yielding (1,8-dimesityl-3,6-dimethylcarbazol-9yl)gallium dichloride (3b) as a pale purple crystalline solid. Crystals suitable for X-ray diffraction were obtained by layering a concentrated toluene solution with hexanes (ca. 1 : 5) and storage at -30 °C for 1 week. Isolated yield: 0.488 g, 54%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  1.75 (12H, s, ortho-CH<sub>3</sub> of Mes), 1.78 (6H, s, para-CH<sub>3</sub> of Mes), 2.13 (6H, s, CH<sub>3</sub> of carbazole), 6.49 (2H, s, CH of carbazole), 6.61 (4H, s, CH of Mes), 7.59

(2H, s, CH of carbazole). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta_c$  19.3 (*para*-CH<sub>3</sub> of Mes), 20.0 (*ortho*-CH<sub>3</sub> of Mes), 20.4 (carbazol-9-yl CH<sub>3</sub>), 119.7 (quaternary aromatic carbon), 123.6 (quaternary aromatic carbon) 126.1 (quaternary aromatic carbon), 129.4 (aromatic CH), 131.8 (aromatic CH), 132.8 (quaternary aromatic carbon), 136.3 (quaternary aromatic carbon), 140.0 (aromatic CH), 140.9 (quaternary aromatic carbon), 142.8 (quaternary aromatic carbon). EI-MS (*m*/*z*): 571.1 {10%, [M]<sup>+</sup>}, 431.2 {100%, [M–GaCl<sub>2</sub>]<sup>+</sup>}; exact mass: calc. for [M]<sup>+</sup> 569.1168, meas. 569.1149. Microanalysis: calc. C 67.28, H 5.65, N 2.45; meas. C 67.66, H 5.88, N 2.33.

#### 3. Results and discussion

2,6-Diarylphenyl ligand systems (I) have been widely exploited in the isolation of complexes containing highly unsaturated metal centres protected, in part, by the remarkable degree of steric shielding afforded by the flanking aryl rings.<sup>3,4</sup> Given that monoanionic carbazol-9-yl ligands have been reported to act as very strong donors in transition metal chemistry,<sup>6,7</sup> and that the ability to functionalize such ligands at the 1 and 8 positions via Suzuki/Miyaura coupling has previously been reported,<sup>9</sup> we have targeted the 1,8-diarylcarbazol-9-yl framework (II) as the basis for a range of possible alternative ligands. In particular, we sought answers to the following questions: (i) how do the ligand families I and II compare in terms of the spatial and angular extent of the sterically shielded cavity produced? and (ii) how are the properties of II influenced by the bulk of the flanking aryl rings? Additionally, we were interested to examine (as a function of aryl substituent bulk) to what extent the coordination geometry at the metal is likely to be augmented via either intra- or inter-molecular interactions. With this in mind, and in the knowledge that the coordination geometry at the metal centre (and the degree of aggregation) found for complexes of the type 2,6-(2,4,6-R<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>GaCl<sub>2</sub> is highly sensitive to the bulk of the peripheral R substituents (Scheme 2),<sup>8</sup> we targeted dichlorogallium complexes of the type  $(1,8-Ar_2,3,6-$ Me<sub>2</sub>C<sub>12</sub>H<sub>4</sub>)GaCl<sub>2</sub> for comparative structural studies.



Scheme 2 Variation in the degree of aggregation for 2,6-diarylphenylgallium dichloride complexes as a function of the steric bulk of the flanking aryl rings.

Ligand syntheses can readily be carried out using 1,8-dibromo-3,6-dimethylcarbazole and the corresponding arylboronic acids (R = Ph, Mes) according to the methodology developed by Spitzmesser and Gibson (Scheme 3).<sup>9</sup> The propensity of carbazole itself to undergo bromination reactions at the 3 and 6 positions,



Scheme 3 Syntheses of carbazolylgallium dichloride complexes 3a and 3b. Key reagents and conditions: (i)  $ArB(OH)_2$  (10–15 equiv.),  $Pd(PPh_3)_4$ ,  $Na_2CO_3$ , toluene : ethanol (4 : 1), 80 °C, 18 h, 43% for 1b; (ii) "BuLi (1.2 equiv.), hexanes, 20 °C, 3 h, then  $GaCl_3$  (1.0 equiv.), hexanes, -30 to 20 °C, 12 h, 54% for 3b.

necessitates the use of the protected 3,6-dimethyl derivative, which then undergoes bromination at the desired 1 and 8 positions. In common with previous observations of Suzuki/Miyaura chemistry,11 the yields of the final coupling reactions used to generate 1a and 1b are strongly dependent on the steric bulk of the boronic acid. Thus, while **1a** has been reported to be synthesized in yields of up to 85% using a Pd(PPh<sub>3</sub>)<sub>4</sub>/Na<sub>2</sub>(CO)<sub>3</sub>/10 : 3 ethanol : water protocol, 1b is synthesized from mesitylboronic acid in 43% yield, and only a trace of the corresponding 2,4,6triisopropylphenyl (Trip) derivative is obtained from TripB(OH)<sub>2</sub> using the same catalytic cocktail. Nevertheless 1a and 1b are available using this methodology in multi-gramme quantities and can be used to synthesize the desired dichlorogallium complexes 3a and 3b in moderate yields by a simple one-pot lithiation, electrophilic GaCl<sub>3</sub> quenching procedure. While the lithiated intermediates 2a and 2b were typically generated in situ without isolation we were successful in structurally characterizing the potassium analogue of 2a (see Fig. 1 and ESI¶).



**Fig. 1** Molecular structure of (1,8-diphenyl-3,6-dimethylcarbazol-9-yl)potassium dimer. Hydrogen atoms omitted for clarity; ORTEP ellipsoids set at the 50% probability level. Key bond lengths (Å) and angles (°): K(1)–N(1) 2.745(2), K(1)–C(15) 3.181(2), K(1)–C(20) 3.227(2), K(1)–C(22) 3.202(2), K(1)–C(5') 3.059(2), K(1)–C(6') 3.080(2) K(1)–N(1)–centroid of five membered ring 150.4(1). Symmetry operations used to generate equivalent atoms: -x + 1, -; y, -z + 1.

The solid state structure of 1,8-diphenyl-3,6-dimethylcarbazol-9-yl potassium provides evidence that rotation of the phenyl rings within the 1,8-diphenyl-substituted ligand about the  $C_{ipso}-C_{ipso}$ bonds is sufficiently facile such as to accommodate secondary metal–arene interactions. Each (1,8-Ph<sub>2</sub>-3,6-Me<sub>2</sub>C<sub>12</sub>H<sub>4</sub>N)K unit features not only a relatively short K–N distance [2.745(2) Å],<sup>12,13</sup> but also intramolecular contacts with the *ipso* and *ortho* carbons of both pendant phenyl rings [3.181(2)-3.227(2) Å] which are also well within the sum of the respective van der Waals radii (*ca.* 4.0 Å).<sup>12</sup> These secondary interactions also fall within the range of previously reported potassium–arene contacts,<sup>14</sup> and are presumably responsible for the observed disrotatory rotation of the phenyl substituents about the  $C_{ipso}-C_{ipso}$  bonds. This orientation of the phenyl rings allows for further intermolecular interactions involving the potassium centre. Thus, a centrosymmetric dimeric structure is adopted in the solid state through pairwise interaction of each potassium with C(5) and C(6) of the second carbazolyl ligand [at distances of 3.059(2) and 3.080(2) Å]. These intermolecular contacts lead to significant bending of the K–N vector out of the parent carbazolyl ligand plane; the angle defined by K(1), N(1) and the centroid of the central five-membered carbazolyl ring is 150.37(5)°.

Dichlorogallium complexes 3a and 3b have been characterized by standard spectroscopic and analytical techniques and 3b by single crystal X-ray diffraction. While <sup>1</sup>H and <sup>13</sup>C NMR data are consistent with the presence of the respective 1,8diaryl-3,6-dimethylcarbazol-9-yl units, and mass spectrometric data (including accurate mass determination) are consistent with the formulation of each species as the desired GaCl<sub>2</sub> complex, determination of the state of aggregation hinges on single crystal X-ray diffraction studies. Several sets of crystals of 3a were obtained (from various solvent systems), but these were sufficient only to obtain very poor quality structure solutions. While such data are consistent with a monomeric structure for 3a, it is apparent from the structure of  $[(1,8-Ph_2-3,6-Me_2C_{12}H_4N)K]_2$  that the conformational flexibility inherent in diphenyl substituted ligands of this type is unlikely to be compatible with the isolation of low coordinate metal systems, allowing as it does close secondary inter- or intramolecular metal-arene interactions. Attention was therefore switched to the corresponding dimesityl derivatives in the hope that the increased bulk of the flanking arene rings would restrict such flexibility. In practice the 1,8-dimesitylcarbazol-9-yl ligand does indeed prove to offer a more rigid sterically protected 'pocket'. Thus, the solid state structure of the parent ligand itself (Fig. 2) features mesityl substituents which, despite the minimal steric demands of the carbazolyl substituent (i.e. hydrogen) are



Fig. 2 Molecular structures of (left) one of the two independent molecules in the unit cell of **1b** and (right) of **3b**. Solvent molecules and hydrogen atoms [except that attached to N(2)] omitted for clarity; ORTEP ellipsoids set at the 50% probability level. Key bond lengths (Å) and angles (°): (for **1b**) N(2)–C(33) 1.392(4), N(2)–C(44) 1.389(4), angles between least squares mesityl and carbazolyl planes 74.2, 82.3; (for **3b**) Ga(1)–Cl(1) 2.127(1), Ga(1)–Cl(2) 2.112(1), Ga(1)–N(1) 1.852(2), Ga(1)–C(13) 3.179(2), Ga(1)–C(24) 2.851(2), Ga–C(24) N(1)–Ga(1)–Cl(1) 120.36(8), N(1)–Ga(1)–Cl(2) 124.75(8), Cl(1)–Ga(1)–Cl(2) 113.28(4), angles between least squares mesityl and carbazolyl planes 87.7, 89.0.

inclined at angles with respect to the carbazolyl backbone which are significantly closer to perpendicular (74.1-82.3° for the two independent molecules in the asymmetric unit). The corresponding angles measured for GaCl<sub>2</sub> complex 3b are even closer to 90° (89.0 and 87.7°); in addition relatively long  $Ga \cdots C_{inso}$  contacts [2.851(2) and 3.179(2) Å] are observed. While the shorter of these distances is actually shorter than that measured by Schmidbaur and co-workers for 1,2,4,5-tetramethylbenzene coordinated to gallium [closest Ga-C contact 2.965(4) Å, albeit for Ga(I) rather than Ga(III)],<sup>15,16</sup> much shorter  $M \cdots C_{ipso}$  contacts have been observed by Power and co-workers for complexes containing 2,6-diarylphenyl ligands [e.g. 2.294(1) Å for  $(2,6-\text{Dipp}_2C_6H_3Cr)_2$ ;  $Dipp = 2,6^{-i}Pr_2C_6H_3$ ].<sup>4c</sup> Thus, despite the noticeable asymmetry in the positioning of the GaCl<sub>2</sub> unit between the flanking arene rings in 3b, the relatively long Ga-C<sub>ipso</sub> distances and the trigonal planar coordination geometry [ $\sum$ angles at gallium = 358.95(8)°] are consistent with weak secondary contacts for this ligand.

To our knowledge 3b represents the first monomeric threecoordinate amidogallium dihalide to be reported in the literature, although the Ga-N distance [1.852(2) Å] is similar to that reported for other trigonal planar gallium monoamides featuring sterically bulky substituents [1.829(9)-1.937(3) Å].<sup>17</sup> Ga-Cl distances [2.127(1), 2.112(1) Å] are similar to those measured for 2,6-(Trip)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>GaCl<sub>2</sub> [2.113(4), 2.124(3) Å] which also features a trigonal planar gallium centre, and significantly shorter than the terminal Ga-Cl bonds found in dimeric  $[2,6-(Mes)_2C_6H_3GaCl_2]_2$  which features tetra-coordinate gallium [2.172(5), 2.290(4) Å].<sup>8</sup> Further analysis of the structures of **3b** and of  $[2,6-(Ar)_2C_6H_3GaCl_2]_n$  (Scheme 2; Ar = Trip, n = 1; Ar = Mes, n = 2) allows useful comparison of the steric properties of the 1,8-diarylcarbazol-9-yl and 2,6-diarylphenyl ligand classes. Thus, from a superficial perspective, the fact that **3b** is mononuclear, featuring a three-coordinate trigonal planar gallium centre while 2,6-(Mes)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>GaCl<sub>2</sub> dimerizes via bridging chloride ligands (to give four-coordinate metal centres) implies that for a given flanking aryl ring (i.e. Mes in this case) the carbazolyl framework offers greater bulk in the vicinity of the metal centre.<sup>8</sup> Indeed, comparison of the spatial and angular extent of the cavity between the flanking aryl rings confirms this inference. The separation between the two mesityl ring centroids in **3b** is 6.53 Å, while the mean distance in  $[2,6-(Mes)_2C_6H_3GaCl_2]_2$  is 7.44 Å (7.35 Å for the corresponding mononuclear Trip complex); similarly the angle between the two mesityl least squares planes in **3b** is 35.1°, compared to 58.7° (mean) for [2,6-(Mes)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>GaCl<sub>2</sub>]<sub>2</sub> and 64.6° for the Trip analogue.<sup>8</sup> All-in-all such, geometric data imply a significantly wider cone angle for the 1,8-dimesitylcarbazol-9-yl ligand system than its 2,6-dimesitylphenyl counterpart, an inference which is confirmed by calculation of the Tollman cone angle  $(\Theta)$  using an established method for ligands of this type (*i.e.* with  $\Theta > 180^{\circ}$ ).<sup>18</sup> Thus, a cone angle of 269° is calculated for the 1,8-dimesitylcarbazol-9-yl ligand based on the distances measured from the crystal structure of 3b, with the analogous values of 185° and 201° being calculated for the 2,6-Mes<sub>2</sub> and 2,6-Trip<sub>2</sub> derivatized phenyl ligands, respectively.<sup>8,18</sup>

#### 4. Conclusions

Sterically encumbered amido ligands based on a 1,8-diarylcarbazol-9-yl backbone can be synthesized from the corresponding 1,8-dibromo derivative by Suzuki/Miyaura chemistry and have been investigated as potential alternatives to the widelyused terphenyl ligand class in the stabilization of low-coordinate metal complexes. Studies of the parent 1,8-diphenylcarbazol-9-yl derivatives are consistent with facile rotation about the  $C_{ipso}$ - $C_{ipso}$ bonds leading to structurally characterized main group derivatives in which the coordination geometry at the metal centre is augmented by close metal-arene interactions. By contrast, the extra bulk inherent in the corresponding 1,8-dimesityl ligand results in essentially perpendicular alignments of the arene and carbazole planes, and a substituent-enforced sterically protected pocket. Moreover, comparative structural studies imply that the 1,8dimesitylcarbazol-9-yl framework offers significantly greater steric protection at the metal centre than does the corresponding 2,6dimesitylphenyl ligand. As such, further studies of the reactivity of 3b with respect to reduction, halide abstraction and halide metathesis chemistries are currently ongoing.

#### Acknowledgements

We acknowledge the EPSRC for funding and for access to the National Mass Spectrometry Service Centre, Swansea University.

#### References

- 1 See for example: (a) P. P. Power, J. Organomet. Chem., 2004, 689, 3904.
- 2 C. Stanciu, A. F. Richards, J. C. Fettinger, M. Brynda and P. P. Power, J. Organomet. Chem., 2006, 691, 2540.
- 3 For recent reports in main group chemistry, see for example: (a) P. P. Power, Organometallics, 2007, 26, 4362; (b) Y. Wang and G. H. Robinson, Organometallics, 2007, 36, 2; (c) Z. Zhu, M. Brynda, R. J. Wright, R. C. Fischer, W. A. Merrill, E. Rivard, R. Wolf, J. C. Fettinger, M. M. Olmstead and P. P. Power, J. Am. Chem. Soc., 2007, 129, 10847; (d) B. Qunllian, Y. Wang, P. Wei, A. Handy and G. H. Robinson, J. Organomet. Chem., 2006, 691, 3765; (e) X.-J. Yang, Y. Wang, B. Quillian, P. Wei, Z. Chen, P. v. R. Schleyer and G. H. Robinson, Organometallics, 2006, 25, 925; (f) R. J. Wright, M. Brynda, J. C. Fettinger, A. R. Betzer and P. P. Power, J. Am. Chem. Soc., 2006, 128, 12498; (g) R. J. Wright, M. Brynda and P. P. Power, Angew. Chem., Int. Ed., 2006, 45, 5953; (h) Y. Wang, B. Quillian, X.-Y. Yang, P. Wei, Z. Chen, C. S. Wannere, P. v. R. Schleyer and G. H. Robinson, J. Am. Chem. Soc., 2005, 127, 7672; (i) J. D. Young, M. A. Khan and R. J. Wehmschulte, Organometallics, 2004, 23, 1965.
- 4 For recent reports in transition metal chemistry, see for example: (a) R. Wolf, M. Brynda, C. Ni, G. J. Long and P. P. Power, J. Am. Chem. Soc., 2007, **129**, 6076; (b) D. L. Kays and A. Cowley, Chem. Commun., 2007, 1053; (c) T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettinger, G. J. Long and P. P. Power, Science, 2005, **310**, 844.
- 5 See, for example:G. H. Spikes, J. C. Fettinger and P. P. Power, *J. Am. Chem. Soc.*, 2005, **127**, 12232.
- 6 For examples of homoleptic main group and transition metal complexes containing the carbazol-9-yl ligand see: (a) M. A. Beswick, C. N. Harmer, P. R. Raithby, A. Steiner, K. L. Verhorevoort and D. S. Wright, J. Chem. Soc., Dalton Trans., 1997, 2029; (b) D. Barr, A. J. Edwards, P. R. Raithby, M.-A. Rennie, K. Verhorevoort and D. S. Wright, J. Chem. Soc., Chem. Commun., 1994, 1627.
- 7 For examples of carbazol-9-yl ligands bearing additional donors tethered at the 1 and 8 positions see: (a) M. Moswer, B. Wucher, D. Kunz and F. Rominger, Organometallics, 2007, 26, 1204; (b) J. A. Gaunt, V. C. Gibson, A. Haynes, S. K. Spitzmesser, A. J. P. White and D. J. Williams, Organometallics, 2004, 23, 1015; (c) V. C. Gibson, S. K. Spitzmesser, A. J. P. White and D. J. Williams, Dalton Trans., 2003, 2718; (d) G. J. P. Britovsek, V. C. Gibson, O. D. Hoarau, S. K. Spitzmesser, A. J. P. White and D. J. Williams, Inorg. Chem., 2003, 42, 3454.
- 8 (a) B. Twamley and P. P. Power, *Chem. Commun.*, 1999, 1805; (b) J. Su, X.-W. Li and G. H. Robinson, *Chem. Commun.*, 1998, 2015; (c) R. C. Crittendon, X.-W. Li, J. Su and G. H. Robinson, *Organometallics*, 1997, 16, 2443.

- 9 S. K. Spitzmesser and V. C. Gibson, J. Organomet. Chem., 2003, 673, 95.
- 10 (a) Denzo: Z. Otwinowski and W. Minor, in *Methods in Enzymology*, ed. C.W. Carter and R. M. Sweet, Academic Press, New York. 1996, vol. 276, p. 307; (b) Sir-92: A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, J. Appl. Crystallogr., 1993, 26, 343; (c) G. M. Sheldrick, Acta Crystallogr., Sect. A, 1990, A46, 467; (d) G. M. Sheldrick, University of Göttingen, 1997; (e) R. H. Blessing, Acta Crystallogr., Sect. A, 1995, A51, 33.
- 11 N. Miyaura and A. Suzuki, Chem. Rev., 1995, 95, 2457.
- 12 J. Emsley, in *The Elements*, Oxford University Press, Oxford, 2nd edn, 1991.
- 13 Related K–N distances in the range: 2.740(7)-3.019(4) Å are listed in the Cambridge Structural Database (27/09/2007) with a bond length of 2.774(2) Å having been determined for the [K(18-crown-6)]\* salt of the parent carbazol-9-yl ligand: H. Esbak and U. Behrens, Z. Anorg. Allg. Chem., 2005, 631, 1581.
- 14 See, for example: P. C. Junk and M. L. Cole, *Chem. Commun.*, 2007, 1579.
- 15 H. Schmidbaur, R. Nowak, B. Huber and G. Müller, *Polyhedron*, 1990, 9, 283.
- 16 Covalent radii for Ga(I) and Ga(III): 1.13 and 0.62 Å, respectively<sup>12</sup>.
- 17 C. J. Carmalt, Coord. Chem. Rev., 2001, 223, 217.
- 18 C. A. Tollman, Chem. Rev., 1977, 77, 313.