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FULL PAPER

Double lithiation of 2,4,6-triphenylbromobenzene: synthesis of bis-amidines and an aluminium bis-amidinate complex

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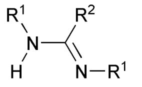
Received 18th June 2002, Accepted 5th August 2002
First published as an Advance Article on the web 23rd September 2002

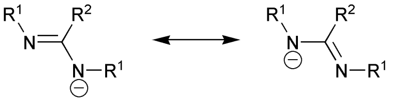
The substituted *m*-terphenyl 2,4,6-triphenylbromobenzene (**2Br**) reacts cleanly with two equivalents of *n*-butyllithium in diethyl ether/hexane solution to produce the dilithiated species **2Li$_2$**. Treatment of **2Li$_2$** with dialkylcarbodiimides (RN=C=NR, R = isopropyl or cyclohexyl) followed by aqueous work-up of the reaction mixture results in the formation of sterically hindered bifunctional amidines **5H$_2$** and **6H$_2$**. Two bis-amidine derivatives were crystallographically characterised. Compound **5H$_2$** reacts readily with trimethylaluminium to form a novel dialkylaluminium bis-amidinate complex **5[AlMe$_2$]$_2$**.

Introduction

The 4-electron donor, monoanionic amidinate ligand **1** is an important substituent in organometallic chemistry. This ligand readily binds to numerous main group elements, transition metals, lanthanides, and actinides to form stable amidinate complexes.[1] Research on alkyl aluminium amidinate complexes has indicated that these complexes may serve as potential ethylene polymerisation catalysts.[2–4] In addition, interest has also been focused on the applicability of aluminium amidinate complexes as potential single source precursors to materials containing the nitride ion.[5] Amidinate complexes such as these are easily prepared by reacting AlX$_3$ (X = halide or alkyl) with the corresponding amidines **1H**.[6]



1H



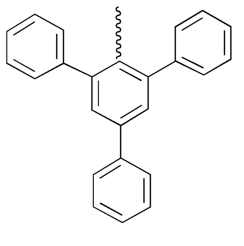
1

The first use of an *m*-terphenyl substituted amidine was an insightful study by Schmidt and Arnold[7] in which they identified the first mono-amidinate complexes of yttrium. It was found that the sterically demanding *m*-terphenyl group on the central carbon atom provided steric protection in the plane of the ligand as well as above and below that plane. This created a bowl-shaped environment for the amidinate ligand that could stabilize unusual coordination patterns in main group and transition metals. Subsequently, we used the triphenylphenyl substituent **2** to prepare the amidines **3H** and **4H** in high yield.[8,9]

Treatment of **3H** and **4H** with AlMe$_3$ produced robust aluminium amidinate complexes **3[AlMe$_2$]** and **4[AlMe$_2$]**. During these studies we identified a novel reaction leading to asymmetric bis-amidines.[10] Herein we report a simple preparation of **2Li$_2$** and the bulky bis-amidines **5H$_2$** and **6H$_2$**. The preparation (Scheme 1) and characterisation of the aluminium bis-amidinate complex **5[AlMe$_2$]$_2$** are reported, as well as the crystallographic characterisation of the mono-protonated bis-amidine salt **6H$_3$Cl**.

Results and discussion

Synthesis and characterisation of amidines



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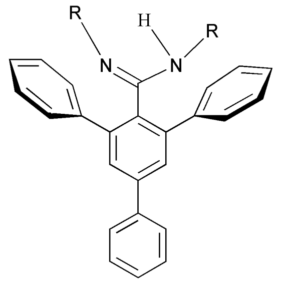
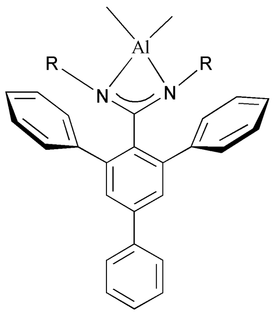


3H, R = isopropyl
4H, R = cylcohexyl



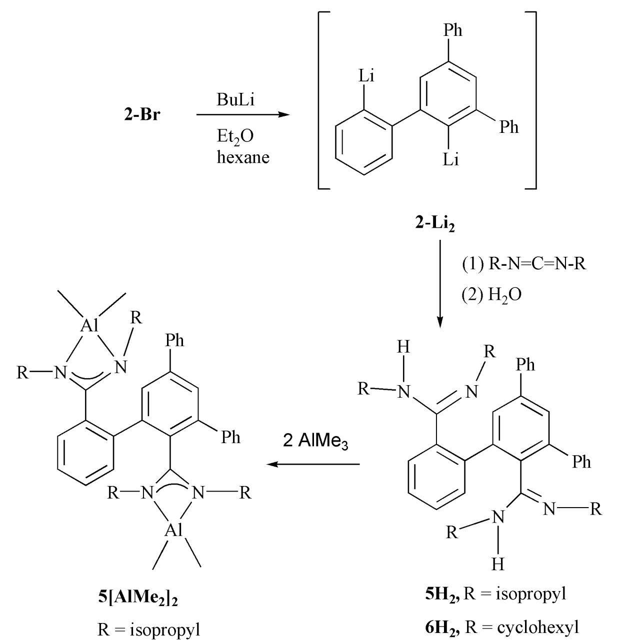
3AlMe$_2$, R = isopropyl
4AlMe$_2$, R = cylcohexyl

The substituted *m*-terphenyl, 2,4,6-triphenylbromobenzene **2Br**,[11] is easily metallated on the central ring by treatment with one equivalent of 1.6 M *n*-BuLi in hexane and stirring for four hours.[12] Serendipitously, and under similar reaction conditions, **2Br** reacts cleanly with *two* equivalents of 1.6 M *n*-BuLi at room temperature to form the dilithium salt **2Li$_2$**.[13,14] Attempts to isolate a crystalline sample of **2Li$_2$** failed, but evidence for its intermediacy is supported by its treatment with carbodiimides to produce bis-amidines **5H$_2$** and **6H$_2$**.

Conversion of **2Li$_2$** to a bis-amidine is achieved *via* treatment of the reaction mixture with a carbodiimide R–N=C=N–R (R = isopropyl or cyclohexyl). This produces the lithium amidinate intermediate, which upon aqueous work-up gives **5H$_2$** and **6H$_2$**. Purification of these compounds is achieved by extraction with CH$_2$Cl$_2$ and recrystallisation from toluene to produce the highly soluble bis-amidines **5H$_2$** and **6H$_2$** in 72% and 29% yield, respectively.

The N–H (**5H$_2$** $\nu = 3420, 3208$ cm^{-1}; **6H$_2$** $\nu = 3402, 3205$ cm^{-1}), C=N (**5H$_2$** $\nu = 1614$ cm^{-1}; **6H$_2$** $\nu = 1623$ cm^{-1}), and C–N (**5H$_2$** $\nu = 1298$ cm^{-1}; **6H$_2$** $\nu = 1256$ cm^{-1}) stretching frequencies of

DOI: 10.1039/b205875h



Scheme 1 Preparation of bis-amidines **5H$_2$** and **6H$_2$** and the bis-aluminium amidinate **5[AlMe$_2$]$_2$**.

5H$_2$ and **6H$_2$** are in agreement with IR spectral frequencies previously reported for other amidines.[15,16] NMR studies (^{1}H and ^{13}C) in CD_2Cl_2 solution are consistent with the proposed structures. Some of these resonances are broadened due to interconversion between *Z-syn* and *E-syn* isomers that occurs on the NMR timescale.[17]

X-Ray crystallographic studies were performed on **5H$_2$** to evaluate the steric demands of the *m*-terphenyl group with respect to the two amidine fragments. The structure of **5H$_2$** is shown in Fig. 1 and full crystallographic details are given in Table 1. The molecular structure indicates that **5H$_2$** exists in the solid state in the *E-syn* configuration. In general, the *E* conformation is energetically more favoured than its *Z* counterpart.[15]

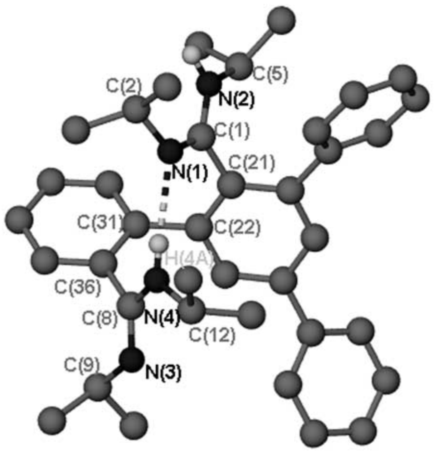


Fig. 1 Selected bond lengths (Å), angles (°) and torsion angles (°) for **5H$_2$** (thermal ellipsoids are shown at 50% probability level): N1–C1 1.295(2), N1–C2 1.466(3), N2–C1 1.350(2), N2–C5 1.458(2), C1–C21 1.507(2), N3–C8 1.289(2), N3–C9 1.461(3), N4–C8 1.365(2), N4–C12 1.457(3), C8–C36 1.507(3), N1 ··· N4 3.094(2), N1 ··· H4A 2.240(19); C1–N1–C2 120.18(17), C1–N2–C5 128.12(18), C8–N3–C9 120.83(18), C8–N4–C12 123.01(19), N1–CI–C21 114.62(16), N2–C1–C21 119.13(17), N3–C8–C36 127.54(17), N4–C8–C36 111.09(17), NI ··· H4A–N4 173.3(19); C35–C36–C8–N3 68.5(3), C36–C31–C22–C23 64.2(2), C22–C21–C1–N1 61.1(2), C21–C26–C51–C56 45.8(3).

The structure of **6H$_2$** was also confirmed by X-ray crystallography. In one experiment, several crystals of **6H$_3$Cl** were isolated in low yield from an attempted metallation reaction.[18] This compound was subsequently prepared systematically by treatment of **6H$_2$** with a 4.0 M dioxane solution of HCl. The resulting white solid was isolated and characterised as **6H$_3$Cl**. The structure is shown in Fig. 2.

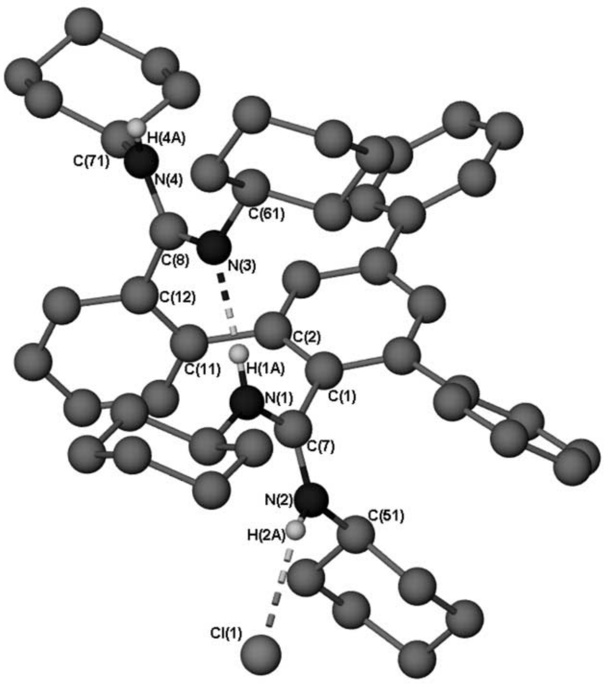


Fig. 2 Selected bond lengths (Å), angles (°) and torsion angles (°) for **6H$_3$Cl** (thermal ellipsoids are shown at 50% probability level): N1–C7 1.315(4), N1–C41 1.453(4), N2–C7 1.301(4), N2–C51 1.479(4), C7–C1 1.524(4), N3–C8 1.273(4), N3–C61 1.468(5), N4–C8 1.366(5), N4–C71 1.478(4), C8–C12 1.504(5), Cl1 ··· N2 3.287(3) Cl1 ··· H2A 2.4812, N3 ··· N1 2.812(4), N3 ··· HIA 1.9467; C7–N1–C41 126.5(3), C7–N2–C51 126.3(3), C8–N3–C61 121.1(3), C8–N4–C71 122.9(3), N1–C7–C1 115.6(3), N2–C7–C1 120.8(3), N3–C8–C12 117.5(3), N4–C8–C12 115.8(3), Cl1 ··· H2A–N2 154.43, N3 ··· H1A–N1 172.45; N1–C7–C1–C2 −60.6(4), N4–C8–C12–C13 −53.6(4), C12–C11–C2–C3 −83.5(4).

The molecule **6H$_3$Cl** crystallises in the space group *Cc*. Location of the protonation was determined *via* measurements of the hydrogen bond interactions between the cation and anion, as well as by examination of the metrical parameters for the amidine unit. For instance, as shown in Fig. 2, the chloride anion engages in hydrogen bonding with the protonated nitrogen (Cl1–N2 = 3.287(3), Cl1 ··· H2A = 2.4812 Å) consistent with other Cl ··· H–N interactions.[19] Also, the C–N bond lengths within the central amidine fragment are 1.301(4) (C7–N2) and 1.315(4) Å (C7–N1). Since they are close in length, and both are intermediate in length between the C–N and C=N lengths observed in the neutral **5H$_2$**, this is the chemically reasonable site of protonation. The flanking amidine fragment possesses asymmetric C=N (C8–N3 = 1.273(4) Å) and C–N (C8–N4 = 1.366(5) Å) bonds, consistent with the neutral amidine moiety.

A notable structural feature (Fig. 2) of **6H$_3$Cl** is the N–H ··· N hydrogen bond (N1 ··· N3 = 2.812(4) Å, N3 ··· H1A = 1.9467 Å, N3 ··· H1A–N1 = 172.45°) that locks the two amidine units. A bridging N–H ··· N interaction (Fig. 1) is also observed in **5H$_2$** (N1 ··· N4 = 3.094(2) Å, N1 ··· H4A = 2.240(19) Å, N1 ··· H4A–N4 = 173.3(19)°). This type of bridging hydrogen bond fits the definition of a moderately strong hydrogen bond.[20] The N–H ··· N hydrogen bond observed in **6H$_3$Cl** is shorter than that seen in **5H$_2$** because of charge assistance.

Synthesis and characterisation of the aluminium complex 5[AlMe$_2$]$_2$

Drop-wise addition of a slight excess of AlMe$_3$ to a toluene

Table 1 Crystal data and structure refinement for $\mathbf{5H_2}$ and $\mathbf{6H_3Cl}$

Compound	$\mathbf{5H_2}$	$\mathbf{6H_3Cl}$
Empirical formula	$C_{38}H_{46}N_4$	$C_{50}H_{63}ClN_4\cdot1.5CH_2Cl_2$
M	558.79	882.88
T/K	223(2)	213(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	Cc
a/Å	9.0339(16)	16.300(2)
b/Å	10.1074(18)	15.3088(19)
c/Å	18.511(3)	20.157(3)
α/°	98.273(3)	90
β/°	90.256(4)	95.155(2)
γ/°	99.322(4)	90
V/Å^3	1649.8(5)	5009.9(11)
Z	2	4
μ/mm^{-1}	0.066	0.273
Reflections collected	9644	14236
Independent reflections	6389 [R(int) = 0.0232]	8381 [R(int) = 0.0171]
Final R indices [I>2σ(I)]	$R1 = 0.0529$, $wR^2 = 0.1016$	$R1 = 0.0596$, $wR^2 = 0.1693$
R indices (all data)	$R1 = 0.1045$, $wR^2 = 0.1160$	$R1 = 0.0693$, $wR^2 = 0.1764$

solution of $\mathbf{5H_2}$ affords the bis-aluminium amidinate $\mathbf{5[AlMe_2]_2}$ as a white solid. This compound was characterised by ^{1}H and ^{13}C NMR, as well as elemental analysis and infrared spectroscopy. Unfortunately, we were unable to crystallographically characterise this material.

The IR spectrum of the solid white reaction product $\mathbf{5[AlMe_2]_2}$, indicates that the N–H stretching frequency of the amidine $\mathbf{5H_2}$ (3420–3400 cm^{-1}) is absent. Likewise, ^{1}H NMR studies show the disappearance of the signal attributed to the N–*H* resonance. The elemental analysis is consistent with the proposed formula, and the ^{1}H NMR spectrum exhibits features anticipated for this molecule. Most striking is the presence of four unique ^{1}H signals for the Al–CH_3 fragments, which occur at −0.66, −0.73, −0.94, and −1.19 ppm.

In an attempt to gain more insight into the structure of $\mathbf{5[AlMe_2]_2}$ semi-empirical calculations (PM3) were performed, and the results are shown in Fig. 3. An important feature is the proximity of one Al–CH_3 fragment to an aryl ring. The high-field resonance tentatively assigned to it appears at −1.19 ppm. Note that the Al–CH_3 groups are in different environments and the ^{1}H NMR data obtained for $\mathbf{5[AlMe_2]_2}$, namely four Al–CH_3 as well as four CH(CH_3)$_2$ peaks, are consistent with the proposed structure. The ^{27}Al NMR signal was broad and uninformative as expected for an asymmetric aluminium centre.

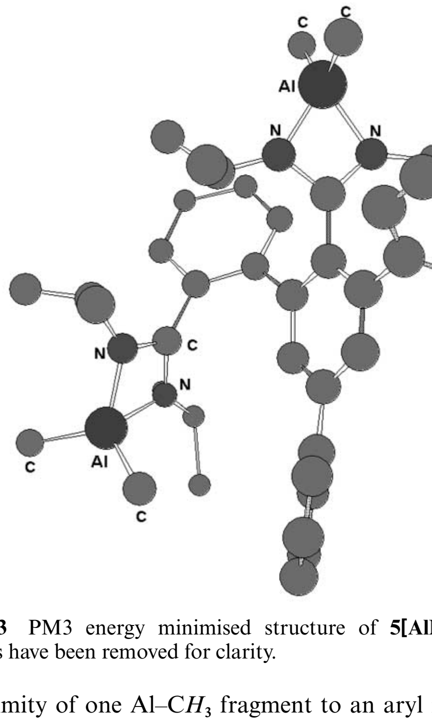


Fig. 3 PM3 energy minimised structure of $\mathbf{5[AlMe_2]_2}$. Hydrogen atoms have been removed for clarity.

Experimental

General

An MBraun UL-99-245 dry box and standard Schlenk techniques on a double manifold vacuum line were used in the manipulation of air and moisture sensitive compounds. NMR spectra were recorded on a Bruker AMX 400 spectrometer in five millimeter quartz tubes. ^{1}H and ^{13}C{^{1}H} chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) and are calibrated to the residual signal of the solvent. Infrared spectra were obtained using a Bomem MB spectrometer with the % transmittance values reported in cm^{-1}. Melting points were measured using a Mel-Temp apparatus and are uncorrected.

Syntheses

$\mathbf{5H_2}$. To a suspension of 15.0 g (38.9 mmol) 2,4,6-triphenylbromobenzene in 60 cm^3 anhydrous diethyl ether and 10 cm^3 anhydrous hexane, 50.0 cm^3 (80.0 mmol) of 1.6 M butyllithium was added drop-wise and stirred for 4 h at room temperature. To the resulting solution, 10.0 g (80 mmol) of *N,N′*-diisopropylcarbodiimide dissolved in *ca.* 30 cm^3 THF was added drop-wise and stirred overnight. After quenching with water, the reaction mixture was extracted with CH_2Cl_2. The organic layer was then washed with water and saturated NaCl and dried over anhydrous $MgSO_4$. After removal of solvent, the remaining solid was dissolved in warm toluene and filtered to remove insoluble LiBr. Upon cooling, the filtrate formed well-defined crystals that were characterised as $\mathbf{5H_2}$ (15.65 g, 28.0 mmol, 72%); mp 197–198 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.18–1.43 (br, 24H, alkyl CH_3), 3.25 (br, 2H, (CH$_3$)$_2$C*H*), 3.50 (br, 2H, (CH$_3$)$_2$C*H*), 3.25–3.74 (br, 2H, N*H*), 7.16–8.02 (m, 16H, phenyl C*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 23.0, 23.3, 24.3, 25.8, 26.1, 46.2, 53.3, 53.5, 53.8, 54.1, 54.3, 126.8, 127.4, 127.7, 127.9, 128.3, 128.6, 129.1, 129.7, 136.4, 140.7, 142.0, 142.2, 152.9 (quaternary carbons not observed). IR (Nujol) 3420 (br), 3208, 1614, 1546, 1493, 1298, 1173, 1120, 1030, 921, 886, 785, 767, 700. Anal. Calc. for $C_{38}H_{46}N_4$: C, 81.68; H, 8.30; N, 10.03%. Found: C, 81.48; H, 8.43; N, 9.82%.

$\mathbf{6H_2}$. Preparation same as for $\mathbf{5H_2}$. Yield 8.14 g, 11.3 mmol, 29%; mp 202–205 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00–1.69 (m, 40H), 2.82 (br, 2H), 3.06 (br, 2H), 3.50 (br, 2H, N*H*), 7.13–7.71 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8, 25.1, 25.2, 25.3, 25.4, 25.5, 26.0, 26.2, 31.9, 33.1, 34.3, 35.9, 36.1, 52.0, 126.6, 126.9, 127.4, 127.6, 128.2, 128.3, 129.0, 137.8, 140.0, 140.5, 141.5. IR (Nujol) 3402, 3205, 2727, 2668, 1947, 1623, 1548, 1343, 1302, 1256, 1150, 1105, 1074, 1030, 977, 886, 761.

Anal. Calc. for $C_{50}H_{62}N_4$: C, 83.52; H, 8.69; N, 7.79%. Found: C, 83.69; H, 8.80; N, 7.52%.

$6H_3Cl$. To a solution of 0.26 g (0.36 mmol) of **$6H_2$** in *ca.* 25 cm^3 of warm toluene, 0.09 mL of 4.0 M HCl in dioxane was added. The solution was stirred for 1.5 h at room temperature and then allowed to sit overnight. The resulting white solid was isolated by filtration and characterised as **$6H_3Cl$** (0.22 g, 0.29 mmol, 81%); mp 300 °C (decomp.). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.82–1.93 (m, 40H), 2.85 (br, 2H), 3.17 (br, 2H), 3.74 (br, 3H, N*H*), 7.16–7.75 (m, 16H).^{13}C NMR (100 MHz, CD_2Cl_2) δ 22.9, 26.3, 26.6, 26.8, 27.0, 27.2, 27.3, 27.5, 33.0, 34.4, 35.6, 36.3, 37.1, 56.9, 127.1, 128.6, 129.8, 130.2, 130.6, 130.9, 131.7, 133.3, 140.9, 142.0, 143.0, 144.0, 157.2, 159.9. IR (Nujol) 3668, 3410, 3129, 2728, 1941, 1594, 1492, 1347, 1307, 1261, 1152, 1074, 1029, 978, 890, 766. Anal. Calc for $C_{50}H_{63}N_4Cl$: C, 79.49; H, 8.40; N, 7.42%. Found: C, 79.59; H, 8.42; N, 7.11%.

$5[AlMe_2]_2$. **$5H_2$** (1.00 g, 2.31 mmol) was dissolved in *ca.* 20 cm^3 of toluene. An aliquot (2.8 cm^3, 4.62 mmol) of 2 M $AlMe_3$ in hexane was added drop-wise and stirred overnight. The solvents were removed *in vacuo*. The resulting white solid was washed with hexane, dried *in vacuo*, and characterised as **$5[AlMe_2]_2$**. Yield, 0.89 g, 1.32 mmol, 73%; mp 192–197 °C (decomp.). ^{1}H NMR (400 MHz, CD_2Cl_2) δ −1.19 (s, 3H, Al–C*H*$_3$), −0.94 (s, 3H, Al–C*H*$_3$), −0.73 (s, 3H, Al–C*H*$_3$), −0.66 (s, 3H, Al–C*H*$_3$), 0.55 (d, J_{HH} = 6 Hz, 6H), 0.72 (d, J_{HH} = 6 Hz, 6H), 0.74(d, J = 6 Hz, 6H), 0.96 (d, J = 6 Hz, 6H), 3.12 (m, 2H), 3.19 (m, 2H), 8.18–7.36 (m, 16H, aromatic C*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ −10.5, −10.4, −9.7, 22.3, 22.6, 24.4, 25.2, 25.7, 26.3, 45.9, 46.0, 46.3, 49.5, 127.3, 127.7, 127.9, 128.0, 128.1, 128.2, 128.4, 129.0, 129.2, 129.3, 129.4, 129.6, 130.1, 130.5, 131.1, 136.9, 140.1, 140.5. IR (Nujol) 3442, 2725, 1598, 1499, 1347, 1311, 1268, 1182, 1157, 1120, 1023, 995, 967, 892, 786, 772, 744 Anal. Calc.: C, 75.19; H, 8.41; N, 8.35%. Found: C, 74.90; H, 8.55; N, 8.12%.

X-Ray crystallography

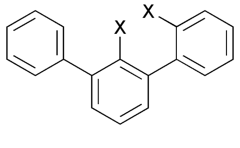
A single crystal of **$5H_2$** or **$6H_3Cl$** was mounted on a glass fibre and centred on a Siemens 1K SMART/CCD diffractometer. Data were collected at −50 °C using Mo(Kα) radiation. Lorentz and polarisation corrections were applied and data were also corrected for absorption using redundant data and the SADABS program.[21] Direct methods and Fourier techniques were used to solve the crystal structures. Refinement was conducted using full-matrix least-squares calculations and SHELXTL-PC V 5.03.[22] All non-hydrogen atoms were refined with anisotropic displacement parameters. Full crystallographic details can be found in Table 1. Diagrams were drawn using X-Seed.[23]

CCDC reference numbers 180739 and 190139.

See http://www.rsc.org/suppdata/dt/b2/b205875h/ for crystallographic data in CIF or other electronic format.

Conclusion

The preparation of **$2Li_2$** provides an easy route to asymmetrical bifunctional aryl compounds[24] broadly based on the biphenyl framework (Fig. 4). Such compounds are of great interest as asymmetric alternatives to binaphthyl and biphenyl ligands for catalysts in organic reactions.[25,26] This reaction may be applied to the preparation of a wide variety of bifunctional polyaromatic compounds. Such systems will be of interest as frameworks for supporting polyfunctional Lewis acids.[27]



X = $B(OH)_2$, OH, SH, Br, I

Fig. 4 Asymmetric bifunctional aryl compounds.

Acknowledgements

Financial support for this research was provided by Saint Mary's University, Simon Fraser University, and the Natural Sciences and Engineering Research Council of Canada (NSERC). The Atlantic Region Magnetic Resonance Centre at Dalhousie University and Marcy Tracey (SFU) collected the NMR data. We also thank Dr Noham Weinberg for advice regarding molecular modeling.

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