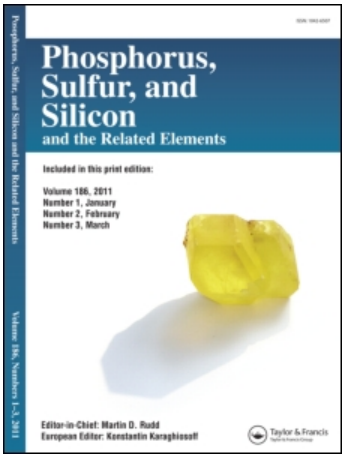

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Synthesis of *B*-Aryl Boron-Sulphur Heterocycles from Arylborondibromides

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SYNTHESIS OF *B*-ARYL BORON-SULPHUR HETEROCYCLES FROM ARYLBORONDIBROMIDES

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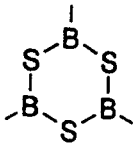
Abstract The synthesis and characterization of some aryl-substituted boron-sulphur heterocycles ($Ar_2B_2S_3$ and $Ar_3B_3S_3$) from $ArBBr_2$ (Ar = Ph, 2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 4-EtC_6H_4, 3,5-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$) and sulphur containing reagents $(Me_3C)_2S_2$, $(Me_3Si)_2S$ and HgS are described.

INTRODUCTION

We have become interested in the syntheses of *B*-aryl boron-sulphur heterocycles with the aim of exploring their coordination chemistry. The heterocyclic systems that interest us are 1,2,3-trithia-2,4,6-triborinanes (structure 1), 1,2,4-trithia-3,5-diborolanes (structure 2), and 1,2-dithia-2,4-diboretanes (structure 3). Literature reports[1,2] in this area are restricted to the *B*-phenyl derivatives (of structures 1, 2, and 3), the *B*-*p*-tolyl derivative (of structure 2), and to group 6 metal carbonyl complexes of $Ph_3B_3S_3$.



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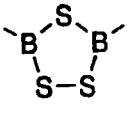

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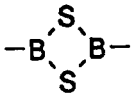

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RESULTS AND DISCUSSION

The syntheses of $Ar_3B_3S_3$ and $Ar_2B_2S_3$ (Ar = 2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 4-EtC_6H_4, 3,5-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$) were achieved by methods reported[3,4] for the phenyl derivatives by reaction of $ArBBr_2$ and either HgS or $^tBu_2S_2$ in refluxing

toluene respectively. $ArBBr_2$ derivatives were prepared by standard methods from either ArHgBr or $ArSiMe_3$ with BBr_3. Attempts to prepare the 4-membered ring derivatives, $Ar_2B_2S_2$, by a route reported[5] for $Ph_2B_2S_2$ using $(Me_3Si)_2S$ and $ArBBr_2$ were unsuccessful; however, these reactions cleanly yielded the corresponding $Ar_3B_3S_3$ 6-membered rings. The new heterocycles have been characterized by NMR (^{11}B, ^1H, ^{13}C), IR and MS. Boron-11 chemical shift data are given in Table 1. Full details of the synthesis and characterization of these *B*-aryl boron-sulphur heterocycles are reported elsewhere.[6,7]

TABLE I Boron-11 NMR data (δ/ppm, C_6D_6 solution) for triarylborthiins and diaryltrithiadiborolanes.

Aryl group	$Ar_3B_3S_3$	$Ar_2B_2S_3$
3-MeC_6H_4	+60.4	+65.1
4-MeC_6H_4	+59.9	+65.7
4-EtC_6H_4	+59.7	+66.1
3,5-$Me_2C_6H_3$	+60.4	+65.4
2-MeC_6H_4	+62.2	+64.8
2,4,6-$Me_3C_6H_2$	+65.4	+63.7

The syntheses and characterization of these heterocyclic compounds has been hampered by their extreme water/air sensitivity, and in air all compounds are rapidly hydrolysed to the related boroxine/boronic acid. We are currently investigating the reactions of these diaryltrithiadiborolanes and triarylborthiins with the following transition metal reagents ($[M(CO)_3(C_7H_8)]$, M = Cr, Mo; $[Fe_2(CO)_9]$; $[Fe(CO)_3$(PhCH:CH COMe)]; $[Pt(PPh_3)_n]$, n = 3, 4; $[Co_2(CO)_8]$; $[Co(CO)_2(C_5H_5)]$; $[\{Rh(COD)Cl\}_2]$; $[MCl(PPh_3)_3]$, M = Rh, Ir) and plan to report these results at a later date.

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