SHORT PAPER

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Unexpected formation of a borated P-Azulene *via* the reaction of a borated diazaphospholidine with phenyllithium[†]

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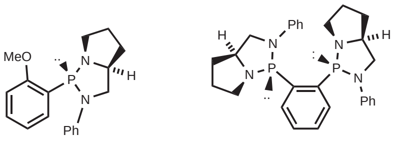
The reaction of a borated diazaphospholidine with phenyllithium provides a means for the formation of P-azulene hetereocycles *via* an addition/nucleophilic aromatic substitution reaction.

Keywords: diazaphospholidine, azulene, rearrangement, borane, phenyllithium

We have recently reported the results from a number of our investigations into the preparation and use in catalysis of both mono- and bis(diazaphospholidine) ligands such as **1** and **2**.[1,2] Whilst the monodonor ligands such as semi-ESPHOS **1** excel at the control of allylic substitution reactions, bisdonor ligands such as ESPHOS **2** demonstrate exceptional enantiocontrol in asymmetric hydroformylation reactions.[2] Similar ligands to ours have also been reported by Buono and others.[3]



Semi-ESPHOS **1**

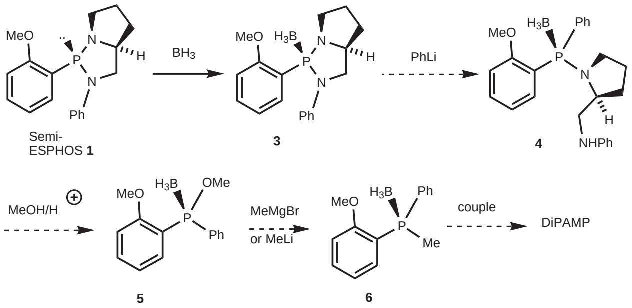
ESPHOS **2**

Compounds 1 and 2

Since the two P-N bonds in semi-ESPHOS **1** are electronically distinct, we reasoned that the reaction of a borated (N-protected) derivative such as **3** with a nucleophilic reagent such as an alkyllithium would result in selective cleavage of one of the bonds (Scheme 1). We anticipated that the N-aryl group would act as a leaving group in this process, since the resulting charged atom benefits from stabilisation into the phenyl ring which is not available to the nitrogen atom on the pyrrolidine ring. Should this reaction prove to be diastereoselective, then this might provide a means for the formation of **4**. Methanolysis of **4**, on the basis of a known precedent by Genet,[4] would be predicted to give **5**, and its subsequent reaction with a source of methyl anion would complete an enantioselective formation of **6**, a known precursor of the important homochiral diphosphine ligand DiPAMP.[5] Similar approaches to **6**, also dependant on sequential displacements at phosphorus, have been reported by a number of researchers.[4,5]

The borane complex **3** of semi-ESPHOS was prepared *via* the reaction of borane with **1** in 70% isolated yield after recrystallisation. Complex **3** proved to be highly crystalline and stable to both moisture and air, and column chromatography, in common with related compounds which we have reported.[6]

Since the relative stereochemistry of semi-ESPHOS **1** is known (it is derived from L-glutamic acid and has the absolute stereochemistry depicted)[1] and the phosphorus atom is known to be configurationally stable in such compounds, we have assumed that this stereochemistry is retained in the product **3**.[3b] Upon reaction with either methylmagnesium bromide or methyllithium, no reaction was observed.



Scheme 1 Proposed route to DiPAMP precursor **6**.

However, the treatment of **3** with phenyllithium resulted in the formation of a new product. Following chromatographic separation and recrystallisation a new product **7** was isolated in 33% yield, the majority of the mass balance being unchanged **3**. Whilst many of the spectroscopic features of **7** matched those predicted for **4**, it was clear from the 1H-NMR spectrum that the methoxy group had been displaced. Since this ruled out the expected product, we obtained an X-ray crystal structure of **7** (Figure 1) which revealed it to have the P-azulene heterocyclic structure illustrated.§ Remarkably this compound appeared to have been formed as a single diastereoisomer, presumably through the intermediates **8** and **9** (Scheme 2).

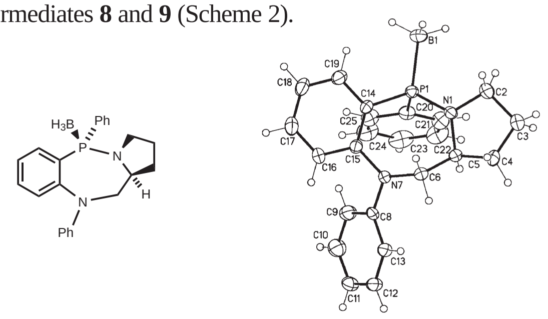
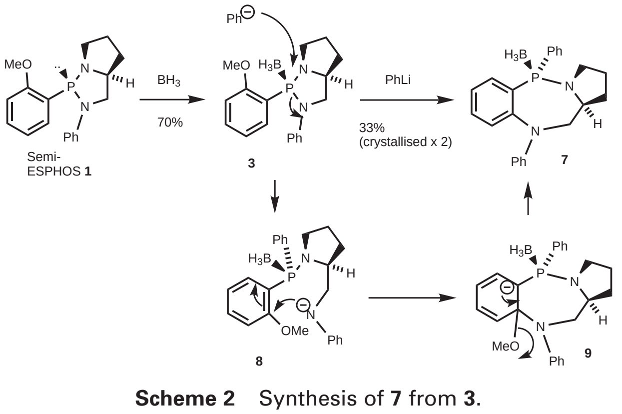


Fig. 1 X-ray crystal structure of **7**.



Scheme 2 Synthesis of **7** from **3**.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

As far as we are aware, this represents a novel rearrangement mechanism and provides a convenient entry to an otherwise challenging series of hetereocyclic compounds. A closely-related rearrangement reaction has been reported by Buono, however this operates on species containing a P=O bond.[6] Since the stereochemical environment around the phosphorus atom in **7** is well-defined, compounds of this type may have potential, following deboration, for use as ligands for asymmetric catalysis.

Experimental

Synthesis of semi-ESPHOS.BH3 precursor **3:** To a solution of semi-ESPHOS **1** (2.00g, 6.4 mmol) dissolved in freshly distilled tetrahydrofuran (50 ml) was added BH_3.THF (1M, 9.6 ml, 9.6 mmol) and the resulting clear solution allowed to stir at ambient temperature for 72 hours. The reaction mixture was concentrated *in vacuo* to give the crude product as a white crystalline solid which was recrystallised under nitrogen from the minimum amount of boiling anhydrous toluene to furnish the pure product **3** as a white highly crystalline solid (2.56g, 70% yield), mp 148°C. $[\alpha]^{22}_D$ –91 (c=1, benzene); ν_{max} (nujol)/cm^{-1} 2367 (BH),1598, 1588, 1572, 1304, 1274, 1246, 1052,1016; δ_H (300 MHz, $CDCl_3$, TMS); 7.79 (1H, ddd, *J* 1.7, 7.5, 13.7, Ar-H), 7.34 (1H, t, *J* 7.9, Ar-H), 7.10 (2H, t, *J*, 8.1, Ar-H), 6.94–6.88 (3H, m, Ar-H), 6.78–6.72 (2H, m, Ar-H), 4.06–3.94 (1H, m, CH), 3.87–3.74 (1H, m, CH_2), 3.70–3.62 (1H, m, CH_2), 3.59 (3H, s, CH_3), 3.32–3.23 (1H, m, CH_2), 3.12–2.99 (1H, m, CH_2), 2.13–2.00 (1H, m, CH_2), 1.98–1.77 (2H, m, CH_2), 1.32–0.41 (3H, brm, BH_3); δ_C (75 MHz, $CDCl_3$, TMS); 160.2 (*ipso* C), 143.4 (d, J_{C-P}, 7.7, *ipso* C),134.7 (d, J_{C-P}, 15.3, Ar-H), 133.6 (Ar-H), 128.6 (Ar-H), 120.4 (d, J_{C-P}, 11.5, *ipso* C), 119.1 (Ar-H), 116.8 (d, J_{C-P}, 5.4, Ar-H), 111.0 (d, J_{C-P}, 3.8, Ar-H), 61.8 (CH), 55.4 (CH_3), 53.6 (CH_2), 47.9 (d, J_{C-P}, 7.7, CH_2), 32.5 (CH_2), 26.3 (d, J_{C-P}, 3.8, CH_2); δ_P (121 MHz, $CDCl_3$) 101.3 (d); δ_B (400 MHz, $CDCl_3$) –38.13 (qu); *m/z* (EI) 326 (M^+), 312 (M^+-BH_3), 243 (M^+-C_5H_9N), 205, 136, 91, 77 (C_6H_5); HRMS (EI) found [M^+] 326.1729, $C_{18}H_{24}BN_2OP$ requires 326.1719.

Synthesis of azulene heterocycle **7:** To a solution of borane protected semi-ESPHOS **3** (9.0g, 27.6 mmol) dissolved in freshly distilled tetrahydrofuran (200 ml) and cooled to –78°C was added phenyllithium (1.8M, 55.2 mmol, 30.67 ml, 2eq) slowly dropwise and the mixture heated to reflux for 17 hours in an atmosphere of dry nitrogen. The resulting solution was allowed to cool to ambient temperature and diluted with degassed dichloromethane (300 ml) and washed with saturated degassed sodium hydrogen carbonate solution, the organic phase separated and dried over magnesium sulphate, filtered and concentrated *in vacuo* to give a viscous orange oil which solidified on drying at high vacuum (0.5 torr) for four hours. The crude product was purified by crystallisation from ethyl acetate/hexane to afford the pure product **7** as white crystals (3.3g, 33% yield), m.p. 181°C; (found C, 74.27; H, 7.09; N, 7.5. $C_{23}H_{26}BN_2P$ requires C74.21; H, 7.04; N, 7.53%); $[\alpha]^{22}_D$ –98.5 (c=1, chloroform); ν_{max} (solid)/cm^{-1} 3324, 2970, 2907, 2847, 2327, 2337, 1593, 1575, 1557; δ_H (300 MHz, $CDCl_3$, TMS); 8.25 (1H, ddd *J* 1.5, 7.7, 13.3, Ar-H), 7.48 (1H, t, *J* 7.5 Ar-H), 7.35 (1H, m, Ar-H), 7.24 (1H, m, Ar-H), 7.10 (5H, m, Ar-H), 6.96 (2H, m, Ar-H), 6.63 (1H, t, *J* 7.3, Ar-H), 6.46 (2H, d, *J* 8.8 Ar-H), 4.03 (1H, d, *J* 15.1,CH), 3.82 (2H, m, CH_2), 3.37 (1H, m, CH*H*), 3.05 (1H, dd, *J* 9.6, 15.1,CH*H*), 2.15 (1H, m, CH*H*), 1.93 (2H, m, CH_2), 1.56 (1H, m, CH*H*), 1.64–0.40 range (3H, m, BH_3););δ_C (75 MHz, $CDCl_3$, TMS); 151.2, 146.3, 137.2 (d, J_{C-P}, 18.6), 133.0, 132.9, 132.1, 130.8 (d, J_{C-P}, 10.4), 130.3 (d, J_{C-P}, 2.1), 129.1, 128.6 (d, J_{C-P}, 10.7),127.9 (d, J_{C-P}, 5.0), 125.7 (d, J_{C-P}, 13.0), 119.3, 115.1, 57.8 (d, J_{C-P}, 4.8), 56.6, 49.9 (d, J_{C-P}, 9.8), 31.0 (d, J_{C-P}, 6.3), 26.1 (d, J_{C-P}, 9.3); δ_P (121 MHz, $CDCl_3$) 54.9 (d, *J* 79.7); *m/z* (EI) 372 (M^+), 358, 289, 261, 212, 198, 182, 167, 152, 109, 89, 77 (C_6H_5); HRMS (EI) found [M^+] 372.1929, $C_{23}H_{26}BN_2P$ requires 372.1927.

X-ray crystallographic details of azulene heterocycle **7:** Crystal dimensions 0.6 × 0.5 × 0.4 mm, $C_{23}H_{26}BN_2P$, M = 372.24, orthorhombic, a=9.1139(2), b=9.3657(2), c=23.83710(10) Å, U = 2034.69(6) Å^3, T =180(2) K, space group P2(1)2(1)2(1), Z = 4, μu(MoK_α) = 0.145 mm^{-1}, λ = 0.71073 Å, D(cal) = 1.215 mg/m^3, F(000) = 792. 13328 reflections measured, 5031 unique [R_{int} = 0.0413]. Absorption correction by semi-empirical methods; minimum and maximum transmission factors: 0.82; 0.96.

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