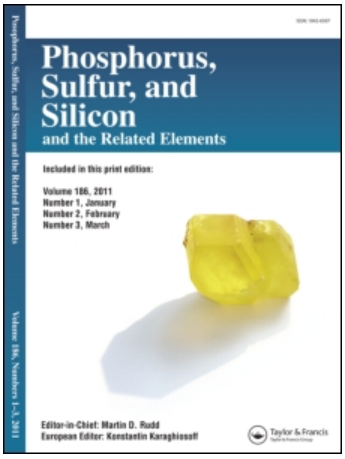

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From a Heterocycle Through a Hetero(spiro)cycle to a "Genuine Heterocycle"

Pierre Losier[a]; Neil Burford[a]; Simon Mason[a]; Sergey V. Sereda[a]; T. Stanley Cameron[a]
[a] Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada

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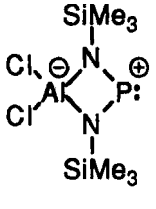
FROM A HETEROCYCLE THROUGH A HETERO(SPIRO)CYCLE TO A "GENUINE HETEROCYCLE"

PIERRE LOSIER, NEIL BURFORD, SIMON MASON, SERGEY V. SEREDA & T. STANLEY CAMERON
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada

Abstract A "Genuine Heterocycle" containing a PNAlS framework is obtained from a heterocyclic phosphenium species with a novel heterobis(spiro)tricycle as an isolable intermediate.

Reaction of the zwitterionic heterocyclic phosphenium derivative **1**[1] with elemental sulfur in toluene yields the novel dimeric bis(spiro)tricyclic compound **2**.[2] If the mixture is allowed to stir at room temperature for two weeks, a complex reaction involving toluene gives the unexpected heterocycle **3**. Interestingly, toluene solutions of compound **2** in pure form are indefinitely stable. Spectroscopic[3] and X-ray crystallographic investigations[4] confirm **3** (Figure 1) as a new example of a "Genuine Heterocycle" (a ring system containing only one atom of each element in the heterocyclic framework).[5] The PNAlS framework of **3** has been previously observed in **4** and the structural parameters are comparable.[6] Although the mechanism of the reaction has not been assessed, the formation of **3** most likely involves the insertion of a P-N bond into the methyl C-H bond of a toluene molecule, cleavage of the Al-N bond and formation of an Al-S heterocyclic bond.



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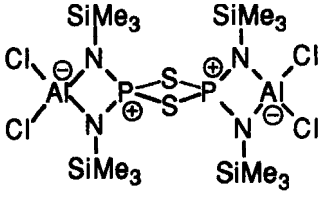

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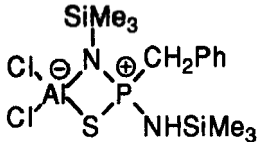

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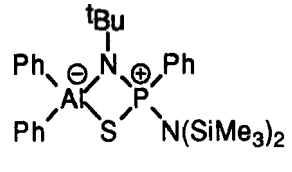

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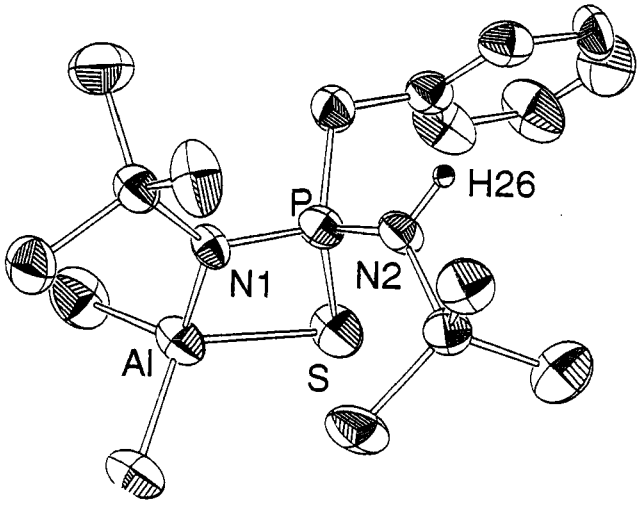

FIGURE 1 ORTEP view of **3**. Selected parameters: P-N1, 1.636(8)Å; N1-Al, 1.855(8)Å; Al-S, 2.272(5)Å; P-S, 2.045(4)Å; N1-P-S, 99.9(3)°; Al-N1-P, 98.4(4)°; N1-Al-S, 85.9(3)°; Al-S-P, 75.4(2)°.

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2. N. Burford, P. Losier, S. Mason, P.K. Bakshi and T.S. Cameron, Inorg. Chem. Submitted.
3. Spectroscopic data for **3**: Isolated yield 37%; NMR (CD_2Cl_2) $^{31}P\{^1H\}$: 55 ppm; $^{13}C\{^1H\}$: 130, 129.9, 129.5, 128.5 (d, J = 3.8Hz), 46.9, 2.2, 1.2 ppm; ^1H: 7.36 (m, 5H), 3.51 (m, 2H), 2.48 (s, 1H), 0.31 (s, 6H), 0.24 ppm (s, 6H); IR (Nujol, CsI, cm^{-1}): 3313m, 2722w, 1953w, 1602w, 1587w, 1493m, 1411w, 1258s, 1187w, 1130w,1070sh, 1050s, 979s, 912s, 880sh, 846s, 829sh, 809s, 777s, 758s, 699s, 673m, 647m, 612w, 595m, 551s, 531s, 508s, 487s, 439w, 417m.
4. X-ray data for **3**: $C_{13}H_{26}AlCl_2N_2PSSi_2$ MW = 427.45, colourless plates, monoclinic, $P2_1/n$, Z = 4, a = 12.694(2)Å, b = 12.275(3)Å, c = 15.541(3)Å, ß = 107.95(1)°, V = 2303.8(8)$Å^3$, D_c = 1.232 g cm^{-3}, F(000) = 896, reflections with $I > 3\sigma_I$ = 1269, parameters = 199, R = 0.0406, R_w = 0.0551, GOF = 2.441.
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