

The reaction of tetraphenyldiphosphazane (Ph₂P)₂NH with mesitylazide 2,4,6-Me₃C₆H₂N₃ and a bulky azide 2,6-iPr₂C₆H₃N₃ affords new [N,N'] chelating ligands, [HN(Ph₂PN(2,4,6-Me₃C₆H₂))₂] (L1H) and [HN(Ph₂PN(2,6-iPr₂C₆H₃))₂] (L2H), respectively. The ligands can be easily deprotonated using nBuLi or Li[N(SiMe₃)₂] in Et₂O to yield [N(Ph₂PN(2,4,6-Me₃C₆H₂))₂Li·OEt₂] L1Li·OEt₂ (1.1) and [N(Ph₂PN(2,6-iPr₂C₆H₃))₂Li·OEt₂] L2Li·OEt₂ (1.2), respectively. The reactions of 1.1 with the trihalides, MX₃ of group 13 elements afford the corresponding dihalide complexes, [N(Ph₂PN(2,4,6-Me₃C₆H₂))₂MX₂] L1MX₂ (M = B, X = F (1.3); M = Al, X = Cl (1.4); M = Ga, X = Cl (1.5); M = In, X = Br (1.6)). The reactions of L1H and L2H with BH₂Cl·SMe₂ give the corresponding mononuclear complexes [N(Ph₂PN(2,4,6-Me₃C₆H₂))₂BHCl] L1BHCl (1.7) and [N(Ph₂PN(2,6-iPr₂C₆H₃))₂BHCl] L2BHCl (1.8), respectively; rare examples of monochloroborane complexes. Similarly, the reactions of L1H with AlMe₃, AlH₃·NMe₂Et and BH₃·SMe₂ respectively, gives the corresponding mononuclear complexes [N(Ph₂PN(2,4,6-Me₃C₆H₂))₂AlMe₂] L1AlMe₂ (1.9), [N(Ph₂PN(2,4,6-Me₃C₆H₂))₂AlH₂] L1AlH₂ (1.10), and a rare borondihydride [N(Ph₂PN(2,4,6-Me₃C₆H₂))₂BH₂] L1BH₂ (1.11). All the complexes reported in this chapter have been isolated in good yields and would serve as useful synthons to elaborate their reaction chemistry. Solid state structures of L1H, L2H and compounds 1.1-1.7, 1.9-1.11 have been investigated by single crystal X-ray structural analysis