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Title: Bis(phosphinimino)amide Supported Monomeric Heteroleptic Boron Complexes: Synthetic,

Reactivity and Structural Studies

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Abstract: 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))2}Li·OEt2] L1Li·OEt2 (1.1) and [{N(Ph2PN(2,6-iPr2C6H3))2}Li·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))2}MX2] 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))2}BHCl] L1BHCl (1.7) and [{N(Ph2PN(2,6-iPr2C6H3))2}BHCl] 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-iPr2C6H2))2}AlH3·NMe2Et and BH3·SMe2 respectively, gives the corresponding mononuclear complexes [{N(Ph2PN(2,4,6-iPr2C6H2))2}AlH3·NMe2Et and BH3·SMe2 respectively, gives the corresponding mononuclear complexes [{N(Ph2PN(2,4,6-iPr2C6H2))2}AlH3·NMe2Et and BH3·SMe2 respectively, gives the corresponding mononuclear complexes [{N(Ph2PN(2,4,6-iPr2C6H2))2}AlH3·NMe2Et and BH3·SMe2 respectively, gives the corresponding mononuclear complexes [{N(Ph2PN(2,4,6-iPr2C6H3))2}AlH3·NMe2Et and BH3·SMe2 respectively.

BH3·SMe2 respectively, gives the corresponding mononuclear complexes [{N(Ph2PN(2,4,6-Me3C6H2))2}AlMe2] L1AlMe2 (1.9), [{N(Ph2PN(2,4,6-Me3C6H2))2}AlH2] L1AlH2 (1.10), and a rare borondihydride [{N(Ph2PN(2,4,6-Me3C6H2))2}BH2] 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

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