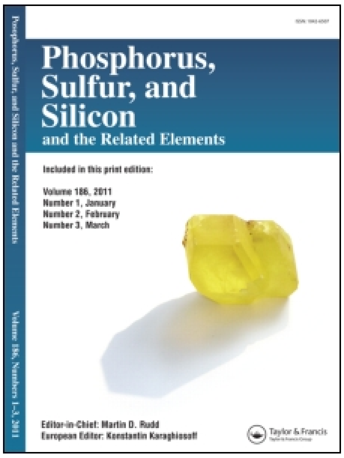

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BIS(DIAZASILAPHOSPHETIDINES) AND THEIR METAL COMPLEXES

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BIS(DIAZASILAPHOSPHETIDINES) AND THEIR METAL COMPLEXES

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The syntheses and solid-state structures of bis(diazasilaphosphetidines) of the type $[Me_2Si(\mu\text{-}N^tBu)_2P]_2NR$, *R* = *Ph*, ^iPr, ^tBu, *of the P-chiral analogue* $[Me_2Si(\mu\text{-}N^tBu)(\mu\text{-}N\text{-}2,6\text{-}^iPrPh)P]_2(C_2H_4)$, *and of some of their metal complexes are reported. The highly electron-rich, modular bis(phosphines) are easy to synthesize and may have applications in catalysis.*

Keywords: Bis(diazasilaphosphetidines); bis(phosphines); diazadiphosphetidines; P,N-heterocycles; Si,N,P-heterocycles

Diazadiphosphetidines, ambidentate phosphorus-nitrogen molecules, have been known for some time, but the comparatively low nucleophilicity of their phosphorus atoms has made them poor phosphine ligands, thereby limiting their role to building blocks for polymers[1] and scaffolds for chelating amido ligands (Chart 1, **1** and **2**).[2,3] Recent studies on tethered bis(diazasilaphosphetidines) (**3**), however, have shown that the silicon-phosphorus analogues are much better phosphorus donors than diazadiphosphetidines.[4] This electron-richness makes these bis(diazasilaphosphetidines) good candidates for reactions requiring electron-donating phosphines, e.g., homogenous hydrogenations and polyolefin catalysis by late-transition metal complexes.[5] Thus, for example, $[(Me_2Si(\mu\text{-}N^tBu)_2P)_2C_2H_4Rh]BF_4$ reduces alkenes to alkanes under mild conditions.

Enantioselective, homogeneous hydrogenations—key steps in the synthesis of fine chemicals—are typically catalyzed by transition-metal complexes bearing C_2-symmetric ancillary ligands. For this reason we developed a synthetic route for a C_2-symmetric bis(diazasilaphosphetidine) (Scheme 1) which yields a diphosphine with two

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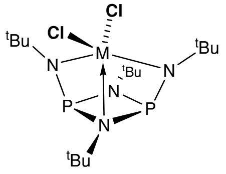

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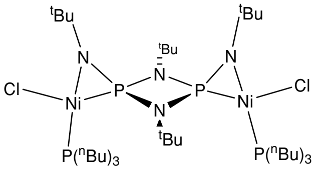

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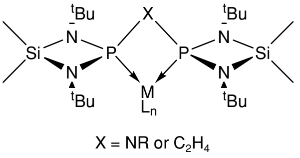
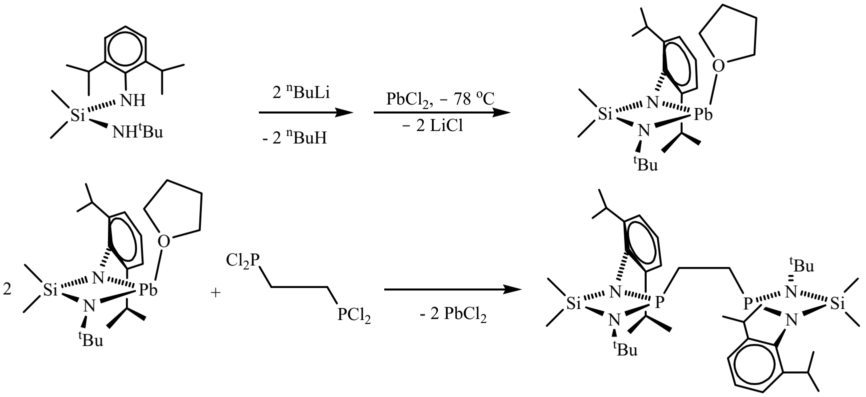


3

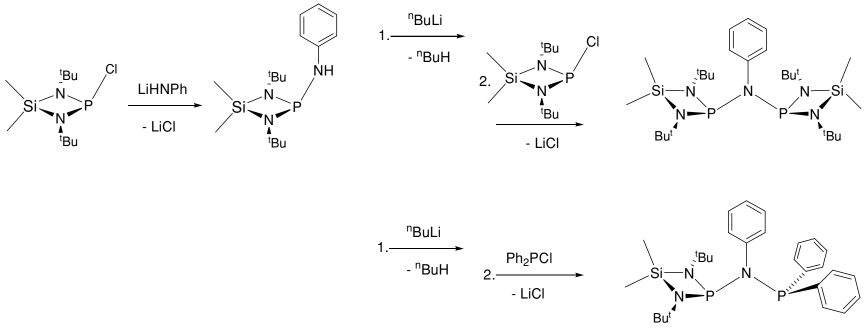
CHART 1

chiral phosphorus centers. Of the three possible products only the desired *S,S/R,R* enantiomer pair was formed, as NMR-spectroscopic and single-crystal x-ray diffraction studies showed. A clean separation of the enantiomers, either in their pristine form or complexed to metals, has thus far eluded us.



SCHEME 1

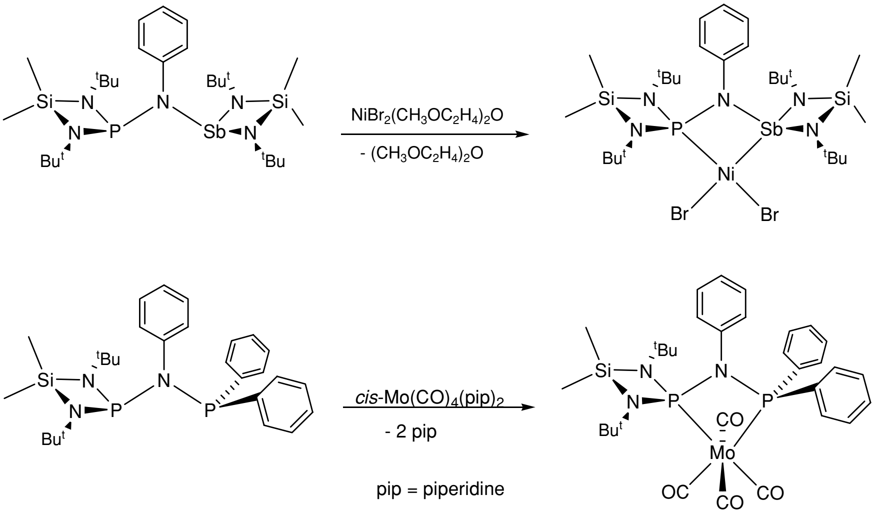
The high cost of $Cl_2PC_2H_4PCl_2$ and the comparatively low yield make the synthesis of bis(diazasilaphosphetidino)ethanediyl via the appropriate diazasilaplumbetidine (Scheme 1) inefficient. An attractive alternative for tethering two such heterocycles is by primary organoamines, because of their low cost and ready availability. Concerns over the presumed lower electron-donating ability of tris(amino)phosphines, compared to analogous alkylbis(amino)phosphines,[6] proved unfounded, because IR-spectroscopic studies showed that *tert*-butylamine-tethered bis(diazasilaphosphetidines) are even more electron-rich than alkyl-tethered species. The versatility of constructing bis(phosphines) in this manner is illustrated in Scheme 2, which shows that symmetrical and



SCHEME 2

asymmetrical bis(phosphines) can be synthesized with relative ease. Even amine-linkers of appreciable length, such as 1,6-diaminohexane, may be used to synthesize tetrakis(diazasilaphosphetidino)phosphines for the construction of one-dimensional coordination polymers or for the synthesis of complexes with two remote catalytic sites.

To derivatize these organoaminobis(diazasilaphosphetidines) we have, thus far, synthesized mainly nickel dibromide and molybdenumtetracarbonyl derivatives, Scheme 3, but these ligands are equally well suited for the coordination of zero-valent nickel and other late transition metals.



SCHEME 3

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