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From New Zirconium-Phosphanide to Phosphinidene Complexes

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Lithiated primary silylphosphanes and -arsanes react with zirconocene-chloride-hydride to give planar Zr(III)₂-E₂-ringsystems (R = SiMe₂Thex (1), Si(i-Pr)₃, SiF(t-Bu)Is). However, the complexes can also be synthesized by conversion of zirconocene-dichloride with lithiated silylphosphanes. Reductive dehydrogenation of 1 through heating with Pd on activated charcoal or [(Ph₃P)₂Pt(C₂H₄)] in toluene leads to 2.

The new cycle 2 can be understood as the dimer of the respective Zr-phosphinidene complex A. Indeed, the ³¹P-NMR resonance signal in benzene at very low field indicates dissociation in solution, giving the Zr-P double bond monomer A. The conversion of decamethylzirconocene-dichloride with lithiated silylphosphane furnishes the compound 3. This Zr(IV)phosphide-chloride also offers access to the terminal phosphinidene A, simply by elimination of HCl through an auxillary base. Further, compounds of the type A can be prepared directly by the reaction of the corresponding Zr-dichloride with the respective dilithium silylphosphanediides.

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[1] M. Driess, J. Aust, K. Merz, H. Pritzkow, to be published.