Synthesis and Structure of the Substituted Lithium Benzyl 
\([\text{Li(tmeda)}_2]^+\text{[C(PMe}_2\text{)(SiMe}_3\text{)C}_6\text{H}_3\text{-3,5-Me}_2]}\). The First Metal Phosphinomethanide Consisting of Solvent-Separated Ion Pairs

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Lithium Phosphinomethanides, Lithium Benzyls

The lithium dimethylphosphinomethanide with trimethylsilyl and 3,5-dimethylphenyl substituents in α position \([\text{Li(tmeda)}_2]^+\text{[C(PMe}_2\text{)(SiMe}_3\text{)C}_6\text{H}_3\text{-3,5-Me}_2]}\) (2) was synthesized from Me\(_2\)P-CH(SiMe\(_3\))C\(_6\)H\(_3\)-3,5-Me\(_2\) (1) and Li\(_n\)Bu/tmeda in hexane in 56% yield (tmeda = \(N, N, N', N'\)-tetramethylethylenediamine). In the solid state it consists of solvent-separated ion pairs which probably is also the case in solution (crystal structure data: tetragonal, space group \(I\bar{4}_1\cd, a = b = 19.303(3), c = 34.905(7) \) Å, \(Z = 16, R(F) = 0.054\) for 2309 unique data and 299 refined parameters). The α-substituted lithium benzyl 2 is the first metal phosphinomethanide containing “free”, uncoordinated anions in the solid state. The lack of metal coordination of the anion is reflected in the bonding parameters at the planar carbanionoid benzylic carbon atom C1 (C1-P 1.773(8), C1-Si 1.846(8), C1-C2(Ph) 1.442(9) Å; C2-C1-P 125.3(5), C2-C1-Si 127.1(5), P-C1-Si 107.5(3)°; sum of the angles at C1: 359.9°).