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CALLERY™ Lithium hexamethyldisilazane, 24% solution in tetrahydrofuran Catalog # 03-1275

Technical Notes:

Lithium hexamethyldisilazane (LiHMDS) is a strong non-nucleophilic, hindered amine base, with higher base strength than alkali metal alkoxides (p $K_a=26$). LiHMDS is a useful reagent for wide variety of chemical reactions and transformations. Applications include alkylation, arylation, acylation, ring formation, isomerization, rearrangements, aldol condensations, Wittig and Horner-Emmons reactions and polymerization. In addition, LiHMDS is able to catalyze transition metal-free reactions and to act as a ligand while reacting with a wide range of metal halides forming M(HMDS)_x catalysts.

Transition metal-free application

- 1. Catalyst used for synthesis of tertiary aminocyclopropanes.
- 2. Coupling reactions. Catalyst for dehydro-coupling of boranes with amines leading to the formation of a B-N bond.
- 3. Vinylation. Catalyst for chemo- and regioselective vinylation of azaallyls.
- 4. Ring opening/polymerization. Catalyst used in the superfast ring opening polymerization of alpha-amino acid N-carboxvanhvdrides.
- 5. **Defluorosilylation**. Catalyst for the defluorosilylation of C(sp²)–F and C(sp³)–F bonds.
- 6. Direct amidation. Catalyst for the highly chemoselective, transamidation of unactivated amides and direct amidation of alkyl esters by N-C/O-C cleavage.
- Catalyst for the tandem synthesis of 2-azaaryl tetrahydroquinolines.
 Cross coupling. Catalyst for the amide/ester cross-coupling via C–N/C–H bond Cleavage to generate βketoesters.



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References:

- 1. Org. Lett. 2016, 18, 6448.
- 2. RSC Adv., 2016, 6, 35648.
- 3. Nat. Chem. 2017, 9, 997.
- 4. Nat. Commun. 2018, 9, 5297.
- 5. Angew. Chem. Int. Ed. 2019, 58, 2064.
- 6. J. Am. Chem. Soc. 2019, 141, 11161.
- 7. Org. Lett. 2021, 23, 1594.
- 8. J. Org. Chem. 2021, 86, 5943.

Application with transition metals

- 1. Hydrosilylation. Ligand for the Fe-catalyzed hydrosilylation of carbonyl compounds.
- 2. Coupling. Base additive used in Pd-catalyzed arylation of 2-benzylfurans.
- 3. Asymmetric arylation. Base additive used in Pd-catalyzed asymmetric α -arylation of alkylnitriles.
- 4. **Arylation**. Base additive used in Pd-catalyzed carbon-sulfur or carbon-phosphorus bond metathesis by reversible arylation.
- Allylic substitution. Base additive for enantioselective Ir-catalyzed allylic substitution with 2methylpyridines.
- 6. **Hydroboration**. Ligand for the Fe-catalyzed selective hydroboration of carbonyls with HBpin.
- 7. Cross-coupling. Base additive for the Pd-catalyzed cross-coupling of thiols with aromatic electrophiles.
- Polymerization. Ligand for the Mg-catalyzed polymerization to prepare poly(propylene oxide) by employing Lewis pair polymerization via zwitterions based on nucleophilic *N*-heterocyclic olefins in cooperation with Mg(HMDS)₂ as an epoxide-activating Lewis acid.
- 9. Alkylation. Used in Co-catalyzed umpolung alkylation of imines to generate α -branched aliphatic amines.

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References:

- 1. Angew. Chem. Int. Ed. 2010, 49, 10186.
- 2. J. Am. Chem. Soc. 2016, 138, 4260.
- 3. J. Am. Chem. Soc. 2016, 138, 16240.
- 4. Science 2017, 356, 1059.
- 5. Angew. Chem. Int. Ed. 2017, 56, 4002.

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- <u>Dalton Trans.</u>, **2018**, 47, 9231.
 <u>ACS Catal.</u> **2019**, 9, 6461.
 <u>Angew. Chem. Int. Ed.</u> **2019**, 58, 10737.
 <u>Org. Lett.</u> **2021**, 23, 3818.