## Strem Chemicals, Inc.

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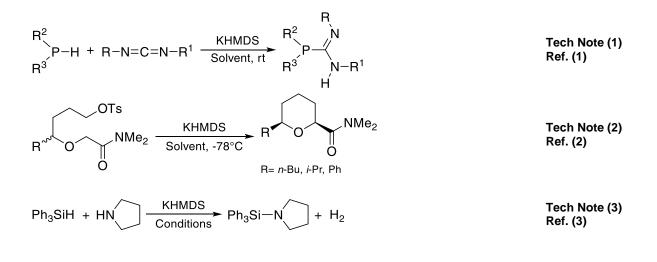
Catalog # 19-1090 CALLERY™ Potassium hexamethyldisilazane, 20% solution in tetrahydrofuran

**Technical Notes:** 

Lithium hexamethyldisilazane (KHMDS) is a strong non-nucleophilic, hindered amine base, with higher base strength than alkali metal alkoxides ( $pK_a=26$ ). KHMDS 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, KHMDS 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)<sub>x</sub> catalysts

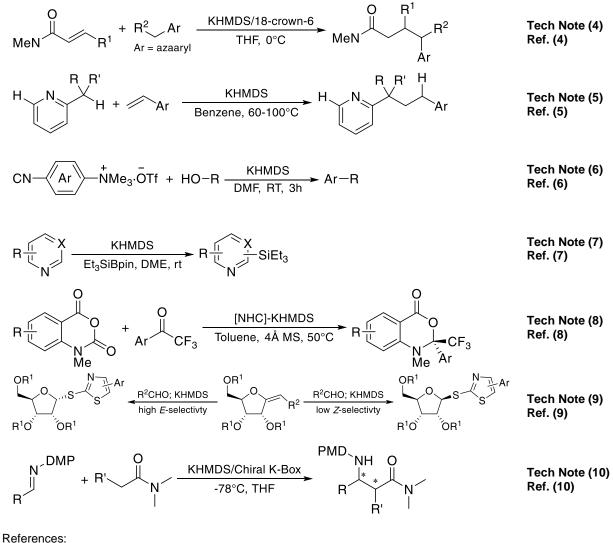
#### **Transition metal-free application**

- 1. Catalyst for the addition of primary and secondary phosphines to carbodiimides to generate substituted phosphaguanidines.
- 2. **Total synthesis.** Catalyst used in the synthesis of 2,6-*cis*-disubstituted tetrahydropyran systems via intramolecular amide enolate alkylation.
- 3. Cross-couplings. Catalyst for the cross-dehydrogenative couplings of hydrosilanes with amines.
- 4. **1,4-Addition reactions**. Catalyst for the 18-crown-6 assisted direct-type 1,4-addition reactions of alkylazaarenes.
- 5. Catalyst for the selective benzylic C–H bond addition of alkylpyridines to styrenes.
- Catalyst for the synthesis of aryl ethers by reacting alcohols/phenols (ROH) with aryl ammonium salts (ArNMe<sub>3</sub><sup>+</sup>), which are readily prepared from anilines (ArNR'<sub>2</sub>, R'=H or Me).
- 7. Silylation of (poly)azines. Catalyst for the mild and direct site-selective sp<sup>2</sup> C–H silylation of (poly)azines.
- 8. Used in the NHC-catalyzed enantioselective decarboxylative annulations to access dihydrobenzoxazinones and quinolones.
- 9. **Olefination**. Catalyst for the stereoselective synthesis of ribofuranoid exo-glycals by olefination using ribofuranosyl sulfones.
- 10. Mannich Reactions. Catalyst for the asymmetric Mannich reactions with simple amides.



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- 4. Angew. Chem. Int. Ed. **2017**, 56, 4520.
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- 10. J. Am. Chem. Soc. 2021, 143, 5598.

#### Application with transition metals

- 1. Hydrosilylation of carbonyls. Ligand for the Fe-catalyzed hydrosilylation of carbonyl compounds.
- 2. Arylation. Base additive used in Pd-Catalyzed C(sp3)–H arylation of diarylmethanes at room Temperature.
- 3. **Selective hydrogenation**. Base additive used in Fe-catalyzed selective hydrogenation of activated amides to amines and alcohols.
- 4. Hydrosilylation of alkenes. Ligand for the Co-catalyzed hydrosilylation of alkenes with tertiary silanes.

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- 5. Alkylation of alcohols. Base additive Co-catalyzed alkylation of secondary alcohols with primary alcohols via borrowing hydrogen/hydrogen autotransfer.
- 6. Hydroboration. Ligand for the REM catalyzed hydroboration of imines and nitriles (REM = Er, Y, Dy or Gd).
- 7. Asymmetric allylic alkylation. Base additive in the direct intermolecular Pd-catalyzed asymmetric allylic alkylation of a-aryl cyclic vinylogous esters, enabling a straightforward enantioselective synthesis of 6-allyl-6aryl-3-ethoxycyclohex-2-en-1-ones, common motifs embedded in numerous structurally diverse natural products.

#### References:

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