strem.com

Catalog # 19-1045 CALLERY™ Potassium hexamethyldisilazane, 15% in toluene

$$Me_3Si \ N^-SiMe_3$$

 K^+

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)_x catalysts

Transition metal-free application

- Catalyst for the addition of primary and secondary phosphines to carbodiimides to generate substituted phosphaguanidines
- 2. **Total synthesis.** Catalyst used in the synthesis of 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
- 1,4-Addition reactions. Catalyst for the 18-crown-6 assested direct-type 1,4-addition reactions of alkylazaarenes
- 5. Catalyst for the selective benzylic C-H bond addition of alkylpyridines to styrenes
- 6. Catalyst for the synthesis of aryl ethers by reacting alcohols/phenols (ROH) with aryl ammonium salts (ArNMe₃+), which are readily prepared from anilines (ArNR'₂, R'=H or Me)
- 7. Silylation of (poly)azines. Catalyst for the mild and direct site-selective sp² C–H silylation of (poly)azines
- 8. Used inth 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

$$R^{2} = R^{2} - R^{1} + R^{-N} = C = N - R^{1}$$

$$R^{3} = R^{2} - R^{1}$$

$$R^{4} = R^{2} - R^{1}$$

$$R^{2} = R^{2} - R^{1}$$

$$R^{3} = R^{2} - R^{1}$$

$$R^{4} = R^{2} - R^{2} - R^{2}$$

$$R^{4} = R^{2} - R^{2} - R^{2} - R^{2}$$

$$R^{4} = R^{2} - R^{2} - R^{2} - R^{2} - R^{2}$$

$$R^{4} = R^{2} - R^{2} - R^{2} - R^{2} - R^{2}$$

$$R^{4} = R^{2} - R^{2}$$

strem.com

References:

- 1. Chem. Commun., 2006, 3812
- 2. J. Org. Chem. 2015, 80, 3315
- 3. ChemCatChem 2016, 8, 1373
- 4. Angew. Chem. Int. Ed. 2017, 56, 4520
- 5. Angew. Chem. Int. Ed. 2018, 57, 1650
- 6. Angew. Chem. Int. Ed. 2018, 57, 3641
- 7. J. Am. Chem. Soc. 2019, 141, 127
- 8. Angew. Chem. Int. Ed. 2019, 58, 5941
- 9. J. Org. Chem. 2021, 86, 657
- 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

strem.com

- 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)
- Asymmetric allylic alkylation. Base additive in the direct intermolecular Pd-catalyzed asymmetric allylic
 alkylation of α-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

$$\begin{array}{c} O \\ R \\ R' \end{array} + Ph_2SiH_2 \\ \hline \begin{array}{c} Fe(HMDS)_2 \\ \hline 23^\circ C \\ \hline \end{array} \\ \hline \begin{array}{c} OSiPh_2H \\ R' \end{array} \\ \hline \end{array} \\ \hline \begin{array}{c} Ar' \\ Rf. \end{array} \\ \hline \begin{array}{c} Ar' \\ H \\ \hline \end{array} \\ \hline \begin{array}{c} Ar' \\ H \\ \hline \end{array} \\ \hline \begin{array}{c} Ar' \\ H \\ \hline \end{array} \\ \hline \begin{array}{c} Ar' \\ H \\ \hline \end{array} \\ \hline \begin{array}{c} Ar' \\ H \\ \hline \end{array} \\ \hline \begin{array}{c} Ar' \\ H \\ \hline \end{array} \\ \hline \begin{array}{c} Ar' \\ H \\ \hline \end{array} \\ \hline \begin{array}{c} Ar' \\ \hline \end{array} \\ \hline \begin{array}{c} R^1 \\ \hline \end{array} \\ \hline \begin{array}{c} CF_3 \\ \hline \end{array} \\ \hline \begin{array}{c} [Fe] \ Catalyst \\ \hline \end{array} \\ \hline \begin{array}{c} [Fe] \ Catalyst \\ \hline \end{array} \\ \hline \begin{array}{c} R^1 \\ \hline \end{array} \\ \hline \begin{array}{c} R^2 \\ \hline \end{array} \\ \hline \begin{array}{c} [Co] \ Catalyst \\ \hline \end{array} \\ \hline \begin{array}{c} CO \ Catalyst \\ \hline \end{array} \\ \hline \begin{array}{c} CO \ Catalyst \\ \hline \end{array} \\ \hline \begin{array}{c} CO \ Catalyst \\ \hline \end{array} \\ \hline \begin{array}{c} CO \ Catalyst \\ \hline \end{array} \\ \hline \begin{array}{c} CO \ Catalyst \\ \hline \end{array} \\ \hline \begin{array}{c} CO \ Catalyst \\ \hline \end{array} \\ \hline \begin{array}{c} CO \ Catalyst \\ \hline \end{array} \\ \hline \begin{array}{c} CO \ Catalyst \\ \hline \end{array} \\ \hline \begin{array}{c} CO \ Catalyst \\ \hline \end{array} \\ \hline \begin{array}{c} CO \ Catalyst \\ \hline \end{array} \\ \hline \begin{array}{c} CO \ Catalyst \\ \hline \end{array} \\ \hline \begin{array}{c} CO \ Catalyst \\ \hline \end{array} \\ \hline \begin{array}{c} CO \ Catalyst \\ \hline \end{array} \\ \hline \begin{array}{c} R^2 \\ \hline \end{array} \\ \hline \begin{array}{c} Ar \ \end{array} \\ \hline \begin{array}{c} R^2 \\ \hline \end{array} \\ \hline \end{array} \\ \begin{array}{c} R^2 \\ \hline \end{array} \\ \hline \begin{array}{c} R^2 \\ \hline \end{array} \\ \end{array} \\ \begin{array}{c} R^2 \\ \hline \end{array} \\ \begin{array}{c} R^2 \\ \hline \end{array} \\ \end{array} \\ \begin{array}{c} R^2 \\ \hline \end{array} \\ \begin{array}{c} R^2 \\ \hline \end{array} \\ \begin{array}{c} R^2 \\ \hline \end{array} \\ \end{array} \\ \begin{array}{c} R^2 \\ \hline \end{array} \\ \end{array} \\ \begin{array}{c} R^2 \\ \hline \end{array} \\ \end{array} \\ \begin{array}{c} R^2 \\ \hline \end{array} \\ \begin{array}{c} R^2 \\ \hline \end{array} \\ \end{array} \\ \begin{array}{c} R^2 \\ \hline \end{array} \\ \begin{array}{c} R^2 \\ \hline \end{array} \\ \begin{array}{c} R^2$$

References:

- 1. Angew. Chem. Int. Ed. 2010, 49, 10186
- 2. J. Am. Chem. Soc. 2012, 134, 13765
- 3. Chem. Commun., 2016, 52, 5285
- 4. J. Am. Chem. Soc. 2017, 139, 1798
- 5. Chem. Eur. J. 2017, 23, 12110
- 6. Inorg. Chem. 2018, 57, 15069
- 7. Org. Lett. 2021, 23, 920

strem.com