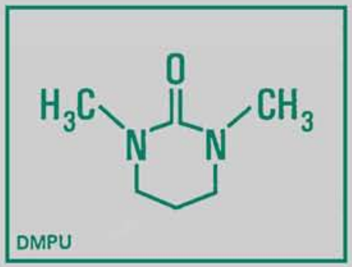
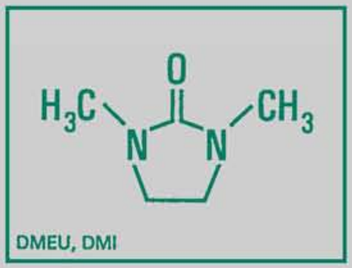
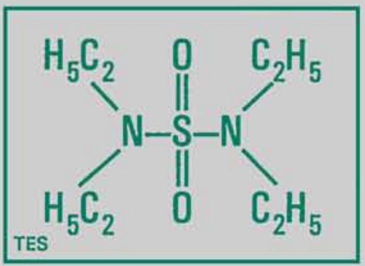
N,N'-DIMETHYLPROPYLENEUREA
1,2-DIMETHYL-2-IMIDAZOLIDINONE
N,N,N',N'-TETRAETHYLSULFAMIDE


DMPU


DMEU, DMI


TES

New Dipolar Aprotic Solvents

FLUKA offers the three new dipolar aprotic solvents **41664 1,3-Dimethyltetrahydro-2(1H)-pyrimidinone (N,N'-Dimethylpropyleneurea) DMPU, 40727 1,3-Dimethyl-2-imidazolidinone (N,N'-Dimethylethyleneurea) DMEU** or **DMI,** and **86718 N,N,N',N'-Tetraethylsulfamide, TES.** These novel solvents for organometallic reactions have been shown in several cases to be favorable substitutes for the carcinogenic HMPA.

DMPU and DMEU are new N-alkylated ureas with high dipole moments and dielectric constants[1]. **DMPU** recently was shown by Seebach et al.[2] to be an excellent replacement of HMPA as cosolvent in oxirane opening with lithium acetylide, in a Wittig olefination, in the double deprotonation of nitroalkanes, in the Michael addition of lithium dithianide to 2-cyclohexenone, and in the selective generation of certain enolates. Some of the attractive properties of DMPU are: a 33% solution in THF is stable to LDA up to at least -35°, DPMU solidifies below -20° and a 50% solution in THF remains clear and homogenous down to at least -78°[2].

DMEU (DMI) was used as solvent for the preparation of trimethylsilyl sodium, one of the strongest bases known[3], and was shown to be more stable than HMPA in the reaction of trimethylchlorosilane with lithium[4]. DMEU was found by T. Mukaiyama et al.[5] to be the solvent of choice for the transformation of allylic iodides into homoallylic alcohols. It may also be used as solvent for dehydrations and dehydrohalogenations with methyltriphenoxyphosphonium iodide[6].

N,N,N',N'-Tetraethylsulfamide, TES, recently was proposed by H. Richey et al.[7] as advantageous solvent for Grignard reagents. TES shows a greater stability towards these strongly basic and nucleophilic reagents than HMPA. Even organolithium compounds have a limited stability at ambient temperatur in TES[7].

41664	**1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone, DMPU purum** >99%(GC); B.P.$_{760}$ 230°; d_4^{25} 1.0596 (N,N'-Dimethylpropyleneurea; 1,3-Dimethyl-2-oxo-hexahydropyrimidine) $\underline{CH_2CH_2CH_2N(CH_3)CON}CH_3$ $C_6H_{12}N_2O$ M_r 126.17 [7226-23-5]	50 ml 250 ml	sFr. 20.— sFr. 85.—	US$ 13.30 US$ 56.70
40727	**1,3-Dimethyl-2-imidazolidinone, DMEU, DMI purum** 99%(GC); 1 lt ≈ 1.06 kg B.P. 221-223° (N,N'-Dimethylethyleneurea) $\underline{CH_2CH_2N(CH_3)CON}CH_3$ $C_5H_{10}N_2O$ M_r 114.10 [80-73-9]	25 ml 100 ml	sFr. 18.— sFr. 65.—	US$ 12.00 US$ 43.30
86718	**N,N,N',N'-Tetraethylsulfamide, TES purum** >99%(GC); B.P.$_{0.02}$ 70°; d_4^{20} 1.044 1 lt ≈ 1.04 kg $(C_2H_5)_2NSO_2N(C_2H_5)_2$ $C_8H_{20}N_2O_2S$ M_r 208.32 [2832-49-7]	100 ml 500 ml	sFr. 25.— sFr. 105.—	US$ 16.70 US$ 70.00

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[4] H. Sakurai, F. Kondo, ibid. *117,* 149 (1976)
[5] T. Mukaiyama et al., Chem. Lett. 1507 (1980)
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[7] H.G. Richey et al., J. Org. Chem. *46,* 2823 (1981)

Besides the three new solvents shown above FLUKA offers a large number of other aprotic dipolar compounds useful as solvents or cosolvents. For specifications and prices see the Catalogue 13, 1982/83.

29545 **1-Cyclohexylpyrrolidone**
34700 **N,N-Dibutylformamide**
32330 **N,N-Diethylformamide**
38401 **N,N-Diisopropylformamide**
38840 **N,N-Dimethylacetamide**
40250 **N,N-Dimethylformamide**
41640 **Dimethyl sulfoxide, DMSO**
04810 **1-Ethylpyrrolidone**
47721 **4-Formylmorpholine**
47725 **1-Formylpiperidine**
47728 **1-Formylpyrrolidine**
52730 **Hexamethylphosphoramide, HMPA**
66179 **N-Methylcaprolactame**
69118 **1-Methylpyrrolidone**
86148 **Sulfolane**
86892 **Tetrabutylurea**
86705 **Tetraethylurea**
87850 **Tetramethylurea**
93230 **Tripiperidinophosphine oxide**
93404 **Tripyrrolidinophosphine oxide**

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8203

Trimethylphosphine-AgI Complex

PMe_3 Now Available in Convenient Solid Form

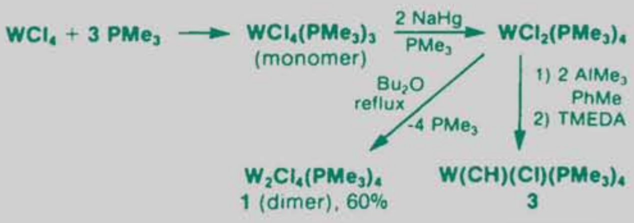
Challenges posed by the synthesis, handling and storage of **trimethylphosphine** make the use of this versatile ligand something less than a joy. Aldrich now offers the **trimethylphosphine-silver iodide complex, $[AgI{\cdot}PMe_3]_4$**, an extremely convenient alternative to neat **PMe_3**. Consider the advantages:

- **minimized hazards** for shipping and handling
- **optimum stability** allowing extended storage in a screw-cap bottle at ambient temperatures (*vs.* ampule and inert gas)
- **extremely pure PMe_3** isolable from the complex simply by heating with a heat gun or an oil bath

Uses of **trimethylphosphine** span the spectrum of synthetic chemistry and extend to studies of catalytic processes.[1] The X-ray structural analyses of novel adducts prepared from *trans*-$[PtCl_2(PMe_3)NH_3]$ and either 18-crown-6 or dibenzo-18-crown-6 have shown that the stability of the crystalline adducts is due in part to hydrogen bonding of the NH_3 ligand to pairs of oxygen atoms comprising the cavity of the crown ether.[2]

A newly synthesized class of complexes containing tungsten-tungsten quadruple bonds (*e.g.*, **1** and **2**) features phosphine ligands such as **PMe_3**;[3] structural studies carried out on several of these derivatives confirm the multiple-bonding character and, in the case of **2**, bridging chlorine atoms.[4]

Variations of this scheme can produce either the novel methylidyne complex **3**,[3] or **1** by thermal dimerization:[4]



Treichel and Komar[6] recently cited the increasing use of **PMe_3** as a ligand in organometallic chemistry in a report of the synthesis of novel cyclopentadienyliron-trimethylphosphine complexes. Similar compounds of cobalt [*e.g.*, $C_5H_5Co(PMe_3)_2$] are precursors of several complexes featuring a disubstituted cyclopentadienyl ligand, a character which permits the study of the influence of steric effects on the Lewis basicity of electron-rich metals.[7]

Phosphines also stabilize nickel in a variety of oxidation states;[8] this property can be exploited to further the understanding of mechanisms involving metal-carbon sigma bonds in organometallic chemistry, including catalytic systems. An example is the homolytic cleavage of the $Ni\text{-}CH_3$ bond in the synthesis of the $17e^-$ Ni(I) d^9 monomeric tetrahedral complex, **4**.[9,10]

$$[Ni(Me)(PMe_3)_4]BPh_4 \rightarrow \underset{\mathbf{4}}{[Ni(PMe_3)_4]BPh_4}$$

Cationic rhodium complexes containing **PMe_3** and other phosphines have been applied to the catalytic hydrogenation of styrene oxide.[11]

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23,086-3	**Trimethylphosphine-silver iodide complex**	**5g $17.25; 25g $69.00; 100g $200.00**
19,804-8	**Trimethylaluminum,** *2M* in toluene	**100ml $8.80; 800ml $32.75**
T2,250-0	***N,N,N',N'*-Tetramethylethylenediamine** (TMEDA)	**100g $7.00; 500g $24.75**
18,665-1	**18-Crown-6**	**5g $7.00; 25g $28.50**
15,839-9	**Dibenzo-18-crown-6**	**2.5g $4.25 10g $11.75; 50g $38.25**

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