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SYNTHESIS ALERTS

Synthesis Alerts is a new monthly feature to help readers of Synthesis keep abreast of new reagents, catalysts, ligands, chiral auxiliaries, and protecting groups which have appeared in the recent literature. Emphasis is placed on new developments but established reagents, catalysts etc are also covered if they are used in novel and useful reactions. In each abstract, a specific example of a transformation is given in a concise format designed to aid visual retrieval of information.

Synthesis Alerts is a personal selection by Paul Blakemore, Brian Dymock, Philip Hall, Philip Kocienski, J.-Y. Le Brazidec and Alessandro Pontiroli of the University of Glasgow. The journals regularly covered by the abstractors are: Angewandte Chemie International Edition, Bulletin de la Societe Chimie de France, Bulletin of the Chemical Society of Japan, Chemische Berichte, Chemistry Letters, Helvetica Chimica Acta, Journal of Organic Chemistry, Journal of Organometallic Chemistry, Journal of the American Chemical Society, Liebigs Annalen, Tetrahedron Letters.

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N,N',N"-Trimethyl-2,5,8,9-tetraaza-1-phos	decane Catalyst	
A new efficient catalyst for silylation of tertiary alcohols and hindered phenols. The title compound is also known as trimethyl-pro-azaphosphatrane.	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Ph TBDMSCI (1.1 eq), A (0.2 eq) Ph OTBDMS (4 examples)
B. A. D'Sa, J. G. Verkade <i>J. Am. Chem. Soc.</i> , 1996, 118, 12832.	A	This catalyst also promotes esterification between a carboxylic acid chloride and an alcohol: B. A. D'Sa, J. G. Verkade <i>J. Org. Chem.</i> , 1996 , <i>61</i> , 2963.

(<i>R</i>)-B-Methyl-4,5,5-triphenyl-1,3,2-oxazab	orolidine			Catalyst
The title compound catalyses the borane reduction of propargylic ketones in high yield with excellant stereocontrol. The dicobalt hexacarbonyl complexes are also suitable substrates. J. Bach, R. Berenguer, J. Garcia, T. Loscertales, J. Vilarassa J. Org. Chem., 1996, 61, 9021.	Ph. Ph HN O Me	oCeH₁1 SiMe₃	BH ₃ *SMe ₂ (1.2 eq), A (1 eq), THF, 0°C, 5 min, 75% 6 examples; er ≥ 95:5.	SiMe ₃ R configuration er = 98:2

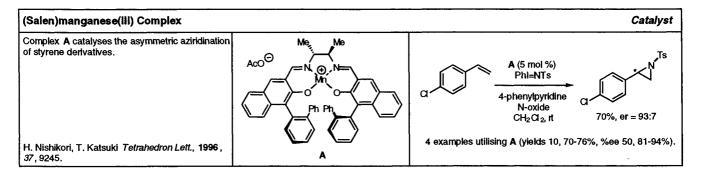
The title compound catalyses the hydrosilylation of prochiral ketones in high yield but modest enantioselectivity. A (10 mol%), HSi(OEt)₃ (6 eq), OSi(OEt)₃ (HSi(OEt)₃ (6 eq), Ph CH₃ 98% er = 78:22 The example shown is the best of 10 examples.

Chromocene		Catalyst
As little as 1 mol% of the title compound together with Mn and TMSCI is sufficient to catalyse the addition of aryl lodides, allyl bromides, iodoalkynes and enol triflates to aldehydes. This is the first example of a <i>catalytic</i> Nozaki-Hiyama-Kishi reaction.	Cp₂ Cr A	O (E)-MeCH=CH-CH ₂ Br OH CO ₂ Me Op ₂ Cr (1 mol%), Mn, TMSCl THF, rt 76% anti:syn = 4:1
A. Fürstner, N. Shi J. Am. Chem. Soc., 1996, 118, 12349.		The active Cr(II) catalyst can also be generatred in situ by Mn reduction of CrCl ₃ (15 mol%) or CpCrCl ₂ .

(1R,2S)-N-Methylephedrine		Catalyst
The potassium alkoxide prepared from the title compound acts as a chiral base in a catalytic enantioselective dehydrohalogenation.	Ph H OH NMe ₂	Ph
M. Amadji, J. Vadecard, JC. Plaquevent, L. Duhamel, P. Duhamel J. Am. Chem. Soc., 1996, 118, 12483.	A	8 examples 82%; er = 98:2

(R)-2-Hydroxy-2'-methoxy-1,1'-binaphthyl		Catalys
The complexes between the title compound and SnCl4 accomplishes enantioselective catalytic protonation of enol silanes and ketene bis(trimethylsilyI) acetals.	H Q Me	OTMS A (5 mol%) Sn Cl ₄ (110 mol%) 2,6-dimethylphenol PhMe, -80°C, 1 h 80%; er = 96:4
K. Ishihara, S. Nakamura, M. Kaneeda, H. Yamamoto <i>J. Am. Chem. Soc.</i> , 1996 , <i>118</i> , 12854.	A	5 examples; er usually >9:1

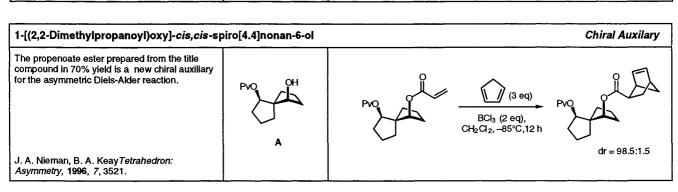
η^4 -(Cycloocta-1,5-diene)platinum (II) Chloride		Catalyst
The Pt(0) species formed from A under the reaction conditions catalyses the vinylation of aryl iodides.	Pt(COD)Cl₂ A	A (2 mol %) PPh ₃ (4 mol %) PPh ₃ (4 mol %) CO 2Me (2 eq) Na ₂ CO ₃ (2 eq) NMP, 130°C, 24 h R = OMe, 79% R = Me, 56% 3% 9 useful examples incorporating 5 simple aryl lodides and 5 conjugated terminal
A. A. Kelkar Tetrahedron Lett., 1996, 37, 8917.		olefins (yields 26-90%, vinylation selectivity 40-95%). Higher yields are obtained for electron rich iodides.



S. Kobayashi, S. Nagayama, T. Busujima *Tetrahedron Lett.*, 1996, *37*, 9221.

24 highly varied examples (yields 73-99%).

Polymer-Supported Scandium Triflate The polymeric species A (PA-Sc-TAD) efficiently catalyses three component reactions between amines, aldehydes and silylated nucleophiles. Ph CHO + PhNH2 OSIMe3 HeO TI, 19 h 73% Me O2G NHPh



Diethylzinc adds to benzaldehyde enantioselectively in the presence of the title ligands. Ligand Diethylzinc adds to benzaldehyde enantioselectively in the presence of the title ligands. H. Kotsuki, M. Wakao, H. Hayawaka, T. Shimanouchi, M. Shiro J. Org. Chem., 1996, 61, 8915. Ligand Diethylzinc adds to benzaldehyde enantioselectively in the presence of the title ligands. Et 2Zn (4 eq), A (2 eq), PhMe-hexane (1:1), 48 h 99% er = 97:3 A was the best of 13 ligands examined with respect to yield and stereocontrol.

Ligand

Reagent

Chiral Crown Ether-Phosphine Complexes

Enantioselective allylations of α -nitro ketones and α -nitro esters with allyl acetate occur in the presence of alkali metal fluorides and 1 mol % of Pd catalysts using chiral ferrocenylphosphine ligands bearing monoaza-18-crown-6 moletles.

M. Sawamura, Y. Nakayama, W-M. Tang, Y. Ito J. Org. Chem., 1996, 61, 9090.

Homochiral Bis(oxazoline) Ligand Ligand An external chiral ligand for the asymmetric (a) n-BuLi (1 eq), addition of allyl zinc reagents to oximes of N (0.8 eq) THF, –78°C→rt α-oxo esters. ÇO₂E1 CO₂Et 15 min ZnBr NHOB (0.9 ea) 72%, er = 96:4 15 min 6 examples (yields 62-90%, %ee 74-94%). S. Hanessian, R.-Y. Yang Tetrahedron Lett.

Homochiral 2-(1,3-Oxazin-2-yl)phenyl Diphenylphosphine

The complex formed from $[Pd(\eta^3-C_3H_5)Cl_2]_2$ (A) and chiral 1,3-oxazine B, catalyses the asymmetric allylic substitution reaction of 1,3-diphenylprop-2-enyl acetate with the sodium salt of dimethyl malonate.

1996, 37, 8997.

P. A. Evans, T. A. Brandt *Tetrahedron Lett.*, **1996**, *37*, 9143.

Optimisation of the above reaction on a single substrate is described.

Trimethylsilyl(methoxy)benzotriazol-1-ylmethane

Aldehydes and ketones are converted into the corresponding one-carbon homologated carboxylic acids in good yields *via* a sequence of Peterson olefination with the title reagent and treatment with ZnBr₂ and HCI.

A. R. Katritzky, D. Toader, L. Xie *Synthesis* 1996, 1425. Different ketones (3 examples) and aldehydes (6 examples) were employed with overall yields between 43 and 57%.

Sodium Azide 1,5-Disubstituted tetrazoles are prepared in a safe and efficient fashion by treatment of imidoyl chlorides with NaN₃ under phase-transfer conditions. NaN₃ Second T.V. Artamonova, A.B. Zhivich, M. Yu. Dubinskii, G. I. Koldobskii Synthesis, 1996, 1428.

2567.

T. G. Back, B. P. Dyck Chem. Commun., 1996,

Homochiral Selenyl Chloride Reagent Diastereoselective cyclisation of unsaturated alcohols and carboxylic acids may be achieved with the homochiral selenyl chloride ${\bf A}$. A (0.95 eq) 4Å mol. sieves °CO₂H CH₂Cl₂, -95°C, 45 min 81%; dr > 95:5 13 examples; yields 61-96%; dr = 2:1 to 95:5 $\boldsymbol{\mathsf{A}}$ is derived in situ from the diselenide and sulfuryl chloride (1 eq). A can be prepared on a large scale. Se also provides a handle for further functionalisation.

Manganese-PbCl₂-Me₃SiCl Reagent This reagent combination promotes the sequential addition of alkyl radicals to allylic acrylates and the subsequent Ireland-Claisen Mn (6 eq), PbCl₂ (cat), Me₃SiCl (3 eq), NMl (3 eq) rearrangement of the ketene silyl acetal formed in situ. THF-DMF (2:1), rt, 30 min 92% C₅H₁₁ 8 examples. E:Z 99:1 K. Takai, T. Ueda, H. Kaihara, Y. Sunami, T. Moriwake J. Org. Chem., 1996, 61, 8728.

Magnesium Methoxide			Reagent
The title reagent effects selective deprotection of alkyl esters. By adjusting the equivalents of reagent, it is possible to selectively cleave primary acetate in the presence of secondary and secondary acetate in the presence of tertiary acetate. Y-C. Xu, A. Bizuneh, C. Walker J. Org. Chem., 1996, 61, 9086.	Mg(OMe) ₂ A	A (8 eq) MeOH, rt, 8h 94% OAc 6 examples.	

Benzyltrimethylammonium Isopropoxide		
α-Substituted aldehydes can be directly alkylated using the title compound as base. Z. Valenta, D. I. MaGee, S. Setiadji <i>J. Org. Chem.</i> 1996, 61, 9076.	[Bn NMe₃]* Me₂CHO − A	A (1.3-1.4 eq) Mel (3 eq) Bu OH, rt, 30 min 71% 11 examples; yields 60-100%. Alkylation can also be accomplished with less reactive halides such as Bul and APri.

Samarium Diiodide		Reagent
Glycosyl phosphates react with carbon radical or anion acceptors in the presence of the title reagent to give a new synthesis of C-glycosides.	Sml₂	BnO OBn cyclopentanone THF, rt, 15-20 mln 81% Sml ₂ cyclopentanone BnO OBn BnO OBn BnO OBn BnO OBnO OBnO
SC. Hung, CH. Wong Angew. Chem. Int. Ed. Engl., 1996, 35, 2671.		12 examples involving 4 different monosaccharide precursors. Electrophiles include t-arryl alcohol (protonation), CO ₂ , acetone, and isobutanal.

The title compound enables regioselective hydroselenation of terminal acetylenes. PhSe-A PhSe-A PhSe-A PhSe-A PhSe-A PhSe-BPh (0.5 eq) PhSe

Isopinocampheylbromoborane		Reagent
The monomeric borane A is a superior reagent for the asymmetric hydroboration of alkenes. U. P. Dhokte, H. C. Brown <i>Tetrahedron Lett.</i> , 1996, 37, 9021.	IpcBBr ₂ + Me ₃ SiH	$(a) pcBBr_2 (1 \ eq) \\ \hline \qquad \qquad$

Samarium		Reagent
Metallic samarium in a methanolic medium reductively dehalogenates <i>vic</i> -dihalides. R. Yanada, N. Negoro <i>Tetrahedron Lett.</i> , 1996 , <i>37</i> , 9313.	Sm A	Ph MeOH Ph MeOH MeOH Rt, 1 h ≥ 98% Rt, 1 h Br MeOH Br MeOH Br MeoH Br Meso 15 examples (yields >92%). Unsurprisingly 2,3-dibromo-1,4-dioic acid derivatives give the corresponding succinic acids.

Indium		Reagent
The reaction between allylic or propargylic bromides and diorganyl diselenides is promoted by indium in aqueous media.		Br (3 eq)
For analogous reaction with α-bromo ketones see: W. Bao, Y. Zhang Synlett, 1996, 1187.	ln A	A (1 eq) THF:H ₂ O (15:5) 50°C, 20 h
W. Bao, Y. Zheng, Y. Zhang, J. Zho <i>Tetrahedron Lett.</i> , 1996 , <i>37</i> , 9333.		11 examples (yields 46-85%). Reactions carried out in either THF/H $_2$ O, DMF/H $_2$ O or EtOH/H $_2$ O.

(–)-10-Mercaptoisoborneol				Reagent
Tandem conjugate addition of the title thiol to enones followed by reduction of the ketone via diastereoselective intramolecular 1,7-hydride shift occurs on treatment with Me ₂ AlCI. After reductive desulfurisation, the overall sequence corresponds to a reduction of the double bond and the asymmetric reduction of the ketone. K. Nishide, Y. Shigeta, K. Obata, M. Node J. Am. Chem. Soc., 1996, 118, 13103.	SH A	Ph Ph Scope	(a) A (1.2 eq), Me ₂ AlCl (1.2 eq) CH ₂ Cl ₂ , rt, 24 h. (b) Reductive desulfurisation 96% and limitations checked on 7 examp	OH Ph er = 98/2 eles.