**Synthesis Alerts** is a 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:

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Article Identifier: 1437-210X:E:2000,0,02,0321,0328,ftx,en:X00200SS.pdf

**Chlorotrism(3,5-dimethylphenyl)/tert-butylamidomolybdenum(IV)**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[MoCl(Nt-Bu/m-Xyl)$_3$] A</th>
<th>[MoCl(Nt-Bu/m-Xyl)$_3$] A</th>
<th>A (10 mol%)</th>
<th>CH$_2$Cl$_2$ (25 eq)</th>
<th>PhMe, 80°C, 20 h</th>
<th>88%</th>
<th>9 examples (yields 60-91%)</th>
</tr>
</thead>
</table>


**Tris(dibenzylideneacetone)dipalladium(0)**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd$_2$(dba)$_3$ A</th>
<th>Pd$_2$(dba)$_3$ A</th>
<th>A (2 mol%), DPEphos (6 mol%), o-BrPhMe (1.0 eq) THF, 80°C, 1 h</th>
<th>56% m:ø = 87:1</th>
<th>17 examples (yields 40-90%, 27:1 meta:ortho:100:0)</th>
</tr>
</thead>
</table>


**Tetrachlorobis(tetrahydrofuranyl)Titanium(IV)**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[TiCl$_4$(THF)$_2$] A</th>
<th>[TiCl$_4$(THF)$_2$] A</th>
<th>A (5 mol%)</th>
<th>EtCOCl (1.2 eq)</th>
<th>i-Pr$_2$NEt (1.5 eq)</th>
<th>CH$_2$Cl$_2$, rt, 10 h</th>
<th>92%, dr &gt; 99:1</th>
<th>10 examples (yields 70-95%, %de = 80-98%)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th><strong>1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene Hydrochloride</strong></th>
<th><strong>Catalyst</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>A and a Pd(0)-source mediate the cross-coupling of aryl chlorides with aryl Grignard reagents.</td>
<td></td>
</tr>
<tr>
<td><img src="image1" alt="Chemical Structure" /></td>
<td><img src="image2" alt="Chemical Structure" /></td>
</tr>
<tr>
<td><strong>J. Huang, S. P. Nolan J. Am. Chem. Soc. 1999, 121, 9689.</strong></td>
<td><strong>16 examples (yields 0, 69-99%).</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Molybdenum Isocyanide Complex</strong></th>
<th><strong>Catalyst</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>A catalyses the regioselective hydrostannation of several types of alkenes, giving preferentially α-stannylated products.</td>
<td></td>
</tr>
<tr>
<td><img src="image3" alt="Chemical Structure" /></td>
<td><img src="image4" alt="Chemical Structure" /></td>
</tr>
<tr>
<td><strong>U. Kazmaier, D. Schauss, M. Pohlm. Org. Lett. 1999, 1, 1017.</strong></td>
<td><strong>11 examples (yields 38-98%, 63.37 ≤ α/β ≤ 95.5) are reported.</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>1,1′-Binaphthalene-2,2′-dilɔ / Dichloro-di-isopropoxytitanium(IV)</strong></th>
<th><strong>Catalyst</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>The title reagent pair catalyse the asymmetric allylation of ketones.</td>
<td></td>
</tr>
<tr>
<td><img src="image5" alt="Chemical Structure" /></td>
<td><img src="image6" alt="Chemical Structure" /></td>
</tr>
<tr>
<td><strong>S. Casolari, D. D’Addario, E. Tagliavini Org. Lett. 1999, 1, 1061.</strong></td>
<td><strong>8 examples (yields 75-91%, 3%ee = 29-65%) are reported.</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>N-p-(Toluenesulfonyl)-1,2-diphenylethanediamine(η^5-arene) ruthenium(II) Chloride</strong></th>
<th><strong>Catalyst</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>The title reagent catalyses the asymmetric transfer hydrogenation of benzils to prepare chiral hydrobenzoin derivatives.</td>
<td></td>
</tr>
<tr>
<td><img src="image7" alt="Chemical Structure" /></td>
<td><img src="image8" alt="Chemical Structure" /></td>
</tr>
<tr>
<td><strong>K. Murata, K. Okano, M. Miyagi, H. Iwane, R. Noyori, T. Ikariya Org. Lett. 1999, 1, 1119.</strong></td>
<td><strong>5 examples (yields 67-100%, 3%ee &gt; 99%) are reported.</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Palladium(II) Acetate</strong></th>
<th><strong>Catalyst</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>A catalyses the Ullmann-type reductive coupling of aryl halides under an air atmosphere in aqueous acetone.</td>
<td></td>
</tr>
<tr>
<td><img src="image9" alt="Chemical Structure" /></td>
<td><img src="image10" alt="Chemical Structure" /></td>
</tr>
<tr>
<td><strong>S. Venkatraman, C.-J. Li Org. Lett. 1999, 1, 1133.</strong></td>
<td><strong>13 examples (yields 0, 64-96%) are reported.</strong></td>
</tr>
</tbody>
</table>
Indium(III) Chloride

The title reagent catalyses the one-pot preparation of α-amino phosphonates from aldehydes or ketones and amines.

\[
\text{InCl}_3 \quad A
\]

\[
\text{Ph} - \text{C} - \text{NHCH}_2\text{Ph}
\]

\[
\text{O} - \text{P(OEt)}_2
\]

Ultrasound

THF, Δ, 9 h

85%

24 examples (yields 76-95%) are reported.


1,3-Bis(2,6-dilodopropylphenyl)imidazol-2-ylidene Hydrochloride

The title reagent catalyses the amination of aryl halides.

\[
\text{MeO} \quad A
\]

\[
\text{PhCl} \quad A
\]

\[
\text{NHPh}
\]

Dioxane, 100°C, 3 h

91%

16 examples (yields 59-99%) are reported.


Guanidinium Phosphine Ligand / Palladium(II) Acetate

The title reagent pair, supported on glass beads, is utilised in Heck reactions and Sonogashira couplings. The catalyst is recyclable and features low leaching of palladium into the system.

\[
\text{Me}_2\text{N} \quad A
\]

\[
\text{Pd(OAc)}_2 \quad B
\]

\[
\text{PhMe, 100°C, 16 h}
\]

87%

7 examples of Heck reactions (yields 55-87%) and 4 examples of Sonogashira couplings (yields 58-87%) are reported.


Chiral Titanocene Dichloride Complex

\[
\text{A}
\]

A catalyses the enantioselective opening of meso-epoxides via a β-titanylo radical intermediate.

\[
\text{Me}_2\text{NCH}_2\text{CH}_2\text{NHCl}
\]

\[
\text{H}_2\text{C} = \text{CHOCCMe}_2(1.25 \text{ eq})
\]

\[
\text{NEt}_3(3 \text{ eq})
\]

\[
\text{PhMe, 100°C}
\]

65%, \%ee = 96:4

6 examples (yields 60-68%, %ee = 74-93%) are reported.


1,6-Bis(dimethylamino)hexane

A is used in the tosylation of various alcohols. The reported method has advantages over the more traditional use of pyridine / TsCl in that the reaction rate is higher, and undesirable chlorination reactions are avoided. A can also be used in mesylation reactions.

\[
\text{Me}_2\text{N(CH}_2)_2\text{NMe}_2
\]

\[
\text{EtOCl} \quad A
\]

\[
\text{EtO}_2\text{C(CH}_2)_2\text{OH}
\]

\[
\text{MeCN, 0°C, 1 h}
\]

94%

6 examples (yields 92-95%) are reported.

**Bis(triethylamino)nickel(II) Dichloride**

The title reagent can be used as an alternative to Pd(PPh₃)₄ in the catalysis of Suzuki reactions. A is effective in the presence of water and the lack of phosphine ligands prevents unwanted side reactions occurring.

N. E. Leadbeater, S. M. Resouly
_Tetrahedron_ 1999, 55, 11889

**Chiral Chromium Salen Catalyst**

A is reported as an efficient catalyst for the kinetic resolution of 2,2-disubstituted epoxides.

H. Lebel, E. N. Jacobsen

**Palladium Catalyst**

A is reported to be a highly active catalyst for the Heck reaction.

F. Miyazaki, K. Yamaguchi, M. Shibusaki

**Ruthenium Catalyst**

A is reported as an effective catalyst for alkene-alkyne coupling.

B. M. Trost, F. D. Toste

**(2,7-Dimethyl-1,8-biphenylenedioxy)bis(diolisopropoxyaluminium)**

The high-speed Tishchenko reaction of aldehydes using A is reported. Highly stereoselective intramolecular Tishchenko reduction of β-hydroxy ketones is also described.

T. Ooi, T. Miura, K. Takaya, K. Maruoka
2.2′-Bis(di-<i>p</i>-tolyphosphino)-1,1′-binaphthyl

A Cu<sup>(I)</sup>-catalyst formed from the title ligand is used in the asymmetric conjugate reduction of α,β-unsaturated esters.


9 examples (yields 84-96%, %ee 80-91%).

PhO<sub>2</sub>P<sub>Ar</sub><br>Ar = <i>p</i>-toly

PMHS = polymethylhydroxilsloxane

α-(Di-tert-butylphosphino)biphenyl

A in combination with Pd(OAc)<sub>2</sub> catalyses the efficient Suzuki-coupling of aryl bromides and chlorides.


21 examples (yields 81-98%).

PhO<sub>2</sub>P<sub>(t-Bu)<sub>2</sub></sub>

Chiral Bis(trifluoromethanesulfonamide) Ligand

Asymmetric acyl halide-aldehyde cyclocondensations are mediated by ligand A and Me<sub>2</sub>Al or Et<sub>2</sub>AlCl.


10 examples (yields 56-91%, %ee = 54-93%).

PhN<sub>2</sub>(S<sub>2</sub>C,F<sub>3</sub>)<sub>2</sub>NH<sub>2</sub></n>CH<sub>2</sub>SO<sub>2</sub>CF<sub>3</sub>

(R,R)-(2′-Benzylkoxyethylphenyl)-2,5-dimethylphospholane

A is reported as an efficient ligand in the Ni-mediated hydrovinylation of styrene.


5 examples (yields 2-94%, %ee = 29-50%).

PhO<sub>2</sub>P<sub>Ar</sub><br>Ar = <i>p</i>-toly

Chiral 2-(phosphinoaryl)pyridine Ligand

Asymmetric allylic alkylations using a palladium catalyst derived from ligand A are reported.


4 examples (yields 77-85%, %ee = 71-93%) are reported.
1,1'-Binaphthyl-2-yl(phenyl)iodonium Tetrafluoroborate

Chiral diaryliodonium salt A and analogues are utilised in the asymmetric α-phenylation of cyclic β-keto esters.


9 examples (yields 15-71%, % ee = 37-53%).

p-Tolylthioglycolic Acid

A and similar thioglycolic acids, undergo N-Mediated cross-couplings with organozinc reagents.


18 examples (yields 40-100%).

2,6-Bis(trimethylsilyl)pyridine

The title reagent is used in Stille-type coupling procedures to prepare new pyridine-based ligands for supramolecular chemistry.


Preparation of A (69%) and 3 examples of ligand synthesis (yields 42-68%) are reported.

Hydroquinone

The title reagent is used as a homogeneous reductant in the palladium-catalysed Ullmann-type homocoupling of aryl halides.


17 examples (yields 54-95%) are reported.

(Dimethylphenylsilyl)pinacolborane

The title reagent is used in the palladium catalysed regioselective elaboration of 3-substituted 1,2-dienes. The utility of the 2-boryl allylsilane derivatives is demonstrated by Pd-catalysed coupling reactions with aryl halides.


7 examples (yields 79-99%, regioselectivity > 86:14) are reported.
Iodoethane / Ethylmagnesium Bromide

The title reagent pair are used in the coupling reaction of arylmagnesium compounds and THF to prepare 2-aryltetrahydrofurans.

\[
\begin{align*}
\text{MeO} & \quad \text{Ph} \\
\text{A} & \quad \text{B (2 eq)} \\
\text{EtMgBr} & \quad \text{THF, rt, 5 h, 43\%}
\end{align*}
\]


8 examples (yields 12-78\%) are reported.

(R)-1-tert-Butylsulfanyl-1-cyclopentene

The title reagent is used in an asymmetric Heck reaction with a variety of para- and meta-substituted arenesulfonamides.

\[
\begin{align*}
\text{A} & \quad \text{Ph-N}_2^+\text{BF}_4^- (2 \text{ eq}) \\
\text{A} & \quad \text{Pb(OAc)}_2 (20 \text{ mol\%}) \\
\text{A} & \quad \text{Ag}_2\text{CO}_3 (2 \text{ eq}) \\
\text{CH}_3\text{CN, rt, 8 h} & \quad \text{72\%} \\
\text{dr} & \quad 96:5
\end{align*}
\]


8 examples (yields 0, 54-79\%, \%de = 82-92\%) are reported.

Molecular Oxygen

Oxygen is used in atom-efficient osmium-catalyzed dihydroxylation in which both oxygen atoms are incorporated into the product.

\[
\begin{align*}
\text{A} & \quad \text{C}_8\text{H}_{13} \\
\text{A} & \quad \text{K}_2[\text{OsO}_2(\text{OH})_4] (0.5 \text{ mol\%}) \\
\text{A} & \quad (\text{DHQD})_2\text{PHAL} (0.15 \text{ mol\%}) \\
\text{H}_2\text{O} & \quad \text{t-BuOH, } 50^\circ\text{C, 18 h} \\
\text{C}_8\text{H}_{13} & \quad \text{98\%, er = 82.18}
\end{align*}
\]


10 examples (yields 51-98\%, \%ee = 54-96\%) are reported.

\[N,N,N,N^\prime\text{-Tetramethylazodicarboxamide (TMAD) / Tributylphosphine}\]

The title reagent pair are utilised in the direct transformation of primary and secondary alcohols to the corresponding nitriles in the presence of acetone cyanhydrin.

\[
\begin{align*}
\text{Me}_2\text{NCON=NCONMe}_2 & \quad \text{A} \\
\text{PBu}_3 & \quad \text{B} \\
\text{Et}_3\text{O, rt, 1 d} & \quad \text{91\%}
\end{align*}
\]


7 examples (yields 6, 75-96\%) are described.

Trimethylsilylsulfanyl Chloride / Iodosobenzene

A method for the preparation of sulfur trioxide in situ from the title reagent pair in the absence of Lewis bases is described. The procedure is utilised in the preparation of sulfones from alkenes.

\[
\begin{align*}
\text{Me}_3\text{SiSO}_2\text{Cl} & \quad \text{A} \\
\text{PhO} & \quad \text{B (0.7 eq), Ph} (0.7 eq) \\
\text{CH}_2\text{Cl}_2, \text{70\%} & \quad \text{rt, 1 h, 60\%}
\end{align*}
\]


6 examples (yields 50-69\%) are reported.
**iso-Propylmagnesium Bromide**

A (or i-Pr$_3$Mg) is utilised in the preparation of polyfunctional ary1 or heteroaryl magnesium reagents from brominated precursors. Excellent chemoselectivity is observed in the Br-Mg exchange of di- or tribromoheterocycles.

M. Abarebri, F. Dehnel, P. Knochel

18 examples using A or i-Pr$_3$Mg (yields 55-88%) are described.

**Diethylaminotrimethylsilane / Methyl Iodide**

The title reagents mediate the ring-opening iodosilation of cyclic ethers.

J. Ohshita, A. Iwata, F. Kanetani, A. Kural, Y. Yamamoto, C. Matsui

24 examples, including the use of different halide sources (yields 33-90%) are described.

**1-Trisopropylsilyloxy-1,2-propanediene**

The title reagent reacts with aldehydes or ketones to give α,β-unsaturated acyl silanes.

I. A. Stergiades, M. A. Tius

21 examples (yields 27-92%) are described.

**4-Nitrophenyltrifluoromethanesulfonate**

The title reagent is reported as a new trifluoromethanesulfonyl transfer agent.

L. Neuville, A. Bigot, M. E. T. H. Dau, J. Zhu

9 examples (yields 60-92%) are reported.

**Cyanomethylenetriethylphosphorane (CMMP)**

The title compound mediates the alkylation of arylmethyl phenyl sulfones with primary and secondary alcohols. Arylmethyl phenyl sulfones of pKa up to 23.5 can be utilized in the CMMP mediated Mitsunobu reaction.

T. Tsunoda, K. Uemoto, T. Ohtani, H. Kaku, S. Itô

12 examples (yields 83-100%).