Acetic anhydride.

Dehydration. Ketoximes of alkyl aryl ketones afford pyrrolines on heating with Ac₂O in dimethylacetamide. Cyclization probably proceeds via H-abstraction after the nitrenium ions are formed.

\[
\begin{align*}
\text{AcO} & \quad \text{AcMe_2} \\
\mu \text{w} & \\
\text{H} & \\
\text{NOH} & \\
\text{AcO} & \\
\text{AcMe_2} & \\
\mu \text{w} & \\
\text{H} & \\
\text{N} & \\
\text{NOH} & \\
\end{align*}
\]

68%


Acetylacetonato(1,5-cyclooctadiene)rhodium(I).

Aryltrialkoxysilanes. Preparation of ArSi(OR)₃ from ArX and HSi(OR)₃ is readily accomplished with the aid of (acac)Rh(cod) in DMF.¹

\[\text{Murata, M., Yamasaki, H., Ueta, T., Nagata, M., Ishikura, M., Watanabe, S., Masuda, Y. T 63, 4087 (2007).}\]

Acetylacetonato(dicarbonyl)rhodium(I).

Alkylation. Addition of 1-alkynes to α-keto esters is catalyzed by (acac)Rh(CO)₂ in the presence of a hindered phosphine ligand [e.g., 2-(di-i-butylphosphino)biphenyl].¹ Complexes containing more electron-rich analogues of the acetylacetonato ligand favor the reaction.

Coupling. Allylic carbonylation and coupling with boronic acids transform 2,3-diazabicyclo[2.2.1]hept-5-enes into 5-hydrazinyl-2-cyclopentenyl ketones.²

\[\text{Fiesers' Reagents for Organic Synthesis, Volume 25. By Tse-Lok Ho}
\]

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1
Addition to α-dicarbonyl compounds. α-Diketones and α-keto esters react in aqueous DME with ArB(OH)$_2$ to produce the monadducts.

Reduction. Conjugated acids are converted to saturated aldehydes by syngas at room temperature, using (acac)Rh(CO)$_2$ in conjunction with a special guanidine as catalyst. Only CO is liberated as stoichiometric side product. Furthermore, conditions for this highly selective reaction do not disturb acetals, esters, carbamates, ethers, silyl ethers, sulfides and many other functional groups.

Hydroformylation. With the Rh complex as catalyst (and a phosphite ligand) enamides and N-vinylimides are converted under syngas to α-amidoacetaldehydes.

Acetyl chloride. Nitration of arylamines. Nitration is performed by treatment of the [ArNHR$_2$]NO$_2$ salts with two equivalents of AcCl. Apparently, the active nitrating agent, AcONO$_2$, is formed.

N-Alkoxy carbonyl azoles. Allyl carbonates. 1-Allyloxy carbonylimidazole is an allyloxy carbonylating agent for enolate ions (e.g., generated from ketones and NaHMDS in DME, $-78^\circ$). O-Allylation occurs under the influence of BF$_3$·OEt$_2$. Substituted allyl groups are similarly transferred from homologous reagents.

Carbamates, carbonates, and thiocarbonates are also readily prepared from the highly stable, nonhygroscopic, and usually crystalline mixed carbamates of 3-nitro-1,2,4-triazole.
Alkylaluminum chlorides.

Rearrangement. $\alpha$-Siloxyarylacetdehyde$\ddagger$ gives aryl ketones on treatment with Me$_2$AlCl. On the other hand, chloroaluminum biphenyl-2,2'-bis(triflylamide) catalyzes an alternative rearrangement pathway.\textsuperscript{1}

\begin{align*}
\text{Et}_3\text{SiO} & \text{CHO} \\
& \text{Ar} \\
& \text{R} \\
\xrightarrow{\text{Me}_2\text{AlCl}} & \text{Ar} \\
& \text{O} \\
& \text{SiEt}_3 \\
\end{align*}

\textsuperscript{1}Ohmatsu, K., Tanaka, T., Ooi, T., Maruoka, K. \textit{ACIE} \textbf{47}, 5203 (2008).

$S$-Alkylisothiouronium salts.

Thiol surrogates. These readily available compounds (RX + thiourea) release RSH in the presence NaOH for conjugate addition. Essentially they are odorless thiolating agents.\textsuperscript{1}

\textsuperscript{1}Zhao, Y., Ge, Z.-M., Cheng, T.-M., Li, R.-T. \textit{SL} 1529 (2007).

$\eta^3$-Allyl(1,5-cyclooctadiene)palladium tetrafluoroborate.

Allylation.\textsuperscript{1} The Pd salt in the presence of 6-diphenylphosphino-2-pyridone catalyzes C-allylation of indoles (at C-3) and pyrroles (at C-2) with allyl alcohol in toluene at 50°, generating water as the only byproduct. The key to activation of the allylating agent is by H-bonding.
**Nucleophilic substitution.** Benzylic acetates react with nucleophiles such as amines, sodium arenesulfonates, and malonic esters under the influence of the title reagent together with DPPF and a mild base [Et$_3$N in EtOH or K$_2$CO$_3$ in \(\text{t-AmOH}\)].

1Usui, I., Schmidt, S., Keller, M., Breit, B. *OL* 10, 1207 (2008).

**\(\eta^3\)-Allyl(cyclopentadienyl)palladium.**

**Cycloaddition.** The Pd complex is useful for generating internal salts containing a \(\pi\)-allylpalladium complex from (\(\omega\)-1)-methylene lactones. Trapping of the intermediates by other 1,3-dipoles such as nitrones results in the products of different types of heterocycles (with larger ring size).\(^1\)

\[\begin{align*}
\text{Ar} & \quad \text{COOMe} \\
\text{Ar} & \quad \text{COOMe}
\end{align*}\]

The subtle ligand effects are manifested in the reaction of dipolar species with acrylic esters, apparently due to different number of P-ligands on the \(\pi\)-allylpalladium complex. With two additional ligands (phosphites) on Pd the \(\pi\)-allyl segment suffers attack at the central carbon to eventually generate spiro[2.4]heptanes, whereas only one additional ligand (phosphine) engenders an electronic bias toward bond formation at the terminus.\(^2\)

\[\begin{align*}
\text{Ph} & \quad \text{COOMe} \\
\text{Ph} & \quad \text{COOMe}
\end{align*}\]

**Carboboration.** An alkyl group is delivered from (alkyl)zirconocene chlorides to a triple bond accompanied by the formation of an oxaborolidine unit. Remarkably, Me$_3$P (vs. other phosphine ligands) has a unique stereochemical influence.
Elimination.°\(^4\) \(\sigma\)-Quinodimethane is generated from \((\sigma\text{-trimethylsilylmethyl})\text{benzyl methyl carbonate}\) on heating with the Pd complex and DPPE in DMSO at 120°.


\(\eta^3\)-Allyldichloro(triphenylphosphine)palladium.

Borylsilylation.°\(^1\) (Chlorodimethylsilyl)pinacolatoborane adds to 1-alkynes to give 1-pinacolatoboryl-2-silylalkenes. The relative amount of the addends is the determinant factor in the stereochemical outcome of the reaction

Allylstannanes.

Allyl addition.°\(^1\) Diastereoselectivity for the addition of an allyl group to hexacarbonyldicobalt complexes of 4-hydroxy-2-alkynals is much higher using allyltriphenylstannane instead of the tributyl congener.
Aluminum bromide.

Reductive phenylation.¹ Naphthalenediols and benzene combine to afford hydroxytetralones. The transformation occurs when the mixtures of the aromatic compounds are treated with an excess of AlBr₃.


Aluminum chloride.

Friedel–Crafts acylation. A synthesis of chilenine is completed by a two-fold Friedel–Crafts acylation of an N-(arylethyl)amide with oxalyl chloride.¹

Acylation of arylidenecyclobutanes is accompanied by ring expansion.² A route to norbornen-7-ones entails an intramolecular desilylative Friedel–Crafts acylation.³ Such compounds are not directly accessible by a Diels–Alder reaction.
Carbimination. Thiophene and N-substituted pyroles and indoles undergo electrophilic substitution with ArNC at room temperature. The reaction gives imines as products.4

Aromatization. Treatment of 6-hydroxy-1,2,3,6-tetrahydro-N-tosyl-3-pyridones with AlCl3 in MeNO2 at –78° brings about dehydration and O-tosylation to give 3-tosyloxy pyridines.5

4Tobisu, M., Yamaguchi, S., Chatani, N. OL 9, 3351 (2007).

Aluminum dimethylamide.

Transamination.1 Tertiary amides are converted to secondary amides on reaction with secondary amines in the presence of Al2(NMe2)6.


Aluminum iodide.

Baylis–Hillman reaction. Ethyl propynoate apparently undergoes iodoalumination to generate a nucleophilic species that adds onto carbonyl compounds. (Z)-β-Iodoacrylic esters are produced.1


Aluminum tris(2,6-diphenylphenoxide), ATPH.

Macrolide synthesis.1 By way of an intramolecular aldol reaction using ATPH and LiTMP, macrocyclic (10-, 12-, and 14-membered) lactones are formed.
Aluminum triflate.

Cycloisomerization. An oxime function is liable to add to a double bond at an appropriate distance and the reaction is realized by heating unsaturated oximes with Al(OTf)$_3$ in MeNO$_2$.

Aminocarbenes.

Reviews. Applications of heterocyclic carbenes in organic synthesis have been reviewed.

Aldol reactions. Enolization of ketones at room temperature (and ensuing silylation) is readily effected by 1,3-bis(1-adamantyl)imidazol-2-ylidene. Accordingly, Mukaiyama aldol reaction is accomplished under the appropriate conditions.

Baylis–Hillman reaction products are obtained in an unconventional manner from α-silylpropargyl alcohols and aldehydes, using 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene as catalyst.

Acyloin condensation. Carbene species (for promoting intramolecular acyloin condensation) are more readily generated from 1,2,4-triazolium salts when one of the N-substituents is highly electron-deficient (e.g., 1). The bicyclic triazolium salt 2 derived
from pyroglutamic acid catalyzes benzoin condensation in modest yields, in which electron-rich ArCHO is less reactive but better asymmetric induction is observed.\(^7\)

\[
\begin{align*}
\text{(1)} & \quad \text{Me}_3\text{SiO} & & \text{Ph} & & \text{BF}_4^- \\
\text{(2)} & \quad \text{CF}_3 & & \text{H} & & \text{N} \\
\end{align*}
\]

Analogous condensation of ArCHO and aldimines gives \(\alpha\)-amino ketones.\(^8\)

**Carboxylic derivatives.** A mixture of an aldehyde and a nitrosoarene is converted into an \(N\)-arylhydroxamic acid on treatment with 3 and DBU,\(^9\) whereas \(\alpha,\alpha\)-dichloro aldehydes gives \(\alpha\)-chloro carboxamides in the presence of amines under similar conditions.\(^10\) A mild organic base is needed to generate the carbene (and a slight variation of the catalyst system for the same reaction comprises the \(N\)-mesityltriazolium chloride and imidazole base.\(^11\))

\[
\begin{align*}
\text{(3)} & \quad \text{Ph} & & \text{CHO} & & \xrightarrow{\text{RNH}_2} & & \text{Ph} & & \text{CONHR} \\
\end{align*}
\]

There is a significant difference in reaction profile for the reaction of enals with nitrosoarenes. Isoxazolidin-5-ones are formed and alcoholysis of which leads to \(\beta\)-arylamino esters.\(^12\) With the nitroarenes replaced by aryazo carbonyl compounds to perform the reaction 3-oxopyrazolidinones result.\(^13\)

As a redox process, the ring expansion of \(\beta\)-formyl-\(\beta\)-lactams to furnish succinimides\(^14\) and the ring scission of 2-nitrocyclopropanecarbaldehydes\(^15\) are also mediated by an azocarbene.
Enals generated by oxidation of allylic alcohols with MnO$_2$ in the presence of azolium ylides are trapped to form secondary allylic alcohols. These are subject to further oxidation and the resulting ketones undergo alcoholysis in situ.$^{16}$

**Antimony(V) chloride.**

**Indanones.**$^1$ trans-2,3-Disubstituted indanones are produced in reasonably good yields from a mixture of arylalkynes and aldehydes with EtOH (1 equiv.) as additive, by treatment with SbCl$_5$.

Arylboronic acids.

Amide formation. o-Halophenylboronic acids catalyze the Diels–Alder reaction of acrylic acid as well as condensation of carboxylic acids with amines at room temperature (in the presence of 4A-molecular sieves).\(^1\)

A thorough study indicates that (1-methyl-4-pyridinio)boronic acid iodide is a superior catalyst for amidation under azeotropic conditions, and esterification of 2-hydroxyalkanoic acids.\(^2\)

\(^1\)Al-Zoubi, R.M., Marion, O., Hall, D.G. ACIE 47, 2876 (2008).

N-Arylsulfinylimines.

Imido transfer.\(^1\) Aldehydes are converted into RCH─NAr on reaction with ArN─S─O, using catalysts such as VOCl\(_3\), MoOCl\(_3\), and MoO\(_2\)Cl\(_2\).


Azobisisobutyronitrile.

Deallylation. Allyl carboxylates are hydrolyzed under neutral conditions on treatment with AIBN (10 mol%) and water. This radical deallylation generally proceeds in high yields.\(^1\)

Oxidative cyclization. Alkynamyllactams cyclize by reaction with PhSH and AIBN, involving carbon radical shuffle.\(^2\)

\(^2\)Denes, F., Beaufis, F., Renaud, P. OL 9, 4375 (2007).