TSE-LOK HO

Fiesers' Reagents for Organic Synthesis

VOLUME
28

WILEY

Reagents for Organic Synthesis

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VOLUME TWENTY EIGHT

Tse-Lok Ho

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PREFACE

This volume covers progress of synthetic organic methodologies for the period between the second half of 2011 and the end of 2012, also a few items of yester-years. The major advances have been refinements of reagent applications and expansion of the scope. Although ligands still figure prominently in affecting reactivities of transition metal ions, work aiming at finding ligand-free reactions remains an honorable goal. Fruitful developments concerning oxidative coupling reactions that eschew halogen compounds are also in evidence. It is noted that burgeoning contributions to synthetic methodology are coming from Chinese chemists, perhaps reflecting societal changes from one of most populous nations. Or they are spiritually ingrained in the expostulation of the benevolent Han tribe leader, King Tang of the Shang Dynasty (商湯), who had a bath tub engraved to remind himself to refine his character while cleansing:

REINVIGORATE TODAY　　苟日新
REINVIGORATE EVERY DAY　日日新

Doesn't this maxim somehow coincide with the effort of synthetic organic chemists?

GENERAL ABBREVIATIONS

Ac	acetyl
acac	acetylacetonate
Ad	1-adamantyl
AIBN	2,2′-azobisisobutyronitrile
aq	aqueous
Ar	aryl
9-BBN	9-borabicyclo[3.3.1]nonane
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
BINOL	1,1′-binaphthalene-2,2′-diol
Bn	benzyl
Boc	*t*-butoxycarbonyl
bpy	2,2′-bipyridyl
bpz	2,2′-bipyrazine
BQ	1,4-benzoquinone
Bs	benzenesulfonyl
Bu	*n*-butyl
Bz	benzoyl
18-c-6	18-crown-6
c-	cyclo-
CAN	cerium(IV) ammonium nitrate
cap	caprolactamate
Cbz	benzyloxycarbonyl
cod	1,5-cyclooctadiene
Cp	cyclopentadienyl
*Cp**	1,2,3,4,5-pentamethylcyclopentadienyl
CSA	10-camphorsulfonic acid
Cy	cyclohexyl
DABCO	1,4-diazabicyclo[2.2.2]octane
DAST	(diethylamino)sulfur trifluoride
dba	dibenzylideneacetone
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	1,3-dicyclohexylcarbodiimide
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DEAD	diethyl azodicarboxylate

DIAD	diisopropyl azodicarboxylate
Dibal-H	diisobutylaluminum hydride
DMA	*N,N*-dimethylacetamide
DMAP	4-dimethylaminopyridine
DMDO	dimethyldioxirane
DME	1,2-dimethoxyethane
DMF	*N,N*-dimethylformamide
DMPU	*N,N′*-dimethylpropyleneurea
DMSO	dimethyl sulfoxide
DPM	dipivaloylmethane
DPPB	1,4-bis(diphenylphosphino)butane
DPPE	1,2-bis(diphenylphosphino)ethane
DPPF	1,1′-bis(diphenylphosphino)ferrocene
DPPP	1,3-bis(diphenylphosphino)propane
DTTB	4,4′-di-*t*-butylbiphenyl
ee	enantiomer excess
Et	ethyl
Fc	ferrocenyl
Fmoc	9-fluorenylmethoxycarbonyl
Fu	2-furyl
HMDS	hexamethyldisilazane
HMPA	hexamethylphosphoric amide
Hx	*n*-hexyl
L	ligand
LAH	lithium aluminum hydride
LDA	lithium diisopropylamide
LHMDS	lithium hexamethyldisilazide
LiDBB	lithium 4,4′-di-*t*-butylbiphenylide
LTMP	lithium, 2,2,6,6-tetramethylpiperidide
LN	lithium naphthalenede
MCPBA	*m*-chloroperbenzoic acid
Me	methyl
MEM	methoxyethoxymethyl
Mes	mesityl
MOM	methoxymethyl
Ms	methanesulfonyl
MS	molecular sieve
MTO	methyltrioxorhenium
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
NIS	*N*-iodosuccinimide

NMO	*N*-methylmorpholine *N*-oxide
NMP	*N*-methylpyrrolidone
Np	naphthyl
Ns	*p*-nitrobenzenesulfonyl
Nu	nucleophile
Oc	*n*-octyl
PEG	poly(ethylene glycol)
Ph	phenyl
Phen	1,10-phenanthroline
Pht	phthaloyl
Pin	pinacolato
Piv	pivaloyl
PMB	*p*-methoxybenzyl
PMHS	poly(methylhydrosiloxane)
PMP	*p*-methoxyphenyl
Pr	*n*-propyl
Py	pyridine
RaNi	Raney nickel
RCM	ring-closing metathesis
R^F	perfluoroalkyl
ROMP	ring opening methathesis polymerization
s-	secondary
salen	*N,N′*-ethenebis(salicylideneiminato)
SAMP	(*S*)-1-amino-2-methoxymethylpyrrolidine
SEM	2-(trimethylsilyl)ethoxymethyl
SES	2-[(trimethylsilyl)ethyl]sulfonyl
TBAF	tetrabutylammonium fluoride
TBDPS	*t*-butyldiphenylsilyl
TBS	*t*-butyldimethylsilyl
TEMPO	2,2,6,6-tetramethylpiperidinoxy
TES	triethylsilyl
Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid
TFAA	trifluoroacetic anhydride
THF	tetrahydrofuran
THP	tetrahydropyranyl
TIPS	triisopropylsilyl
TMEDA	*N,N,N′,N′*-tetramethylethanediamine
TMS	trimethylsilyl
Tol	*p*-tolyl
tpp	tetraphenylporphyrin

Ts	*p*-toluenesulfonyl
TSE	2-(trimethylsilyl)ethyl
Z	benzyloxycarbonyl
Δ	heat
))))	ultrasound

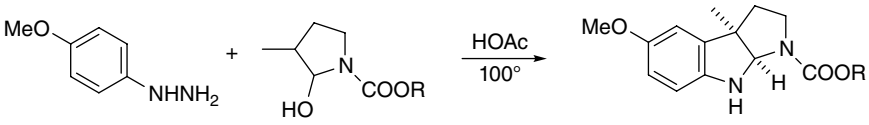
REFERENCE ABBREVIATIONS

ACIE	Angew. Chem. Inter. Ed.
ASC	Adv. Synth. Catal.
CAJ	Chem. Asian J.
CC	Chem. Commun.
CEJ	Chem. Eur. J.
ChJC	Chinese. J. Chem.
CL	Chem. Lett.
CO	ChemistryOpen
CS	Chem. Science
CSR	Chem. Soc. Rev.
EJOC	Eur. J. Org. Chem.
HCA	Helv. Chim. Acta
JACS	J. Am. Chem. Soc.
JCCS	J. Chinese Chem. Soc.
JOC	J. Org. Chem.
OBC	Org. Biomol. Chem.
OL	Org. Lett.
S	Synthesis
SL	Synlett
T	Tetrahed.
TL	Tetrahed. Lett.

A

Acetic acid

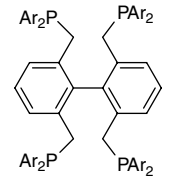
Fischer indole synthesis. The pyrroloindole ring system characterized of the physostigmine alkaloids is formed in the interrupted indolization between an arylhydrazine and *N*-protected 2-hydroxy-3-methylpyrrolidine, and it is accomplished in hot HOAc.[1]



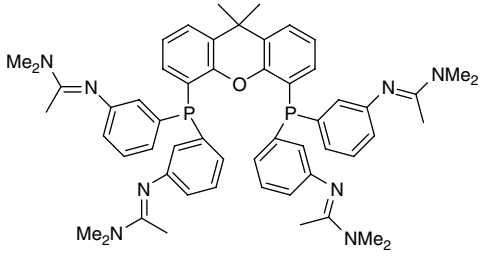
[1] Schammel, A.W., Chiou, G., Garg, N.K. *JOC* **77**, 725 (2012)

Acetylacetonato(dicarbonyl)rhodium(I)

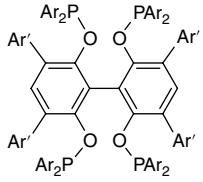
Addition. With ligand **1** hydroformylation of 2-alkenes catalyzed by (acac)Rh(CO)$_2$ proceeds via a double bond shift.[1] In the presence of an amine the reaction becomes a hydroamination process (amino group introduced at the carbon chain terminus).[2]



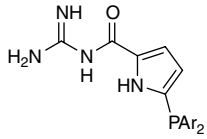
(**1**)



(**2**)



(**3**) Ar = pyrrol-1-yl
Ar′ = 2,4-$F_2C_6H_3$



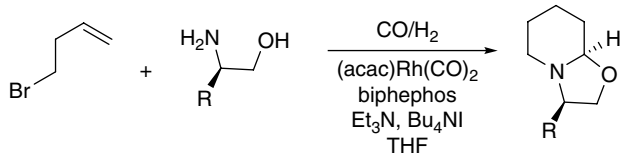
(**4**)

Fiesers' Reagents for Organic Synthesis, First Edition. Tse-Lok Ho.

Ligand **2** is for linear hydroformylation of 1-alkenes, in which the amidate groups bring the catalyst into the aqueous phase as the bicarbonate salt is formed.[3] Developed for highly linear hydroformylation of 1-alkenes, including allyl cyanides, is a ligand series represented by **3**.[4]

When ligands such as **4** for the Rh catalyst are used the aldehyde products undergo reduction to yield primary alcohols.[5] Simpler ligands such as $(4\text{-}FC_6H_4)_3P$ can be used in the hydroacylation of enamides to form 1,4-dicarbonyl compounds.[6]

Homoallylic alcohols form 5-membered cyclic products even if the new CC bond formation is with the internal sp^2-carbon atom.[7] Double trapping of the homologous aldehyde derived from 4-bromo-1-butene with 2-phenyl-2-aminoethanol leads to a bicyclic heterocycle which is amenable to substitution at the α-carbon to the nitrogen atom.[8]



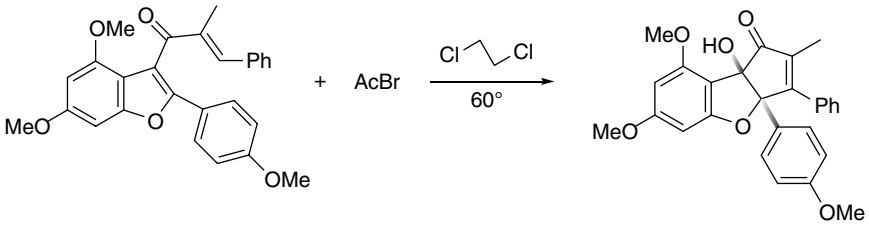
Under normal hydroformylation condition but with addition of a secondary amine and 2,2′,6,6′-tetrakis(diphenylphosphinomethyl)biphenyl to the reaction mixture, Schiff bases are formed and then reduced.[9]

Decarbonylation. The removal of CO from 2-(2-acylaryl)pyridines by heating with $(acac)Rh(CO)_2$ is of synthetic interests because the ketone substrates are generally more readily accessible.[10]

[1] Cai, C., Yu, S., Liu, G., Zhang, X., Zhang, X. *ASC* **353**, 2665 (2011)
[2] Liu, G., Huang, K., Cao, B., Chang, M., Li, S., Yu, S., Zhou, L., Wu, W., Zhang, X. *OL* **14**, 102 (2012)
[3] Mokhadinyana, M., Desset, S.L., Williams, D.B.G., Cole-Hamilton, D.J. *ACIE* **51**, 1648 (2012)
[4] Cai, C., Yu, S., Cao, B., Zhang, X. *CEJ* **18**, 9992 (2012)
[5] Fuchs, D., Rousseau, G., Diab, L., Gellrich, U., Breit, B. *ACIE* **51**, 2178 (2012)
[6] Zhang, H.-J.,Bolm, C. *OL* **13**, 3900 (2011)
[7] Ueki, Y., Ito, H., Usui, I., Breit, B. *CEJ* **17**, 8555 (2011)
[8] Zill, N., Schoenfelder, A., Girard, N., Taddei, M., Mann, A. *JOC* **77**, 2246 (2012)
[9] Liu, G., Huang, K., Cai, C., Cao, B., Chang, M., Wu, W., Zhang, X. *CEJ* **17**, 14559 (2011)
[10] Lei, Z.-Q., Li, H., Li, Y., Zhang, X.-S., Chen, K., Wang, X., Sun, J., Shi, Z.-J. *ACIE* **51**, 2690 (2012)

Acetyl bromide

Nazarov cyclization. Cross-conjugated ketones in which one of the double bonds belongs to a benzofuran nucleus undergo Nazarov cyclization.[1] Enolacetylation to create a highly electrophilic moiety for the reaction to proceed is most likely.



[1] Magnus, P., Freund, W.A., Moorhead, E.J., Rainey, T. *JACS* **134**, 6140 (2012)

1-Acyl-1,5-diazabicyclo[4.3.0]non-5-ene tetraphenylborates

O-Acylation. These reagents are excellent acyl donors to OH-compounds.[1]

[1] Taylor, J.E., Williams, J.M.J., Bull, S.D. *TL* **53**, 4074 (2012)

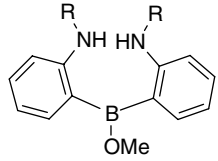
1-Acylpyrazoles

Acylation. A review of the acylating capability of 1-acylpyrazoles has been published.[1]

[1] Goldys, A.M., McErlean, C.S.P. *EJOC* 1877 (2012)

Alkoxybis(2,2′-aminomethylphenyl)boranes

Alcoholysis. Alkoxyboranes **1** are useful catalysts for cleavage of 1,3-dicarbonyl compounds such as β-keto esters and *N*-acylamides by alcohols under essentially neutral conditions. These boranes perform activation on both reactants.[1]

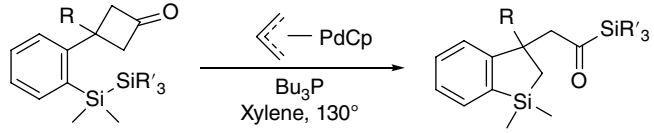


(**1**) R = Me, Cy

[1] Oishi, S., Saito, S. *ACIE* **51**, 5395 (2012)

η^3-Allyl(cyclopentadienyl)palladium

Cyclomutation.[1] Cleavage of the small ring of 3-arylcyclobutanones that is *o*-substituted by a heteroatom group such as disilane is attended by heterocyclization.



Decarboxylation. Benzyl cyanoacetates extrude CO_2 while the remaining parts recombine to afford 3-arylpropanenitriles. In the case of 2-furylmethyl cyanoacetates the choice of the phosphine ligand affects the recombination step. It can be coaxed toward formation of 2-cyanomethyl-5-methylfurans.[2]

[1] Ishida, N., Ikemoto, W., Murakami, M. *OL* **14**, 3230 (2012)
[2] Recio III, A., Heinzman, J.D., Tunge, J.A. *CC* **48**, 142 (2012)

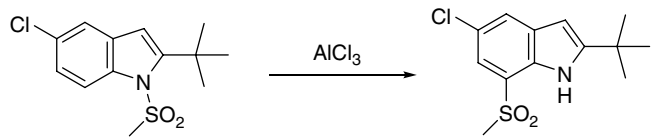
η^3-Allylpalladium molybdosulfide

Allylation.[1] In the presence of $(\eta^3\text{-}C_3H_5)Pd(S_4Mo_3)$ the allylation of arylamines can use allyl alcohol. The allyl group is to be attached to C-3 of an indole nucleus.

[1] Tao, Y., Wang, B., Zhao, J., Song, Y., Qu, L., Qu, J. *JOC* **77**, 2942 (2012)

Aluminum chloride

Group migration. On treatment with $AlCl_3$, the protecting group of *N*-mesylindoles migrates to C-7.[1]



Mannich reaction.[2] Condensation of ArCHO, MeCN and MeCOAr' to afford $ArCH(NHAc)CH_2COAr'$ is observed on treatment with $AlCl_3$ and AcCl. β-Keto esters undergo a similar reaction.

Cyclization. γ,δ–Unsaturated ketones cyclize to form a benzene ring in the presence of $AlCl_3$ in dioxane.[3]

Ether cleavage.[4] Ethers are split by silyldealkylation of ethers using R_3SiCl, with $AlCl_3$ or $FeCl_3$ or $BiCl_3$ as promoter. The other products are RCl.

[1] Prasad, B., Adepu, R., Sandra, S., Rambabu, D., Krishna, G.R., Reddy, C.M., Deora, G.S., Misra, P., Pal, M. *CC* **48**, 10434 (2012)
[2] Ali, Z.M., Ardeshir, K., Mohammad, M., Abdolkarim, Z., Maliheh, S., Fatemeh, D.-P., Hassan, K., Ahmad, A.D.-F., Maria, M. *ChJC* **30**, 345 (2012)
[3] Narender, T., Sarkar, S., Rajendar, K., Tiwari, S. *OL* **13**, 6140 (2011)
[4] Wakabayashi, R., Sugiura, Y., Shibue, T., Kuroda, K. *ACIE* **50**, 10708 (2011)

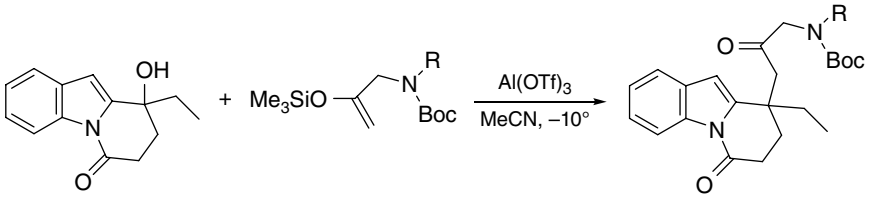
Aluminum fluoride

CH activation. High-surface AlF_3 is able to activate aliphatic C-H bond under very mild conditions (at 40°), and this property can be exploited by deuteration.[1]

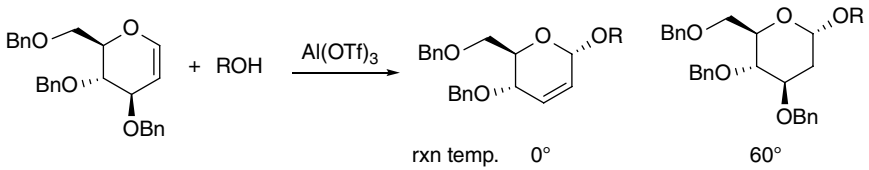
[1] Prechtl, M.H.G., Teltewskoi, M., Dimitrov, A., Kemnitz, E., Braun, T. *CEJ* **17**, 14385 (2011)

Aluminum triflate

Substitution. Benzyl and cinnamyl alcohols are easily converted into the corresponding amines with the aid of $Al(OTf)_3$.[1] Substitution using other nucleophiles are equally smooth, as exemplified in the construction of an intermediate for a synthesis of mersicarpine.[2]



The reaction of tri-*O*-benzylglucal with an alcohol on catalysis by $Al(OTf)_3$ temperature can change the reaction mechanism.[3] At 0° Ferrier rearrangement products are formed but at 60° addition to the double bond is favored.



[1] Ohshima, T., Ipposhi, J., Nakahara, Y., Shibuya, R., Mashima, K. *ASC* **354**, 2447 (2012)
[2] Zhong, X., Li, Y., Han, F.-S. *CEJ* **18**, 9784 (2012)
[3] Williams, D.B.G., Simelane, S.B., Kinfe, H.H. *OBC* **10**, 5636 (2012)

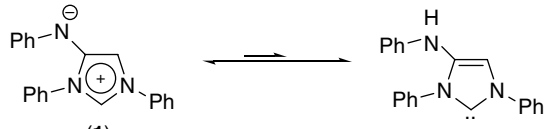
Aluminum tris(2,6-di-β-naphthoxide)

Vinylogous aldol reaction.[1] The title reagent is a more bulky analog of ATPH and perhaps more sensitive to steric effects. Its application as catalyst in site-selective condensation such as reaction between crotonic esters and aldehydes to form 5-hydroxy-2-alkenoates has been demonstrated.

[1] Gazaille, J.A., Sammakia, T. *OL* **14**, 2678 (2012)

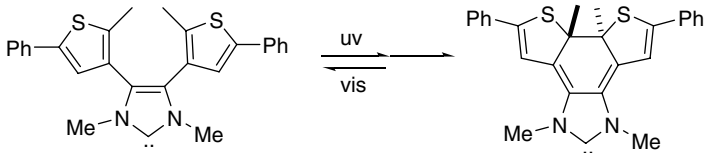
Aminocarbenes

Structural variations. The commercially available mesionic "Nitron" has an *N*-heterocyclic carbene (NHC) tautomer, but its application in directing reactions has yet to be explored.[1] Electron properties and stability of imidazole-based mesionic carbenes (imidazol-5-ylidenes) are found to be inversely correlated.[2]



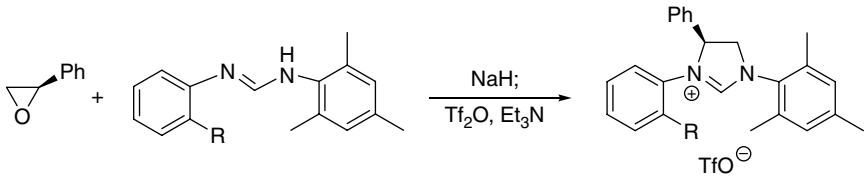
(**1**)

Imidazolium and imidazolinium bicarbonate salts are air-stable precursors of NHC's.[3] 1,3-Bis(2,6-dimethoxyphenyl)imidazol-2-ylidene is a typical electron-rich carbene.[4] A photoswitchable NHC pair is **2A** and **2B**, interconverted by uv and visible lights.[5]

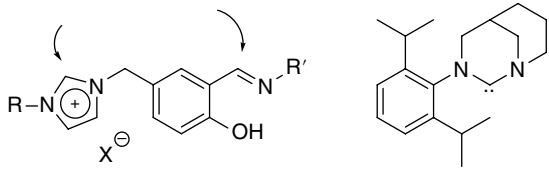


(**2A**) (**2B**)

A convenient method for synthesis of chiral imidazolium salts, precursors of NHC's, is based on reaction of *N,N′*-disubstituted amidines and chiral oxiranes.[6]

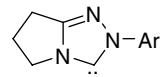


Imidazolium salts that bear an *N*-substituent extended to a salicyldiminato function are versatile precursors of multipurpose and tunable catalysts. Two sites for metal bonding are obvious.[7] A new type of the carbene is represented by **3** which in placing one of the nitrogen atoms at a bridgehead prevents its lone pair electrons to delocalize and therefore increases the electrophilicity of the carbene center while keeping nucleophilicity the same.[8]



(**3**)

Reduction. Transfer reduction of carbonyl compounds by *i*-PrOH is effected with 1,3-diarylimidazolium tetrafluoroborate (each aryl group being 4-substituted) and KOH.[9] Ketones and imines are reduced via hydrosilylation, with **4A** as catalyst.[10] By this procedure the multiple bond of propargylic alcohols and cinnamyl alcohols are reduced, the former class of compounds to be converted into allylic alcohols.[11]

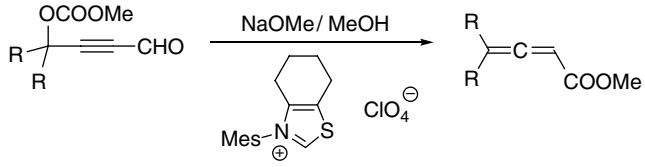


(**4A**) Ar = Ph
(**4B**) Ar = Mes
(**4C**) Ar = C_6F_5

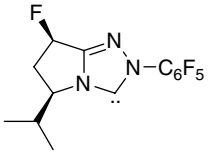
Formation of 3-acyloxy-2-indolinones from isatins and aldehydes is achieved by heating with **4B** and *t*-BuOK in toluene.[12] The aldehydes become the acyl moiety. The effect of **4B** on tri-*O*-benzylfuranoses such as the ribose derivative is that debenzyloxylation occurs at C-2 while oxidation to the γ-lactones is the complementary reaction.[13]

Oxidative functionalization of aldehydes. The most extensive uses of NHC's appear to involve transformation of aldehydes. For example, under oxygen aldehydes and alkyl halides form esters under the influence of the ylide (carbene) derived from 3,4-dimethylthiazole iodide.[14] Type **4** NHC unites aldehydes and thiols to give thioesters,[15] and carboxylic acids are obtained when **4C** exerts its effect.[16] Aldehydes and $ArB(OH)_2$ also combine to yield aryl esters,[17] otherwise anodic oxidation of aldehydes in alcohols to furnish esters is catalyzed by a thiazole carbene.[18]

α-Halocinnamaldehydes lose the halogen substituent during conversion to the cinnamic esters,[19] and an intramolecular redox transformation of 2-alkynals with a carbonato substituent at C-4 leads to 2,3-alkadienoic esters.[20]



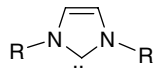
Addition. α-Cyanohydrin ester formation[21] from aldehydes on NHC-catalyzed reaction with acetyl cyanide or ethyl cyanoformate is somewhat unusual. The fluorinated carbene **5** is useful for promoting hydroacylation of cinnamic esters by aldehydes.[22]



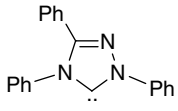
(**5**)

Perhaps the perennial favorite among NHC's, **6A** (often called IPr), helps the union of dimethylamine and CO to form DMF.[23] Actually a general procedure for formylation of amines is that involving a polysiloxane.[24]

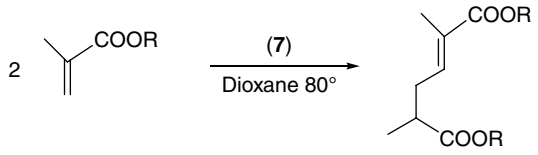
The triazole-based carbene **7** can cause tail-to-tail dimerization of methacrylic esters[25] because it confers the β-carbon of the ester with anionic properties.[26]



(**6A**) R = 2,6-*i*Pr$_2$C$_6$H$_3$
(**6B**) R = 2,4,6-Me$_3$C$_6$H$_2$
(**6C**) R = Cy



(**7**)

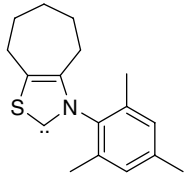


Conjugate addition of aldehydes to vinyl sulfones is akin to the Stetter reaction. A bicyclic thiazole carbene **8** is an active catalyst.[27] However, a carbene can transform α-bromo enals into acylate azolium salts which act as Michael acceptors for β-keto esters.[28]

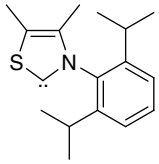
Stable esters can be activated by carbenes to form enolates (not involving ketene intermediates), as shown by a synthesis of 3,4-dihydropyridones from reaction with conjugated imines.[29]

In conjunction with metallic catalysts that fashion and combine a 2-diazo-1,3-diketone and a functionalized alkene ready for Michael addition, an NHC effectively completes the final step leading to a spirolactone or lactam.[30]

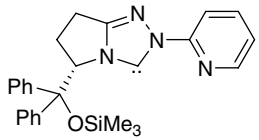
Benzoin condensation and related reactions. Cross-benzoin condensation using **9** which is generated in situ also from a perchlorate salt is successful.[31] As for asymmetric benzoin condensation, **10** has been developed.[32]



(**8**)

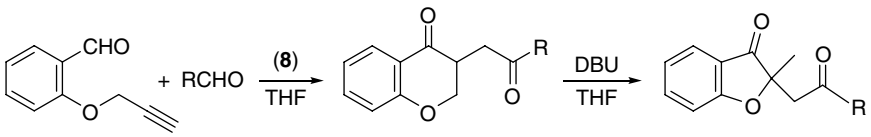


(**9**)

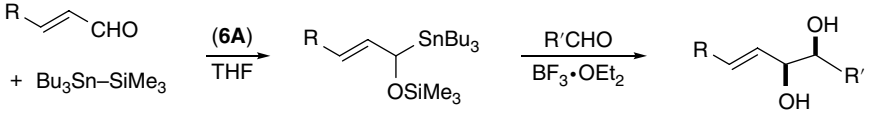


(**10**)

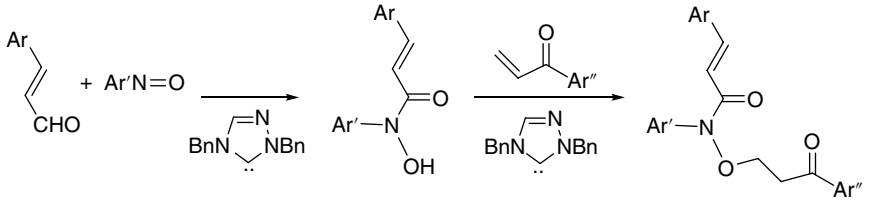
It is quite remarkable that two research groups reported at about the same time the same kind of transformation using the same bicyclic thiazole carbene **8**.[33,34]



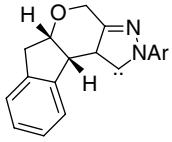
Conjugated aldehydes form 1-tributylstannyl-1-trimethylsiloxy-2-alkenes in a carbene-mediated reaction. The adducts are useful for synthesis of unsaturated diols by further reaction with RCHO in the presence of $BF_3{\cdot}OEt_2$.[35]



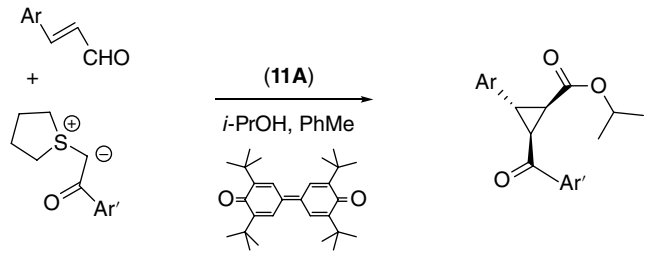
N-(2-Aroylethoxyl) cinnamides are assembled from cinnamaldehydes, nitrosoarenes and aryl vinyl ketones. The first step which forms the hydroxamic acids can be considered as an aza-benzoin condensation.[36]



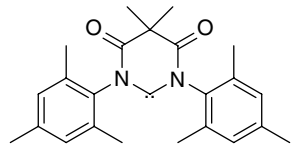
Annulation. The sulfur ylide reaction with electron-deficient alkenes to form cyclopropane derivatives as applied to conjugated aldehydes can give ester products by intervention of carbene **11A**.[37] In the case of spirlactonization of isatin a conjugated aldehyde is transformed into an equivalent of a chiral carboxylic acid β-anion by *ent*-**11B**.[38] Oxindole-3-imines form spirolactams on reaction with conjugated aldehydes.[39]



(**11A**) Ar = Mes
(**11B**) Ar = 2,6-$Et_2C_6H_3$

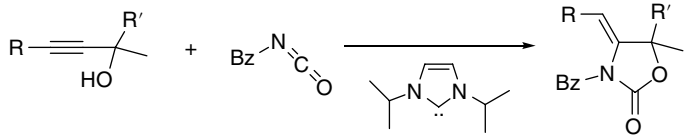


Total consumption of **12** on reaction with alkynes is as expected, adducts of which afford cyclopropenones on hydrolysis.[40] Nitriles also undergo cycloaddition with **12**.



(**12**)

Along with a Lewis acid, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene **6A** or its dihydro derivative is capable of mediating insertion of CO_2 into oxiranes to yield dioxolan-2-ones.[41] A similar transformation is the formation of 4-alkylidene-oxazolidin-2-ones where a carbene serves as a Brønsted base.[42]

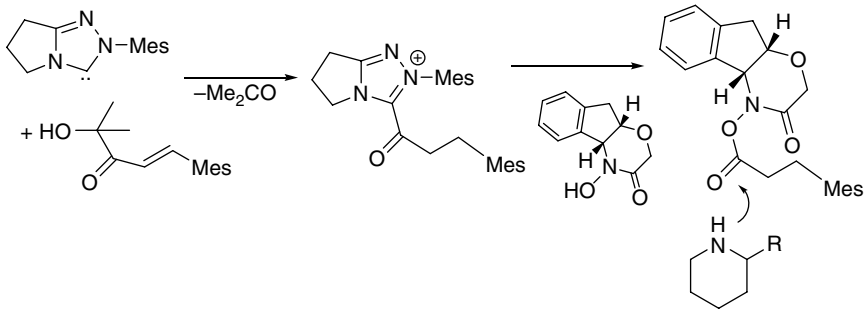


NHC's help unfold the nucleophilicity of saturated aldehydes, as seen in the facile assemblage of 3,4-dihydro-2-pyrones and 2-pyridones.[43] A formal [3+2]cycloaddition between conjugated aldehydes and isatin imines leads to spiroannulated oxindoles, with the formyl group being converted into a lactamic carbonyl by intervention of **6B**.[44]

Decomposition of the Diels-Alder adduct of 1-trimethylsiloxy-1,3-butadiene and acrylyl fluoride to afford 1,3-cyclohexadiene is a favorable reaction, in which Me_3SiF and CO_2 are eliminated.[45] The role of carbene for the two-step process is not clear.

A theoretical study (DFT calculation) indicates the cocatalytic NHC and $Ti(OR)_4$ to develop *cis*-3,4-disubstituted cyclopentenes is due to involvement of a chelated intermediate.[46]

Kinetic resolution. 2-Substituted cyclic amines are resolved via *N*-acylation. The acylating agent is derived from a chiral *O*-acylhydroxamate.[47]



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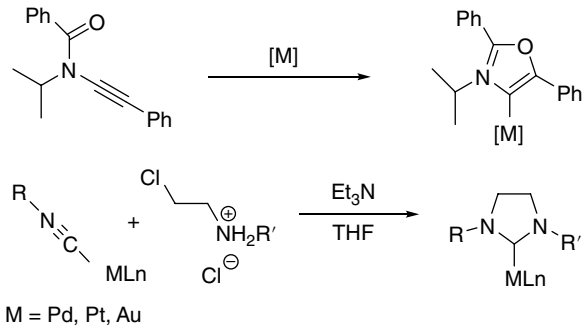
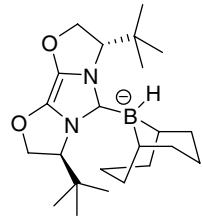
Aminocarbene - metal complexes

The more extensively employed metal-carbene complexes are grouped and discussed individually.

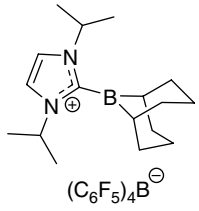
Preparation. Ynamides are useful precursors of unstable NHC's.[1]



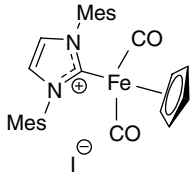
Reduction. Ligand exchange removes Me_2S from borane and the boron atom is linked to a carbene center, the resulting stable solid (to air, water and chromatography) retains power of reducing the carbonyl group with silica promotion.[2] One, two or all three hydrides is transferrable, and no quench or workup is needed. Furthermore, aldehydes can be reduced selectively in the presence of ketones. The use of a more complex entity **12** for asymmetric reduction also has been reported.[3] The salt **13** is a catalyst for hydrogenation of imines and enamines,[4] whereas the iron complex **14A** is active in hydrosilylation of imines under visible light.[5] Complex **14B** is prepared from the imidazolium iodide with an N-substituent bearing a terminal cyclopentadiene unit and $Fe_3(CO)_{12}$, and it serves as a catalyst for sulfoxide reduction.[6]



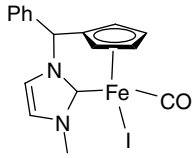
(**12**)



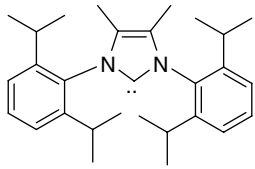
(**13**)



(**14A**)



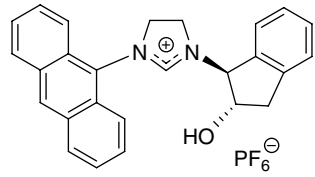
(**14B**)



(**15**)

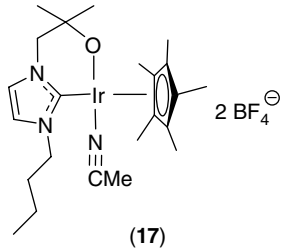
Catalyzing semihydrogenation of alkynes, allenes and dienes with hydrosilane assisted by the complex **15** is a pleasing discovery.[7]

Substitution. Regioselective S_N2' displacement of allyl phosphates with organoboronates is achieved, using the unsymmetrical carbene complex generated from **16** and CuCl.[8] For carboxylation of benzoxazole and benzothiazole the effectiveness of a 1,2, 3-triazol-5-ylidene CuCl is recognized.[9]



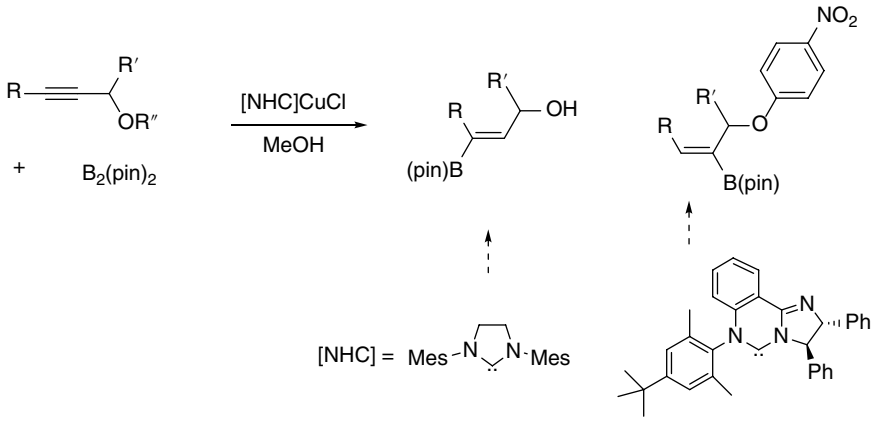
(**16**)

Primary alcohols are viable substrates for *N*-alkylation of amines, when the iridium complex **17** is present in the reaction media.[10]



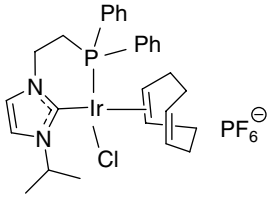
(**17**)

Addition. Hydroboration of propargylic alcohols with (bispinacolato)diboron places the boryl group at the carbon farther from the hydroxyl function, but that of their *p*-nitrophenyl ethers shows an opposite regioselectivity, although different Cu-carbenoids are involved.[11]

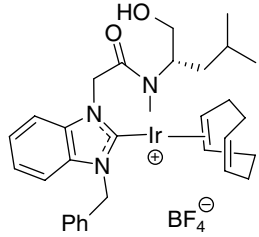


Alkylboranes obtained from hydroboration with 9-BBN deliver 1-aminoalkanes on reaction with hydroxylamine *O*-benzoates in the presence of **5C**-CuCl.[12] Carboxylation is done with CO_2 (catalyst from **6A**-CuCl and MeOLi).[13] Borylcarboxylation of alkynes catalyzed by a copper(I)-carbene provides 4-borato-2-buten-4-olides which are valuable substrates for Suzuki coupling.[14]

An iridium(I) salt in which the metal center is surrounded by **6B**, 1,5-cyclooctadiene, and Bn_3P is serviceable for hydrogenation of alkenes.[15] Another complex (**18**) that one of the imidazoline nitrogen atoms is connected to a phosphinated sidechain is able to catalyze transfer hydrogenation of conjugated ketones (to give saturated alcohols), as well as alkylation of α-arylethanol with primary alcohols [to yield ArCH(OH)CH_2CH_2R],[16] hydrosilylation to produce chiral benzylic alcohols is effected in the presence of **19**.[17]

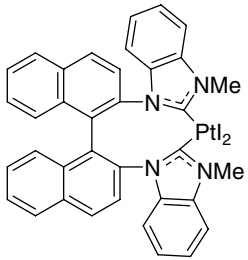


(**18**)

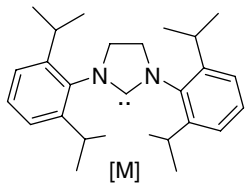


(**19**)

An ionic Pt-complex derived from **20** and $AgBF_4$ is shown to promote intramolecular hydroamination.[18] For accomplishing selective cyclization involving one of two double bonds a lanthanide complex (**21**) proves its value.[19]

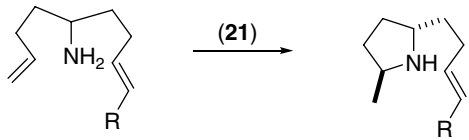


(**20**)



[M] = $Sc(NSiMe_3)_2$, $Y(NSiMe_3)_2$

(**21**)



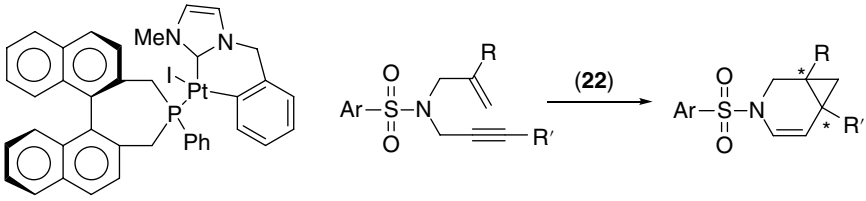
Condensation of RCHO, amines and 1-alkynes to form propargylic amines is also effected by a carbene-AgOAc complex.[20]

(*E*)-3-Chloro-2-alkenoylarenes are adducts of ArCOCl and 1-alkynes, formed in a reaction catalyzed by **6A**-Ir(cod)Cl.[21]

Upon conversion of the type **6** carbene-bound CuCl to CuF·HF by $AgHF_2$ or $Et_3N(HF)_3$ - *t*-BuOK, a catalytic activity for promoting diastereoselective allylation of *N*-*t*-butanesulfinyl aldimines is revealed.[22]

Change of a non-carbene ligand to modify properties of the complex is also the case of **6A**-$GaCl_3$, the replacement of a chlorine atom with a 2,4,6-trifluorophenylcyanide ligand renders the resulting complex more active as a π-Lewis acid with increasing resistance to hydrolysis.[23]

Cycloisomerization. The Pt-carbenoid **22** is the motivator for transforming 1,6-enynes to bicycle[4.1.0]heptenes.[24]



(**22**)

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[2] Taniguchi, T., Curran, D.P. *OL* **14**, 4540 (2012)
[3] Curran, D.P., Solovyev, A., Brahmi, M.M., Fensterbank, L., Malacria, M., Lacôte, E. *ACIE* **50**, 10294 (2011)
[4] Farrell, J.M., Hatnean, J.A., Stephan, D.W. *JACS* **134**, 15728 (2012)
[5] Castro, L.C.M., Sortais, J.-B., Darcel, C. *CC* **48**, 151 (2012)
[6] Cardoso, J.M.S., Royo, B. *CC* **48**, 4944 (2012)
[7] Semba, K., Fujihara, T., Xu, T., Terao, J., Tsuji, Y. *ASC* **354**, 1542 (2012)
[8] Shintani, R., Takatsu, K., Takeda, M., Hayashi, T. *ACIE* **50**, 8656 (2011)
[9] Inomata, H., Ogata, K., Fukuzawa, S., Hou, Z. *OL* **14**, 3986 (2012)
[10] Bartoszewicz, A., Marcos, R., Sahoo, S., Inge, A.K., Zou, X., Martin-Matute, B. *CEJ* **18**, 14510 (2012)
[11] Park, J.K., Ondrusek, B.A., McQuade, D.T. *OL* **14**, 4790 (2012)
[12] Rucker, R.P., Whittaker, A.M., Dang, H., Lalic, G. *JACS* **134**, 6571 (2012)
[13] Ohishi, T., Zhang, L., Nishiura, M., Hou, Z. *ACIE* **50**, 8114 (2011)
[14] Zhang, L., Cheng, J., Carry, B., Hou, Z. *JACS* **134**, 14314 (2012)
[15] Bennie, L.S., Fraser, C.J., Irvine, S., Kerr, W.J., Andersson, S., Nilsson, G.N. *CC* **47**, 11653 (2011)
[16] Gong, X., Zhang, H., Li, X. *TL* **52**, 5596 (2011)
[17] Kawabata, S., Tokura, H., Chiyojima, H., Okamoto, M., Sakaguchi, S. *ASC* **354**, 807 (2012)
[18] Zhang, R., Xu, Q., Mei, L., Li, S., Shi, M. *T* **68**, 3172 (2012)
[19] Jiang, T., Livinghouse, T., Lovick, H.M. *CC* **47**, 12861 (2011)
[20] Chen, M.-T., Landers, B., Navarro, O. *OBC* **10**, 2206 (2012)
[21] Iwai, T., Fujihara, T., Terao, J., Tsuji, Y. *JACS* **134**, 1268 (2012)
[22] Vergote, T., Nahra, F., Welle, A., Luhmer, M., Wouters, J., Mager, N., Riant, O., Leyssens, T. *CEJ* **18**, 793 (2012)
[23] Tang, S., Monot, J., El-Hellani, A., Michelet, B., Guillot, R., Bour, C., Gandon, V. *CEJ* **18**, 10239 (2012)
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O-(2-Aminoethyl)diphenylborinate

Alcohol functionalization. With the title reagent as catalyst, regioselectivity for mono-acylation, sulfonylation and alkylation of diols and sugars is observed.[1] It can also be used in Koenigs-Knorr glycosylation.[2]

[1] Lee, D., Williamson, C.L., Chan, L., Taylor, M.S. *JACS* **134**, 8260 (2012)
[2] Gouliaras, C., Lee, D., Chan, L., Taylor, M.S. *JACS* **133**, 13926 (2011)

Antimony(III) chloride

Benzylation. Friedel-Crafts benzylation with ArCH(OH)R succeeds by using $SbCl_3$ as catalyst.[1]

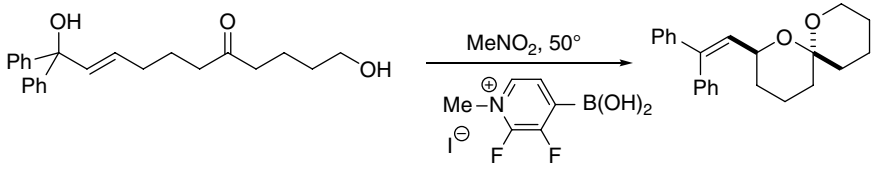
[1] Shukla, P., Choudhary, M.K., Nayak, S.K. *SL* 1585 (2011)

Arylboronic acids

Functionalization. For conversion of $ArB(OH)_2$ into $ArNH_2$, 2,4-dinitrophenoxyamine is an adequate reagent,[1] and phenols are produced by oxidation with tolyldimethylamine oxide.[2]

Condensation. 2-Iodo-5-methoxyphenylboronic acid acts as a stable and recyclable catalyst for the direct amidation of carboxylic acids at room temperature, 4A-MS is also required for the dehydration.[3]

Friedel-Crafts reaction. 2,3-Difluoro-1-methylpyridinium-4-boronic acid iodide is a useful activator of allylic alcohols for cyclization onto an aromatic ring and formation of spiroacetals.[4] Friedel-Crafts alkylation of arenes with propargylic alcohols is catalyzed by $C_6F_5B(OH)_2$.[5]



Suzuki coupling. Coupling procedures using $ArBF_3K$ are now recognized as providing the same results as with $ArB(OH)_2$. It is due to hydrolysis of the aryltrifluoroborate salts.[6]

[1] Zhu, C., Li, G., Ess, D.H., Falck, J.R., Kürti, L. *JACS* **134**, 18253 (2012)
[2] Zhu, C., Wang, R., Falck, J.R. *OL* **14**, 3494 (2012)
[3] Gernigon, N., Al-Zoubi, R.M., Hall, D.G. *JOC* **77**, 8386 (2012)
[4] Zheng, H., Ghanbari, S., Nakamura, S., Hall, D.G. *ACIE* **51**, 6187 (2012)
[5] McCubbin, J.A., Nassar, C., Krokhin, O.V. *S* 3152 (2011)
[6] Butters, M., Harvey, J.N., Jover, J., Lennox, A.J.J., Lloyd-Jones, G.C., Murray, P.M. *ACIE* **49**, 5156 (2010)

2-Azido-1,3-dimethylimidazolinium hexafluorophosphate

Alkyl azides. Alcohols are converted into azides the title phosphate reagent.[1]

[1] Kitamura, M., Koga, T., Yano, M., Okauchi, T. *SL* 1335 (2012)

1-Azidosulfonyl -2,3-dimethylimidazolium triflate

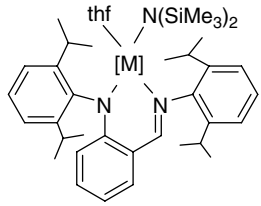
Sulfamoyl azides.[1] The reagent is prepared by methylation of the product of NaN_3, SO_2Cl_2, and 2-methylimidazole. It is used in derivatizing amines.

[1] Culhane, J.C., Fokin, V.V. *OL* **13**, 4578 (2011)

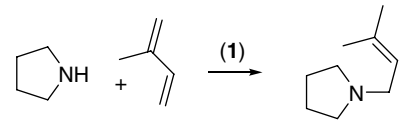
B

Barium iminoanilide

Hydroamination. Preparation from BaI_2, $KN(SiMe_3)_2$, and the N,N-ligand in THF, the amido complex **1** is the most active of a series (Ba > Sr >Ca) of *anti*-Markovnikov hydroamination catalysts for styrenes and conjugated dienes.[1]



(**1**)



[1] Liu, B., Roisnel, T., Carpentier, J.-F., Sarazin, Y. *ACIE* **51**, 4943 (2012)

Barium hydroxide

Baylis-Hillman reaction. For hydroxyalkylation of 2-cycloalkenones in 5:1 aqueous methanol, a promising catalyst system is composed of $Ba(OH)_2$ and *N*-methylpyrrolidine.[1]

[1] Guerra, K.P., Afonso, C.A.M. *T* **67**, 2562 (2011)

***o*-Benzenedisulfonimide**

Substitution. The title reagent is a reusable and mild Brønsted acid that is useful to convert dimethylacetals to homoallylic methyl ethers with allylsilanes.[1] The hydroxyl group of benzyl alcohols is similarly replaced (also by an alkynyl group). Ultimately ArCHO are converted into triarylmethanes by this method.[2]

Condensation. The Mukaiyama aldol reaction can be carried out in the neat with *o*-benzenedisulfonimide as catalyst.[3] Other uses are in bringing about the Pictet-Spengler reaction[4] and the Strecker reaction.[5]

[1] Barbero, M., Bazzi, S., Cadamuro, S., Dughera, S., Piccinini, C. *S* 315 (2010)
[2] Barbero, M., Cadamuro, S., Dughera, S., Magistris, C., Venturello, P. *OBC* **9**, 8393 (2011)

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[3] Barbero, M., Bazzi, S., Cadamuro, S., Dughera, S., Magistris, C., Smarra, A., Venturello, P. *OBC* **9**, 2192 (2011)
[4] Barbero, M., Bazzi, S., Cadamuro, S., Dughera, S. *TL* **51**, 6356 (2010)
[5] Barbero, M., Cadamuro, S., Dughera, S., Ghigo, G. *OBC* **10**, 4058 (2012)

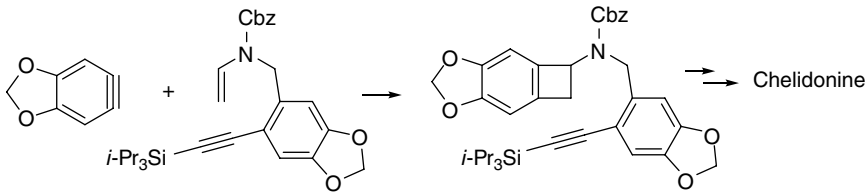
Benzyne

Preparation. A new precursor for the fluoride-induced decomposition is *o*-trimethylsilylphenyl 1-imidazolesulfonate.[1]

Alkenes. Benzyne removes the heteroatoms from 2-thiazolidinethiones to leave behind alkenes.[2] It completes a two-step defunctionalization of *vic*-amino alcohols.

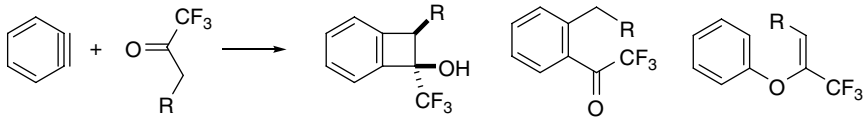
Condensation. Benzyne is trapped by isonitriles and the adducts in turn deprotonate 1-alkynes and cause a union to yield alkynyl arylketimines. An excess of the alkynes can be engaged to form pyridines or isoquinolines.[3]

Access by a [2+2]cycloaddition with enamides, the substituted benzocyclobutenes are valuable precursors of aminoquinodimethanes. A synthesis of chelidonine based on this reactivity is most rewarding.[4]

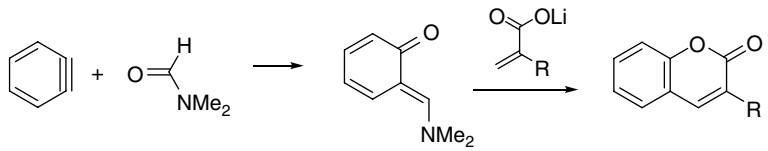


The condensation of benzyne with 2-vinylazetidines leads to 1-benzazocines.[5] An expedient method for preparing aza-bridged benzotropones is by trapping benzyne with pyridinium 3-oxides.[6]

Three different kinds of benzyne adducts with trifluoromethyl ketones CF_3COCH_2R may be isolated, depending on the electronic and steric nature of the CH_2R group.[7]



Generation of benzyne in DMF furnishes an *o*-quinomethide which on reaction with ester enolates or ketenimine anions delivers coumarins.[8]



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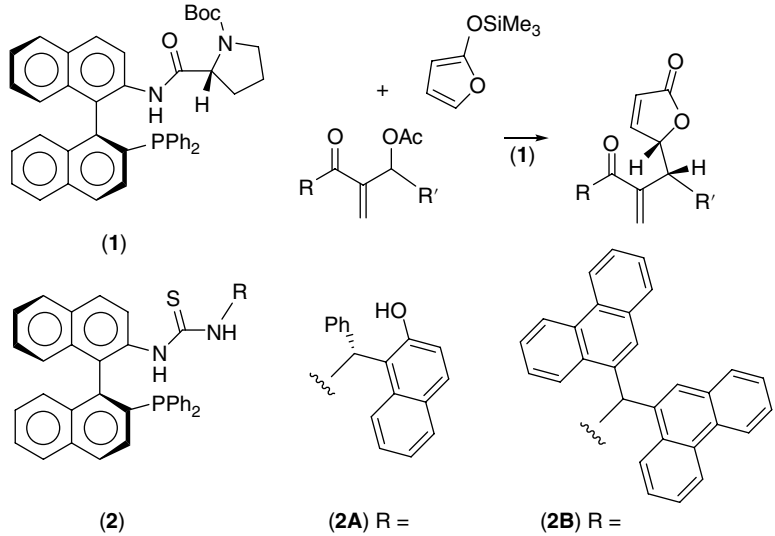
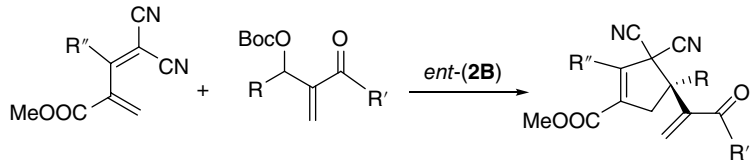
[2] Hwu, J.R., Hsu, Y.C. *CEJ* **17**, 4727 (2011)
[3] Sha, F., Wu, L., Huang, X. *JOC* **77**, 3754 (2012)
[4] Ma, Z.-X., Feltenberger, J.B., Hsung, R.P. *OL* **14**, 2742 (2012)
[5] Aoki, T., Koya, S., Yamasaki, R., Saito, S. *OL* **14**, 4506 (2012)
[6] Ren, H., Wu, C., Ding, X., Chen, X., Shi, F. *OBC* **10**, 8975 (2012)
[7] Yoshida, H., Ito, Y., Yoshikawa, Y., Ohshita, J., Takaki, K. *CC* **47**, 8664 (2011)
[8] Yoshida, H., Ito, Y., Ohshita, J. *CC* **47**, 8512 (2011)

1,1′-Binaphthalene-2-amine-2′-phosphines

Substitution. The chiral binaphthyl **1** containing both a phosphino group and a prolinamide unit has been used to conduct S_N2 reaction on Baylis-Hillman esters by 2-trimethylsiloxyfuran.[1] Another catalyst is the thiourea **2A**, capable of inducing reaction using as *P*-nucleophile such as secondary phosphine oxides.[2]



Cycloaddition. Baylis-Hillman esters also engage in enantioselective reaction with electron-deficient dienes.[3] A chirality center is created as the cyclopentene adducts are formed.

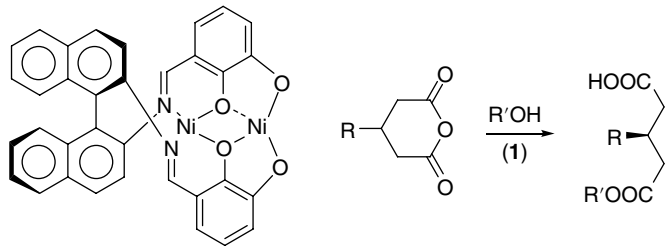


[1] Wei, Y., Ma, C.-N., Shi, M. *EJOC* 5146 (2011)
[2] Deng, H.-P., Shi, M. *EJOC* 183 (2012)
[3] Zhang, X., Deng, H.-P., Huang, L., Wei, Y., Shi, M. *CC* **48**, 8664 (2012)

1,1′-Binaphthalene-2,2′-diamine and derivatives

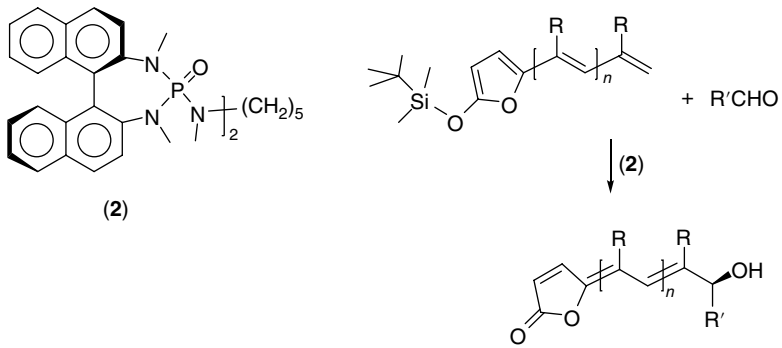
Derivatization. On milling with 3,5-bis(trifluoromethyl)phenyl isothiocyanate, BINAMINE is converted into an adduct containing two thiourea moieties.[1]

Alcoholysis. Desymmetrization of 3-substituted glutaric anhydride by addition of an alcohol furnishes chiral monoesters when conducted in the presence of **1**.[2]



(**1**)

Addition. Deprotonated 2-methyl-3-butenenitrile is nucleophilic toward aldehydes, both saturated and conjugated. An asymmetric carbinol center is established when the reaction is carried out in the presence of **2**. Using the same phosphoramide the condensation of 5-alkenyl-2-trialkylsiloxyfurans with aldehydes leads to 4-alkylidene-2-butenolides with a chiral alcohol sidechain.[3]



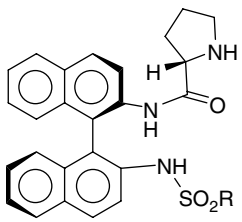
(**2**)

For aldol reaction a reusable catalyst is **3A**.[4] Serving well in a solvent-free synthesis of the Wieland-Miescher ketone and analogs is **3B**.[5] The diamide **4** is employed in the reaction of α-keto esters (acceptor).[6]

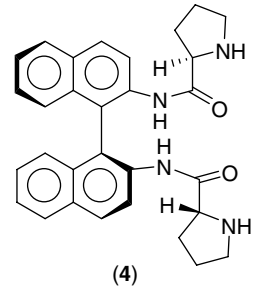
Asymmetric carbonyl-ene reaction involving α-keto esters, formaldehyde *t*-butylhydrazone and the bis-urea adduct of BINAMINE and 3,5-bis(trifluoromethyl)phenyl isocyanate relies on attainment of a multiple H-bonding transition state, one urea unit for each addend.[7]

The cycloalkoxylation initiated by attack of *N*-phenylthiophthalimide on unsaturated alcohols is rendered enantioselective by having the selenophosphoramide **5** present.[8]

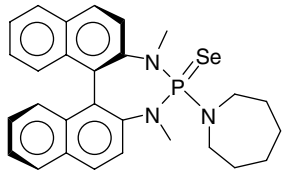
A magnesium complex of (6), an analog to (1), is active for promoting the asymmetric addition of *N*-Boc isoindolinone to *N*-sulfonylimines.[9]



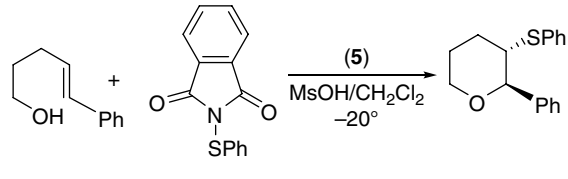
(**3A**) R = polymer
(**3B**) R = Tol

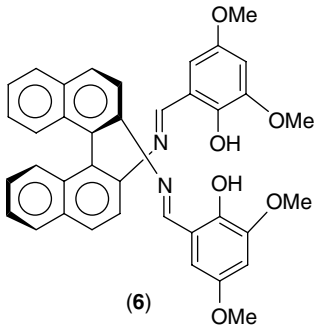


(**4**)

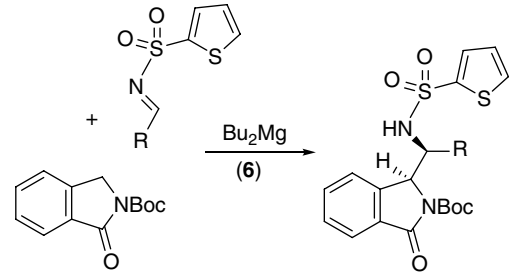


(**5**)





(**6**)



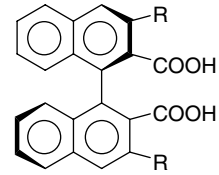
[1] Strukil, V., Irgc, M.D., Eckert-Maksic, M., Friscic, T. *CEJ* **18**, 8464 (2012)
[2] Gopinath, P., Watanabe, T., Shibasaki, M. *OL* **14**, 1358 (2012)
[3] Curti, C., Battistini, L., Sartori, A., Lodola, A., Mor, M., Rassu, G., Pelosi, G., Zanardi, F., Casiraghi, G. *OL* **13**, 4738 (2011)

[4] Bañon,-Caballero, A., Guillena, G., Najera, C. *HCA* **95**, 1831 (2012)
[5] Bradshaw, B., Bonjoch, J. *SL* 337 (2012)
[6] Viozquez, S.F., Bañon-Caballero, A., Guillena, G., Nájera, C., Gómez-Bengoa, E. *OBC* **10**, 4029 (2012)
[7] Crespo-Peña, A., Monge, D., Martin-Zamora, E., Alvarez, E., Fernandez, R., Lassaletta, J.M. *JACS* **134**, 12912 (2012)
[8] Denmark, S.E., Kornfilt, D.J.P., Vogler, T. *JACS* **133**, 15308 (2011)
[9] Suzuki, Y., Kanai, M., Matsunaga, S. *CEJ* **18**, 7654 (2012)

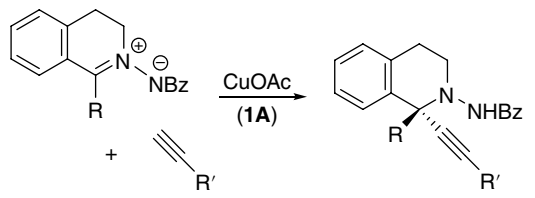
1,1′-Binaphthalene-2,2′-dicarboxylic acids

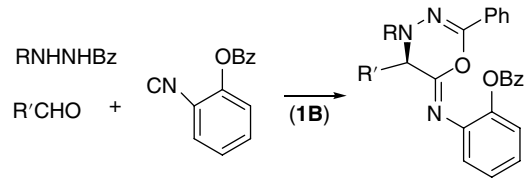
Addition to imines. In the Cu(I)-catalyzed addition of 1-alkynes to *N*-benzoylamino-3, 4-dihydroisoquinoline zwitterions, chiral products are obtained on adding diacid **1A** to the reaction media.[1]

Cycloaddition. The 1,3,4-oxadiazine ring system emerges as aldehydes, benzoylhydrazines, and aryl isonitriles condense in the presence of **1B**.[2]



(**1A**) R = Si(Ph)Me$_2$
(**1B**) R = C$_6$H$_3$[3,5-(NO$_2$)$_2$]





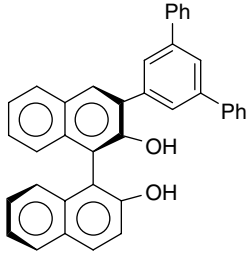
[1] Hashimoto, T., Omote, M., Maruoka, K. *ACIE* **50**, 8952 (2011)
[2] Hashimoto, T., Kimura, H., Kawamata, Y., Maruoka, K. *ACIE* **51**, 7279 (2012)

1,1′-Binaphthalene-2,2′-diol and analogues

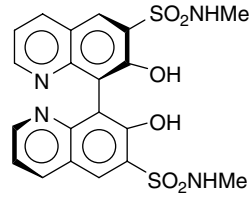
Addition. The BINOL **1**, while displacing two alkoxy groups from (*i*-PrO)$_4$Ti, forms an asymmetric catalyst for the Grignard reaction that forms diarylmethanols.[1] Aryl(triisopropoxy)titanium reagents attack RCHO in a chiral manner as influenced by the complex derived from octahydro-BINOL.[2] Asymmetric induction is also examined in the addition of alkynyl(alkyl)zinc reagents in the presence of BINOL,[3] and to *N*-phosphinoylimines, the 3,3′-dibromo-BINOL.[4]

The dibromo-BINOL also mediates enantioselective propargylation of carbonyl compounds by allenylboronates under microwave irradiation.[5]

The unusual BINOL analog **2** that is actually a 8,8′-Biquinoline-7,7′-diol **1NN** catalyzes the addition of Me_3SiCN to carbonyl compounds and imines.[6] The homocyclic analog itself is inactive.

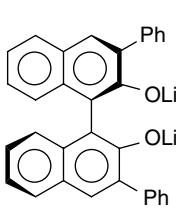


(**1**)

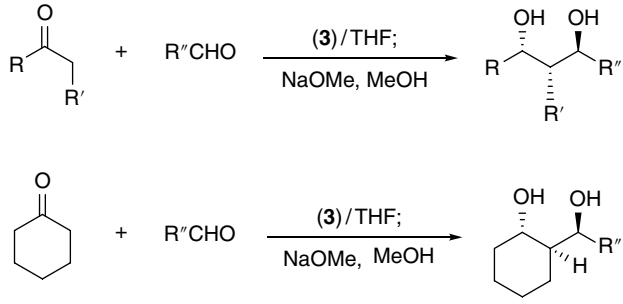


(**2**)

The dilithium salt of a chiral 3,3′-dichloro-BINOL is useful to catalyze the Mukaiyama aldol reaction.[7] *anti*-1,3-Diols are formed from reaction of ketones and aldehydes, as a Tishchenko reaction can be easily realized after an aldol condensation that is promoted by dilithium 3,3′-diphenyl-BINOLate.[8]



(**3**)

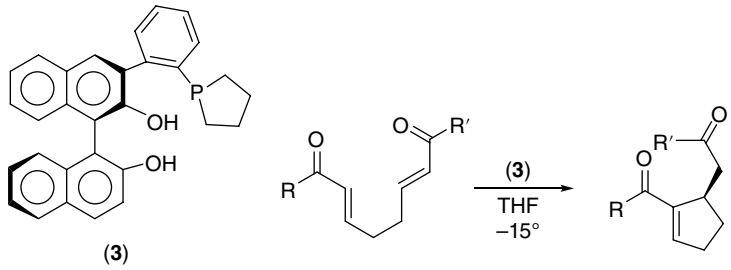


A Zr(IV) complex of 3,3′-bis[3,5-di(trifluoromethyl)phenyl]-BINOL is responsible for asymmetric induction during Friedel-Crafts reaction of pyrrole by α-keto esters.[9]

Many versions of conjugate addition are catalyzed by BINOLs and their metal salts. For example, introduction of a chiral sidechain to C-3 of the indole nucleus is accomplished by addition to enones, catalyzed by zirconium di-*t*-butoxide 3,3′-dibromo-BINOLate.[10] *N*-Acetyltryptophan methyl ester is obtained from the reaction with the α-acetamidoacrylic ester using an analogous dibromo-BINOL complex derived from $SnCl_4$.[11]

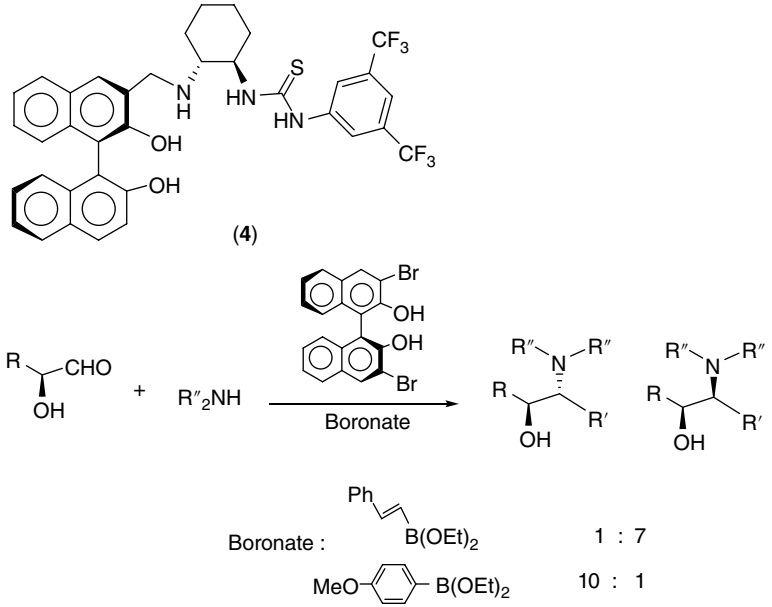
Chain elongation at the γ-position of *N*-acyl 2-butenelactams by conjugate addition is rendered asymmetric by using the Mg salt of a chiral 3,3′-diphenyl-BINOL.[12]

Cyclization involving intramolecular addition of one conjugated carbonyl unit to another is initiated by BINOL **3** which contains a tertiary phosphine.[13]



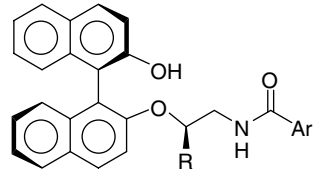
Conjugate addition of organoboronates to enones has been studied employing 3,3′-dichloro-BINOL[14] and 3,3′-bis(pentafluorophenyl)-BINOL.[15] *o*-Quinone methides generated in situ also are serviceable as acceptors for alkenylboronates.[16]

Based on the Petasis reaction of salicylaldehyde for access to chiral benzylamines, BINOL **4** is employed.[17] Interestingly, diastereocontrol for synthesis of β-amino alcohols is obtained on variation of the boronates.[18]

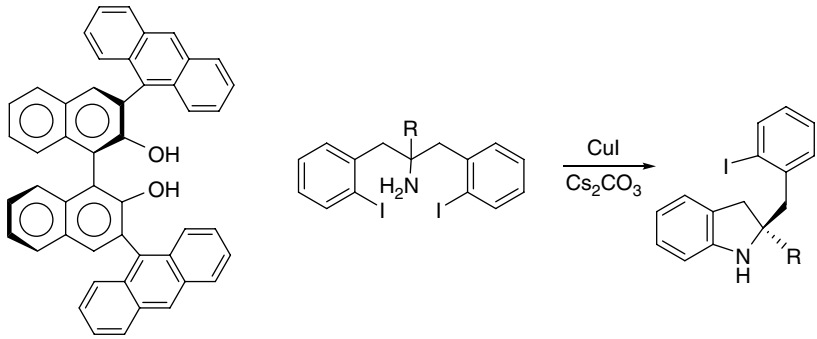


Substitution. In replacement of the sulfonyl group from α-amino sulfones to acquire propargylic amines, chiral products are obtained when the zinc alkynides are associated with an antipodal 3,3′-bis[3,5-di(trifluoromethyl)phenyl]-BINOL.[19]

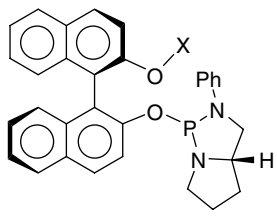
(*R*)-BINOL is used in kinetic resolution of *N*-aroylaziridines.[20]



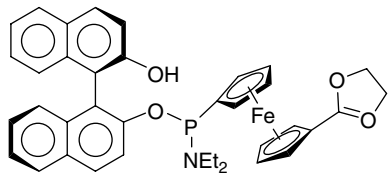
Enantioselective formation of 2-substituted indolines involving desymmetrization directed by (*R*)-3,3′-di(9-anthryl)-BINOL.[21]



A number of BINOL derivatives, represented by **5A** and **5B**, are useful ligands for Pd to promote S_N2' reactions.[22, 23] The complex ligand **5B** which is obtained from (*R*)-BINOL is also employed in a Pd-catalyzed allylation of acylsilanes.[24]



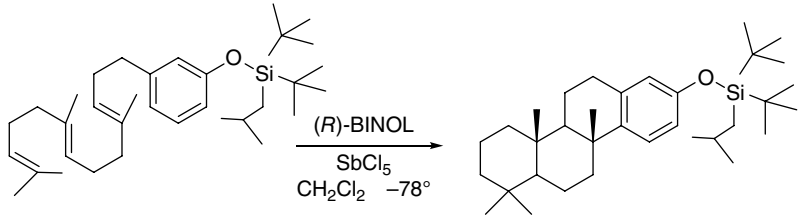
(**5A**) X = Ts, CH_2Py



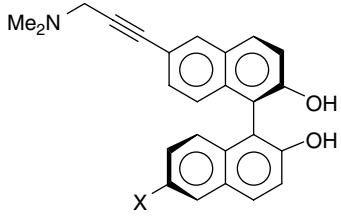
(**5B**)

Cyclization. Transformation of 3-(*N*-acyl-*N*-alkenyl)aminopropanals to 1,2,3, 4-tetrahydropyridin-4-ols is catalyzed by Lewis acids. A chiral diisopropoxytitanium BINOLate is effective.[25]

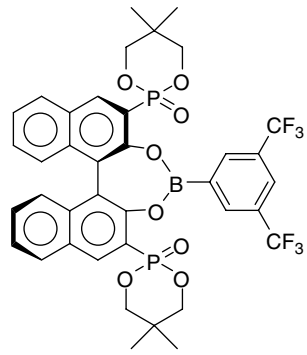
Polyene cyclization that generates four contiguous stereocenters in highly enantioselective manner is very desirable. It can be achieved with a combination of $SbCl_5$ and BINOL.[26]



Cycloaddition. Amphophilic BINOLs such as **6A** and **6B** show catalytic activities for epoxidation of enones.[27] Association of boronate **7** with tris(pentafluorophenyl)borane creates a supramolecular catalyst for directing asymmetric Diels-Alder reaction (e.g., between cyclopentadiene and α-substituted acroleins).[28]



(**6A**) X = H
(**6B**) X = $CCCH_2NMe_2$



(**7**)

Oxidation. A combination of a chiral BINOL and Bi_2O_3 is used in asymmetric oxidation of sulfides.[29]

[1] Itakura, D., Harada, T. *SL* 2875 (2011)
[2] Wu, K.-H., Zhou, S., Chen, C.-A., Yang, M.-C., Chiang, R.-T., Chen, C.-R., Gau, H.-M. *CC* **47**, 11668 (2011)
[3] Turington, M., Pu, L. *SL* 649 (2012)
[4] Blay, G., Ceballos, E., Monleon, A., Pedro, J.R. *T* **68**, 2128 (2012)
[5] Barnett, D. S.,Schaus, S. E. *OL* **13**, 4020 (2011)
[6] Sephton, S.M., Wang, C., Zakharov, L.N., Blakemore, P.R. *EJOC* 3249 (2012)
[7] Ichibakase, T., Kaneko, T., Orito, Y., Kotani, S., Nakajima, M. *T* **68**, 4210 (2012)
[8] Ichibakase, T., Nakajima, M. *S* 3145 (2012)
[9] Blay, G., Fernandez, I., Muñoz, M.C., Pedro, J.R., Recuenco, A., Vila, C. *JOC* **76**, 6286 (2011)
[10] Blay, G., Cano, J., Cardona, L., Fernandez, I., Muñoz, M.C., Pedro, J.R., Vila, C. *JOC* **77**, 10545 (2012)
[11] Kieffer, M.E., Repka, L.M., Reisman, S.E. *JACS* **134**, 5131 (2012)
[12] Lin, L., Zhang, J., Ma, X., Fu, X., Wang, R. *OL* **13**, 6410 (2011)
[13] Zhang, X.-N., Shi, M. *EJOC* 6271 (2012)

[14] Turner, H.M., Patel, J., Niljianskul, N., Chong, J.M. *OL* **13**, 5796 (2011)
[15] Lundy, B.J., Jansone-Popova, S., May, J.A. *OL* **13**, 4958 (2011)
[16] Luan, Y., Schaus, S.E. *JACS* **134**, 19965 (2012)
[17] Han, W.-Y., Wu, Z.-J., Zhang, X.-M., Yuan, W.-C. *OL* **14**, 976 (2012)
[18] Muncipinto, G., Moquist, P.N., Schreiber, S.L., Schaus, S.E. *ACIE* **50**, 8172 (2011)
[19] Blay, G., Brines, A., Monleon, A., Pedro, J.R. *CEJ* **18**, 2440 (2012)
[20] Cockrell, J., Wilhelmsen, C., Rubin, H., Martin, A., Morgan, J.B. *ACIE* **51**, 9842 (2012)
[21] Zhou, F., Guo, J., Liu, J., Ding, K., Yu, S., Cai, Q. *JACS* **134**, 14326 (2012)
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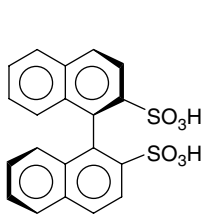
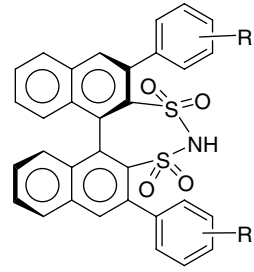
[23] Zheng, B.-H., Ding, C.-H., Hou, X.-L. *SL* 2262 (2011)
[24] Chen, J.-P., Ding, C.-H., Liu, W., Hou, X.-L., Dai, L.-X.. *JACS* **132**, 15493 (2010)
[25] Tong, S., Wang, D.-X., Zhao, L., Zhu, J., Wang, M.-X. *ACIE* **51**, 4417 (2012)
[26] Surendra, K., Corey, E.J. *JACS* **134**, 11992 (2012)
[27] El Kadiri, M.Y., Framery, E., Andrioletti, B. *TL* **53**, 6335 (2012)
[28] Hatano, M., Mizuno, T., Izumiseki, A., Usami, R., Asai, T., Akakura, M., Ishihara, K. *ACIE* **50**, 12189 (2011)
[29] Malik, P., Chakraborty, D. *TL* **53**, 5652 (2012)

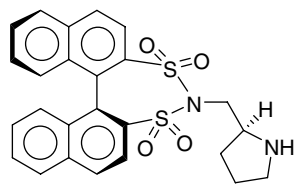
1,1′-Binaphthalene-2,2′-disulfonic acid and imides



(**1**)



(**2A**) R = 3,5-$(CF_3)_2$
(**2B**) R = 3,5-$[(CF_3)_2CF]$
(**2C**) R = 3,5-$(O_2N)_2$-4-Me

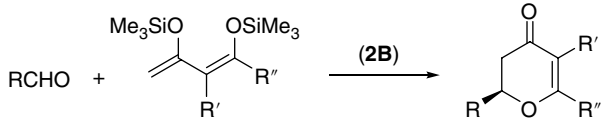


(**3**)

Addition. The Hosomi-Sakurai reaction is affected by a chiral counter-anion as shown by the catalysis of **2C**.[1] Chiral α,α-diaminomethylarenes are acquired by the addition of amides to ArCH=$NCOOCH_2$Ar', using the 2,6-bis(2,4,6-triisopropylphenyl) pyridinium salt of **1** as catalyst.[2] Addition of indole (C-3) to *N*-sulfonylaldimines in the presence of **2A** is enantioselective.[3]

Catalyst **3** possesses two chiral elements and its use in promoting Michael addition to alkylidenemalonic esters has been studied.[4]

Cycloaddition. The pyranone synthesis pioneered by Danishefsky has many applications and numerous catalysts for inducing enantioselectivity are on record. A new catalyst is **2B**.[5]



[1] Mahlau, M., Garcia-Garcia, P., List, B. *CEJ* **18**, 16283 (2012)
[2] Hatano, M., Ozaki, T., Sugiura, Y., Ishihara, K. *CC* **48**, 4986 (2012)
[3] Chen, L.-Y., He, H., Chan, W.-H., Lee, A.W.M. *JOC* **76**, 7141 (2011)
[4] Jia, S., Luo, C., Du, D. *ChJC* **30**, 2676 (2012)
[5] Guin, J., Rabalakos, C., List, B. *ACIE* **51**, 8859 (2012)

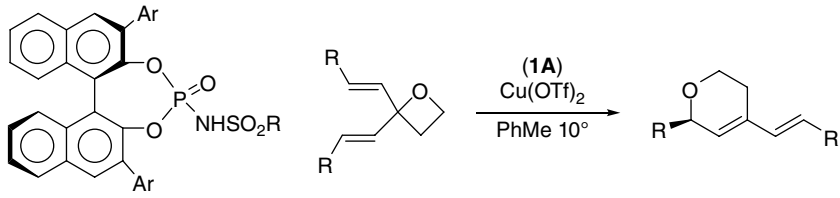
1,1′-Binaphthalene-2,2′-diyl di-*t*-butanesulfinate

Grignard reaction. The title reagent, in either chiral series, is obtained from BINOL on consecutive treatment with BuLi and *t*-BuSOCl. Chiral *t*-butyl sulfoxides can be prepared by a Grignard reaction with the reagent, from which the BINOL is recovered.[1]

[1] Gaggero, N., Albanese, D.C.M. *T* **68**, 7129 (2012)

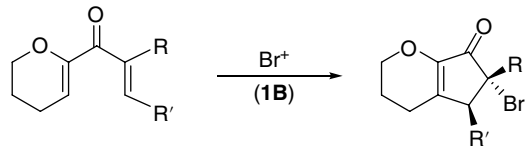
1,1′-Binaphthalene-2,2′-diyl *N*-sulfonylaminophosphates

Ring enlargement. 2,2-Dialkenyloxetanes isomerized by **1A** to 4-alkenyl-5, 6-dihydro-2*H*-pyrans.[1]

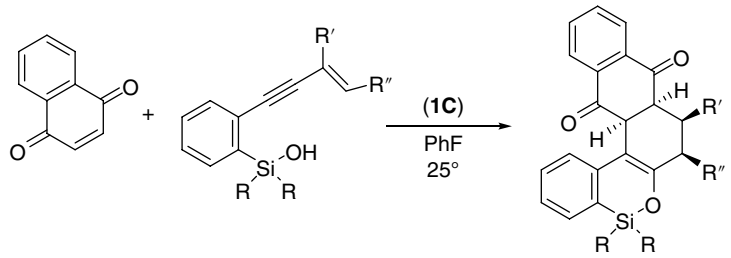


(**1A**) Ar = 9-anthryl, R = Tol
(**1B**) Ar = 9-phenanthryl, R = CF_3
(**1C**) Ar = 1-pyrenyl, R = CF_3

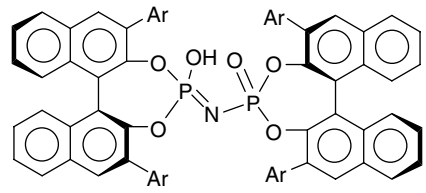
Nazarov cyclization. As chiral Brønsted acids, both **1B** and its octahydro derivative are effective to catalyze cyclization of 2-alkoxy-1,4-alkadien-3-ones.[2] A further modification is to use a Br^+ source to initiate the reaction.[3]



Cycloaddition. Asymmetric Diels-Alder reaction involving *o*-(3-alken-1-ynyl)phenylsilanols as latent dienes has been realized, while employing **1C** to exert chiral guidance.[4]



Oxidation. Enantioselective oxidation of sulfides is accomplished with H_2O_2 and **2**.[5]

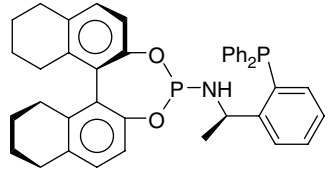


(**2**) Ar = 2,4,6-$Et_3C_6H_2$

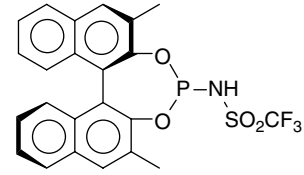
[1] Guo, B., Schwarzwalder, G., Njardarson, J.T. *ACIE* **51**, 5675 (2012)
[2] Raja, S., Ieawsuwan, W., Korotkov, V., Rueping, M. *CAJ* **7**, 2361 (2012)
[3] Rueping, M., Ieawsuwan, W. *CC* **47**, 11450 (2011)
[4] Han, Z.-Y., Chen, D.-F., Wang, Y.-Y., Guo, R., Wang, P.-S., Wang, C., Gong, L.-Z. *JACS* **134**, 6532 (2012)
[5] Liao, S., Coric, I., Wang, Q., List, B. *JACS* **134**, 10765 (2012)

1,1′-Binaphthalene-2,2′-diyl *N*-alkylaminophosphites

Addition. Asymmetric hydrogenation of ketimines based on iridium complexes can rely on aminophosphite **1**[1] or a combination of **2** and $Ph_2PNHSO_2C_6H_4Bu$.[2]



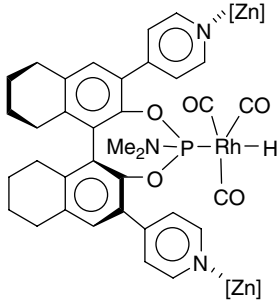
(**1**)



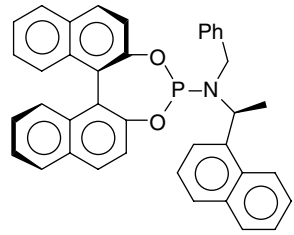
(**2**)

For hydroboration of β,γ-unsaturated Weinreb amides a Rh(I) salt is supported by the BINOL-derived *N*-methylanilinophosphite. The optical yield is highly dependent on the borane used.[3]

Supramolecular axial complexes typified by **3** show excellent activity and selectivity for asymmetric hydroformylation of alkenes.[4] Addition of ethylene to styrenes provides 3-aryl-1-butenes, and this Ni-catalyzed process is subject to chiral manipulation by **4.**[5]

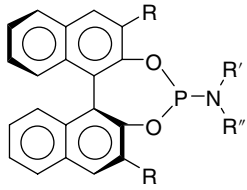


(**3**)

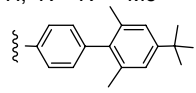


(**4**)

Nickel(0)-mediated gathering of a conjugated diene, an aldehyde and a silylborane serves to construct a carbon chain containing three contiguous stereocenters and a silyl and hydroxyl substituent each. By involving **5D** an enantioselective process is achieved.[6]

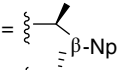


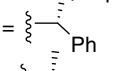
(**5A**) R = H, R′ =R″ = Me

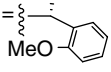
(**5B**) R =  R′ = R″ = Me

(**5C**) R = 9-anthryl, R′ = R″ = Et

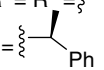
(**5D**) R = $CHPh_2$, R′ = R″ = Bn

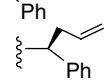
(**5E**) R = H, R′ = R″ = 

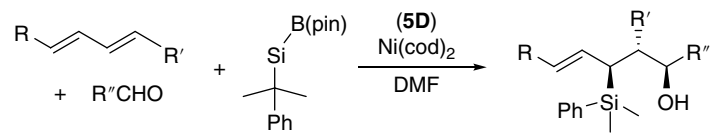
(**5F**) R = H, R′ = R″ = 

(**5G**) R = H, R′ = R″ = 

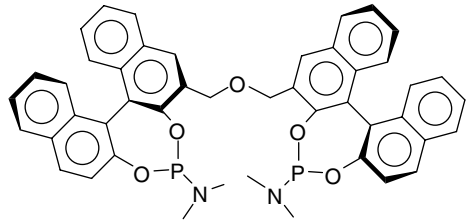
(**5H**) R = 9-anthryl, R′ = R″ = 

(**5I**) R = Me, R′ = R″ = 

(**5J**) R = H, R′ = Bn, R″ = 

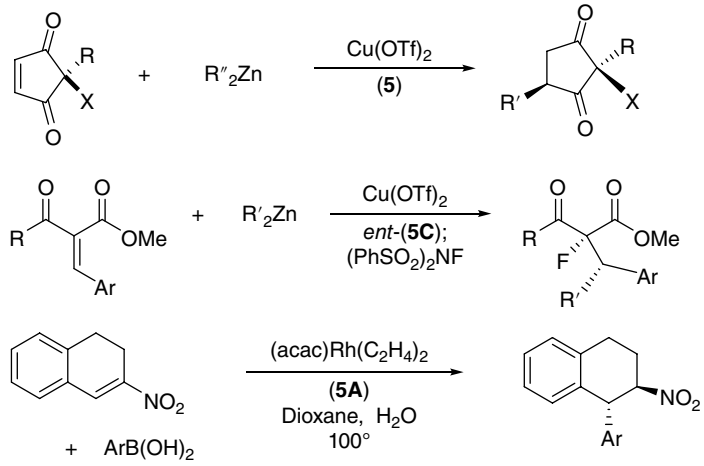


The dimeric BINOL derivative **6** forms with $(Ph_3P)_2RuCl_2$ a catalyst that directs addition of $ArB(OH)_2$ to glyoxylate esters in enantioselective manner.[7]



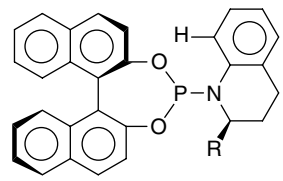
(**6**)

Conjugate addition of R_2Zn and R_3Al to 2,2-disubstituted 4-cyclopentene-1,3-diones is Cu(II)-catalyzed. It favors the *syn* face to the more polar substituent, and enantioselectivity is governed by **5B**.[8]

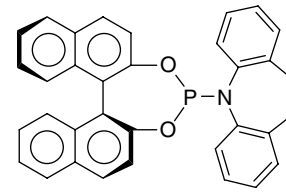


After adding diorganozinc reagents to α-benzylidene-β-keto esters the quenching with $(PhSO_2)_2NF$ establishes two new stereocenters, and the whole process is rendered asymmetric by the presence of *ent*-**5C**.[9] 3-Nitro-1,2-dihydronaphthalene picks up the Ar group from $ArB(OH)_2$ asymmetrically to afford *trans*-1-aryl-2-nitrotetralins when a Rh complex and **5A** are added.[10]

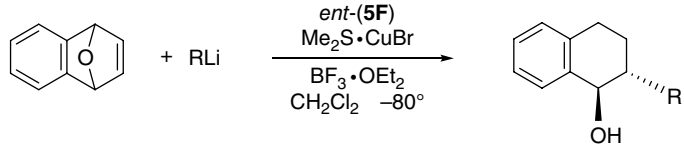
Substitution. The iridium complex with **7** controls the S_N2' reaction of malonate esters and cinnamyl carbonate.[11] An iridacycle is formed in which the metal is covalently bonded to C-8 of the tetrahydroquinoline.



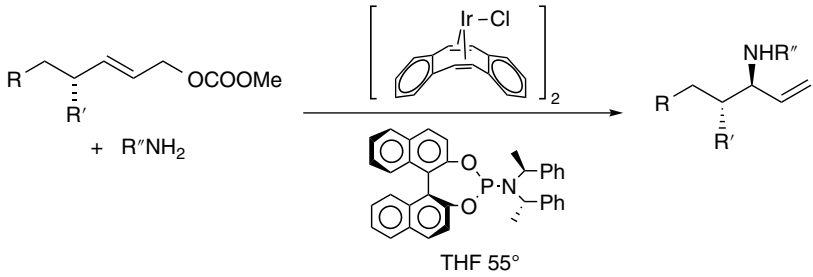
(**7A**) R = H
(**7B**) R = Me



(**8**)

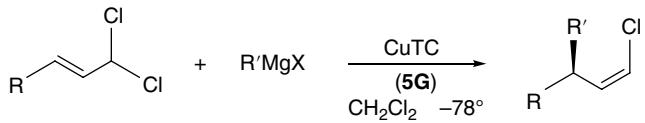


Iridium catalysts always favor bond formation at the secondary allylic center, therefore the reaction can be exploited to access 3-amino-1-alkenes with an additional chirality center at C-4.[12]



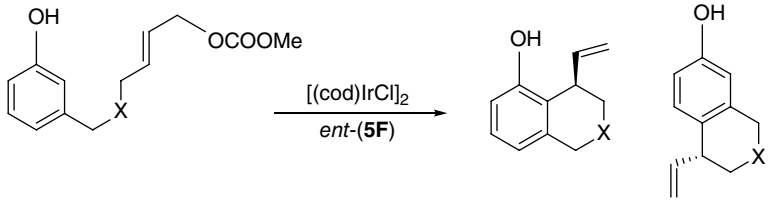
Enantioconvergent access to 3-organothio-1-alkenes is attained in the reaction of allylic alcohols using **8** and $(BuO)_2POOH$.[13] Similarly, chiral 3-aryl-3-aryloxy-1-propenes are synthesized from cinnamyl carbonates and phenols [catalyst: Ir(I) complex + **5E**].[14]

Reaction with RLi opens 1,4-oxa-1,4-dihydronaphthalene in the S_N2' fashion (catalysts: $Me_2S.CuBr$, $BF_3{\cdot}OEt_2$), and it is rendered enantioselective by *ent*-**5F**.[15] Attack of Grignard reagents on 1,1-dichloro-2-alkenes can be made regioselective and stereoselective, giving (*Z*)-1-chloro-1-alkenes which are useful for Suzuki coupling.[16] A similar reaction with RLi on 1-alkoxy-2-alkenes[17] or 1-halo-2-alkenes[18] to produce 1-alkenes with a chirality center at C-3 is then a routine extension.



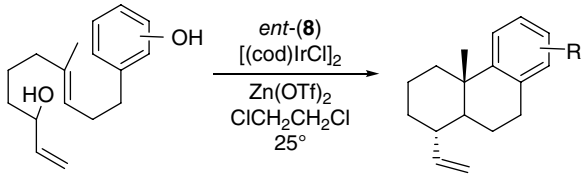
1-Chloro-2-alken-4-ynes are converted by the Cu(I)-catalyzed Grignard reaction into 1-alken-4-ynes while a new chirality center at C-3 is being created.[19]

Further examples of iridium(I)-catalyzed substitution may be mentioned. Thus, using sulfamic acid as nucleophile enables enantioselective replacement of the hydroxyl group of 1-alken-3-ols by NH_2 in the presence of **8**.[20] Cycloallylation of phenols occurs when a *m*-substituent is equipped with the necessary leaving group.[21] Products from substitution at both an *o*- and a *p*-position results have the same absolute configuration at the new chirality center. A similar process serves to form a spirocycle at C-3 of the indole nucleus.[22]



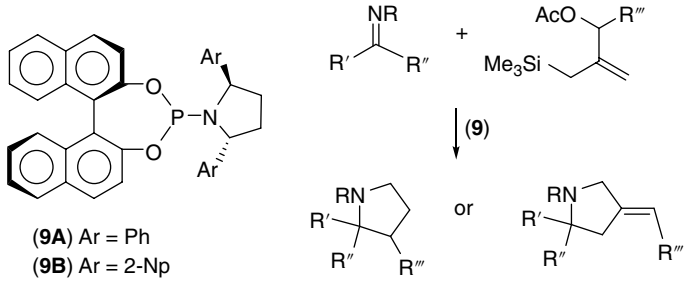
Coupling of 2-vinylaniline with cinnamyl methyl carbonate is interesting, as it produces a 1,4-diene.[23]

A tricyclic structure emerges from exposure of 10-aryl-1,7-decadien-3-ols to a mixture of $[(cod)IrCl]_2$ and $Zn(OTf)_2$, and the products containing three contiguous asymmetric centers are obtained by introducing *ent*-**8** into the reaction media.[24]



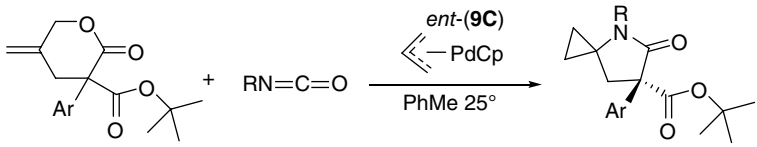
For Pd-catalyzed allylic substitution, **5J** can be employed as a chiral catalyst.[25]

Cycloaddition. [3+2]Cycloaddition involving trimethylenemethanes that are generated from silylated allylic esters is amenable to deliver chiral products on ligating the Pd catalyst with **9A/9B**, as illustrated in the combination with imines[26] and with nitroalkenes.[27]

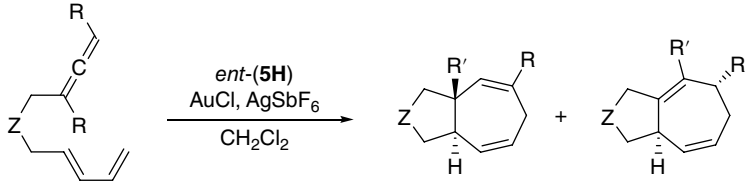


(**9A**) Ar = Ph
(**9B**) Ar = 2-Np
(**9C**) Ar = 3,5-$Me_2C_6H_3$

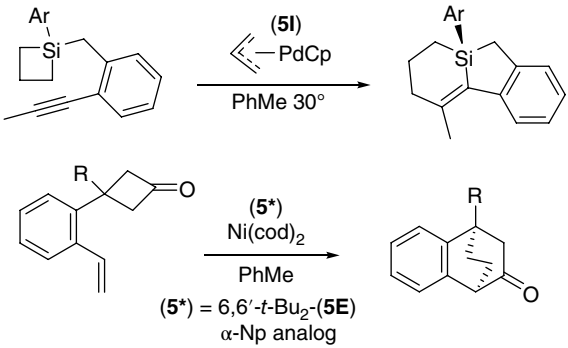
Decarboxylation of γ-methylene-δ-lactones gives rise to more complex trimethylenemethanes, and the capture of which by isocyanates results in the formation of spirolactams. Those with chirality residing in the α-carbon are promptly prepared by ligating the Pd center with **9C**.[28]



Intramolecular [4+3]cycloaddition to unite diene and allene units is induced by Au(I)-activation of the allene. With *ent*-**5H** to ligate the metal center it yields fused cycloheptadienes.[29]



Ring enlargement. Silacyclobutanes insert alkynes to form 1-sila-2-cyclohexenes in a Pd-catalyzed reaction. The ligand H_8-**5I** is useful for asymmetric induction at the silicon atom.[30] A very unusual reaction of 3-(*o*-vinylaryl)cyclobutanones is their conversion into benzonorbornenones. Produced in optically active form is by catalysis of $Ni(cod)_2$ and the 6,6′-di-*t*-butyl derivative of **5E**′.[31]



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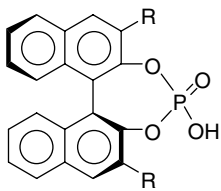
1,1′-Binaphthalene-2,2′-diyl phosphates and 3,3′-diaryl analogs

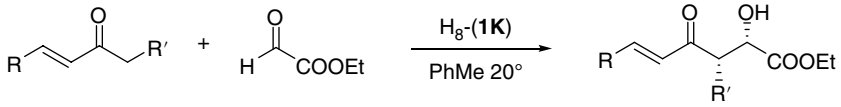


(**1A**) R = H
(**1B**) R = Ph
(**1C**) R = 4-PhC_6H_4
(**1D**) R = 4-(β-Np)C_6H_4
(**1E**) R = 4-MeOC_6H_4
(**1F**) R = 4-O_2NC_6H_4
(**1G**) R = 4-XC_6H_4
(**1H**) R = 4-FC_6H_4
(**1I**) R = 3,5-$F_2C_6H_4$
(**1J**) R = 3,5-(*i*-Pr)$_2C_6H_3$
(**1K**) R = 2,4,6-$Me_3C_6H_2$
(**1L**) R = 2,4,6-(*i*-Pr)$_3C_6H_2$
(**1M**) R = 2,6-Me_2-4-(*t*-Bu)C_6H_2
(**1N**) R = 3,5-(*i*-Pr)$_2$-4-(MeO)C_6H_2
(**1O**) R = 9-anthryl
(**1P**) R = 9-phenanthryl
(**1Q**) R = β-Np
(**1R**) R = 2-thienyl
(**1S**) R = 3-thienyl
(**1T**) R = Ph_3Si

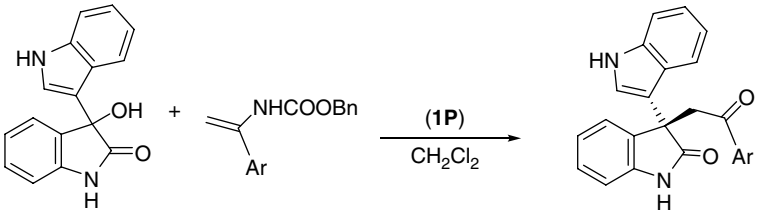
Kinetic resolution. A catalyst composed of **1L** and DABCO is for controlled enantioselective acetylation of secondary alcohols.[1] 1,2-Alkadien-4-ols are half-converted into the (*R*)-2-alkyl-2,5-dihydrofurans, leaving the (*S*)-alcohols alone, on exposure to **1C**.[2]

Selective cyclization of one enantiomer of an unsymmetrically substituted 1,5-diketone is realized by catalysis of **1L**.[3] For kinetic resolution of an *N*-sulfonylated benzylamine, a method is based on desulfonylation of one enantiomer by BnSH, using either **1B** or **1F** as catalyst.[4]

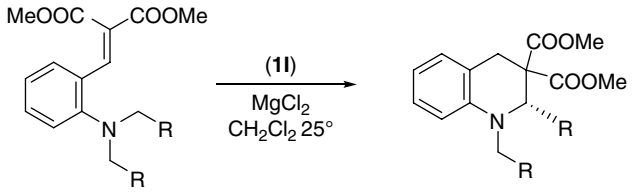
Substitution. Creation of a chiral quaternary benzylic center from allylation of α-substituted arylacetaldehydes is accomplished in a Pd(0)-catalyzed reaction, provided that Brønsted acids such as **1L** and benzhydrylamine are enlisted as participants.[5] Regioselective and enantioselective aldol reaction of conjugated ketones with ethyl glyoxylate occurs at the α′ -position, and in such case H_8-**1K** is of excellent service.[6]



Ketones are alkylated by 3-hydroxy-3-(β-indolyl)oxindole under acidic conditions. It provides chiral products with two contiguous chirality centers when (*ent*)-**1E** is employed.[7] This method was initially developed for a synthesis of (+)-folicanthine using an α-(*N*-benzyloxycarbonyl)aminostyrene as the nucleophile (and **1P** the catalyst).[8]



Cooperative actions from Brønsted acid **1I** and Lewis acid $MgCl_2$ smooth the cyclization of 2-aminoarylidenemalonic esters, which is initiated by a 1,5-hydride shift to create an ion pair.[9]



Addition. For transfer hydrogenation of 2-alkylquinolines to deliver the (*S*)-tetrahydro derivatives, Au(I)-carbene and *ent*-**1L** are a valuable combination, a Hantzsch ester acts as the hydrogen source (>99% yield, 98% ee, turnover up to 10000).[10] A reusable transfer hydrogenation catalyst is prepared from a polymer based on *ent*-**1R**, which has high surface area and shows increased selectivity.[11]

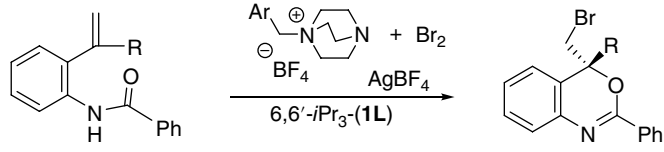
The DMAP salt of *ent*-**1O** effectively mediates the reduction of aryl methyl ketones by catecholborane.[12] Transfer hydrogenation with a Hantzsch ester also converts *N*-protected α-iminoarylacetic esters into the (*S*)-amino esters (catalyst: **1P**).[13] To enentioselectively introduce a deuterium into the α-position of amines one can starts from the corresponding ketimines, which accept the D-atom from 2-aryl-2-deuteriobenzothiazolines in the presence of (*ent*)-**1L**.[14] The same system (but with the ordinary 2-phenylbenzothiazoline as hydrogen source) is effective to conduct asymmetric reductive amination of ketones with *p*-anisidine.[15] Another report describes the use of **1T** and a Hantzsch ester to hydrogenate aryl *o*-hydroxylaryl ketimines.[16]

In the Rh(II)-catalyzed decomposition of α-diazo carbonyl compounds intervention of a proximal carbonyl group offers an opportunity for asymmetric reduction of the latter functionality (through carbonyl ylide). During formation of 1-arylisochroman-4-ones, a Hantzsch ester provides a hydride, while *ent*-**1P** can furnish a proton.[17]

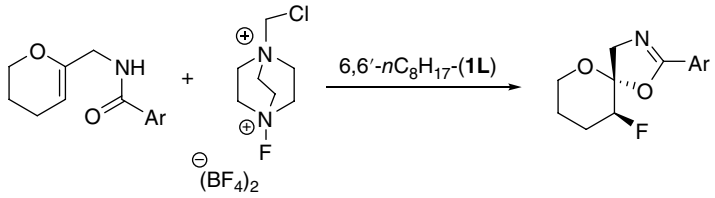
Consecutive hydroamination and asymmetric reduction to access chiral secondary amines employs a phosphine-ligated Au(I) salt for the first step and hydrogenation is catalyzed by a half-sandwich iron complex with **1L** to steer the stereochemical course.[18]

The popularity of **1L** and its enantiomer for asymmetric processes is apparent. Spiroacetalization in its presence is found to be diastereoselective and enantioselective.[19] Internal alkenes with a terminal polar group are coaxed to cyclize on reaction with NBS, and chiral adducts are obtained by furnishing **1L** to the reaction media.[20] Bromosuccinimidation of enecarbamates in the presence of *ent*-**1L** and the calcium salt is stereochemically illuminating, the acid enforces formation of products with the (*1R, 2S*)-configuration, whereas the calcium salt the (*1S, 2R*)-isomers.[21]

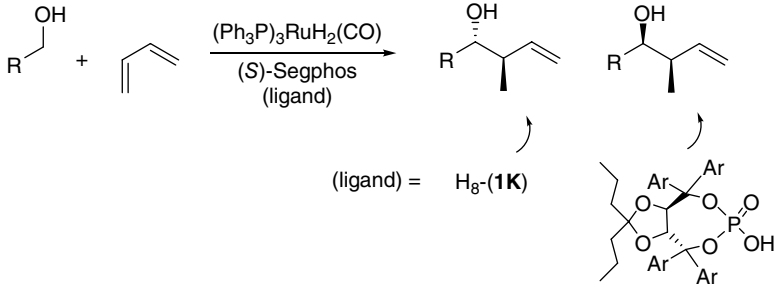
Halocyclization in enantioselective sense is accomplished as shown in the following example.[22] Note that the chiral catalyst is a 6,6′-bis(triisopropylsilyl) derivative of *ent*-**1L**.



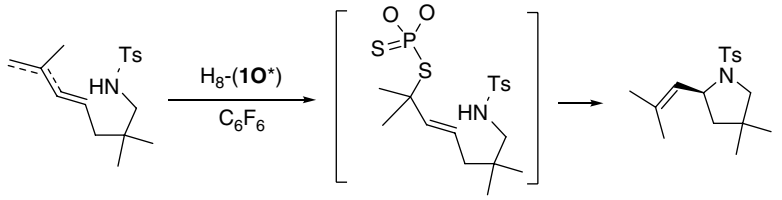
Asymmetric fluorination of enamides with Selectfluor also has been carried out with the 6,6′-dioctyl derivative of **1L**.[23,24]



1,2-Addition to conjugated dienes such as 3-vinylindoles by 2,4-diaryl-5-oxazolinones is found to be highly stereoselective. Two chirality centers appear in the adducts when *ent*-**1C** is employed as the catalyst.[25] Primary alcohols add to 1,3-butadiene under the influence of a Ru hydride complex, which is mainly catalyzed by a chiral Segphos ligand, but the Brønsted acid additive is also of utmost importance to determine the absolute configuration of the carbinolic center.[26]

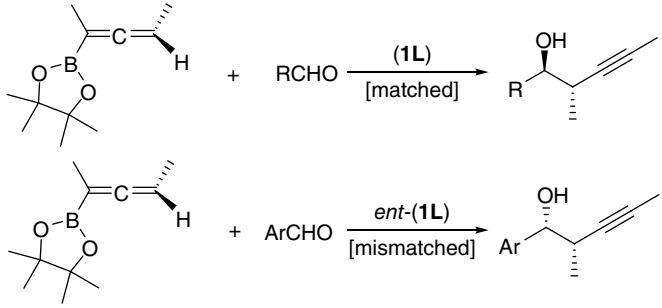


When a conjugated diene undergoes 1,2-addition with a dithiophosphoric acid based on a H_8-BINOL, the addition is able to trigger an intramolecular S_N2' reaction by an N-nucleophile.[27]



(**1O***) : 3,3′-[10-(Mes)An]$_2$-(**1A**)

Propargylation of aldehydes with allenylboronates catalyzed by**1L** proceeds via a matched pairing in the transition state. In switching to *ent*-**1L**, the pairing of the reactants is mismatched therefore it leads to a different diastereomeric series.[28] The same reaction can be conducted with the biphenylphosphoric acid analogous to **1L**.[29]



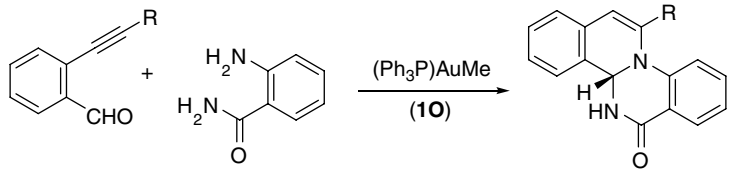
The silver salt of *ent*-**1N** is added to the InCl-catalyzed reaction of 1-methoxy-1-benzaminoalkanes with allylboronates (and allenylboronates). Actually it proceeds by an elimination-addition sequence, to produce the chiral homoallylic amine derivatives (and those of allenyl analogs).[30] Conjugated ketene silyl ethers add to *N*-(*p*-anisyl)aldimines to yield 5-amino-2-alkenoic esters with an *anti*-configuration, *ent*-**1L** is able to exert its effects to make the reaction asymmetric.[31]

N-Boc ketimines derived from isatin have been presented to pyrrole and indole in an asymmetric environment imposed by close association with *ent*-**1C**.[32] Anthranilide and certain aldimines (e.g., *N*-aryl and *N*-sulfonyl derivatives) react via imino exchange and intramolecular addition. The acid *ent*-**1O** can serve as catalyst for both steps.[33] Di-*t*-butyl α-diazomethylphosphonates and *N*-Boc aldimines combine enantioselectively as influenced by *ent*-**1L**,[34] and the same with thiols serving as one group of addends.[35]

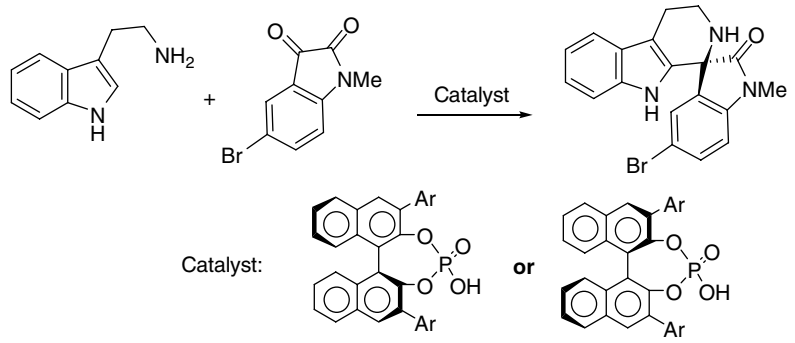
A report on Mannich reaction between oxazolinones and *N*-tosyl imines with the Ag salt of *ent*-**1T** as catalyst is found in recent literature.[36]

The noninterfering dual catalyst system of a phosphine-ligated Au(I) complex and **1L** works well to promote cyclization of 4-pentynol and then alkylation by 2,4-diaryl-5-oxazolinones at C-4, in the second step enantioselectivity is invoked.[37]

A similar strategy is deployed for the synthesis of quinazolinones which are further annulated, from mixtures of anthralinamide and 2-alkynylbenzaldehydes.[38] In this case (Ph_3P)AuMe and **1O** cooperate to deliver an excellent result.



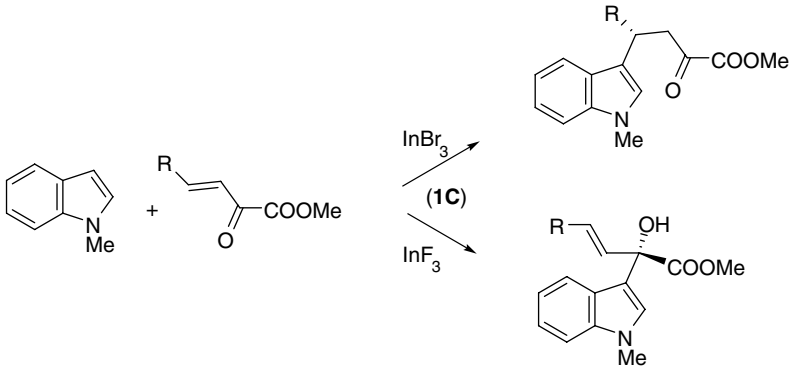
Establishment of the first chirality center in a recent synthesis of corynantheidine enlists H_8-*ent*-**1T** to conduct a Pictet-Spengler reaction.[39] The most remarkable observation is that Pictet-Spengler reaction with tryptamine and an isatin the product of same configuration is obtained from using either a (*R*)- or (*S*)-3,3′-diaryl-1,1′-binaphthalene-2,2′-diyl phosphate.[40]



Asymmetric addition of electron-rich arenes such as indole to ethyl 3,3,3-trifluoro-2-oxopropanoate gives rise to the fluorinated mandelic esters. Calcium salt of an octahydro-3,3′-diaryl-1,1′-binaphthalene-2,2′-diyl phosphate is a useful catalyst.[41]

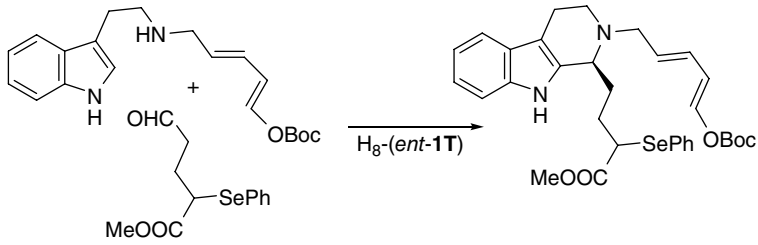
Double Michael addition involving N_b-methoxycarbonyltryptamine and 1-alken-3-ones gives rise to pyrrolo[2,3-*b*]indolines, *ent*-**1L** has shown value of stereoinduction at the ring junction.[42]

The InX_3-catalyzed addition of 1-methylindole to 2-oxo-3-alkenoic esters proceeds in either 1,2- or 1,4-fashion, depending on the halogen atoms associated with indium (F vs. Br).[43] The asymmetric versions are accomplished by adding **1C** and the like.



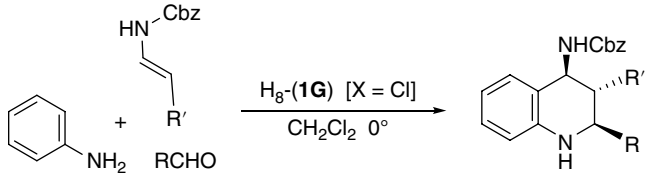
The Friedländer quinoline synthesis from 2-aminobenzaldehyde and 4-substituted cyclohexanones is rendered enantioselective by using *ent*-**1C** as catalyst.[44] Perhaps the Brønsted acid comes into play during enolization.

A synthesis of (+)-yohimbine featuring the C/D-ring construction by an intramolecular Diels-Alder reaction is dependent on enantioselective attachment of the dienophilic chain by a Pictet-Spengler reaction, and this is achievable by using *ent*-H_8-**1T** to catalyze the union.[45]



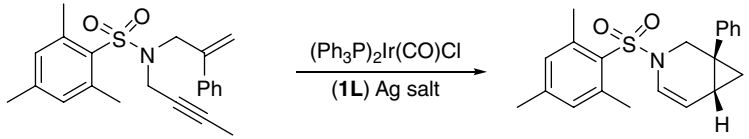
Cycloaddition. The 3,3-oxydimethylene-connected *ent*-**1A** is active in promoting the [3+2]cycloaddition of enones and imines to furnish chiral products.[46] Aldimines formed in situ from α–amino esters and aldehydes also undergo cycloaddition with 1-alkyn-3-ones, and experimentation using catalyst *ent*-**1O** has been reported.[47] Synthesis of pyrazolidines by the cycloaddition employs a catalyst generated from *ent*-**1D** and Ph_2SiCl_2.[48]

The Pavarov reaction has enjoyed much attention in recent years. Tetrahydroisoquinolines in optically active modification are now very readily assembled from anilines, aldehydes and functionalized alkenes that include enamides,[49] *N*-alkenylthioureas,[50] and nuclear hydroxylated styrenes.[51,52] In all these cases the acquisition of chiral products employs various members of **1** [e.g., *ent*-**1L**, **1J**, **1T**, and H_8-**1G** (X= Cl)].

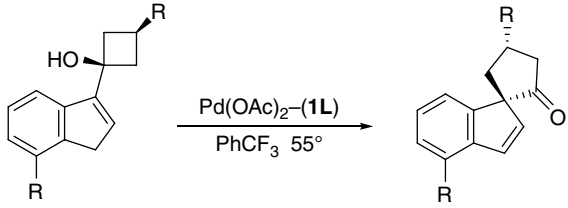


Modification of the Friedländer quinoline synthesis can yield the same type of products as the Pavaro reaction, e.g., by providing a Hantzsch ester to reduce the proper intermediates. Here a catalyst system made up of *ent*-**1L** and $Mg(OTf)_2$ is used to advantage.[53]

As iridium complexes are able to extract an allylcarbenoid activity from an alkyne, intramolecular cyclopropanation of properly distanced ene/yne units is readily practiced, and such reaction is also subject to asymmetric induction (e.g., by the silver salt of **1L**).[54]



Rearrangement. 1-(Inden-3-yl)cyclobutanols undergo rearrangement upon C-H bond activation (at C-1 of the indene nucleus) by a Pd salt to yield spirocyclic ketones under oxidative conditions, and **1L** is for producing chiral products.[55]



Imidates of 2-alkenols are converted into chiral 3-acylamino-1-alkenes. The Claisen rearrangemnt is facilitated by a palladcycle and enantioselectivity is conferred by the 2:2-complex with **1L** (the palladacycle also contains a chiral element).[56]

Oxidation. Asymmetric oxidation of sulfides (including 1,3-dithianes) by H_2O_2 is mediated by *ent*-**1Q**.[57] Alternatively, change can be made of the oxidant to PhIO and the catalyst to an iron(III) complex of salicylimine and a 3,3′-di(4-*t*-butylphenyl) derivative of **1A**.[58]

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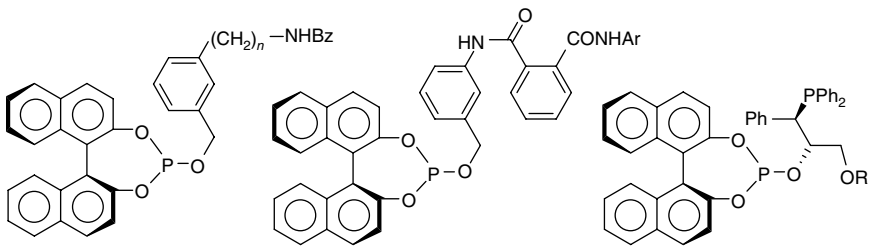
1,1′-Binaphthalene-2,2′-diyl phosphites

Hydrogenation. Enantioselective hydrogenation of functionalized alkenes is achieved on Rh(I) complexed to BINOL-derived phosphites **1**, **2**, or **3**.[1,2,3]



(**1**) (**2**) (**3**)

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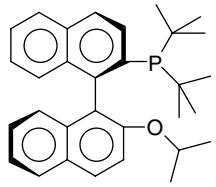
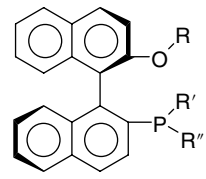
1,1′-Binaphthalen-2-ol-2′-phosphines and derivatives

Substitution. The binaphthyl-based ether/phosphine **1** has found use as a monodentate ligand for Pd-catalyzed *N*-arylation of $ArNH_2$,[1] and 1,2-bis(*t*-butoxycarbonyl)hydrazine.[2] Different Pd species are used in the two reactions, as the *t*-Boc groups in substrate of second reaction is acid-sensitive.



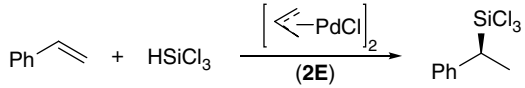
(**1**)



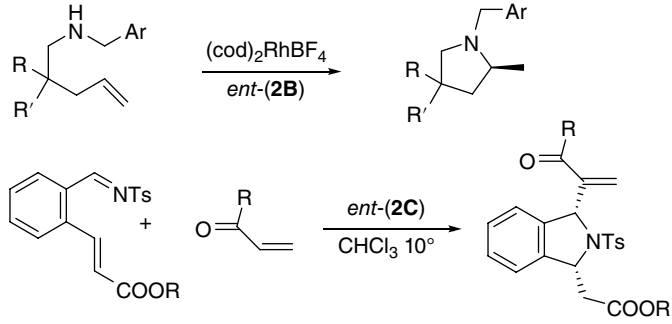
(**2A**) R = CH_2(β-Np), R′ = R″ = Cy
(**2B**) R = $CHPh_2$, R′ = R″ = Cy
(**2C**) R = H, R′ = R″ = Ph
(**2D**) R = *i*-Pr, R′ = R″ = Ph
(**2E**) R = *i*-Pr, R′ = Ph, R″ = *i*-Pr
(**2F**) R = Me, R′ = R″ = Ph

By arylation of ketene silyl ethers to access chiral α–arylalkanoic esters the H_8-derivative of an ether/phosphine **2** may be gainfully employed.[3]

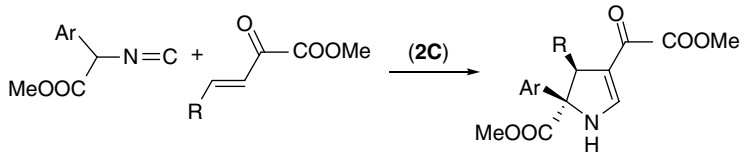
Addition. The ligand **2E**, prepared in five steps from (*R*)-BINOL, can promote enantioselective hydrosilylation of styrenes (with $HSiCl_3$) and thence (*S*)-1-arylethanols.[4]



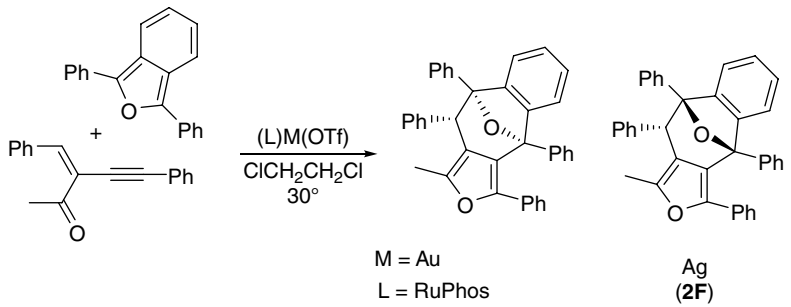
Intramolecular hydroamination in the presence of a Rh(I) salt sequestered by *ent*-**2B** results in the formation of (*S*)-2-methylpyrrolidines.[5] Taking advantage of the ability of tertiary phosphines to catalyze the Baylis-Hillman reaction, an application of *ent*-**2C** to elaborate *cis*-1,3-disubstitited isoindolines in chiral modification is realized.[6]



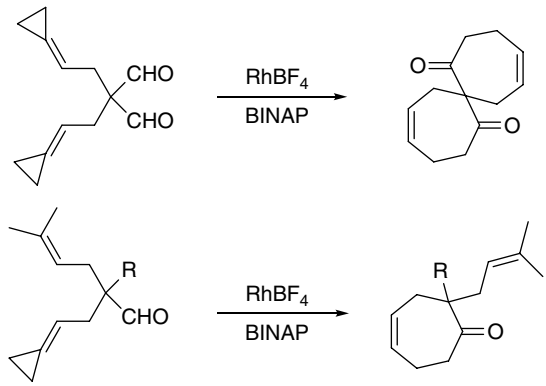
Annulation. An enantioselective route to 2,3-dihydropyrrole-2-carboxylic esters also employs **2C** to catalyze the union of α–isocyano esters and conjugated carbonyl compounds.[7]



Induced by noble metal complexes α-benzylidene-3-alkyn-1-ones are converted into 4-metallo-2-oxoniafulvenes which would actively pursue cycloaddition. In the reaction with isobenzofurans the stereochemical influence by a silver complex of *rac*-**2D** is different from that of a gold complex to RuPhos.[8]



3-Formylpropylidenecyclopropanes undergo intramolecular hydroacylation that breaks up the three-membered ring in a reaction catalyzed by a Rh(I) salt.[9]



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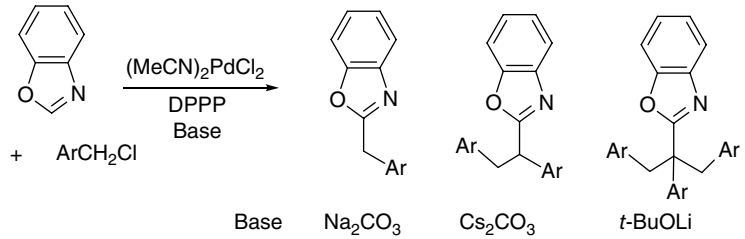
Bis(acetonitrile)dichloropalladium(II)

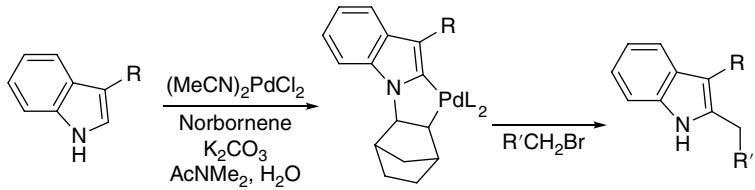
Coupling. Stille coupling for preparation of 3-alkynoic esters and amides starts with tributylstannylalkynes and the α-bromo esters/amides.[1] Arenesulfonyl compounds (chlorides, and sodium salts) are converted to ArCN on reaction with CuCN, the Pd catalyst is assisted by $Cu(acac)_2$.[2] Benzylation at C-2 of benzoxazole can go further at the α-carbon by changing the base from Na_2CO_3 to Cs_2CO_3 and *t*-BuOLi.[3] Hiyama coupling of thiophene occurs selectively at a β-position.[4]



Suzuki coupling of polyfluoroarenes containing a 2-oxazolidinyl group is selective, as expected to occurs at the *o*-position of the heterocyclic substituent.[5]

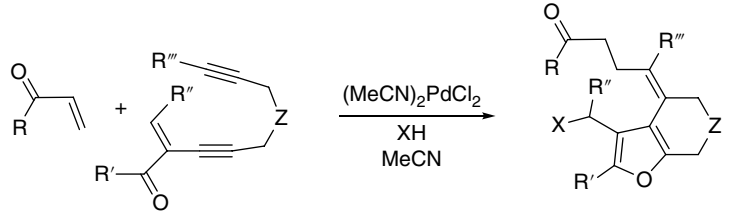
3-Phthalimido-1-alkenes add RZnBr under oxidative conditions [$(MeCN)_2PdCl_2$, $Zn(OTf)_2$, benzoquinone] to afford homologous *N*-alkylphthalimides.[6] Alkyl group transfer to and deoxygenation of isoquinoline-*N*-oxide take place when it is heated with a dialkyl sulfoxide; with $SOCl_2$ chlorination occurs. Besides the Pd(II) catalyst, additives present are Bu_3N, $(Bu_4N)OAc$, and ZnO.[7]

Norbornene is a participant in palladation and then alkylation of indoles at C-2, but its role is transient.[8]



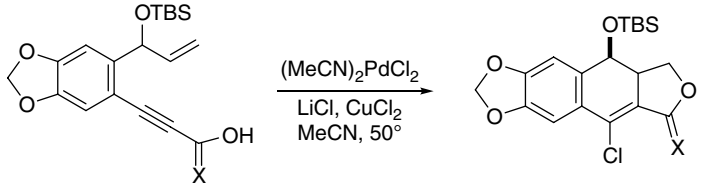
3-Alkylidene-1-isoindolinones are formed in a coupling reaction of *o*-halobenzamides and 1-alkynes. A ligand to assist the metal catalyst is *N,N′*-di(4-pyridinemethylene) hydrazine.[9]

Certain enediynes are susceptible to push-pull bicyclization in the presence of a nucleophile, a Michael acceptor besides the Pd catalyst.[10]



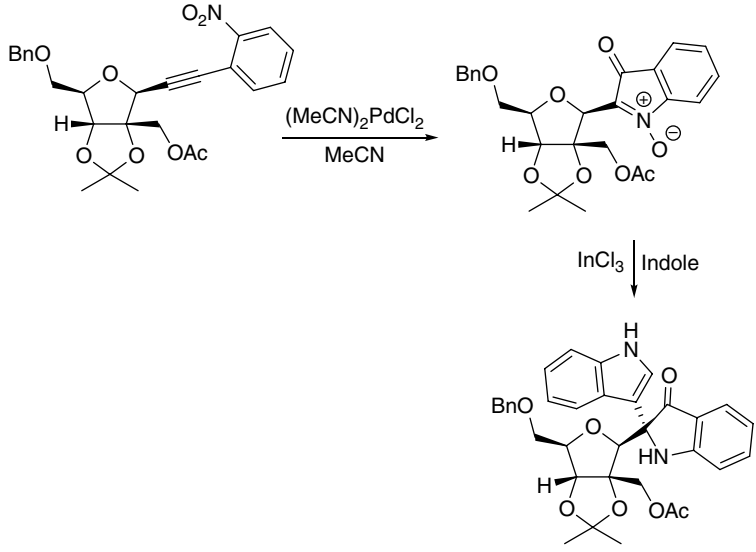
Addition to CC multiple bonds. The passage of styrenes to arylacetaldehydes is >99% regioselective, by oxidative hydration in a reagent system composing of $(MeCN)_2PdCl_2$, benzoquinone, *t*-BuOH and water.[11] The Pd-catalyzed oxidation of 1-alkenes in the presence of pinacol furnishes the aldehyde acetals.[12]

A combination of $(MeCN)_2PdCl_2$ and $CuCl_2$ induces the cycloaddition of *N*-(ω-alkenyl) carbamates with loss of the *O*-alkyl group, to form bicyclic oxazolidinones.[13] An intramolecular cycloaddition is apparently initiated by chloropalladation of a triple bond, in this case sufficient concentration of the chloride ion is provided by LiCl.[14]



X = O; H,H

In a synthesis of (–)-isatisine-A the indolizidinedione unit is constructed in three steps starting from an intramolecular addition.[15]



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Bis(allyl)calcium

Metallation. 2-Picoline undergoes metallation at the methyl group for reaction with electrophiles.[1]

[1] Jochmann, P., Leich, V., Spaniol, T.P., Okuda, J. *CEJ* **17**, 12115 (2011)

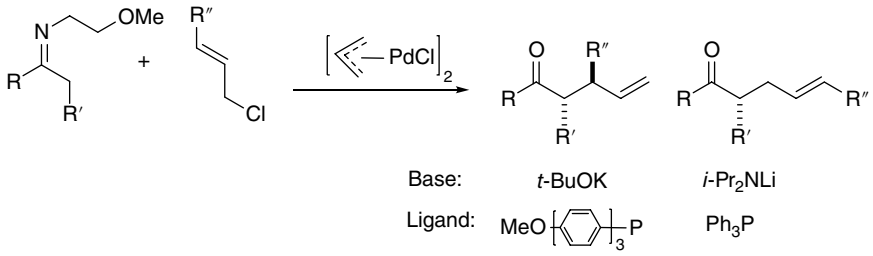
Bis(η³-allyl)dichlorodipalladium

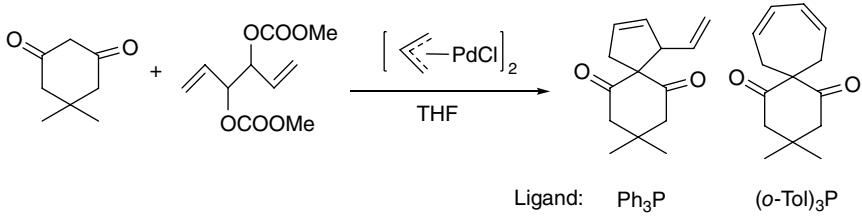
Addition. π-Allylpalladium chloride (dimer) is catalytically active for promotion of hydrohalogenation of 1-haloalkynes by LiX in HOAc, leading to (*Z*)-1,2-dihalo-1-alkenes.[1]

Substitution. The primary carbonate of an (*E*)-2-alkene-1,5-diol can be transformed into *syn*-1-alkene-3-5-diols via Pd-catalyzed hemiacetalization with an added aldehyde, followed by an intramolecular S_N2' reaction. 4-Vinyl-1,3-dioxanes that are formed have an all-*cis* configuration.[2]

In an alkyl aryl ether synthesis from ArX and RR'CHOH it seems that the catalyst is best supported by an encumbered phosphine such as BrettPhos.[3]

Allylation of ketimines by 1-chloro-2-alkenes can follow S_N2 or S_N2' pathway, and a choice of base and ligand becomes the determining factor.[4] A related finding is the double allylation of 5,5-dimethyl-1,3-cyclohexadione by a dicarbonate of 1,5-hexadiene-3,4-diol.[5]





The applicability of allylamines such as *N*-allylpyrrolidine as electrophiles in the reaction with ketones is quite novel.[6] However, the transition of 3-aryl-2-propen-1-ols to amines is straightforward,[7] although whether the ligand, 1,7-bis(diphenylphosphino)indole, has special attributes is unclear.

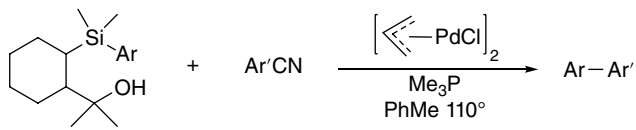
3-Bromo-2,4-pentadienyl acetate undergoes twofold substitution, with the nucleophiles attach themselves at the two terminal carbons in the resulting 2,3-alkadienes.[8]

Amine synthesis based on some substitution/coupling reactions has been extended to using sulfonamides to react with ArX,[9] main purpose seems to be exploration of new catalyst and ligand combinations. More unusual is the substitution of allylic amines to form allyl sulfones on reaction with RSO_2Na.[10]

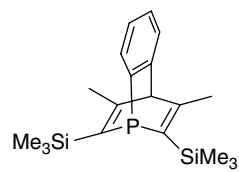
The transformation of ArOTf into ArF is better performed in a microreactor with packed-bed for flow reaction that allows for handling the insoluble CsF, and reaction time control.[11]

The ionic Pd tetrafluoroborate complex containing an allyl and a COD ligand each is active in promoting benzylic displacement by all kinds of nucleophiles, and under such conditions the leaving group selectivity trend is F > OCOOMe >> OAc.[12]

Coupling. Biaryls are formed from coupling reactions. Pairing $(ArSiMe_2)_2O$ with Ar'Br is easily recognized,[13] but that involving Si-C bond cleavage and decyanation is quite unusual.[14] A method for synthesis of $ArCOCH_2CN$ is through coupling of ArI, CO and Me_3SiCH_2CN, here the catalyst system contains bis(η³-methallyl)dichlorodipalladium, $CuBr_2$, and ZnF_2.[15]

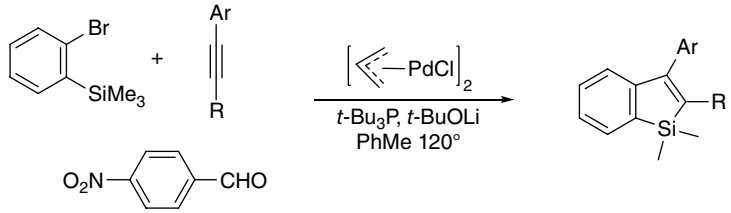


The Negishi coupling can take full advantage of the air-stable phosphabarrelene ligand **1** that forms a catalyst active at room temperature in THF because it allows easy reduction of Pd(II) species to the Pd(0) state.[16]



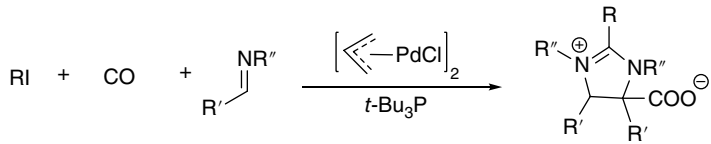
(**1**)

Benzosiloles can be elaborated from 2-bromoaryltrimethylsilanes and alkynes.[17] However, the appropriate Pd catalyst for alkynes having the *sp*-carbons bonded to alkyl groups is $(Ph_3P)_4Pd$.



On converting tertiary amines containing one benzyl group to the tricarbonylchromium complexes, arylation is relatively facile. Thus lithiation on exposure to $LiN(SiMe_3)_2$ is followed by the Pd catalyst, a phosphine ligand and ArOTf to complete the transformation. The use of a chiral ferrocene-based P,N-ligand gives optically active diarylmethylamines.[18]

α-Cyanoalkanoic acid salts (of Na, K) undergo decarboxylative benzylation.[19] In the formation of an imidazolinium salt that bear a carboxylate group at C-4 by coupling of an imine, RI and CO, two equivalents of the imine are consumed.[20]



Many aroylformic acid derivatives can be made in one step from electron-rich ArI, CO and nucleophiles, A base that is preferred is DBU.[21]

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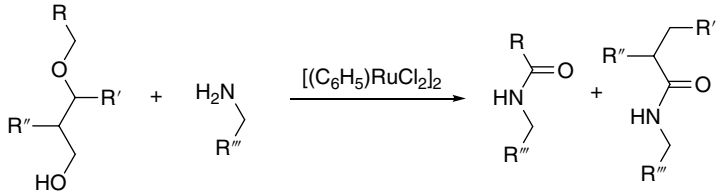
Bis[(η⁶-arene)dichlororuthenium(II)]

Reduction. Under hydrogen the reduction of aroic acid esters to the benzyl alcohols is achieved in the presence of $[(\eta^6\text{-benzene})RuCl_2]_2$ and a 1-methylimidazol-2-ylmethylphosphine ligand (variation of the other *P*-substituents to suit the nature of the ester, ArCOOR or ArCOOAr').[1]

Transfer hydrogenation of nitroarenes and reductive cleavage of azoarenes are readily achieved using $[(\eta^6\text{-cymene})RuCl_2]_2$ as catalyst.[2] The same method is applicable to reduction of sulfinimines [with additive $HOCH_2C(NH_2)Me_2$].[3] A borane complex, $Me_2NH{\cdot}BH_3$, is also a suitable hydrogen source for the reduction of carbonyl compounds, imines, and oximes.[4]

Alkylation of amines by incorporating the carbon chain of allylic alcohols is accomplished by heating the mixtures with HCOOH in toluene at 150° with a modified $[(\eta^6\text{-cymene})RuCl_2]_2$ in which one of the chlorine atom is replaced by an *o*-diphenylphosphinobenzenesulfonate group.[5]

Coupling. 3-Alkoxyalkanols react with primary amines to produce two amides through cleavage of the ethereal carbon bond, each fragment being utilized for oxidative coupling.[6]

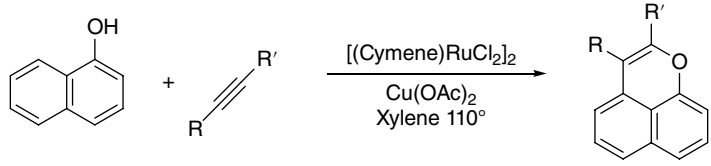


An aroic ester is *o*-hydroxylated on treatment with $[(\eta^6\text{-cymene})RuCl_2]_2$ and an oxidant (e.g., $K_2S_2O_8$) in a mixture of CF_3COOH and $(CF_3CO)_2O$.[7] Amides are similarly *o*-hydroxylated with a slightly different catalyst-oxidant system, $[(\eta^6\text{-cymene})Ru(OCOMes)_2]_2$ and $PhI(OAc)_2$.[8] [Note the dimesylate complex promotes *o*-arylation of functionalized arenes in water by phenols, which are converted into tosylates in situ.[9]]

Phthalides are synthesized by *o*-alkenylation of aroic acids with electron-deficient alkenes, which is followed by lactonization. The oxidant is $Cu(OAc)_2$.[10]

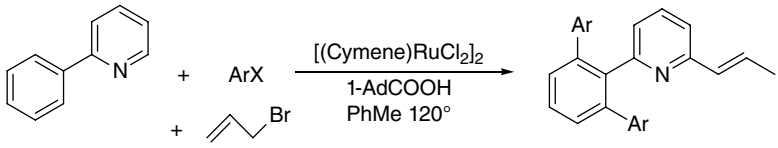
Ring closure via formyl group translocation delivers 3-formylindoles from 2-alkynylformanilines. Heating the substrates with $[(C_{10}H_{14})RuCl_2]_2$ in dichloroethane accomplishes the reaction.[11]

o-Arylation of aromatic amides employs $ArB(OH)_2$, the Ru(II) complex, and Ag_2O – $AgSbF_6$.[12] More extensively investigated is the *o*-alkenylation, involving aroic esters,[13,14] aromatic aldehydes,[15] *O*-aryl carbamates and an acrylic ester in air.[16] In these reactions $Cu(OAc)_2$ and $AgSbF_6$ are essential additives. With alkynes these acids and amides combine to give isocoumarins[17,18] and isoquinolin-1-ones,[19–21] respectively. Tertiary amides furnish *o*-alkenyl derivatives as expected.[22] 1-Naphthol and 4-hydroxycoumarin are annulated across the *peri*-position.[23]



Different results appear in the coupling of aryl ketones with alkynes, as 1-indanols or benzofulvenes are obtained.[24] The latter compounds are the dehydration products produced when larger amounts of $AgSbF_6$ are used.

The familiar activation by the pyridinyl nitrogen atom on a proximal C-H bond of 2-arylpyridines also prevails with the Ru(II) complex. Alkynylation using 1-bromoalkynes[25] and arylation[26] are similarly performed. Interestingly, a 1-propenyl group is selectively introduced to C-6 of the pyridine ring on reaction with allyl bromide.

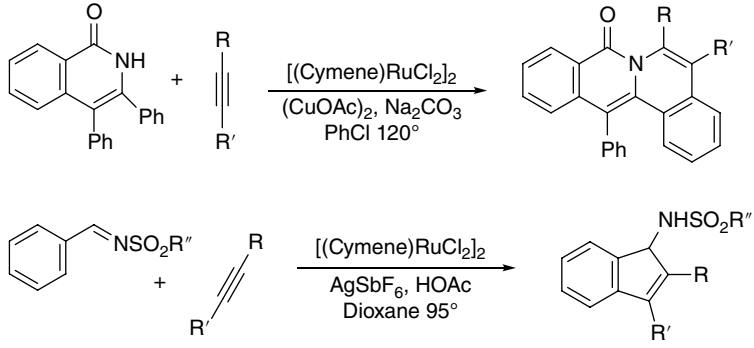


A strategy for *o*-arylation of phenols as developed based on the directive effect of a pyridyl group involves formation of aryl 2-pyridyl ethers. Removal of the pyridyl unit after the arylation completes the transformation.[27]

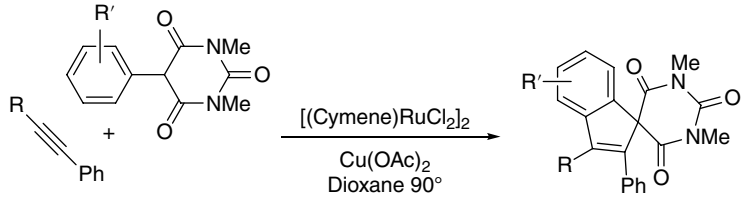
The coupling method is applicable to adding a carbamoyl group, when using RNCO as reactant.[28] *N*-Arylimines of aryl ketones readily undergo *o*-arylation, introduction of the substituent to two open *o*-positions is observed.[29] Similar reactions on oximes and oxime ethers produce substituted isoquinolines.[30]

2-Arylaminopyrimidines form *N*-(2-pyrimidyl)indoles on reaction with alkynes.[31] The *o*-position of the aniline derivatives is activated by the pyrimidyl group.

3-Aryl-1-isoquinolinones offer an opportunity to form a dibenzoquinolizine skeleton.[32] *N*-Sulfonylaldimines derived from araldehydes undergo coupling that ends with addition to the C=N bond.[33]



Activation of a benzylic C-H bond for coupling is exemplified by the method of α-arylation of benzylic amines.[34] On attaching the amino group to C-2 of β-picoline (removable), the pyridyl nitrogen atom can exert its influence on the benzylic position. Spiroannulation of 5-aryl-1,3-dimethylbarbituric acids is quite facile.[35]



Tertiary cyclic amines (pyrrolidines and piperidines) are alkylated by RCHO/HCOOH at a β-carbon in the presence of the slightly modified $[(\eta^6\text{-cymene})RuCl_2]_2$ in which a chlorine atom is replaced by an *o*-phosphinobenzenesulfonato ligand.[36]

N-(α-Diazo-β-oxoalkanoyl)anilines undergo cyclization to furnish 3-acyloxindoles on warming in toluene with $[(\eta^6\text{-cymene})RuCl_2]_2$.[37]

Substitution. *ipso*-Substitution with retention of configuration of cinnamyl acetates/carbonates and their allylomers is a general trend for the Ru(II)-catalyzed reaction. 2-Diphenylphosphinobenzoic acid is a better ligand than Ph_3P. Regarding regioselectivity, the cinnamyl substrates perform poorer than those having the leaving group at the benzylic position.[38]

An unusual arenesulfonylation at a *m*-position of 2-arylpyridine[39] is interpreted as activation of the *p*-position to the metal of a ruthenacycle intermediate. [Note that the *p*-position is *meta* to the pyridyl substituent.]

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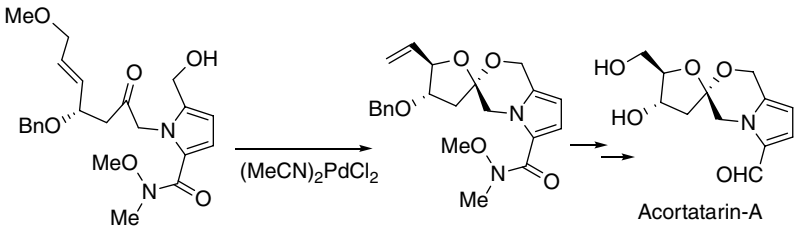
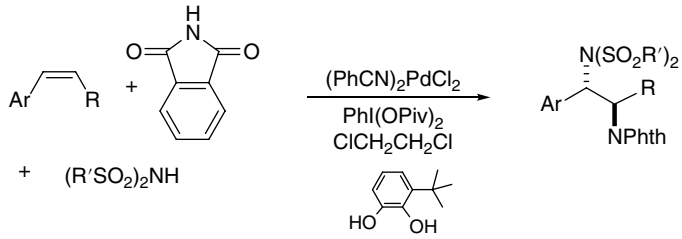
Bis(benzonitrile)dichloropalladium(II)

Coupling. Aryl formates are converted into aroic esters by reaction with ArX, using $(PhCN)_2PdCl_2$ as catalyst (ligand: Xantphos).[1] Unsaturated azacycles undergo C-H arylation at the sp^2-carbon atom adjacent to the nitrogen. The reaction is carried out with RSO_2Na, while the Pd catalyst is supplemented with an oxidant, e.g., $Cu(OAc)_2$.[2]

Substitution. In a synthetic approach to acortatarin-A the spiroketal unit was constructed in a reaction sequence of hemiacetalization and intramolecular S_N2' displacement.[3]



Addition. Functionalization of a double bond by adding two different amino groups is illustrated in the example shown below.[4]



Cyclopentenes are synthesized from a Pd-catalyzed reaction between 1-pinacolatoboryl-1,2-propadiene and doubly activated alkenes.[5]

[1] Fujihara, T., Hosoki, T., Katafuchi, Y., Iwai, T., Terao, J., Tsuji, Y. *CC* **48**, 8012 (2012)
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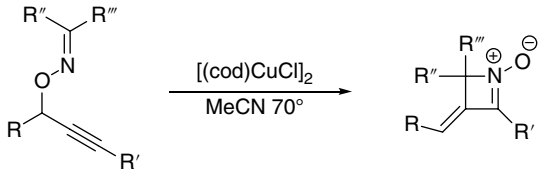
Bis[chloro(1,5-cyclooctadiene)copper(I)]

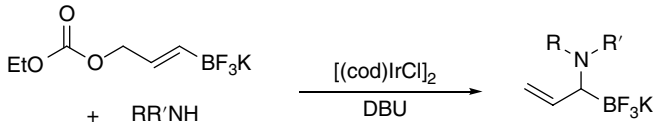
Cycloisomerization. Conversion of oxime propargyl ethers into four-membered nitrones on heating with $[(cod)CuCl]_2$ is a rather unusual reaction.[1]



[1] Nakamura, I., Kudo, Y., Araki, T., Zhang, D., Kwon, E., Terada, M. *S* 1542 (2012)

Bis[chloro(1,5-cyclooctadiene)iridium(I)]

Substitution. Catalyzed by $[(cod)IrCl]_2$, 3-trichloroacetimino-1-alkenes are transformed by $Et_3N{\cdot}3HF$ into the 3-fluoro-1-alkenes.[1] An anionic trifluoroborato group directs the regiochemistry of allylic substitution.[2]



α–Alkylation of nitriles (e.g., MeCN to $ArCH_2CH_2CN$) by primary alcohols is achieved in the presence of a base.[3] Intramolecular reaction is similarly performed.[4]

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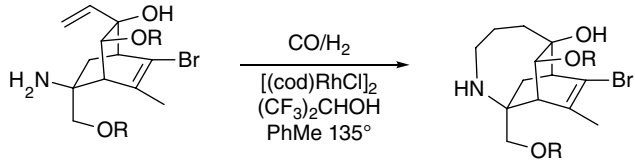
[3] Anxionnat, B., Pardo, D.G., Ricci, G.,Cossy, J. *OL* **13**, 4084 (2011)
[4] Anxionnat, B., Pardo, D.G., Ricci, G.,Cossy, J. *EJOC* 4453 (2012)

Bis[chloro(1,5-cyclooctadiene)rhodium(I)]

Addition. Hydroformylation and reduction are accomplished in one operation to transform styrenes into 2-arylpropanols by syngas in the presence of $[(cod)RhCl]_2$ and 1,4-bis(dimethylamino)butane.[1] Linear homologation of a carbon chain and functionalization can lead to cyclization via a Schiff base.[2]

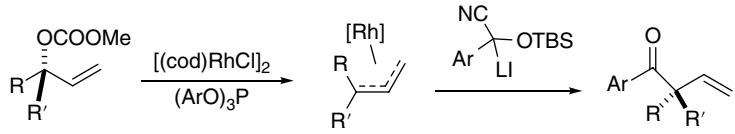


n-Alkenols apparently undergo isomerization to become donors of aldol reaction, and the *syn*-2-alkyl-3-hydroxyalkanals are prepared.[3]

By Rh(I) catalysis, pyridine adds pinacolatoborane to afford *N*-pinacolatoboryl-1, 2-dihydropyridine.[4] A similar reaction is the formation of α-arylamine derivatives from reaction of *N*-sulfinylimines with arylboroxines[5] or (with *S*-chiral imines) sodium tetraarylborates.[6]

Pyridine *N*-oxide and benzannulated azoles add *t*-butyl acrylate at the α-carbon site, when the Rh(I) catalyst supported by a diphosphine is used.[7]

Substitution and coupling. The reaction of cinnamyl halides with triorganoindium reagents is catalyzed by $[(cod)RhCl]_2$.[8] The oxygen function of benzylic acetates is replaced (S_N2') by an allyl group from allylsilanes.[9] However, on reversing the roles of the allylic substrates, the action of the Rh(I) complex on allylic carbonates to render them electrophilic, reaction with masked acyl anions takes place at the internal position.[10]



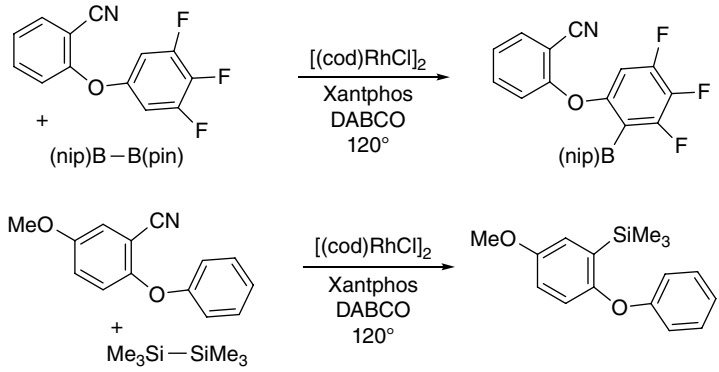
The substitution of 3-(α-sulfonylalkyl)indoles by various nucleophiles usually proceeds by an elimination-addition pathway. It is no exception in the Rh(I)-catalyzed reaction with arylboronic acids under basic conditions.[11] An ester group is introduced at C-3 of the indole nucleus on a carbonylation-trapping sequence promoted by the Rh(I) complex and in the presence of $K_2S_2O_8$.[12]

Substitution (or coupling) of ArI on reaction with Ar'SH in the presence of the Rh complex[13] is of little synthetic significance. Less obvious is the B/CN group exchange from aryl, benzyl and alkenyl cyanides on reaction with cyclic diboronates.[14]

Benzosiloles are synthesized from reaction of *o*-trimethylsilylphenylboronates and alkynes.[15] In the cyclization step loss of a methyl group from the silicon atom occurs.

Bromoarenes couple with acrylic esters at the *m*-position when the Rh(I) complex and $Cu(OAc)_2$ are used as cocatalysts in air. One equivalent of Cl_3CCOOH is also indispensable.[16]

Rhodium insertion into aryl cyanides followed by 1,5-metal migration is featured in certain *o*-cyanodiaryl ethers, and bonding of the coupling partner to the other aryl nucleus is observed.[17]



Annulation. An intricate transformation involves ring cleavage of an alkylidenecyclopropane unit while one of the sp^2-carbon atoms participates in the formation of a five-membered ring.[18] Under the Pauson-Khand reaction conditions (presence of CO) the small ring remains unscathed while the π-bond (although as an allenylidenecyclopropane) is normally engaged.[19]