

Fiesers'

Reagents for Organic Synthesis

VOLUME TWENTY SIX

Tse-Lok Ho



A JOHN WILEY & SONS, INC., PUBLICATION

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PREFACE

Writing in the tradition of my predecessors requires constant inspiration. At least that is the sentiment I espouse. Recently this feeling sprang from my heart again on reading about the life of Friedrich Konrad Beilstein (1838–1906), whose famous *Handbuch der organischen Chemie* is well known to the older generations of organic chemists worldwide.

Beilstein was born in St. Petersburg of German parentage. He studied with Bunsen in Heidelberg, and with Liebig in Munich. After receiving a doctorate degree under Wöhler in Göttingen he spent some time with Wurtz in Paris, at the Ecole de Medicine. After returning to Germany, Beilstein gained experience in editing through a close association with the publication of the *Zeitschrift für Chemie*. When the professorship at the Imperial Technological Institute in St. Petersburg was vacated by Mendeleev in 1866, Beilstein was named to fill it. Apparently, he conceived the idea of writing his *Handbuch* in this period and completed a manuscript in the late 1870s. It was published in two volumes between 1880 and 1882, immediately became a best seller. Revision and amendment to make up 4080 pages in a second edition occupied all the time available to Beilstein and an assistant; he declined callings from German universities because he thought many duties would interfere with his writing.

While surveying the new period (mid-2008 ~ end of 2009) for this volume the author observes that the chemical literature still parades Pd and Au reagents most prominently as the cardinal currency, with torrential pouring out of chiral catalysts in tributaries from proline and cinchona alkaloid sources.

My three-month stay in the campus of Academia Sinica in Taipei was indispensable for collecting information to form the framework of this volume. My heartfelt thanks go to Professor C.-H. Wong (President) and Professor Y.-T. Tao (Director, Institute of Chemistry) for their hospitality and help, as well as the cheerful librarians for facilitating my work.

REFERENCE ABBREVIATIONS

<i>ACIE</i>	Angew. Chem. Inter. Ed.
<i>ASC</i>	Adv. Synth. Catal.
<i>CAJ</i>	Chem. Asian J.
<i>CC</i>	Chem. Commun.
<i>CEJ</i>	Chem. Eur. J.
<i>CJC</i>	Can. J. Chem.
<i>CL</i>	Chem. Lett.
<i>CSR</i>	Chem. Soc. Rev.
<i>EJOC</i>	Eur. J. Org. Chem.
<i>H</i>	Heterocycles
<i>HCA</i>	Helv. Chim. Acta
<i>JACS</i>	J. Am. Chem. Soc.
<i>JCR</i>	J. Chem. Res.
<i>JHC</i>	J. Heterocycl. Chem.
<i>JOC</i>	J. Org. Chem.
<i>JOMC</i>	J. Organomet. Chem.
<i>OBC</i>	Org. Biomol. Chem.
<i>OL</i>	Org. Lett.
<i>OM</i>	Organometallics
<i>OPPI</i>	Org. Prep. Proced. Int.
<i>OS</i>	Org. Synth.
<i>RJOC</i>	Russ. J. Org. Chem.
<i>S</i>	Synthesis
<i>SC</i>	Synth. Commun.
<i>SL</i>	Synlett
<i>T</i>	Tetrahed.
<i>TA</i>	Tetrahed. Asym.
<i>TL</i>	Tetrahed. Lett.

A

4-Acetamido-2,2,6,6-tetramethyl-1-oxopiperidinium tetrafluoroborate.

Ether cleavage. Benzyl ethers undergo oxidative cleavage to release the alcohols (primary and secondary) and benzaldehyde on exposure to the oxopiperidinium salt in aq. MeCN.¹

¹Pradhan, P.P., Bobbitt, J.M., Bailey, W.F. *JOC* **74**, 9524 (2009).

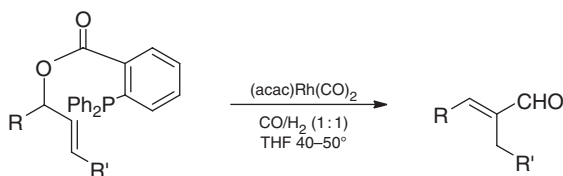
Acetylacetonatobis(cyclooctene)rhodium(I).

Hydroboration. With (acac)Rh(coe) as catalyst and a tertiary phosphine ligand that is attached to silica gel the hydroboration of styrenes leads to benzylic alcohols.¹

¹Geier, M.J., Geier, S.J., Vogels, C.M., Beland, F., Westcott, S.A. *SL* **477** (2009).

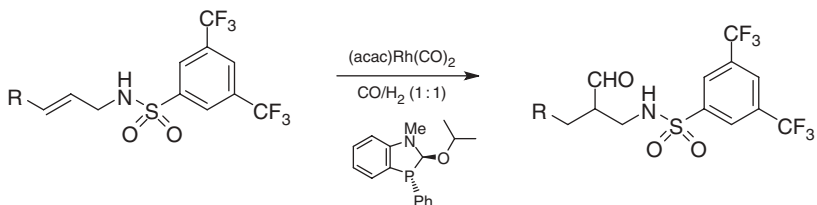
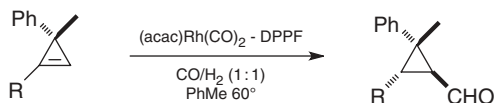
Acetylacetonato(dicarbonyl)rhodium(I).

Hydroformylation. A biphenyl-based diphosphine ligand supports the transformation of 1-alkenes to primary alcohols using the Rh(I) complex in syngas (tandem hydroformylation–hydrogenation).¹ The 2,2',6,6'-tetrakis(diphenylphosphinomethyl)-1,1'-biphenyl ligand exerts high linear selectivity for hydroformylation and confers high performance at high temperatures.² Another ligand is a 2,2',6,6'-tetrakis(dipyrrolylphosphinoxy) derivative for transforming acrylic esters into 3-formylpropanoic esters (regioselectivity >99:1).³ By installing an internal phosphine ligand the regioselective hydroformylation of allylic alcohols is realized.⁴

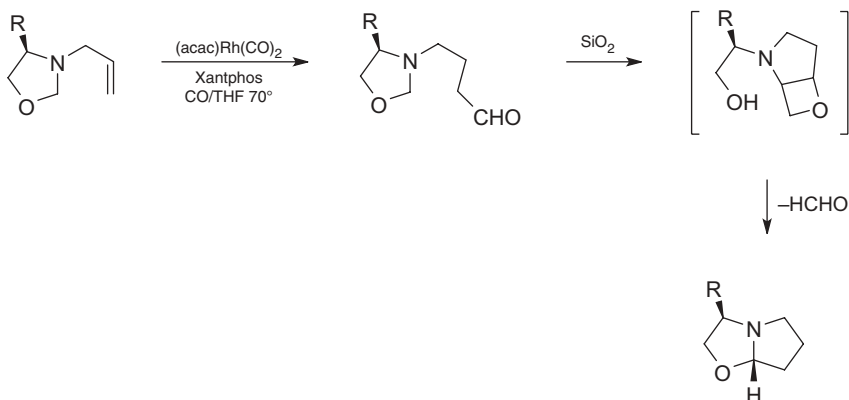


Hydroformylation of cyclopropenes is subject to steric effects,⁵ polar effects seem to dominate in the cases such as *N*-sulfonyl-2-alkenylamines.⁶

2 Acetylacetonato(dicarbonyl)rhodium(I)

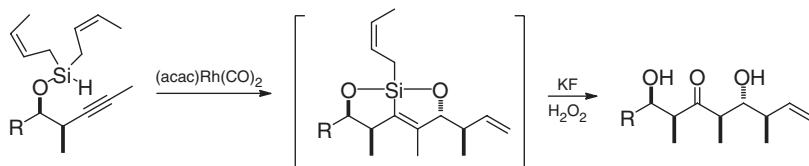


A somewhat unusual reaction occurs on treatment of *N*-allyloxazolidines under hydroformylation conditions.⁷

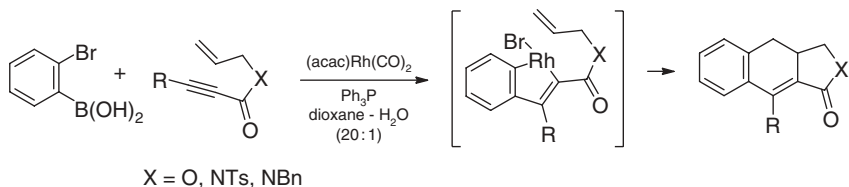


Several valuable tandem reactions that follow the hydroformylation have been designed. Thus, chain elongation by an acrylic acid unit is achieved by a subsequent Knoevenagel reaction and decarboxylation.⁸ Pictet–Spengler cyclization to follow hydroformylation of *N*-(3-butenyl)tryptamine⁹ and *N*-allyl-(3-indolyl)acetamide¹⁰ gives tetracyclic compounds. (Cf. the intermolecular version.¹¹)

A stereoregular methyl-branched carbon chain can be built from homopropargylic silyl ethers. When intramolecular silylformylation is concluded an allyl residue is delivered from the silicon atom to the nascent formyl group.¹²

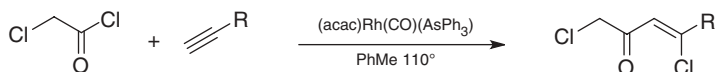


Addition. The Rh complex promotes addition of arylboronic acids to alkynes, with diarylethyne the formation of triarylethenes is achieved.¹³ A more intricate reaction involves *o*-bromophenylboronic acid and allyl 2-alkynoates and amide congeners from which γ -lactones and lactams fused to a dihydronaphthalene nucleus arise.¹⁴



The title complex is also useful as hydrogenation catalyst for enones.¹⁵

A slightly different complex in which one of the CO ligands is replaced by Ph₃As catalyzes acylchlorination of 1-alkynes.¹⁶



¹Ichihara, T., Nakano, K., Katayama, M., Nozaki, K. *CAJ* **3**, 1722 (2008).

²Yan, Y., Zhang, X., Zhang, X. *ASC* **349**, 1582 (2007).

³Yu, S., Chie, Y.-m., Zhang, X. *ASC* **351**, 537 (2009).

⁴Bruch, A., Gebert, A., Breit, B. *S* 2169 (2008).

⁵Sherrill, W.M., Rubin, M. *JACS* **130**, 13804 (2008).

⁶Worthy, A.D., Gagnon, M.M., Dombrowski, M.T., Tam, K.L. *OL* **11**, 2764 (2009).

⁷Vasylyev, M., Alper, H. *ACIE* **48**, 1287 (2009).

⁸Kemme, S.T., Sinejkal, T., Breit, B. *ASC* **350**, 989 (2008).

⁹Airiau, E., Spangenberg, T., Girard, N., Schoenfelder, A., Salvadori, J., Taddei, M., Mann, A. *CEJ* **14**, 10938 (2008).

¹⁰Chiou, W.-H., Lin, G.-H., Hsu, C.-C., Chaterpaul, S.J., Ojima, I. *OL* **11**, 2659 (2009).

¹¹Bondzic, B.P., Eilbracht, P. *OBC* **6**, 4059 (2008).

¹²Spletstoser, J.T., Zacuto, M.J., Leighton, J.L. *OL* **10**, 5593 (2008).

¹³Zhang, W., Liu, M., Wu, H., Ding, J., Cheng, J. *TL* **49**, 5214 (2008).

¹⁴Fang, X., Li, C., Tong, X. *CC* 5311 (2009).

¹⁵Scheuermann, C.J., Jaekel, C. *ASC* **350**, 2708 (2008).

¹⁶Kashiwabara, T., Fuse, K., Hua, R., Tanaka, M. *OL* **10**, 5469 (2008).

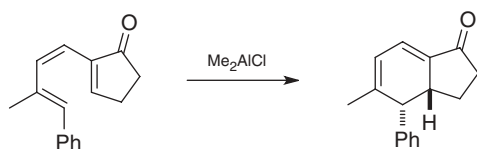
Alkylaluminum chlorides.

Friedel-Crafts reactions. Selective alkylation is observed on mixing ArH and CF₃CH₂CHF₂ with EtAlCl₂ in hexane at room temperature to give CF₃CH₂CHAr₂.¹

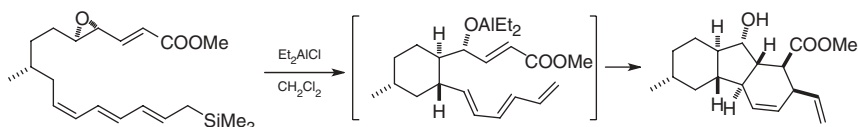
Pyrroles and indoles undergo nuclear carboxylation in the presence of Me₂AlCl and CO₂.²

4 Alkylaluminum chlorides

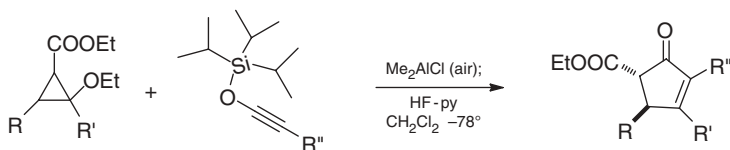
Pericyclic reactions. The rates of electrocyclicization of functionalized conjugated trienes are increased by alkylaluminum chlorides such as Me_2AlCl .³



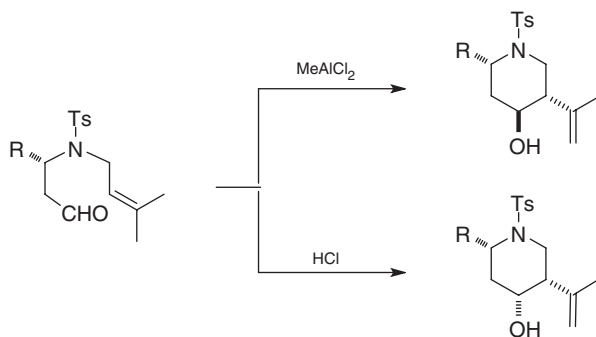
A further example of Diels–Alder reaction as facilitated by dienophile activation with an alkylaluminum chloride is that the preparation of a chiral decalin precursor⁴ for the drimane-type sesquiterpenes. A more intriguing and useful reaction is that the elaboration of a hydrofluorene from an acyclic epoxytetraene, involving epoxide opening to trigger a desilylative cyclization and intramolecular Diels–Alder reaction.⁵



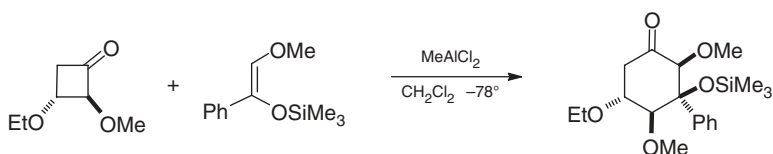
Push-pull cyclopropanes combine with alkoxyalkynes to afford cyclopentenones readily in a reaction mediated by Me_2AlCl , HF-py in the air.⁶



Different steric courses for the intramolecular ene reaction are adopted using HCl and MeAlCl_2 .⁷



Ring expansion. Reaction of cyclobutanones with silyl enol ethers furnishes cyclohexanones. The two carbon units are inserted without disturbing the stereocenters.⁸



Aryldiisobutylaluminum reagents. Barbier reaction conditions suffice to convert ArBr into *i*-Bu₂AlAr directly at room temperature, other reactants consisting of *i*-Bu₂AlCl, LiCl, and magnesium turnings and it is performed in a mixture of THF and heptanes.⁹

¹Ali, M., Liu, L.-P., Hammond, G.B., Xu, B. *TL* **50**, 4078 (2009).

²Nemoto, K., Onozawa, S., Egusa, N., Morohashi, N., Hattori, T. *TL* **50**, 4512 (2009).

³Bishop, L.M., Barbarow, J.E., Bergman, R.G., Trauner, D. *ACIE* **47**, 8100 (2008).

⁴Henderson, J.R., Parvez, M., Keay, B.A. *OL* **11**, 3178 (2009).

⁵Nicolaou, K.C., Sarlah, D., Wu, T.R., Zhan, W. *ACIE* **48**, 6870 (2009).

⁶Qi, X., Ready, J.M. *ACIE* **47**, 7068 (2008).

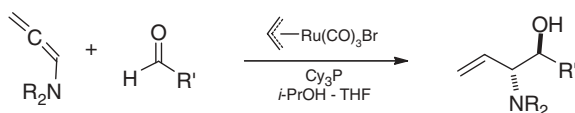
⁷Cariou, C.A.M., Kariuki, B.M., Smith, J.S. *OBC* **6**, 3123 (2008).

⁸Matsuo, J., Negishi, S., Ishibashi, H. *TL* **50**, 5831 (2009).

⁹Gao, H., Knochel, P. *SL* 1321 (2009).

η^3 -Allylbromo(tricarbonyl)ruthenium(I).

Aminoallylation.¹ In the presence of a phosphine ligand a reductive allylation reaction of carbonyl compounds with allenylamines is catalyzed by the Ru(I) complex.¹



¹Skucas, E., Zbieg, J.R., Krische, M.J. *JACS* **131**, 5054 (2009).

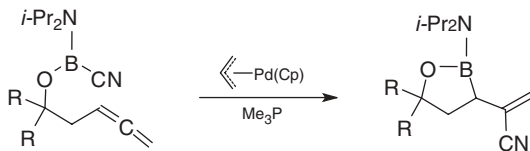
η^3 -Allylbis(triphenylphosphine)palladium tetrafluoroborate.

Allylic substitution.¹ Using this Pd complex to catalyze substitution allylic fluorides show a higher reactivity than the corresponding acetates but less than the benzoates.

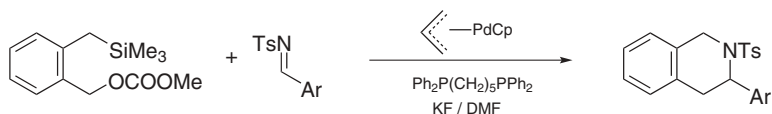
¹Hazari, A., Gouverneur, V., Brown, J.M. *ACIE* **48**, 1296 (2009).

η^3 -Allyl(cyclopentadienyl)palladium.

Cyanoboration.¹ The Pd complex promotes intramolecular addition of a cyanoborate group to a proximal double bond (shown for an allene).



Cycloaddition.² *o*-Trimethylsilylbenezyl carbonates are defunctionalized to form [c]benzopalladacyclopentanes that can be intercepted by *N*-tosylimines to form 3-substituted *N*-tosyl-1,2,3,4-tetrahydroisoquinolines. A formal [4 + 2]cycloaddition of *o*-xylylenes is realized.



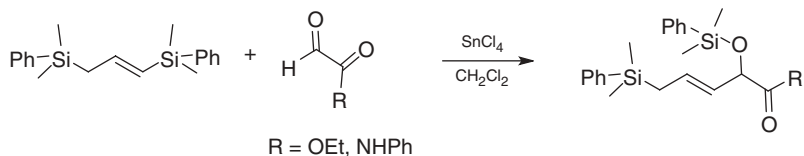
¹Yamamoto, A., Ikeda, Y., Suginome, M. *TL* **50**, 3168 (2009).

²Ueno, S., Ohtsubo, M., Kuwano, R. *JACS* **131**, 12904 (2009).

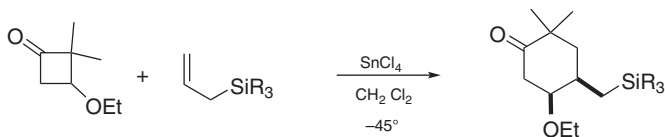
Allylsilanes.

Allylation. Allylation of aldehydes is accomplished with allyltrichlorosilane in the presence of a bithienylbisphosphine dioxide and *i*-Pr₂NEt.¹

Catalyzed by SnCl₄, 1,3-disilylpropenes react with 1,2-dicarbonyl compounds at the aldehyde group. The products retain a *C*-silyl group at an allylic position.²



Ring expansion. The more substituted C_α–C_β bond of a 3-alkoxycyclobutanone is inserted by a two-carbon unit of an allylsilane.³ The reaction course likely involves fragmentation and addition.



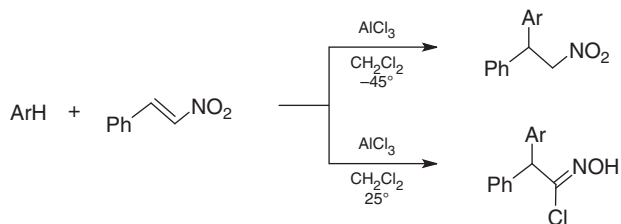
¹Simonini, V., Benaglia, M., Benincori, T. *ASC* **350**, 561 (2008).

²Tuzina, P., Somfai, P. *TL* **49**, 6882 (2008).

³Matsuo, J., Sasaki, S., Hoshikawa, T., Ishibashi, H. *OL* **11**, 3822 (2009).

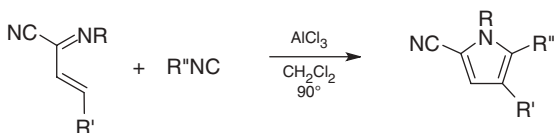
Aluminum chloride.

Addition. Arenes add to conjugated nitroalkenes at -78° but α -chlorooximes are formed at room temperature.¹

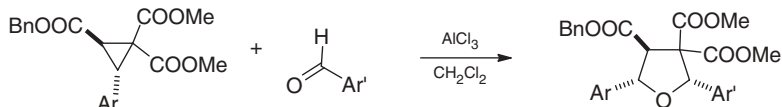


The reaction of benzylzinc bromides with araldehydes provides stilbenes, when they are heated with AlCl_3 in dioxane.²

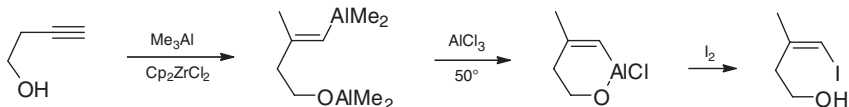
Cycloadditions. Formation of 2-cyanopyrroles from conjugated α -cyanoimines and isonitriles is found to be catalyzed by AlCl_3 .³



1,1-Cyclopropanedicarboxylic esters and araldehydes undergo [3 + 2]cycloaddition to afford tetrahydrofuran derivatives also in the presence of AlCl_3 .⁴



Isomerization. After methylaluminumation of 3-buten-1-ol the (*E*)-alkenylalane is isomerized by heating with AlCl_3 to afford a cyclic species, from which (*Z*)-4-iodo-3-methyl-3-butenol is readily prepared.⁵



¹Tu, Z., Raju, B.R., Liou, T.-R., Kavala, V., Kuo, C.-W., Jang, Y., Shih, Y.-H., Wang, C.-C., Yao, C.-F. *T* **65**, 2436 (2009).

²Peng, Z.-Y., Ma, F.-F., Zhu, L.-F., Xie, X.-M., Zhang, Z. *JOC* **74**, 6855 (2009).

8 Aluminum fluoride

³Fontaine, P., Masson, G., Zhu, J. *OL* **11**, 1555 (2009).

⁴Sanders, S.D., Ruiz-Olalla, A., Johnson, J.S. *CC* 5135 (2009).

⁵Wang, G., Negishi, E. *EJOC* 1679 (2009).

Aluminum fluoride.

Friedel–Crafts reaction.¹ The fluoride is prepared from (*i*-PrO)₃Al and 50% HF. It catalyzes Friedel–Crafts reactions as demonstrated in a synthesis of α -tocopherol from tetramethylhydroquinone and isophytol (100% yield).

¹Coman, S.M., Wuttke, S., Vimont, A., Daturi, M., Kemnitz, E. *ASC* **350**, 2517 (2008).

Aluminum oxide.

Azlactone synthesis. Rapid condensation of 2-phenyl-oxazolin-5-one with ArCHO is readily achieved on contact with Al₂O₃ in chloroform.¹

Arylboronic acids. Hydrolysis of potassium arenetrifluoroborates is conveniently performed by heating (or by microwave) with Al₂O₃ and water.²

¹Conway, P.A., Devine, K., Paradisi, F. *T* **65**, 2935 (2009).

²Kabalka, G.W., Coltuclu, V. *TL* **50**, 6271 (2009).

Aluminum triflate.

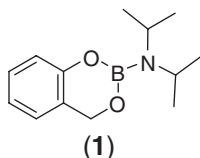
Arylamines.¹ Aryl azides are reduced on exposure to NaI and a mixture of Al(OTf)₃ and Gd(OTf)₃ in MeNO₂.

¹Kamal, A., Markandeya, N., Shankaraiah, N., Reddy, C.R., Prabhakar, S., Reddy, C.S., Eberlin, M.N., Santos, L.S. *CEJ* **15**, 7215 (2009).

Aminoboranes.

Reduction. Reduction of nitriles (to primary amines) by *i*-Pr₂NBH₂ in THF is catalyzed by LiBH₄.¹

Ugi reaction. The aminoborane **1** shows an aptitude for catalyzing the Ugi reaction.²



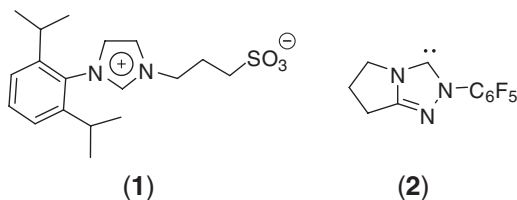
¹Haddenham, D., Pasumansky, L., DeSoto, J., Eagon, S., Singaram, B. *JOC* **74**, 1964 (2009).

²Tanaka, Y., Hasui, T., Suginome, M. *OL* **9**, 4407 (2007).

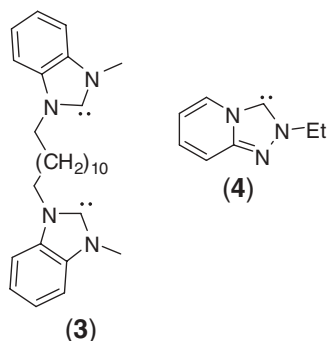
Aminocarbenes.

Dihydrogen splitting. A combination of 1,3-di-*t*-butylimidazol-2-ylidene and tris(pentafluorophenyl)borane forms the imidazolium borate in the presence of dihydrogen, as a result of distributing the two hydrogen atoms to form the salt.¹

Redox processes. Carbene derived from **1** converts ArCHO to ArCOOH in aqueous DMF.² The bicyclic triazolium ylide derived from **2** effects reductive acylation of naphthoquinones with aldehydes.³

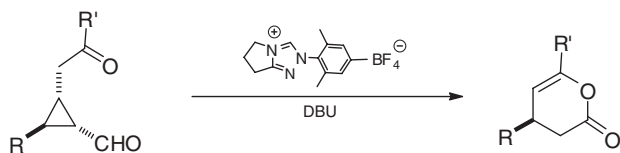


Carbenes **3** and **4** possess catalytic activities in the benzoin condensation.^{4,5} The precursor of **4** is readily available from 2-hydrazinopyridine.⁵

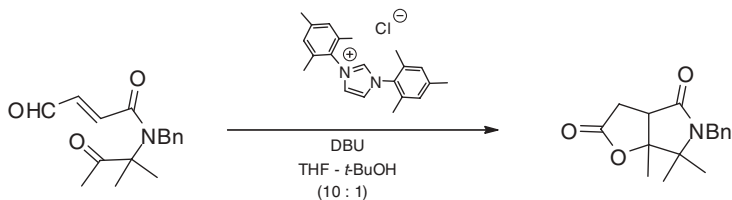


The azocarbene-aldehyde adducts, intermediates in the benzoin condensation, can be trapped by fluoronitroarenes to form diaryl ketones.⁶

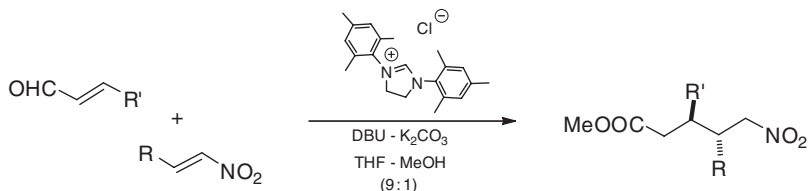
Ring expansion of 2-formyltetrahydrofuran and homologous cyclic ethers is based on the same redox process.⁷ 2-Acylcyclopropanecarbaldehydes give 3,4-dihydro- α -pyrones.⁸



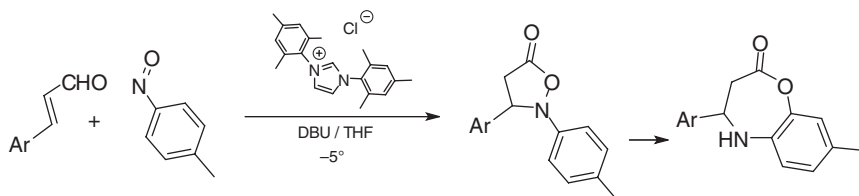
Molecules containing both saturated carbonyl and enal moieties that are conveniently separated cyclize to afford lactones.⁹



Redox reaction of conjugated aldehydes in the presence of nitroalkenes and an alcohol (e.g., MeOH) affords δ -nitroalkanoic esters.¹⁰ α' -Hydroxy- α,β -unsaturated ketones are converted to saturated amides on reaction with amines, involving cleavage of the α -ketol system.¹¹



Interestingly, under similar conditions enals and a nitrosoarene afford conjugated *N*-arylhydroxamic acids¹² or oxazepanones.¹³



The Stetter reaction has been carried out employing a chiral bicyclic azocarbenes but the products are produced only in moderate ee.¹⁴

Ketene intermediates generated from α,β -epoxy aldehydes are trapped by hydrazoic acid to furnish oxazolidin-2-ones. If Me₃SiN₃ is used, carbamoyl azides are obtained.¹⁵

Hydroacylation. Araldehydes containing an *o*-alkenyl sidechain are liable to cyclization (5- and 6-membered ring products) on treatment with thiazole or thiazolidine carbenes.^{16,17}

A hydrosylation agent for conjugated esters is formed when *N*-tosylaldimines are treated with 1,3-dimesitylimidazolyliene.¹⁸

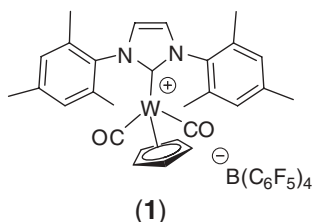
Metal complex activation. π -Allyliron complexes are activated toward allylic substitution by 1,3-dimesitylimidazolin-2-ylidene.¹⁹

- ¹Chase, P.A., Stephan, D.W. *ACIE* **47**, 7433 (2008).
²Yoshida, M., Katagiri, Y., Zhu, W.-B., Shishido, K. *OBC* **7**, 4062 (2009).
³Molina, M.T., Navarro, C., Moreno, A., Csaky, A.G. *JOC* **74**, 9573 (2009).
⁴Iwamoto, K., Kimura, H., Oike, M., Sato, M. *OBC* **6**, 912(2008).
⁵Ma, Y., Wei, S., Lan, J., Wang, J., Xie, R., You, J. *JOC* **73**, 8256 (2008).
⁶Suzuki, Y., Ota, S., Fukuta, Y., Ueda, Y., Sato, M. *JOC* **73**, 2420 (2008).
⁷Wang, L., Thai, K., Gravel, M. *OL* **11**, 891 (2009).
⁸Li, G.-Q., Dai, L.-X., You, S.-L. *OL* **11**, 1623 (2009).
⁹Struble, J.R., Bode, J.W. *T* **65**, 4957 (2009).
¹⁰Nair, V., Sinu, C.R., Babu, B.P., Varghese, V., Suresh, E. *OL* **11**, 5570 (2009).
¹¹Chiang, P.-C., Kim, Y., Bode, J.W. *CC* 4566 (2009).
¹²Wong, F.T., Patra, P.K., Seayad, J., Zhang, Y., Ying, J.Y. *OL* **10**, 2333 (2008).
¹³Yang, L., Tan, B., Wang, F., Zhong, G. *JOC* **74**, 1744 (2009).
¹⁴Enders, D., Han, J., Hensler, A. *CC* 3989 (2008).
¹⁵Vora, H.U., Moncecchi, J.R., Epstein, O., Rovis, T. *JOC* **73**, 9727 (2008).
¹⁶He, J., Tang, S., Liu, J., Su, Y., Pan, X., She, X. *T* **64**, 8797 (2008).
¹⁷Hirano, K., Biju, A.T., Piel, I., Glorius, F. *JACS* **131**, 14190 (2009).
¹⁸Chen, D.-D., Hou, X.-L., Dai, L.-X. *JOC* **73**, 5578 (2008).
¹⁹Holzwarth, M., Dieskau, A., Tabassam, M., Plietker, B. *ACIE* **48**, 7251 (2009).

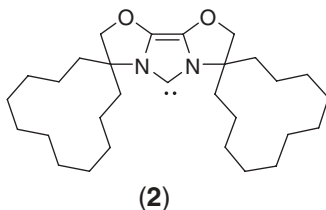
Aminocarbene-metal complexes.

Propargyl amines. The three-component condensation of 1-alkynes, aldehydes and amines to give propargyl amines in one step can be catalyzed by the Ag(I) complex of a polymer-bound imidazolylidene.¹

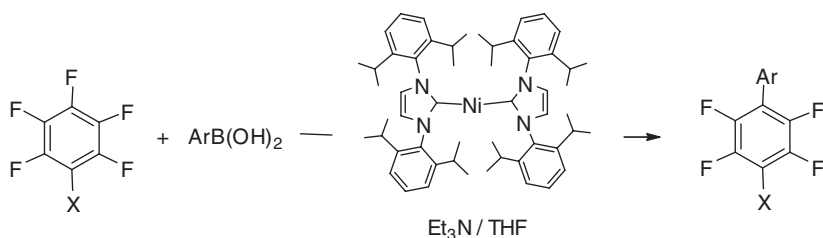
Reduction. The complex **1** is useful for hydrosilylation of ketones with Et₃SiH at room temperature,² reaction is initiated on adding the hydrosilane to the substrate and the catalyst to give a homogeneous solution. At the end of the reaction the catalyst precipitates.



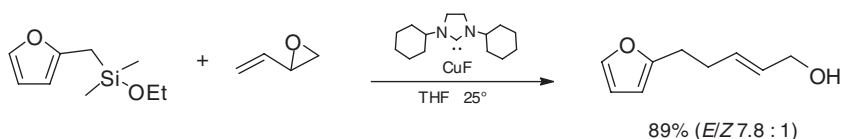
Apparently the Cu(I) complex of carbene **2** is effective in promoting reductive cleavage of propargylic acetates to afford allenes.³



Coupling reactions. A dicarbene-nickel complex is active in the regioselective Suzuki coupling of certain fluoroarenes.⁴



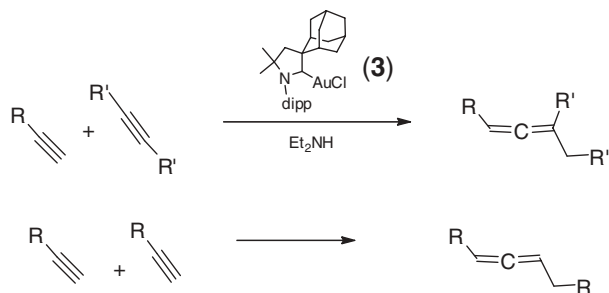
Investigations on the use of azolecarbene-copper complexes are in profusion. These include coupling reactions between ArSi(OEt)₃ and allyl bromide,⁵ benzylic silanes and vinyl epoxides,⁶ ArI and Me₃SiCF₃,⁷ as well as a synthesis of aroylformamides from ArI, CO and amines.⁸ Cross-coupling of β-naphthols (electron-rich + electron-poor) is achieved with a catalyst system containing CuX, AgNO₃, the 1,3-dimesitylimidazolidine carbene, and Oxone.⁹



A synthesis of chiral 3,3-diaryl-1-propenes is based on reaction of ArMgBr with Ar'CH=CHCH₂Br, the Cu(I)-catalyst comprises a C₂-symmetric 4,5-diphenylimidazolidin-2-yl carbene ligand.¹⁰ Unconventional hydroboration of cinnamyl acetate is achieved by a reaction with bis(pinacolato)diboron in the presence of the copper complex of 1,3-dimesitylimidazolin-2-ylidene.¹¹ Formation of a new C–B bond is at the nonbenzylic position.

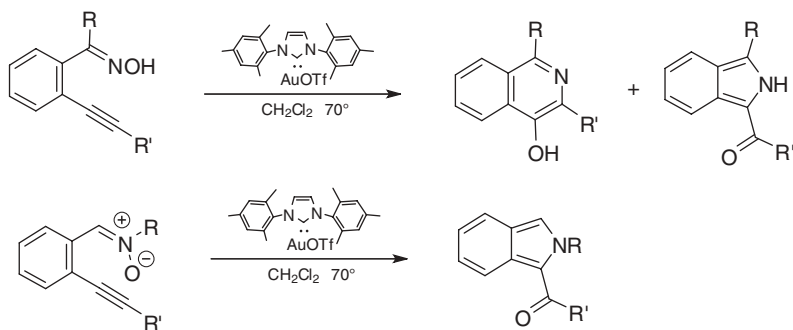
Deborative carboxylation of arylboronic esters and alkenboronic esters is accomplished in the presence of a carbene derived from a hindered imidazolium salt.¹²

The hindered Au(I) complex **3** causes coupling of two 1-alkyne molecules to afford allenes. A mixture of a terminal alkyne and an internal alkyne undergoes cross-coupling.¹³

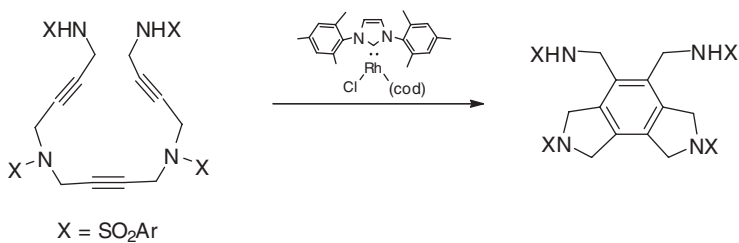


Heterocycles. Application of azocarbene-copper complexes to performing the click reaction for synthesis of 1,2,3-triazoles from alkynes and organoazides is well anticipated. With a complex containing bulky substituents on the nitrogen atoms is employed, the reaction requires slightly elevated temperature and activation by water or DMSO.¹⁴ 1,3-Dicyclohexylimidazol-2-ylidene is perhaps a better ligand.¹⁵ In another procedure DMAP is added to increase reaction rates and yields.¹⁶ Reaction with an azocarbene-copper complex linked to silica gel has also been examined.¹⁷

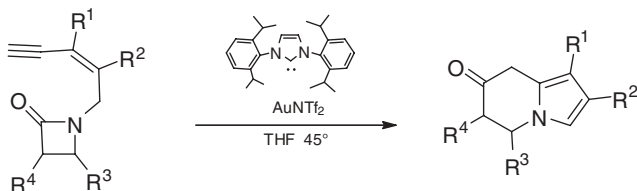
1-Acylisindoles are formed via isomerization of *o*-alkynylbenzylidene *N*-oxides which is catalyzed by a carbene-gold(I) complex. The benzaldoximes also give 4-hydroxyisoquinolines besides the ketones.¹⁸

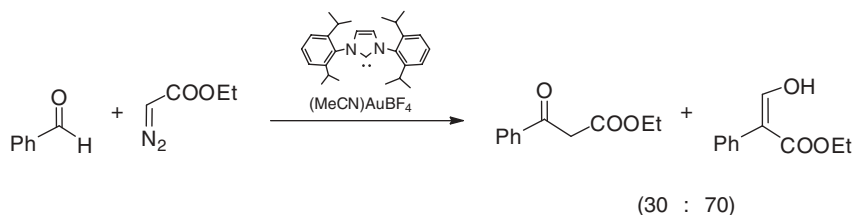


Intramolecular [2 + 2 + 2]cycloaddition of an aza-stitched symmetrical triyne, catalyzed by a Rh-carbene, furnishes a tricyclic product.¹⁹



An Au(I) complex induces intramolecular insertion of two *sp*-carbon atoms from a sidechain of *N*-substituted β -lactam. With double bond migration to follow, 5,6-dihydro-8*H*-indolizin-7-ones result.²⁰





- ¹Li, P., Wang, L., Zhang, Y., Wang, M. *TL* **49**, 6650 (2008).
²Dioumaev, V.K., Bullock, R.M. *Nature* **424**, 530 (2000).
³Deutsch, C. Lipshutz, B.H., Krause, N. *OL* **11**, 5010 (2009).
⁴Schaub, T., Backes, M., Radius, U. *JACS* **128**, 15964 (2006).
⁵Herron, J.R., Ball, Z.T. *JACS* **130**, 16486 (2008).
⁶Herron, J.R., Russo, V., Valente, E.J., Ball, Z.T. *CEJ* **15**, 8713 (2009).
⁷Dubinina, G.G., Furutachi, H., Vivic, D.A. *JACS* **130**, 8600 (2008).
⁸Liu, J., Zhang, R., Wang, S., Sun, W., Xia, C. *OL* **11**, 1321 (2009).
⁹Grandbois, A., Mayer, M.-E., Bedard, M., Collins, S.K., Michel, T. *CEJ* **15**, 9655 (2009).
¹⁰Selim, K.B., Matsumoto, Y., Yamada, K., Tomioka, K. *ACIE* **48**, 8733 (2009).
¹¹Lee, Y., Hoveyda, A.H. *JACS* **131**, 3160 (2009).
¹²Ohishi, T., Nishiura, M., Hou, Z. *ACIE* **47**, 5792 (2008).
¹³Zeng, X., Frey, G.D., Kousar, S., Bertrand, G. *CEJ* **15**, 3056 (2009).
¹⁴Diez-Gonzalez, S., Stevens, E.D., Nolan, S.P. *CC* 4747 (2008).
¹⁵Diez-Gonzalez, S., Nolan, S.P. *ACIE* **47**, 8881 (2008).
¹⁶Teyssot, M.-L., Chevry, A., Traikia, M., El-Ghozzi, M., Avignat, D., Gautier, A. *CEJ* **15**, 6322 (2009).
¹⁷Li, P., Wang, L., Zhang, Y. *T* **64**, 10825 (2008).
¹⁸Yeom, H.-S., Lee, Y., Lee, J.-E., Shin, S. *IBC* **7**, 4744 (2009).
¹⁹Gonzalez, I., Pla-Quintana, A., Roglans, A. *SL* 2844 (2009).
²⁰Peng, Y., Yu, M., Zhang, L. *OL* **10**, 5187 (2008).
²¹Huang, X., de Haro, T., Nevado, C. *CEJ* **15**, 5904 (2009).
²²Brissy, D., Skander, M., Jullien, H., Retailleau, P., Marinetti, A. *OL* **11**, 2137 (2009).
²³Ramon, R.S., Marion, N., Nolan, S.P. *CEJ* **15**, 8695 (2009).
²⁴Cho, J., Hollis, T.K., Helgert, T.R., Valente, E.J. *CC* 5001 (2008).
²⁵Fructos, M.R., Diaz-Requejo, M.M., Perez, P.J. *CC* 5153 (2009).

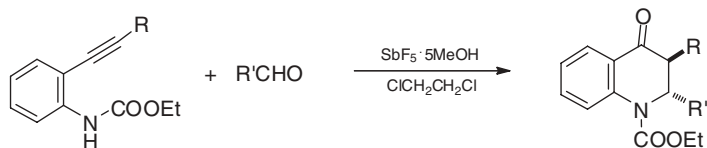
Antimony(III) chloride.

Friedel–Crafts reaction. Deposited on K-10, SbCl₃ forms a catalyst for solvent-free alkylation of pyrroles and indoles with epoxides at room temperature.¹

¹Liu, Y.-H., Liu, Q.-S., Zhang, Z.-H. *TL* **50**, 916 (2009).

Antimony(V) chloride.

Hydroquinolones.¹ 2-Alkynylanilines undergo annulation on reaction with aldehydes in the presence of SbCl₅ · 5MeOH.



¹Sato, A., Kasai, J., Odaira, Y., Fukaya, H., Hanzawa, Y. *JOC* **74**, 5644 (2009).

Arenediazonium tosylates.

Preparation. When arylamines are mixed with nitrite anion-exchange resin and TsOH in HOAc at room temperature the diazonium salts are obtained.¹ Alternatively, diazotization employs a mixture of NaNO₂ and TsOH in water at room temperature.² Such salts show much better thermal stability while retaining good reactivity. They are safer.

¹Filimonov, V.D., Trusova, M., Postnikov, P., Krasnokutskaya, E.A., Lee, Y.M., Hwang, H.Y., Kim, H., Chi, K.-W. *OL* **10**, 3961 (2008).

²Gorushko, D.A., Filimonov, V.D., Krasnokutskaya, E.A., Semenischeva, N.A., Go, B.S., Hwang, H.Y., Cha, E.H., Chi, K.-W. *TL* **49**, 1080 (2008).

2-Azido-1,3-dimethylimidazolium chloride.

Diazo transfer.¹ The title reagent is prepared from the corresponding 2-chloro derivative on treatment with NaN₃ in MeCN at 0°. It reacts readily with 1,3-dicarbonyl compounds in the presence of Et₃N.

¹Kitamura, M., Tashiro, N., Okauchi, T. *SL* 2943 (2009).

1,1'-Azobis(cyclohexane-1-carbonitrile).

Desulfurative carbonylation. The transformation of RSO₂X to RCOX, where X = SR, CN, ... is initiated by the title azo compound.¹

¹Kim, S., Lim, K.-C., Kim, S. *CAJ* **3**, 1692 (2008).

B

Barium.

Propargylation. Barium mediates the addition of an α -branched propargyl group to ketones and imines. The proper organometallic reagents are formed from mixing 1-trimethylsilyl-3-bromo-1-alkynes with Ba.¹

¹Yanagisawa, A., Suzuki, T., Koide, T., Okitsu, S., Arai, T. *CAJ* **3**, 1793 (2008).

Barium permanganate.

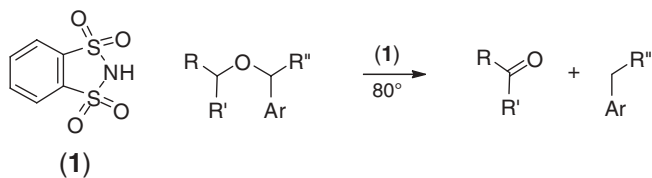
Oxidation. 1, ω -Diols are oxidized in MeCN by BaMnO₄ to afford lactones in good yields. The reaction, promoted by microwave, is demonstrated in the formation of 4-, 5-, 6-, 7-, and 18-membered rings.¹

¹Bagley, M.C., Lin, Z., Phillips, D., Graham, A.E. *TL* **50**, 6823 (2009).

o-Benzenedisulfonimide.

Functional group transformation. The title compound shows catalytic effect in esterification, acetalization, and mixed ether synthesis.¹ Ritter reaction of tertiary alcohols and secondary benzylic alcohols can be conducted in its presence.²

Redox reaction. Alkyl aryl ethers undergo redox cleavage on warming with catalytic amounts of the title compound, which is safe, noncorrosive, and recoverable.³



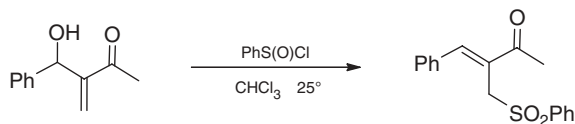
¹Barbero, M., Cadamuro, S., Dughera, S., Venturello, P. *S* 1379 (2008).

²Barbero, M., Bazzi, S., Cadamuro, S., Dughera, S. *EJOC* 430 (2009).

³Barbero, M., Bazzi, S., Cadamuro, S., Dughera, S., Ghigo, G. *EJOC* 4346 (2009).

Benzenesulfinyl chloride.

Phenyl sulfones. Electron-rich benzylic alcohols react with PhSOCl to give benzyl phenyl sulfones, due to facile ionization of benzyl benzenesulfonates.¹



¹Li, H.-H., Dong, D.-J., Jin, Y.-H., Tian, S.-K. *JOC* **74**, 9501 (2009).

N-Benzenesulfonylhydroxylamine.

Cyclic hydroxamic acids. A convenient route to *N*-hydroxylactams (5- and 6-membered) involves treatment of cyclobutanone and cyclopentanone with PhSO₂NHOH under basic conditions.¹

¹Banerjee, R., King, S.B. *OL* **11**, 4580 (2009).

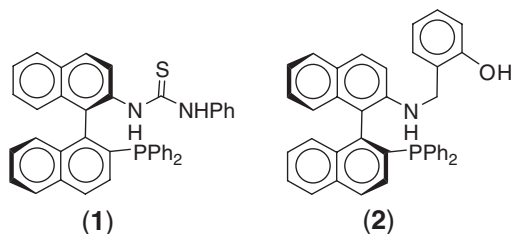
1-Benzyl-3,5-bis(methoxycarbonyl)pyridinium bromide.

Acetalization. The pyridinium salt is an effective catalyst for acetalization and dithioacetalization of carbonyl compounds. Reaction involving diols and dithiols is carried out in THF.¹

¹Procuranti, B., Connon, S.J. *OL* **10**, 4935 (2008).

1,1'-Binaphthalene-2-amine-2'-phosphines.

Baylis-Hillman reaction. Two different heteronuclear ligands **1** and **2** are used together with PhCOOH to catalyze the aza-Baylis-Hillman reaction.^{1,2}



Coupling reactions. An efficient coupling leading to indolenines is observed. This process give partially dearomatized chiral products in excellent yields.³ Arylation and