LEDAC : Ligands with extreme donating character for applications in catalysis
JCJC - 2008

AGENCE NATIONALE DE LA RECHERCHE ANR

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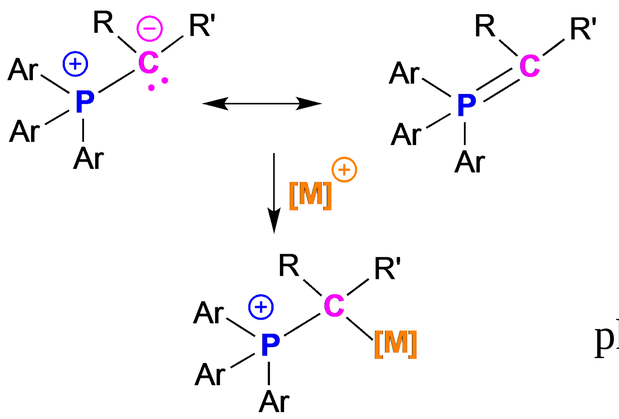
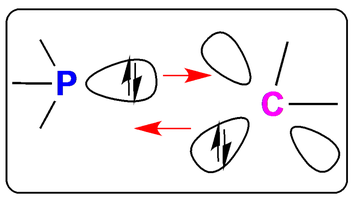
Phosphonium ylides

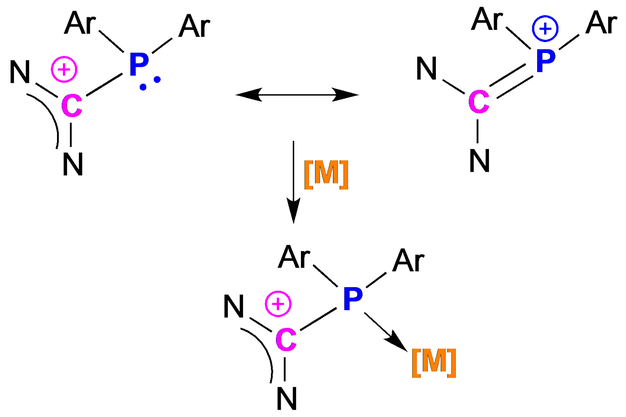


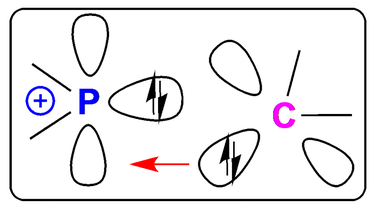


phosphine-carbene adduct

strongly σ-donating P^+C ligand (X-type)

Amidiniophosphines: « reversed ylides »





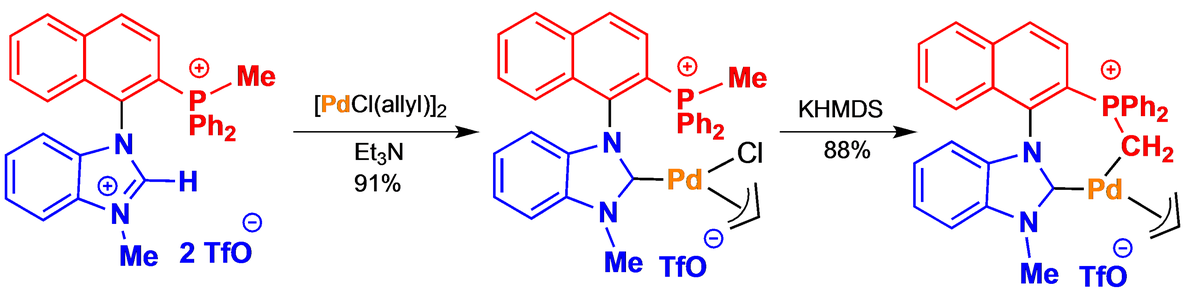
phosphenium-carbene adduct

New. J. Chem. **2012**, *36*, 17.

weakly σ-donating C^+P ligand (L-type)

Atropo-stereogenic strongly donating *ylides*

* NHC-ylide ligands

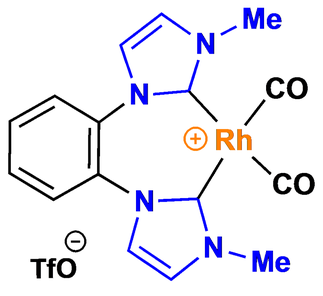


Angew. Chem. Int. Ed. **2007**, *46*, 6313. (série racémique)

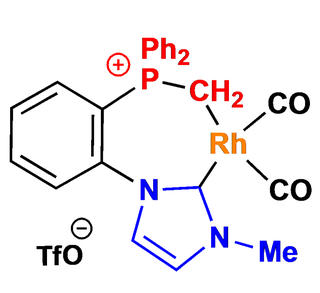
Dalton Trans. **2009**, 7196. (série énantiopure)

Eur. J. Inorg. Chem. **2010**, 2325. (revue)

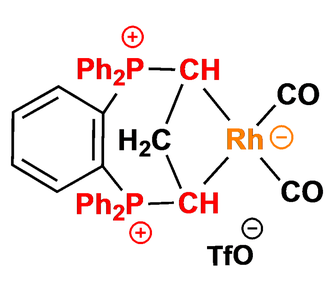
* Phosphonium ylides are stronger donor than NHCs



ν_{CO} = 2030, 2084 cm^{-1}



ν_{CO} = 2008, 2071 cm^{-1}



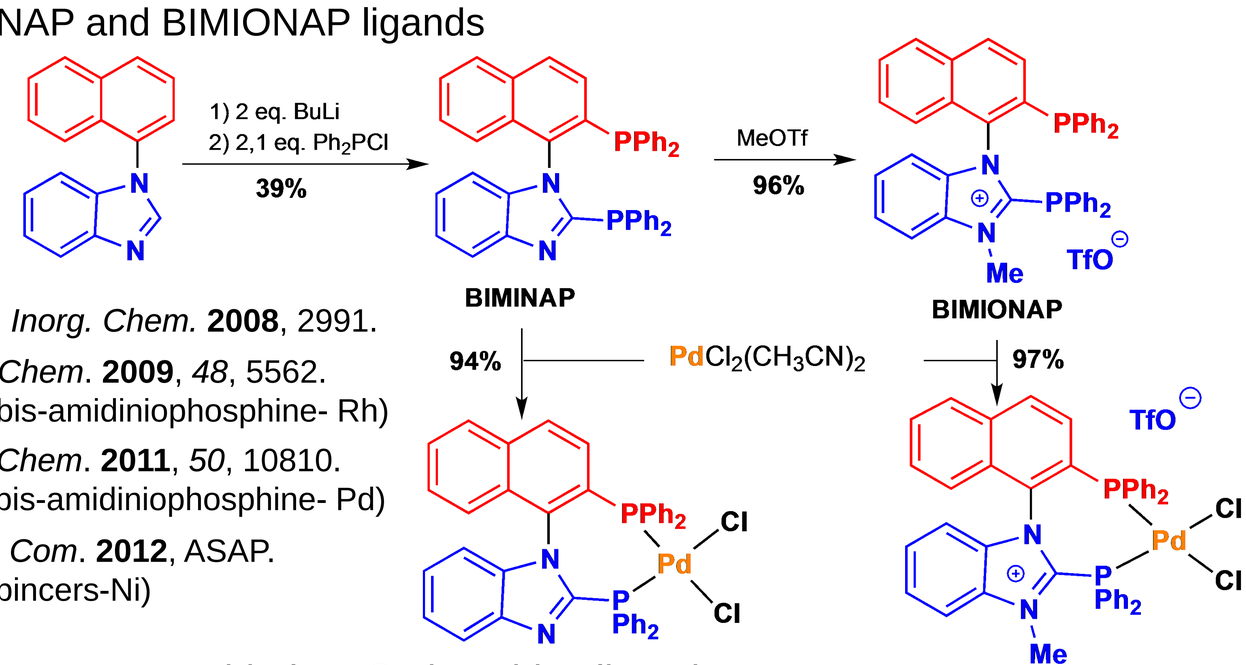
ν_{CO} = 1984, 2051 cm^{-1}

J. Am. Chem. Soc. **2008**, *130*, 8406.

Eur. J. Inorg. Chem. **2012**, 4057. (série méta)

Atropo-stereogenic weakly donating *amidiniophosphines*

* BIMINAP and BIMIONAP ligands



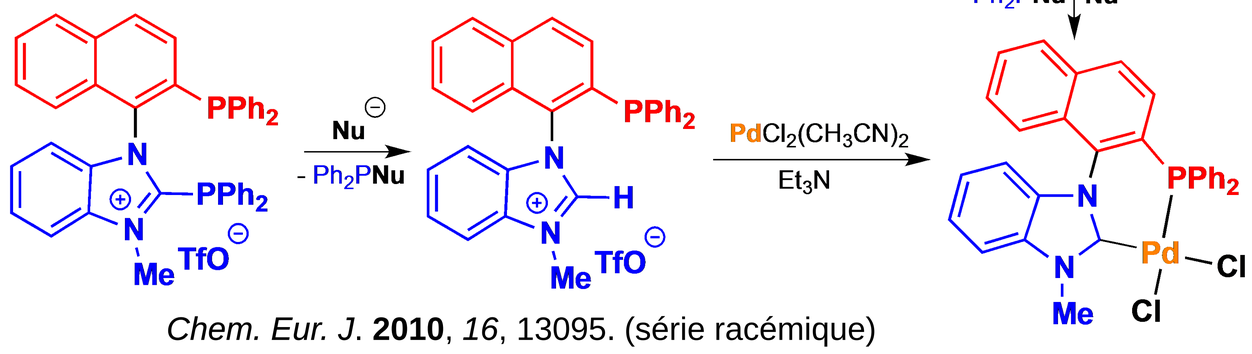
Eur. J. Inorg. Chem. **2008**, 2991.

Inorg. Chem. **2009**, *48*, 5562. (série bis-amidiniophosphine- Rh)

Inorg. Chem. **2011**, *50*, 10810. (série bis-amidiniophosphine- Pd)

Chem. Com. **2012**, ASAP. (série pincers-Ni)

* Access to atropochiral NHC-phosphine ligands



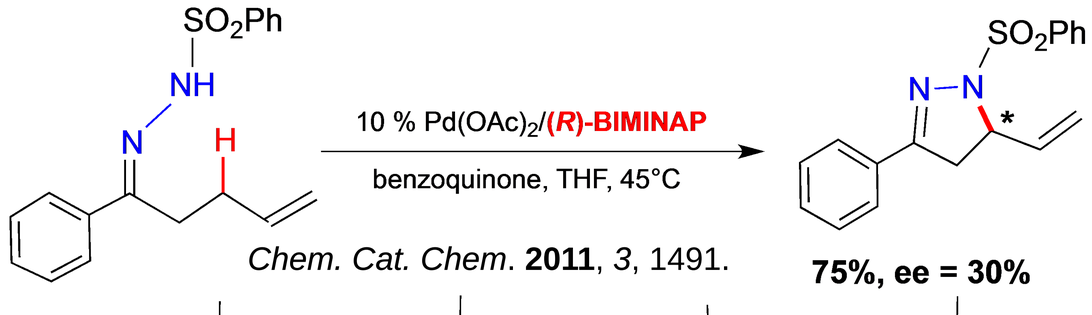
Chem. Eur. J. **2010**, *16*, 13095. (série racémique)

Chem. Eur. J. **2011**, *17*, 5110. (série énantiopure)

Chem. Eur. J. **2012**, *18*, 7705. (série amidiniophosphonite)

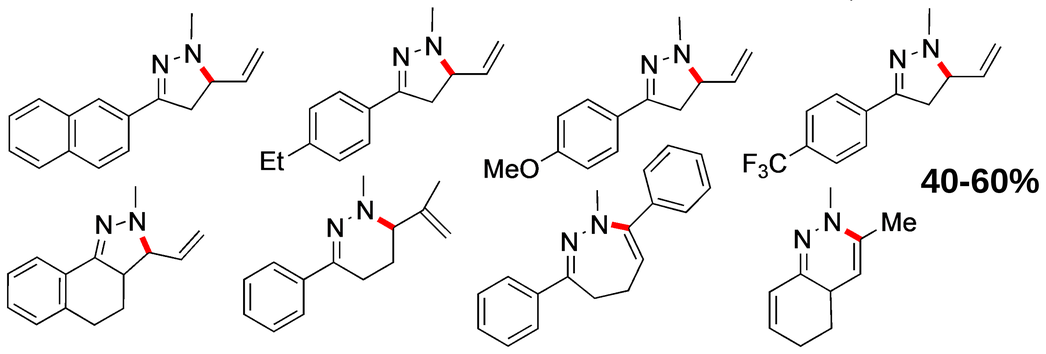
Catalytic applications of the BIMINAP ligand

* Intramolecular oxidative allylation of hydrazones

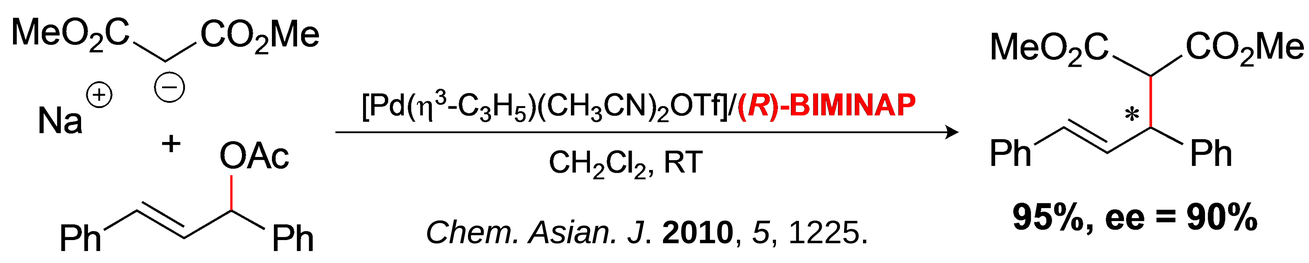


Chem. Cat. Chem. **2011**, *3*, 1491.

75%, ee = 30%



* Tsuji-Trost allylation



Chem. Asian. J. **2010**, *5*, 1225.

95%, ee = 90%

Ligand [L]	[Pd-L][%]	Solvent	ee[%]	Yield %
(*R*)-BIMINAP[a]	2	THF	44(*S*)	96
(*R*)-BIMINAP[a]	2	CH_2Cl_2	77(*S*)	95
(*R*)-BINAP[a]	2	THF	25(*S*)	89
(*R*)-BIMINAP[b]	2	CH_2Cl_2	90(*S*)	95

[a] = 2 eq. of ligand L with respect to $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ in mol %.
[b] = 2 eq. of ligand L with respect to $[Pd(\eta^3\text{-}C_3H_5)(CH_3CN)_2OTf]$ in mol %.

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LCC

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Université de Toulouse