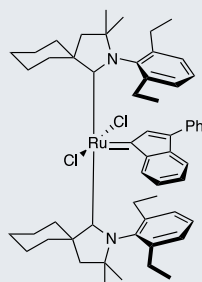


Olefin Metathesis CAAC Family Catalysts

Bis-CAAC Catalyst Group

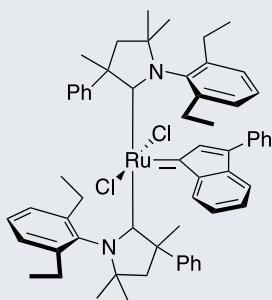
The Apeiron Synthesis' effort to explore versatile ruthenium-based catalysts for olefin metathesis resulted in a new class of complexes: bis(CAAC)ruthenium indenylidenes, which combine the benefits of both the NHC and the CAAC catalyst families. One of these catalysts, UltraCat, has proved to be extremely universal and highly efficient in virtually all metathesis transformations leading to terminal and internal olefins, such as ethenolysis via ring closing metathesis (including challenging macrocyclization), cross metathesis (involving electron deficient partners like acrylates), or ene-yne metathesis. These transformations are highly selective and take place at exceptionally low catalyst loadings. In one industrially relevant example, i.e. self metathesis of 1-decene, a turnover number of over 300000 was obtained. Importantly, these new catalysts were prepared using an efficient, low-cost and scalable synthetic route.



Ultra LatMet

AS2098 CAS: 2501978-79-4

- Excellent for ROMP reaction of DCPD and NBE (catalyst loading as low as 3 ppm).
- Long pot life - several months - in DCPD with a simple additive.
- High stability allows handling in air.



Bis-CAAC Catalyst Group

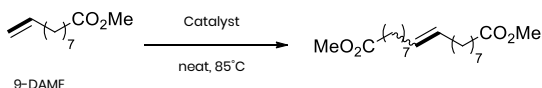
UltraCat

AS2086 CAS: 2055540-61-7

- Versatile catalyst, excellent for CM of terminal, type 1 olefins; excellent for ethenolysis, very good for mRCM and RCM leading to small/medium rings.
- Compatible with toluene, ethyl acetate, dimethylcarbonate, CPME; neat substrate in the temp. range of 40 to 85°C.
- High stability allows handling in air.

case study

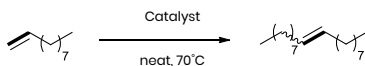
efficiency of UltraCat in cross metathesis



9-DAME

Catalyst	Loading [ppm]	GC yield [%]	TON
Hov-II	1 (4×0.25)	12	60 000
Gru-II	1 (4×0.25)	< 1	-
UltraCat	1 (4×0.25)	88	440 000
	0.5 (2×0.25)	66	660 000
	0.25	41	820 000

ethylene was removed from the reaction mixture by bubbling inert gas



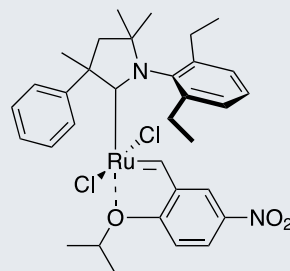
Dec-1-ene

Catalyst	Loading [ppm]	GC yield [%]	TON
UltraCat	0.2 (4×0.05)	84	2 100 000
	0.15 (3×0.05)	75	2 500 000
	0.1 (2×0.05)	59	2 950 000
	0.05	34	3 400 000

ethylene was removed from the reaction mixture by bubbling inert gas

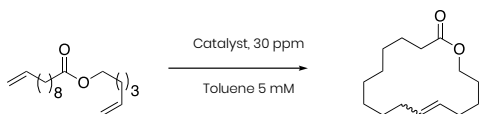
Mono-CAAC Catalyst Group

Apeiron's team found that substitution of the NHC group by carefully selected CAAC ligands significantly improves efficiency and selectivity of ruthenium benzylidene complexes in cross metathesis with acrylonitrile and in macrocyclization reactions. These two types of reactions were studied due to their importance in specialty chemical, pharmaceutical, and F&F industries. The newly designed class of catalysts allowed to accomplish both transformations with extraordinarily high turnover numbers.

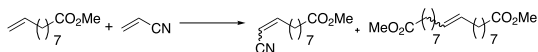


case study

efficiency of UltraNitroCat in macrocyclization



Catalyst	GC yield [%]	TON
UltraNitroCat	90	30 000
nitro-Grela	7	2 300
Grubbs II	12	4 000



Catalyst	GC yield [%]	Selectivity [%]*	TON
UltraNitroCa	75	75	38 000
nitro-Grela	34	81	18 400

* numbers relate to cross metathesis selectivity over self metathesis

Ultra NitroCat

AS2091 CAS: 2106819-64-9

- Exceptional efficiency in cross metathesis with electron deficient partners and in macrocyclizations.
- Compatible with toluene, ethyl acetate, dimethylcarbonate, CPME in the temperature range of 25 to 85°C.
- High stability allows handling in air.

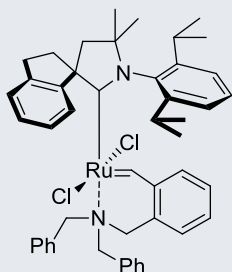


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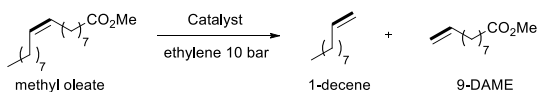
SlashCat

AS2153

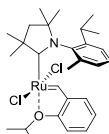
- Shows unmatched efficiency in ethenolysis.
- Compatible with toluene, ethyl acetate, dimethylcarbonate, neat substrate in the temp. range of 30 to 85°C.
- High stability allows handling in air.

case study

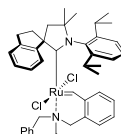
efficiency of SlashCat



Catalyst	Loading [ppm]	Conversion	Selectivity	TON
Reference	1	41	92	378 000
catalyst*	0.5	25	94	472 000
	0.25	16	97	604 000
SlashCat	1	60	96	574 000
	0.5	43	98	848 000
	0.25	32	99	1260 000



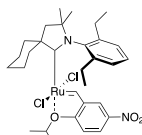
Reference catalyst*



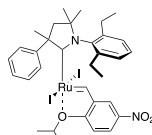
SlashCat

*Grubbs 2015, Angew. Chem. Int. Ed. 2015, 54, 1919–1923.vv

other Catalysts in the Group



AS2100



AS2092

References: Gawin R, Tracz A, Chwalba M., Kozakiewicz A, Trzaskowski B, Skowerski K. ACS Catal. 2017, 7, 5443–5449 Supporting patents: PCT/IB2016/054486, PCT/IB2017/056992, P.419421