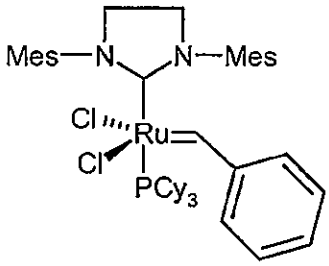
the degradation are still relatively high (see Example 3 of WO-A-03/002613, in which M_w = 180 000 g/mol and M_n = 71 000 g/mol).

US 2004/0127647 A1 describes blends based on low molecular weight HNBR rubbers having a bimodal or multimodal molecular weight distribution and also vulcanisates of these rubbers. To carry out the metathesis, 0.5 phr of Grubbs I catalyst, corresponding to 614 ppm of ruthenium based on the nitrile rubber used, is used according to the examples.

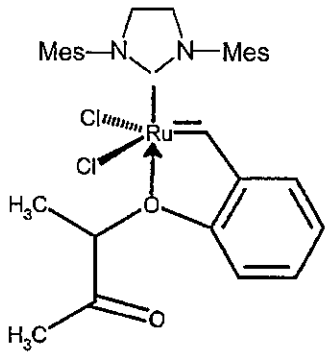
If a "Grubbs (II) catalyst" mentioned in **WO-A-00/71554**, e.g. 1,3-bis(2,4,6-trimethylphenyl)-2-(imidazolidinylidene~~imidazolidenylidene~~) (tricyclohexylphosphine)ruthenium(phenylmethylene) dichloride, is used for the NBR metathesis, this also succeeds without use of a coolefin (**US-A-2004/0132891**). After the subsequent hydrogenation, which is preferably carried out in situ, the hydrogenated nitrile rubber has lower molecular weights and a narrower molecular weight distribution (PDI) than when using catalysts of the Grubbs (I) type. In terms of the molecular weight and the molecular weight distribution, the metathetic degradation thus proceeds more efficiently when using catalysts of the Grubbs II type than when using catalysts of the Grubbs I type. However, the amounts of ruthenium necessary for this efficient metathetic degradation are still relatively high. Long reaction times are also still required for carrying out the metathesis using the Grubbs II catalyst.



Grubbs (II) catalyst

In all the abovementioned processes for the metathetic degradation of nitrile rubber, relatively large amounts of catalyst have to be used and long reaction times are required in order to produce the desired low molecular weight nitrile rubbers.

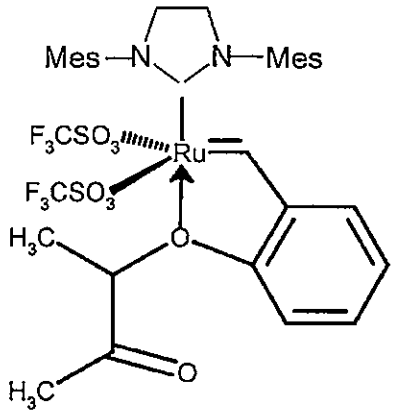
It is therefore an object of the invention to provide a catalyst which makes metathetic degradation of nitrile rubber without gelling possible and makes possible the setting of lower molecular weights of the degraded nitrile rubber at a comparable noble metal content.



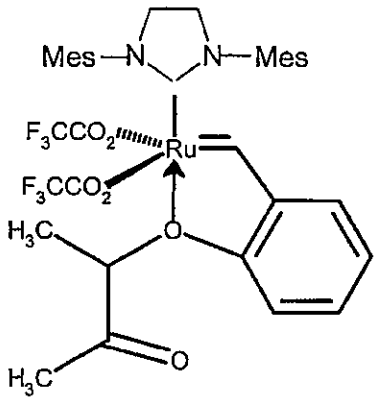
(V)

which is also referred to herein as "Arlt catalyst".

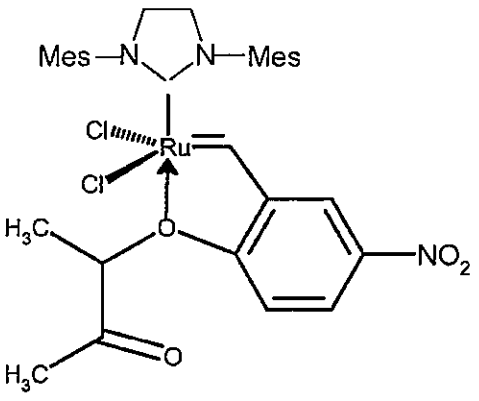
Further suitable catalysts which come under the general structural formula (IV) are those of the formulae (VI), (VII), (VIII), (IX), (X), (XI), (XII) and (~~XII~~XIII), where Mes is in each case a 2,4,6-trimethylphenyl radical.



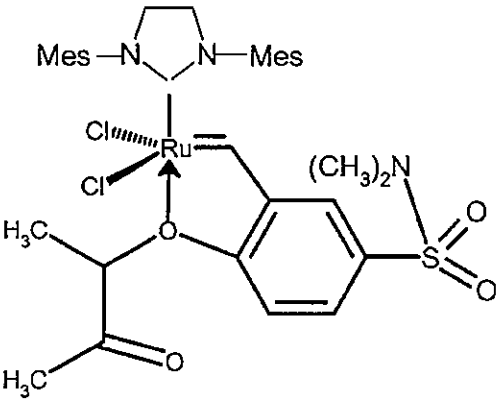
(VI)



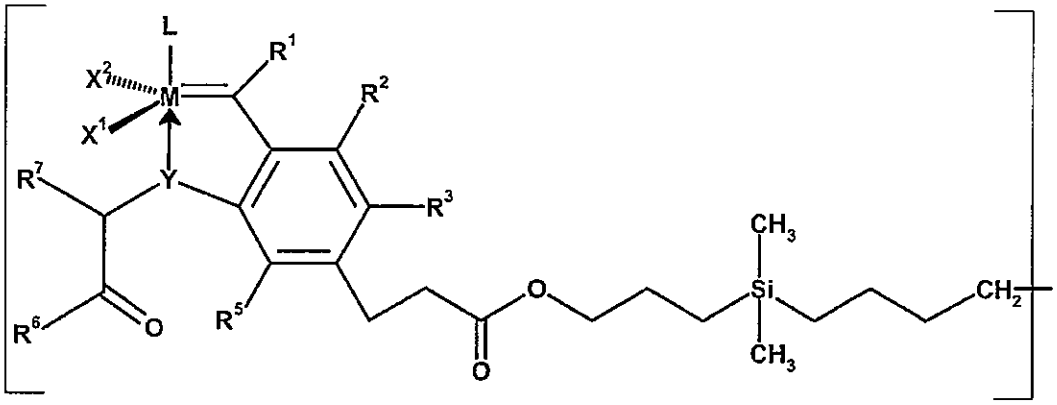
(VII)



(VIII)



(IX)



(XV)

where

M, L, X^1, X^2, R^1, R^2, R^3, R^5, R^6 and R^7 have the meanings given for the general formula (I) or can have the meanings given for all the abovementioned preferred or particularly preferred embodiments.

Such catalysts of the similar formula (XV) are known from **US 2002/0107138 A1** and can be prepared according to the information given there.

All the abovementioned catalysts of the formulae (I), (Ia), (~~II~~Ib), (IV)-(XIII), (XIV), (Iaa) and (XV) can either be used as such for the NBR metathesis or can be applied to and immobilized on a solid support. As solid phases or supports, it is possible to use materials which firstly are inert towards the reaction mixture of the metathesis and secondly do not impair the activity of the catalyst. It is possible to use, for example, metals, glass, polymers, ceramic, organic polymer spheres or inorganic sol-gels for immobilizing the catalyst.
The catalysts of all the abovementioned general and specific formulae (I), (Ia), (~~II~~Ib), (IV)-(XIII), (XIV), (Iaa) and (XV) are highly suitable for the metathetic degradation of nitrile rubber.

In the process according to the invention, a nitrile rubber is subjected to a metathesis reaction in the presence of a catalyst of the general formula (I) or in the presence of a catalyst of one of the formulae (Ia) or (Ib).

The weight amount of the catalyst used according to the invention for the metathesis depends on the nature and the catalytic activity of the specific catalyst. The amount of catalyst used is from 1 to 1000 ppm of noble metal, preferably from 5 to 500 ppm, in particular from 5 to 250 ppm, based on the nitrile rubber used. It has surprisingly been found by the inventors of the present invention that

Example 2.1

"Arlt catalyst" using 0.007 phr of catalyst and 4.0 phr of 1-hexene

NBR	"Arlt catalyst"		1-Hexene		Temperature
Amount [g]	Amount [g]	Amount [phr]	[g]	[phr]	[°C]
75	0.0053	0.007	3.0	4.0	23

Analytical data	"Arlt catalyst~~Umicore catalyst~~"
Brookfield Viscosity	456
Mooney Viscosity*	9,5
M_w [kg/mol]	144590
M_n [kg/mol]	57681
PDI	2.51

*ML 1+4 @ 100 °C

Example 2.2 (comparison)

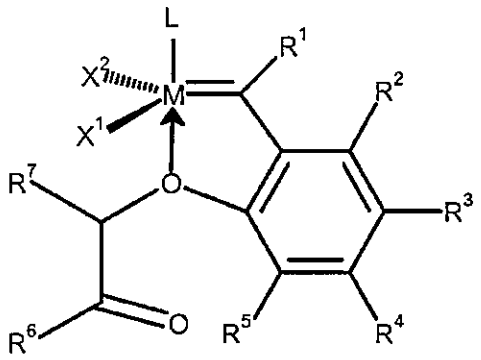
"Grubbs II catalyst" using 0.007phr of catalyst and 4.0 phr of 1-hexene

NBR	"Grubbs II catalyst"		1-Hexene		Temperature
Amount [g]	Amount [g]	Amount [phr]	[g]	[phr]	[°C]
75	0.0053	0.007	3.0	4.0	23

Analytical data	"Grubbs II catalyst"
Brookfield Viscosity	508
Mooney Viscosity*	10,9
M_w [kg/mol]	168364
M_n [kg/mol]	65028
PDI	2.59

*ML 1+4 @ 100 °C

In comparison to the original Perbunan NT 3429, the decrease in the Mooney viscosity and the molecular weight properties M_w and M_n in Examples 2.1 and 2.2 shows that at an amount of catalyst of 0.007phr the activity of the "Arlt catalyst" is higher than that of the "Grubbs II catalyst".



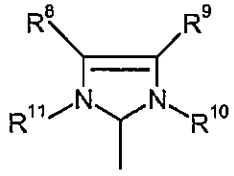
(IV)

where

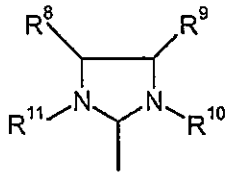
M, L, X^1, X^2, R^1, R^2, R^3, R^4, R^5, R^6, R^7 have the meanings given for the general formula (I) in Claim 1.

6. Process according to Claim 5, wherein, in the general formula (IV),

M	is ruthenium,
X^1 and X^2	are both chlorine,
R^1	is hydrogen,
R^2, R^3, R^4, R^5	are all hydrogen,
R^6	is methyl,
R^7	is methyl and
L	is a substituted or unsubstituted imidazolidine radical of the formula (IIa) or (IIb),



(IIa)



(IIb)

where

R^8, R^9, R^{10}, R^{11} are identical or different and are each hydrogen, straight-chain or branched C_1-C_{30}-alkyl, C_3-C_{20}-cycloalkyl, C_2-C_{20}-alkenyl, C_2-C_{20}-alkynyl, C_6-C_{24}-aryl, C_1-C_{20}-carboxylate, C_1-C_{20}-alkoxy, C_2-C_{20}-alkenyloxy, C_2-C_{20}-alkynyloxy, C_6-C_{24}-aryloxy, C_2-C_{20}-alkoxycarbonyl, C_1-C_{20}-alkylthio, C_6-C_{24}-arylthio, C_1-C_{20}-alkylsulphonyl, C_1-C_{20}-alkylsulphonate, C_6-C_{24}-arylsulphonate or C_1-C_{20}-alkylsulphinyl.

7. Process according to Claim 1, wherein a catalyst of the formula (VI), (VII), (VIII), (IX), (X), (XI), (XII) and (~~XII~~XIII), where Mes is in each case a 2,4,6-trimethylphenyl radical, is used.