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THE DEVELOPMENT OF FUNCTIONAL GROUP TOLERANT ROMP CATALYSTS

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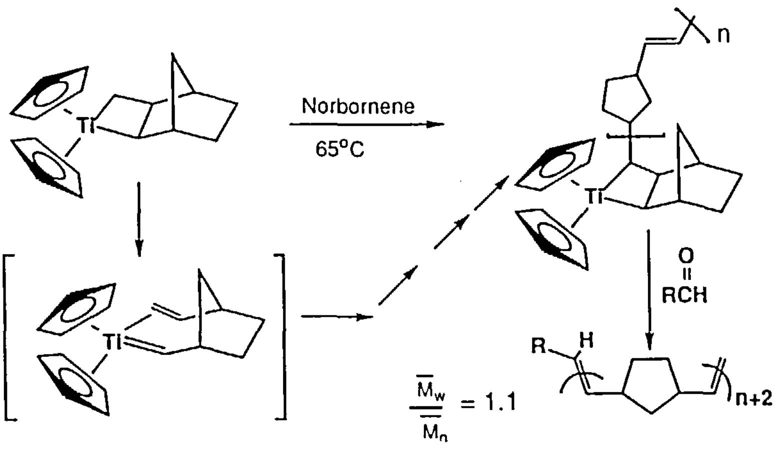
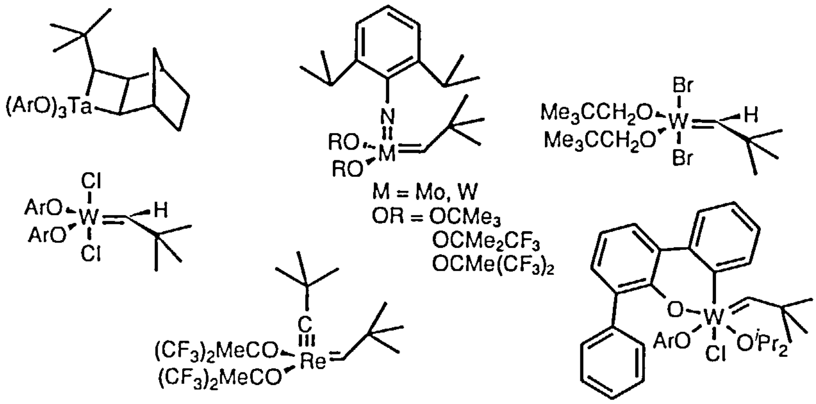
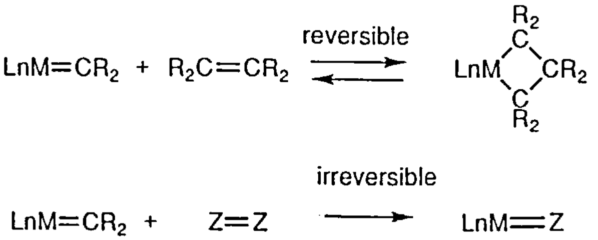
Since the discovery that transition metals salts mixed with organoaluminum reagents catalyze the polymerization of ethylene to crystalline polyethylene, organometallic complexes and reagents have played a major role in the polymer industry [1]. Over the past 20 years a tremendous amount has been learned about the structures and mechanisms of reactions of complexes related to those proposed to be active in these systems [2]. In the related area of olefin metathesis and ring-opening metathesis polymerization (ROMP), metal carbenes and metallacycles were proposed intermediates, and over the past few years a number of complexes with these structures that will catalyze the olefin metathesis reaction have been prepared and studied [3]. In contrast to the ill-defined classical catalysts based on Ziegler-type catalysts, these are living polymerization systems. This was first observed using Tebbe-type reagents [4].



Since this observation, it has been found that many of the well-characterized metal carbene complexes will give living ROMP systems [5–8].



After finding that ROMP systems could be living, a search for catalysts that would be more tolerant of functional groups was initiated. The more functionality tolerated, the larger the variety of functional polymers and block copolymers that would be available. In the catalysts that were subsequently synthesized and explored for living romp polymerization, as the central atom moved to the right in the periodic table from titanium, the tolerance for functionality increased. The key to a successful ROMP catalyst that will function in the presence of a functional group is the relative selectivity of the complex for the relatively soft C=C in the presence of hard complexing functionality such as esters and ketones [9]. It has also been found that functional groups not only reacted with the Lewis acids in the "classical" catalysts but also underwent irreversible reactions with the carbene ligand in the single component catalysts. This reactivity has found application in organic synthesis [10] but is limited to use in endgroup functionalization in polymer chemistry [11].

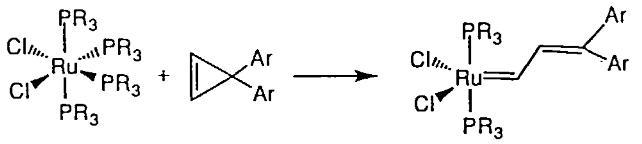


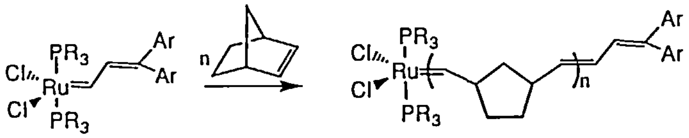
Group VIII catalysts for ROMP were discovered very early. However, their use has been limited to the polymerization of highly strained norbornene derivatives [12]. Although these catalysts showed limited activity had not been reported in any acyclic metathesis reactions or in the ROMP of cyclic olefins with low ring strain, they functioned in protic solvents and showed a high tolerance of functionality.

The finding that ruthenium chloride would function as an outstanding ROMP catalyst in water with a variety of functionalized 7-oxonorbornene derivatives, initiated an exploration of the mechanism and intermediates in these reactions [13]. The key findings of these studies were:

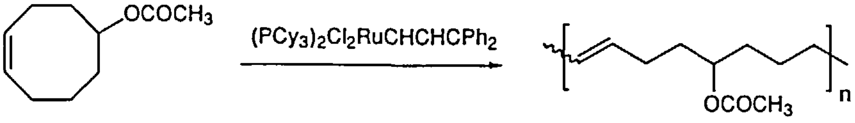
1. Water was essential for the activity of catalyst systems that started with Ru^{3+}.
2. Independent of the initial ruthenium source, a ruthenium(II) olefin complex was formed during the polymerization.
3. The ruthenium(II) olefin complexes were excellent catalyst precursors, and when they were used, the usual induction period was very short.
4. For most cases, $Ru(H_2O)_6(OTs)_2$ was the best catalyst precursor [14].
5. In some cases, if other sources of carbene fragments were added to the system, the ruthenium catalysts showed limited activity toward less strained olefins [15].

These lessons were used to develop a synthesis for a well-defined catalyst for the ROMP of functionalized olefins. It was found that the reaction of a ruthenium(II) complex with a highly strained cyclopropene resulted in the formation of a stable vinylcarbene complex of ruthenium that would ROMP norbornene to a living polymer [16].





The activity of the catalyst could be tuned by changing the structure of the phosphine ligand [17]. The triphenylphosphine complex catalyzed the slow living polymerization of norbornene and would only react with strained or electron-rich olefins. The tricyclohexylphosphine complex was much more active and would polymerize less strained olefins such as cyclooctene and its derivatives [18] and catalyze the metathesis of acyclic olefins [19].



This reaction opens the way to a family of terpolymers of butadiene, ethylene, and a vinyl derivative.

Titanium	*Tungsten*	*Molybdenum*	*Ruthenium*
Alcohols, Water	Alcohols, Water	Alcohols, Water	**Olefins**
Acids	Acids	Acids	Alcohols, Water
Aldehydes	Aldehydes	Aldehydes	Acids
Ketones	Ketones	**Olefins**	Aldehydes
Esters, Amides	**Olefins**	Ketones	Ketones
Olefins	Esters, Amides	Esters, Amides	Esters, Amides

Based on the experience in polymerization chemistry and organic synthesis using the different metathesis catalysts, a reactivity table can be constructed. As the central metal is chosen from further right in the periodic table, the selectivity for olefins over other functionalities increases [20]. It is reasonable that as the central atom moves to the right it becomes softer and contains more *d*-electrons. This trend favors the complexation and reaction with olefins over the harder oxygen-containing functional groups.

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