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Synthesis and comparative behavior of ruthena(II)cycles bearing benzene ligand in the radical polymerization of styrene and vinyl acetate

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ABSTRACT

A series of half-sandwich ruthenium(II) complexes of the type $[Ru(\eta^6\text{-}C_6H_6)(N\cap C)L]PF_6$ (L = PPh_3, $P(n\text{-}Bu)_3$, $SbPh_3$, MeCN), bearing cyclometalated *N*,*N*-dimethylbenzylamine (**1a**–**d**) and 2-phenylpyridine (**2a**–**d**) moieties, has been efficiently prepared by ligand substitution. The molecular structures of the new compounds were unequivocally determined by single-crystal X-ray diffraction. The catalytic activity of the complexes in the radical polymerizations of styrene and vinyl acetate was evaluated, and a comparative structure – activity analysis was performed.

1. Introduction

Cyclometalation of ligands by transition metals is one of the easiest ways to form organometallic compounds with a metal-carbon sigma bond. Due to the stabilization by chelation, these compounds are generally quite robust and therefore may easily be managed without extreme precautions. The platinum group metals are by far the most popular domain used for cyclometalation reactions and a vast number of metallocycles has been prepared by heteroatom-assisted C–H bond activation, with the palladium complexes being the most studied, since cyclopalladated derivatives are known for nearly all classes of ligands [1–4]. The corresponding ruthenium compounds have been much less investigated and their synthesis and properties are less well understood, even though ruthenacycles have shown remarkable photophysical and electrochemical properties. For instance, they have been considered as promising materials for applications in solar cells, intervalence electron-transfer systems or in bioelectronic devices as efficient electron shuttles for oxidoreductase enzymes [1,2,5–11]. The organoruthenium derivatives also possess the required characteristics for the interaction with biomolecules and several ruthenacycles are considered as promising candidates for anticancer drugs [1,12–14]. Although ruthenium complexes have been widely investigated for homogeneous catalysis, their *ortho*-metalated counterparts have not as yet demonstrated their full potential in this area and only a few examples of cycloruthenated compounds showing good activity in homogeneous catalysis have been reported [15–17].

Cycloruthenation is very versatile and of broad scope mostly because of the great diversity and availability of ruthenium precursors. However, one setback is the relative lack of reactivity of ruthenium complexes toward the cyclometalation reaction and frequently the synthetic route requires various steps and results in low yields [1,18]. Our group has been studying the synthesis and possible ways of application of cycloruthenated compounds for almost two decades. Simple and highly effective synthesis of ruthenacycles has been developed which allows easy modification

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Abbreviations: BEB, 1-(bromoethyl)-benzene; MMA, methyl methacrylate; St, styrene; VAc, vinyl acetate; MEK, methyl ethyl ketone; TEMPO, (2,2,6,6-tetramethyl-piperidin-1-yl)oxyl; Cyclometalated ligands: dmba, *N*,*N*-dimethylbenzylamine; phpy, 2-phenylpyridine; tolpy, 2-(*p*-tolyl)pyridine.

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of the compounds in the desirable direction [8,9,19–21].

One of the promising applications of the ruthenacycles in catalysis may be in atom transfer radical polymerization (ATRP) or metal catalyzed living radical polymerization. Indeed, ruthenium(II) complexes were among the first catalysts reported for this reaction and to the date remain one of the most active and versatile catalytic systems [22,23]. Moreover, ruthenium complexes have been known to be among the most efficient for C–C bond formation in the Karasch addition or atom transfer radical addition (ATRA), a reaction mechanistically very similar to ATRP [24–26]. The classical mechanism of ATRP consists in the reversible homolysis of a terminal carbon-halogen bond of the dormant species through the abstraction of the halogen atom by the metallic catalyst resulting in the formation of growing radicals and the complex in +1 higher oxidation state (Scheme 1). The complex participates in a reversible oxidative addition reaction and therefore its catalytic activity should correlate with its redox potential, where a lower redox potential means higher catalytic activity. A direct correlation has been shown for structurally simpler copper catalysts [27], while the structure – ATRP reactivity relationship for the ruthenium-based catalysts is highly sophisticated and no simple dependence has been found, even for structurally similar ruthenium compounds [28–30]. Cyclometalated ruthenium(II) complexes may have advantages here in comparison with their coordinated congeners because of the less positive Ru^{III}/Ru^{II} potential [1,12,31–33]. Several ruthenacycles have been reported as efficient catalysts in ATRP and ATRA reactions of different acrylic and vinylic compounds [26,30,34–36]. They may be better referred to catalyst precursors since all of them are 18 electrons coordinatively saturated molecules and a vacant site must be generated to enable their activation for ATRP [30,34–36]. Recently, the very active catalyst precursor $[Ru(\eta^6\text{-}C_6H_6)(dmba)(MeCN)]PF_6$ has been reported, which was able to polymerize vinyl acetate, one of the most difficult monomers for ATRP, via the reversible activation of the carbon-Cl terminals under specific conditions [37]. Additionally, the investigation demonstrated the importance of the presence of a benzene ligand in the structure of the catalyst, since the complexes having benzene were generally more active than their counterparts with polypyridine ligands. Unfortunately, polymerization of other more conjugated monomers, such as styrene or methyl methacrylate proceeded without control.

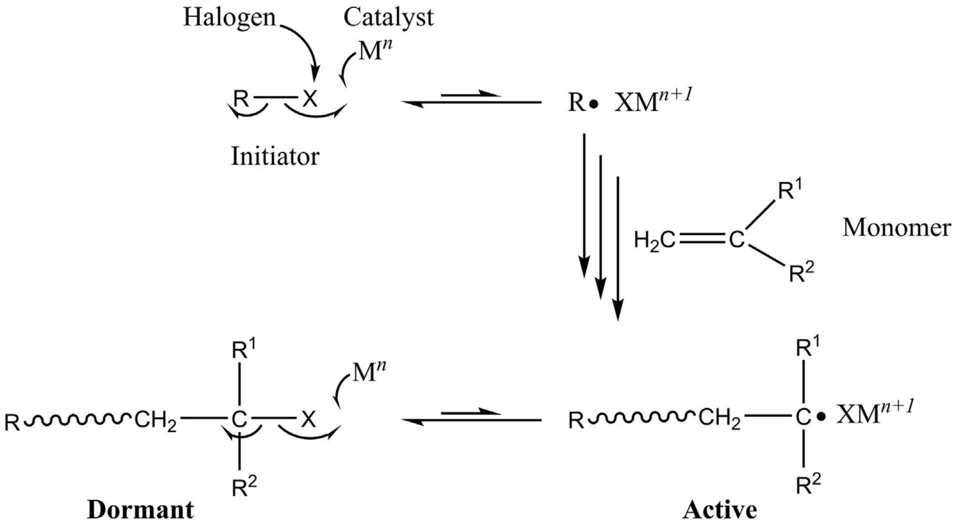
To continue our effort in understanding the role of potentially labile ligands in the catalytic activity, a series of ten cyclometalated ruthenium(II) complexes bearing η^6-C_6H_6 has been prepared (See Fig. 1 for the structures). In order to evaluate the influence of different parameters such as the lability of the ligands and the electron density on the metal centre, the structure of the complexes was gradually modified: (i) two different cycloruthenated moieties, *N*,*N*-dimethylbenzylamine (group **1**) and 2-phenylpyridine (group **2**) were introduced, and, (ii) a substitution reaction allowed the incorporation of various ancillary ligands such as acetonitrile, phosphines and stibines. Such a variety of compounds enabled the investigation of the influence of the different ligands on the catalytic activity and to clarify some mechanistic aspects. The behavior of the complexes was analyzed under conditions of the polymerization of St and VAc. Furthermore, considering that the ionic character of the complexes may also impact on their catalytic performance [26,38,39], two neutral $[Ru(\eta^6\text{-}C_6H_6)(N\cap C)Cl]$ compounds (group **3**), with a phpy-based cyclometalated fragment, were also studied and the results compared with group **1** and **2** catalysts.

2. Experimental

2.1. Materials and reagents

All reactions were carried out under inert atmosphere (dinitrogen or argon) using conventional Schlenk glassware; all solvents were dried using established procedures and distilled under dinitrogen prior to use. Styrene (99%) was washed three times with 1 wt % NaOH solution and passed through a column filled with neutral alumina, vinyl acetate (>99%, Aldrich) was passed through a neutral alumina column, distilled under reduced pressure, and stored under nitrogen. All the others reagents were purchased from Aldrich and used as received: *N*,*N*-dimethylbenzylamine, 2-phenylpyridine, *n*-decane, BEB (97%), carbon tetrachloride, tetrahydrofuran HPLC, tri-*n*-butylphosphine, triphenylphosphine, triphenylstibine, potassium hexafluorophosphate, silver hexafluorophosphate, anhydrous ether and anhydrous acetonitrile. Commercial $RuCl_3$ was purchased from Pressure Chemical Company. Complexes **1d**, **3′**, **3″** and **4** were prepared according to the literature [18,19,40–42].

Mass Spectra were obtained using a JEOL JMS-SX102A instrument with *m*-nitrobenzyl alcohol as the matrix [FAB^+ mode, *m*/*z* (%,



Scheme 1. Mechanism of ATRP.