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Polyisobutylene-Anchored *N*-Heterocyclic Carbene Ligands

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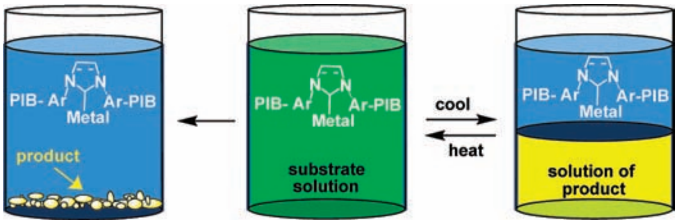
ABSTRACT



The synthesis of polyisobutylene (PIB)-supported *N*-heterocyclic carbenes (NHCs) that are useful as ligands for recoverable/recyclable organometallic complexes is described. Both PIB-bound carbenes analogous to SIMes and IMes as well as carbene precursors bound to PIB via 1,2,3-triazoles by alkyne−azide couplings are described. Both Ag(I) and Ru(II) complexes of these carbenes are shown to be phase selectively soluble in heptane. Hoveyda−Grubbs second-generation catalysts containing a PIB-supported NHC have also been used to catalyze ring-closing metathesis.

N-Heterocyclic carbenes have become widely used ligands for organometallic chemistry since Arduengo's initial reports.[1] While their use in metathesis chemistry is most common, metal complexes derived from these structurally diverse ligands are useful in many catalytic processes.[2,3] *N*-Heterocyclic carbenes themselves are also useful organocatalysts.[4] Thus, there is significant interest in strategies that facilitate separation, recovery and reuse of these ligands and their metal complexes. Below we describe new routes to recoverable, heptane-soluble NHC ligands and their use as supports for recoverable, reusable metathesis catalysts. Insoluble cross-linked polymers or inorganic supports for recoverable reusable NHC-ligated metal complexes useful in catalysis are known.[5,6] Examples of soluble polymer supports for these catalysts have also been described, but these latter reports are limited to the use of poly(ethylene glycol) (PEG) supports.[7,8] PEG supports attached to an imidazolium carbon or to an imidazolium nitrogen yield NHC catalysts that are water-soluble or recoverable by solvent precipitation. Here we describe using heptane-soluble polyisobutylene as a phase anchor to prepare phase-separable NHC metal complexes.[9] As shown below, PIB groups can be attached to these carbene precursors in various ways, and the product PIB-bound NHCs form metal complexes that are phase selectively soluble in the heptane phase of thermomorphic mixtures of heptane and polar solvents. Alternatively, heptane solutions of these NHCs can be extracted with polar solvents with minimal losses of the metal

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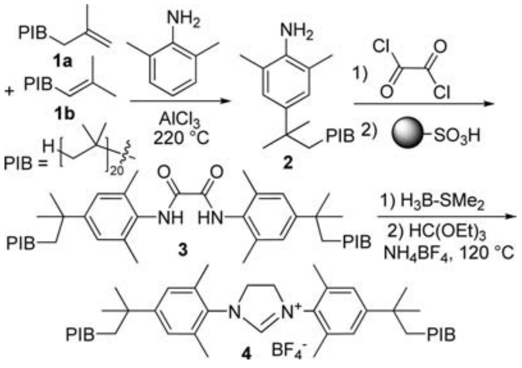
Scheme 1. Synthesis of the PIB-SIMes Salt **4**



complex. This behavior is demonstrated both for Ag(I) complexes and with a separable, recoverable, and reusable Ru catalyst useful in ring-closing metathesis chemistry.

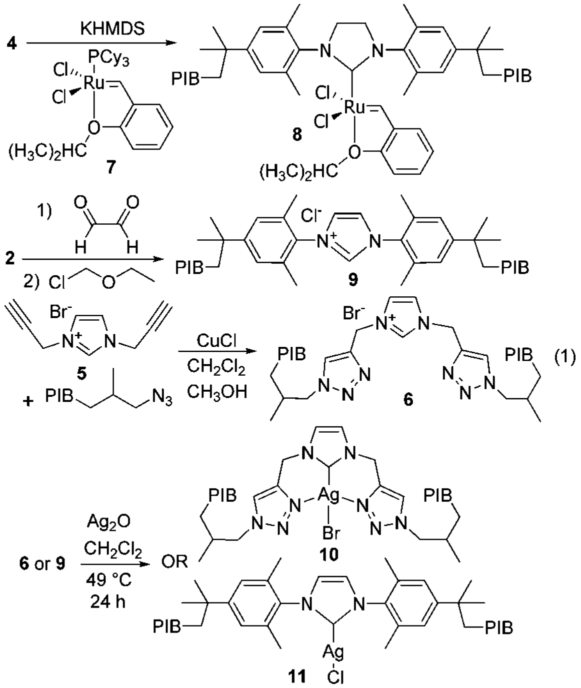
Two approaches were explored as routes for the synthesis of PIB-supported NHC ligands. First, a Friedel−Crafts alkylation of a commercially available mixture of alkene-terminated PIBs **1a** and **1b** afforded 2,6-dimethyl-4-(polyisobutyl)aniline **2** which like mesityl amine reacts with oxalyl chloride to form the diamide **3**. Excess **2** used in this reaction was separated using an Amberlyst resin scavenger.[10] The diamide product was then reduced to form a diamine that was converted into the PIB-bound imidazolium tetrafluoroborate salt **4** using known chemistry (Scheme 1).[7]

A second route to PIB-bound NHC ligands (Scheme 2, eq 1) used a "Click" cycloaddition of a dipropargylic imidazole derivative and a PIB-bound azide.[8] Zeitler's group used similar chemistry to prepare PEG-bound NHCs.[11]

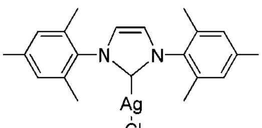
Formation of metal complexes from PIB-bound imidazolium salts used either KHMDS to deprotonate **4** to synthesize a PIB-supported Hoveyda−Grubbs second-generation catalyst **8** from the Hoveyda−Grubbs first-generation catalyst **7**[7] or used the reaction of a basic metal oxide like Ag_2O[12] with **6** or **9** to prepare the Ag(I) complexes **10** and **11** (Scheme 2).

Figure 1. Visually evident phase separation of **8** and **13**: (a) a heptane/acetonitrile mixture; (b) a heptane/DMF mixture; (c) a heptane/EGDA mixture.

Scheme 2. Syntheses of PIB-Supported Ru and Ag Complexes



The metal complexes formed were characterized by solution-state ^1H and ^{13}C NMR spectroscopy. The PIB-bound pincer complex **10** had spectra that were like those of low molecular weight pincer Ag(I) complexes formed using octadecylazide in place of the PIB azide. The Ag(I) complex **11** was directly compared to **12**. In the case of **11**, the carbene carbon also exhibited $^{107,109}Ag$ coupling. An analysis for Ag showed that **10** or **11** contained 4.06% or 3.51% Ag, respectively (4.05% or 3.89% Ag was expected for **10** or **11** if the PIB groups in the product have a degree of polymerization of 20). ICP-MS analyses showed that the Ag(I) complex **10** had a 98:2, 99:1, or 96:4 selective solubility in heptane in mixtures of heptane with CH_3CN, $AcOCH_2CH_2OAc$ (EGDA), or DMF. A direct comparison of **11** with its low molecular weight analogue **12** in a partially thermomorphic heptane/CH_3CN mixture showed that **11** had a 98:2 phase selective solubility in the heptane phase of this solvent mixture at room temperature, while the heptane-phase selective solubility for **12** was <1:1000. This ICP-MS analysis of **11** vs **12** in this equivolume heptane/CH_3CN mixture illustrates the effectiveness of the PIB phase tag.



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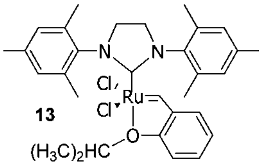

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The phase-selective solubilities of the Ru complexes **8** and **13** mirrored those of the Ag complexes. UV−vis spectroscopy analysis showed a heptane-phase selective solubility difference of 99:1 vs 1:100 for **8** vs **13** in a thermomorphic equivolume mixture of heptane and CH_3CN. This solubility difference is evident in a visual comparison (Figure 1) and

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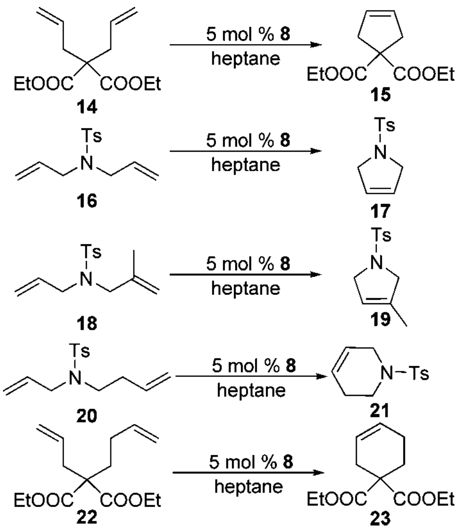
Table 1. RCM Reactions with Catalyst **8**[a]



product	cycle 1 (%)	cycle 2 (%)	cycle 3 (%)	cycle 4 (%)	cycle 5 (%)
15	60	75	85	94	94
17[b]	72	81	99	99	98
19	67	75	93	99	99
21	59	76	84	93	93
23	62	71	97	99	99

[a] [a]Yields in cycles 1−5 are for isolated products in 1 h, 0.5 mmol scale reactions, and increase cycle to cycle because of saturation of the catalyst-containing heptane-phase byproduct. [b] Twenty cycles (average yield of 97%/cycle) were carried out with reaction times of 2 h in the 12th−13th cycles, 4 h in 14th−18th cycles, and 8 h in 19th−20th cycles.

was confirmed by ICP-MS analyses for Ru that showed a 97:3 vs a 1:99 phase selective solubility for **8** and **13** in the heptane versus the CH_3CN phase of a heptane/CH_3CN mixture.

Ru complexes like **8** are structurally analogous to the Ru complex **13** already used in ring-closing metathesis.[13] However, unlike **13**, **8** could be recycled up to 20 cycles in conversion of a variety of 1,6-dienes and 1,7-dienes into cyclic olefins at room temperature (Table 1), though some catalyst deactivation appeared to be occurring after cycle 12.

Recycling of **8** was accomplished in one of two ways. The first approach used for ring-closing metathesis of dienes **14** and **22** used heptane as a solvent, extracting product afterward with CH_3CN. In this approach, the less dense heptane phase containing **8** was reused by simply adding fresh substrate. Products **15** and **23** were then isolated by removal of the CH_3CN.

While most catalyst recovery schemes focus on catalyst separation, the solubility of **8** in heptane and the low solubility of many organic compounds in heptane allowed us to use another recycling scheme for substrates **16**, **18**, and **20**. In these cases, starting materials were soluble in a heptane solution of the catalyst, but the products precipitate from solution and separate themselves from the solution of **8**. Products **17**, **19**, and **21** were recovered by simple filtration and recycling only required adding a fresh substrate to the recovered solution containing **8**. The recyclability/recoverability of **8** was evaluated by ICP-MS analysis. Samples of product **17** from the first, second, fifth, and fourteenth cycles were digested first in concentrated nitric acid and then in sulfuric acid. ICP-MS analysis of this solution showed that only 0.37−0.63% of the starting Ru was in the product phase. This level of leaching of Ru is comparable to that seen for a water soluble PEG-supported SIMes.[14] More significantly, the metal leaching is ca. 10-fold less than observed for Ru catalysts that used a PIB-bound benzylidene ligand chemistry where Ru separation depended on a "boomerang" reaction for catalyst recovery.[15]

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Supporting Information Available: Synthetic procedures and characterization data for PIB-bound metal complexes and procedures for ring-closing-metathesis reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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