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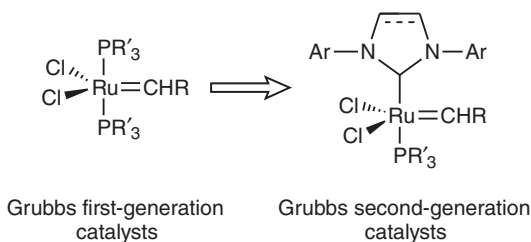
Synthetic Experiments in Current Organic and Organometallic Chemistry

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Stable N-heterocyclic carbenes (NHCs) have become a key class of ligands in organometallic chemistry (1) since their isolation and crystallographic characterization by Arduengo et al. (2). Oftentimes compared to tertiary phosphines because of similarities in their bonding and their transition-metal catalytic activity, the NHCs possess properties that render them more desirable for a number of catalytic applications (3). For instance, the Grubbs second-generation catalysts involve the substitution of one phosphine ligand by a bulky NHC ligand (Scheme I). This modification has produced the mixed phosphine–NHC compounds, $[\text{RuCl}_2(=\text{CHR})(\text{NHC})(\text{PR}'_3)]$, which display dramatically improved metathesis activity, thermal stability, and inertness toward oxygen and moisture in comparison to $[\text{RuCl}_2(=\text{CHR})(\text{PR}'_3)_2]$ (4, 5). These enhanced catalytic performances and higher stabilities are generally attributed to the better σ -donor properties of the NHCs compared to those of the best donor phosphines (6).

A minor hurdle hindering a more widespread use of NHCs as ligands is the need to generate them from their respective imidazolium salt ($\text{NHC}\cdot\text{HX}$, where $\text{X} = \text{Cl}, \text{Br}, \text{I}$), which either requires an additional isolation step or, alternatively, their formation in situ. Recently however, Cowley et al. (7) and Nolan et al. (8) have developed easy-to-do general synthetic procedures to generate $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{NHC})\text{Cl}]$ complexes directly from $\text{NHC}\cdot\text{HCl}$ and $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$. These NHC complexes have been found to be active catalysts in aryl amination and in aryl halide dehalogenation reactions (8).



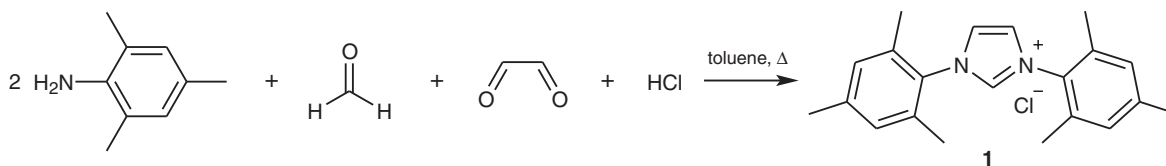
Scheme I. Examples of Grubbs catalysts.

The four-part experiment presented here includes the synthesis of an imidazolium salt; the synthesis of $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ and sodium cyclopentadienide; their reaction together to give nickelocene; and the reaction of the latter with the imidazolium salt to form the corresponding NHC–nickel(II) complex. Each product can be characterized by either ^1H NMR or IR spectroscopy, which allows the students to gain experience in these common characterization techniques. These experiments have been successfully performed by fourth-year students (i.e., equivalent to fourth-year undergraduates in U.S. universities). No specialized techniques or equipment are required apart from access to a dual inert-gas vacuum manifold, fritted filter funnels with side arms designed for use with schlenk-ware, a vacuum pump, and freshly distilled water- and oxygen-free tetrahydrofuran.

Experiment Overview

Each step in this four-part synthesis is of pedagogic interest. The organic reaction, the formation of the 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride (IMes $\cdot\text{HCl}$) **1**, demonstrates the one-pot preparation of an imidazolium salt from the condensation of glyoxal and paraformaldehyde with two equivalents of 2,4,6-trimethylaniline in an acidic medium (Scheme II) (9). This reaction constitutes a good example of the reactivity of carbonyl derivatives towards an amine (see the online material for a possible mechanism).

The product **1** is isolated from the black tar that results from the removal of the volatiles from the reaction medium, by trituration in acetone, precipitation by addition of diethyl ether, filtration, and a thorough washing with acetone (9b). The whitish powder thus obtained is sufficiently pure to be used in a subsequent reaction without the need for additional recrystallization or purification. The ^1H NMR spectrum of **1** in CDCl_3 reveals an effective mirror plane of symmetry that contains the NCHN proton and bisects the $\text{CNH}=\text{CNH}$ bond. Rapid rotation about the $\text{Mes}-\text{N}$ bonds on the ^1H NMR time scale combined with this effective mirror plane of symmetry renders the four ortho Me groups, the four meta H atoms, the two para Me groups and the two olefinic protons respectively equivalent.



Scheme II. Preparation of 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride **1**.

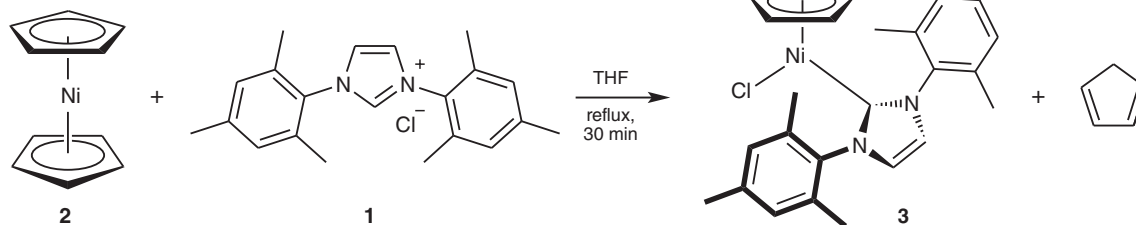
The synthesis of bis(cyclopentadienyl)nickel **2** is of interest because of the importance of metallocenes in modern organo-metallic chemistry (10). Its preparation involves first, the preparations of $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ and of sodium cyclopentadienide (NaCp) (Scheme III). $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ is readily synthesized by adding concentrated aqueous ammonia to an aqueous solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (11). NaCp can be reliably prepared by following the improved synthetic procedure recently published by Roesky et al. (12). This one-pot synthesis avoids the lengthy thermal retro-Diels–Alder “cracking” reaction and the tedious distillation of the cyclopentadiene monomer by directly reacting sodium in neat dicyclopentadiene at 160 °C (Scheme III).

$[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ can be characterized by FTIR spectroscopy. To assign the NH_3 group vibrations, it is convenient to consider the six normal modes of the bound ammonia molecule independently (13). The antisymmetric and symmetric NH_3 stretching, NH_3 degenerate deformation, NH_3 symmetric deformation, and NH_3 rocking vibrations can be easily assigned.

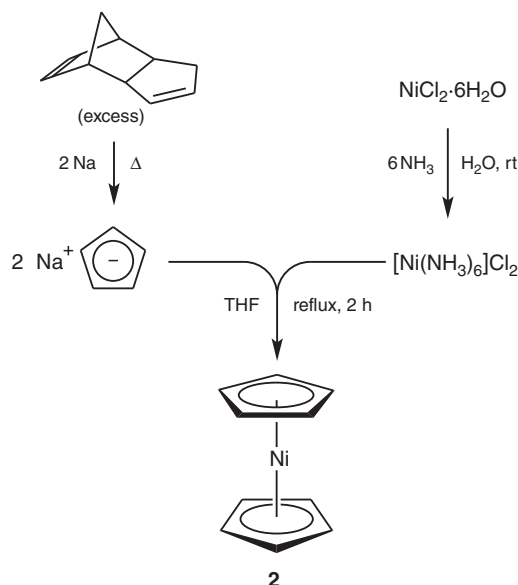
Even solid NaCp is highly air-sensitive, and to avoid product decomposition, it is best not to separate the insoluble powder from excess dicyclopentadiene. Instead, the suspension of NaCp in excess dicyclopentadiene is dissolved in water- and oxygen-free freshly distilled tetrahydrofuran, and this solution is reacted directly with $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ under reflux (Scheme III) (14). The presence of excess dicyclopentadiene in the medium does not interfere with the reaction, and it is easily eliminated when crystallizing the product. This reaction affords $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$ **2**, in which the nickel atom is complexed to the cyclopentadienyl rings via the interaction of its set of 3d orbitals with the cyclopentadienyl π molecular orbitals.

As **2** is paramagnetic, ^1H NMR cannot readily be used for its characterization and it is best characterized by its deep green color and by FTIR spectroscopy. Characteristic vibrations are found for C–H and C=C bonds at 3075 ($\nu_{\text{C-H}}$), 1430 ($\nu_{\text{C=C}}$), 1109 ($\delta_{\text{C-H}}$), and 1002 cm^{-1} ($\delta_{\text{C-H}}$) (14).

The last reaction is the addition of the imidazolium chloride **1** to $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$ **2**. This reaction proceeds rapidly and is over in 30 min (7). The $\text{IMes} \cdot \text{HCl}$ **1** adds onto the nickel atom to form new Ni–C and Ni–Cl bonds while one cyclopentadienyl ring plays the role of a hydrogen abstractor, giving the nickel(II) half-sandwich complex $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{IMes})\text{Cl}]$ **3** and cyclopentadiene (Scheme IV). It should be pointed out to the students that the strong Ni–Cl bond formed in the reaction is believed to be a significant thermodynamic driving force leading to the product (8). It should also be mentioned that the diamagnetic Ni(II) complex **3** observes the 18-electron rule, which is not the case of the paramagnetic 20-electron nickelocene. Loss of coordinated $\eta^5\text{-C}_5\text{H}_5$ ligands is not usually observed, but is frequent in the chemistry of this 20-electron complex.



Scheme IV. Reaction of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$ **2** with the imidazolium chloride **1**.



Scheme III. Preparation of bis(cyclopentadienyl)nickel **2**.

The violet product **3** is purified by filtration on Celite and crystallization from toluene and is analyzed by ^1H NMR in CDCl_3 . The ^1H NMR spectrum shows the presence of one η^5 -bonded cyclopentadienyl ligand and one carbene ligand. Rapid rotation of the cyclopentadienyl ring about the nickel–ring-centroid renders all five aromatic protons of the ligand equivalent on the ^1H NMR time scale, and thus a single signal is seen for these protons. Concerning the carbene ligand, the effective mirror plane of symmetry that bisects the $\text{CNH}=\text{CNH}$ bond and contains the Ni and Cl atoms and the Cp ring centroid, as well as the rapid rotation about the $\text{Mes}-\text{N}$ bonds, render the four ortho methyl groups, the four meta hydrogen atoms, the two para methyl groups, and the two olefinic hydrogen atoms respectively, chemically equivalent as seen for the organic precursor **1**.

Hazards

Pentane and diethyl ether are extremely flammable and are harmful in case of ingestion. Tetrahydrofuran, toluene, acetone, dicyclopentadiene, and $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$ **2** are readily flammable. Diethyl ether and tetrahydrofuran can form explosive peroxides. Tetrahydrofuran is irritating to the eyes and to the respiratory system. Toluene and glyoxal are harmful in case of inhalation. Acetone is irritating to the eyes. 2,4,6-trimethyl-

aniline is very toxic in case of inhalation, and harmful in case of skin contact and ingestion. Paraformaldehyde and $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ are harmful in case of inhalation, skin contact, and ingestion. Paraformaldehyde may cause irreversible damage and can cause burns. Aqueous ammonia and hydrochloric acid can cause burns. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$, and $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$ can cause cancer. In case of ingestion, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ is toxic and $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$ is harmful. Na reacts violently with water forming extremely flammable gases. Special care should be taken when handling sodium. Dicyclopentadiene is harmful when inhaled and ingested. Celite and silica constitute an inhalation hazard owing to their small particle size. The compounds **1** and **3** have not been fully tested for toxicity and therefore should be handled with care.

Summary of Procedure

The reactions are appropriate for an advanced undergraduate inorganic laboratory class or for a graduate class. All the reagents are relatively cheap. The reaction sequence requires four laboratory sessions of approximately one day each to be completed. We recommend the first day to be devoted to the synthesis of $\text{IMes} \cdot \text{HCl}$ **1**, the second to those of $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ and NaCp, the third to that of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$ **2**, and the fourth to that of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{IMes})\text{Cl}]$ **3**. A possible alternative is to bypass the syntheses of $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$, NaCp, and **2** by purchasing **2**. The organic product **1** and $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ can be stored in a closed vial in air till the next session. NaCp should always be kept rigorously under nitrogen and should be used as soon as possible. We thus recommend the second and third laboratory sessions to be held on two consecutive days. Although **2** can be handled quickly in air in the solid state, it is best kept in a Schlenk tube under nitrogen. The final product **3** is stable in solution under nitrogen, and air-stable in the solid state.

The preparation of hexaamminenickel(II) chloride is carried out in air and that of **1** under nitrogen without any other particular precaution. The other reactions are run under nitrogen in freshly distilled tetrahydrofuran. These experiments show the need for manipulating complexes under nitrogen but—except in the case of NaCp—the reactions are forgiving and students are not unduly penalized if some air accidentally enters the system. Except for the preparation of **1** (ca. 40%), the yields of the reactions are close to quantitative. Purification of nickelocene and **3** by crystallization after filtration on silica or Celite provides a good example of how impurities can be removed to obtain a product of high purity.

The experiments presented here are instructive as they link organic and organometallic chemistry and give students an insight onto modern molecular chemistry (15). Moreover, they provide an introduction to a class of ligands, the NHCs, which finds an ever-growing application field in homogeneous catalysis (16). Finally the students are gratified that the ^1H NMR and IR spectra of the products are interpretable and are in agreement with the proposed structures.

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