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LDRD Final Report on New Homogeneous and Supported Oligomerization Catalysts (LDRD 42461)

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Abstract

The overall purpose of this LDRD is multifold. First, we are interested in preparing new homogeneous catalysts that can be used in the oligomerization of ethylene and in understanding commercially important systems better. Second, we are interested in attempting to support these new homogeneous catalysts in the pores of nano- or mesoporous materials in order to force new and unusual distributions of □-olefins to be formed during the oligomerization. Thus the overall purpose is to try to prepare new catalytic species and to possibly control the active site architecture in order to yield certain desired products during a catalytic reaction, much like nature does with enzymes.

In order to rationally synthesize catalysts it is imperative to comprehend the function of the various components of the catalyst. In heterogeneous systems, it is of utmost importance to know how a support interacts with the active site of the catalyst. In fact, in the catalysis world this lack of fundamental understanding of the relationship between active site and support is the single largest reason catalysis is considered an "empirical" or "black box" science rather than a well-understood one. In this work we will be preparing novel ethylene oligomerization catalysts, which are normally P-O chelated homogeneous complexes, with new ligands that replace P with a stable carbene. We will also examine a commercially catalyst system and investigate the active site in it via X-ray crystallography. We will also attempt to support these materials inside the pores of nano- and mesoporous materials. Essentially, we will be tailoring the size and scale of the catalyst active site and its surrounding environment to match the size of the molecular product(s) we wish to make. The overall purpose of the study will be to prepare new homogeneous catalysts, and if successful in supporting them to examine the effects that steric constraints and pore structures can have on growing oligomer chains.

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General Introduction

The overall purpose of this LDRD is multifold. First, we are interested in preparing new homogeneous catalysts that can be used in the oligomerization of ethylene and in understanding commercially important systems better. Secondly, our interest resides in supporting these new homogeneous catalysts in the pores of nano- or mesoporous materials in order to force new and unusual distributions of □-olefins to be formed during the oligomerization. Thus the overall purpose is to try to control the active site architecture in order to yield certain desired products during a catalytic reaction, much like nature does with enzymes.

Described in this report is chemistry involved primarily with the first aspect of the proposed research – the synthesis of new coordinating ligands. We were interested in preparing variations upon the SHOP catalyst system used in the oligomerization of ethylene by Shell Chemical Company. A key feature of the SHOP ligand used with the Ni(2+) metal ion to afford an active catalyst is the chelating nature of the phosphine/carboxylate portions of the ligand, as shown by arrows (Figure 1). It is believed that this ligand chelates to nickel during catalyst formation, and in the presence of a reducing agent such as borohydride, the formation of a ligated nickel hydride is the active species. Ethylene can then react with the Ni-H, form an alkyl group via insertion chemistry, and generate an empty orbital upon insertion. Repeated coordination of ethylene followed by insertion steps affords longer and longer chain alkyls. Eventually, the alkyl group undergoes so-called □-H elimination rather than insertion, and the resulting □-olefin desorbs from the catalyst. This is the traditional view of the catalytic cycle involving olefin oligomerization.

Over the past decade stable carbenes have been shown to function as adequate, or in some cases improved, replacements for phosphines in catalytic applications. We were interested in preparing new ligands based on modifications to these stable carbenes – an important feature would be to attach a arm to the carbene that has an atom that can chelate to the active metal. This would lead to homogeneous catalysts of Ni, Rh, or Pd containing these chelating ligands. We were also interested in potentially attaching these homogeneous ligands to solid supports, and the preparation of a tethered chelating carbene ligand is described.

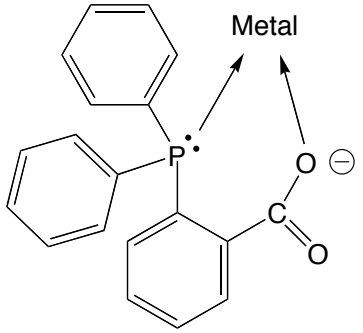


Figure 1. Chelating Nature of SHOP-type Ligand.

Ni-Based Complexes with Carbene Ligands

Introduction

Since the isolation of the first N-heterocyclic carbene (NHC) in 1991, there has been much research into NHC complexes and their applications in catalysis.[1-3] Recently there has been interest in NHCs functionalized with additional donor groups, which can potentially form chelating NHC ligands. NHC ligands have been used in catalysts in place of phosphines and in many cases shown superior catalytic properties, due to their better s-donor abilities, for example in olefin metathesis catalysis.[4] We were interested in preparing chelating nickel complexes of functionalized carbene ligands, which would be analogous to the P–O chelate Ni complexes used as catalysts for the oligomerization of ethylene to α-olefins in the Shell Higher Olefins Process (SHOP).

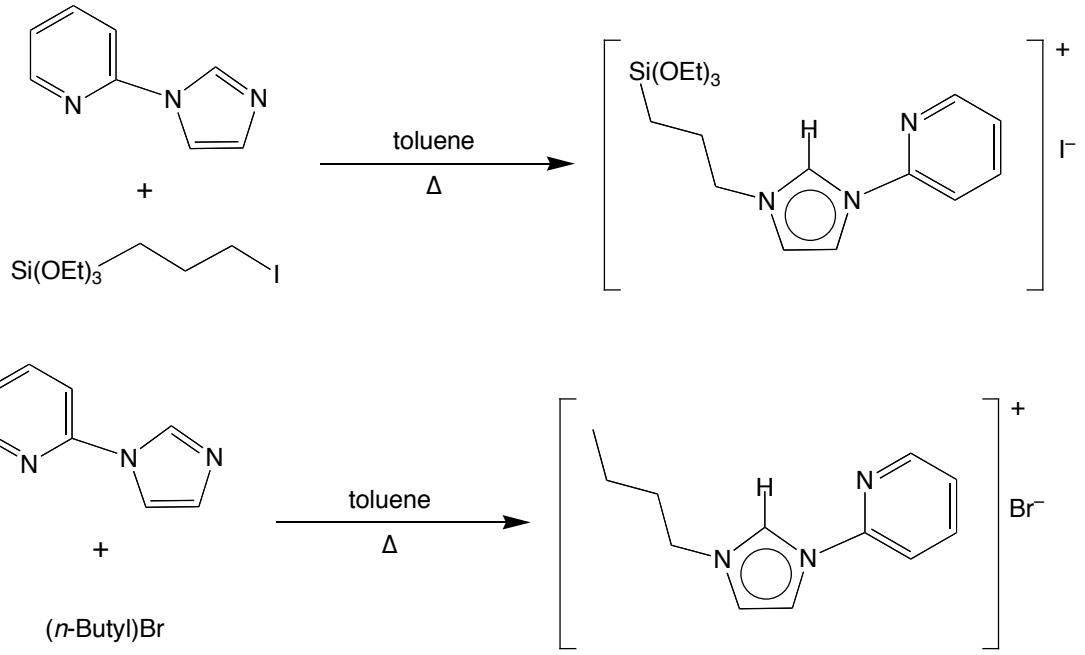
A difficulty in the synthesis of functionalized imidazole based NHC complexes is the formation of the carbene itself. The standard procedure, involving deprotonation of an imidazolium precursor using a strong base, often fails because the additional functional group can possess acidic protons or be otherwise reactive under such conditions. Alternative methods to synthesize functionalized carbene complexes have included (i) formation of an Ag carbene complex, followed by transmetallation, (ii) oxidative addition of imidazolium C–H bonds to a low-valent metal center, and (iii) reaction of an imidazolium salt with a metal complex containing a basic ligand. We have prepared functionalized Ni carbene complexes by method (iii). In this case, the carbene is generated *in situ* through deprotonation by the basic ligand, which is in turn replaced by the carbene. In nickel chemistry, precedence for this type of reaction comes from the work of Cowley *et al.*, in which nickelocene was treated with an imidazolium chloride, leading to displacement of one of the cyclopentadienyl rings and deprotonation of the imidazolium to give a CpNi(carbene)Cl species.[5]

Discussion

Synthesis of Ligands

Imidazolium salts functionalized with N- and O-donors were prepared by known procedures. Pyridine functionalized imidazolium bromides, Im(R, 2-Py), have been synthesized by heating a neat mixture of an N-alkylimidazole and 2-bromopyridine.[6-9] This reaction appears to be quite complex. Others have reported that the reaction also generates dipyridylimidazolium salts[10], and we have seen evidence for the formation of dialkylimidazolium species as well. Nevertheless, reasonable yields of the desired species can be obtained. Cavell has reported syntheses of carbonyl functionalized imidazolium salts by treatment of N-methylimidazole with an α-bromo ester or ketone.[11] These reactions generally proceed readily in THF at room temperature. Using this method, we prepared an analogous imidazolium ketone, derived from N-*n*-butylimidazole, rather than N-methylimidazole, in order to aid solubility of metal complexes.

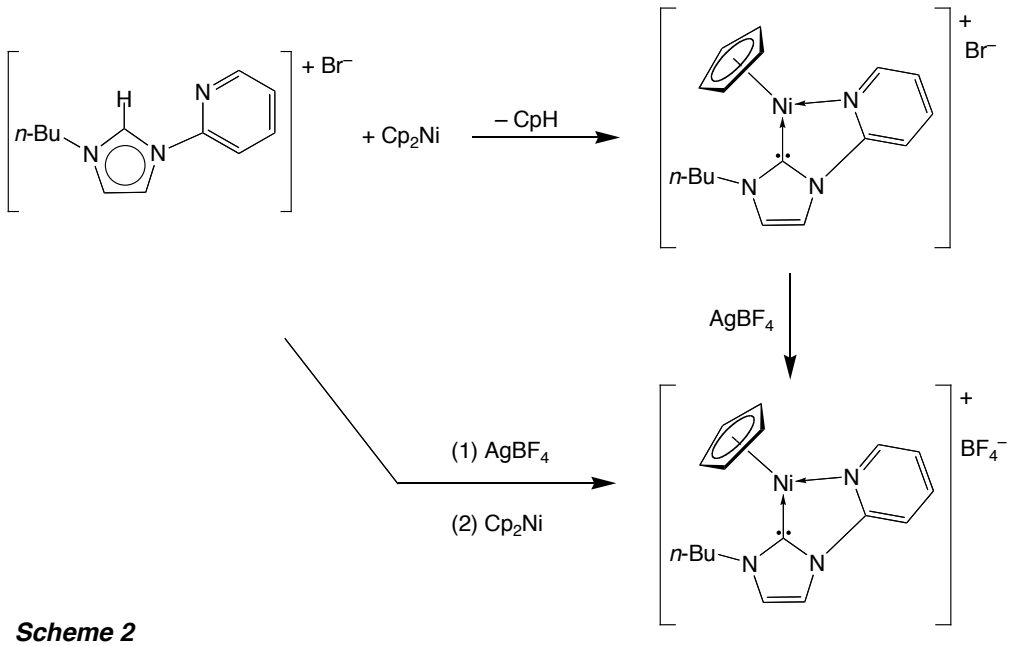
We were also interested in preparing a ligand containing a tether that might allow a carbene complex to be attached to a support such as silica.[12] It was attempted to prepare an imidazolium salt functionalized with pyridine, and 3-propyltriethoxysilane. No reaction was observed, however, between N-(2-pyridyl)imidazole and (3-chloropropyl)triethoxysilane, even in refluxing 1,4-dioxane. It was necessary to convert the chloropropylsilane to the analogous iodo species, by treatment with NaI in refluxing acetone, to allow the functionalized imidazolium $[Im(2\text{-}Py,(CH_2)_3Si(OEt)_3]^+I^-$ to be prepared (Scheme 1). This moiety could potentially be grafted onto silica through reaction of the triethoxysilyl group with Si–OH groups on the silica, with elimination of ethanol and formation of Si–O–Si linkages.



Scheme 1

Synthesis of Nickel Carbene Complexes

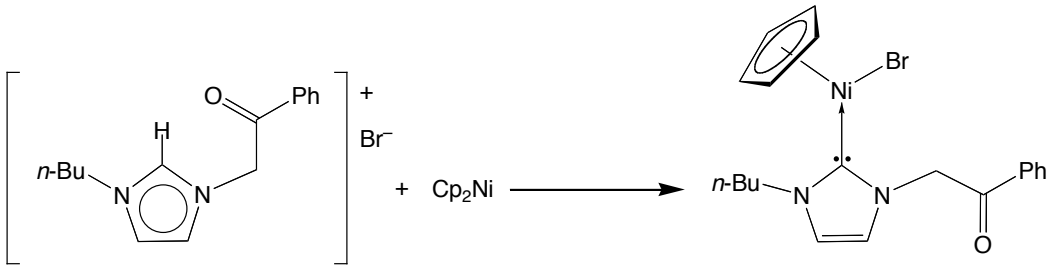
It was first attempted to prepare cyclopentadienyl carbene complexes by treatment of functionalized imidazolium salts with nickelocene, analogous to the previous work[5]. Reaction of Cp_2Ni with the pyridyl functionalized imidazolium bromide, $[Im(Bu,2\text{-}Py)]^+Br^-$, in refluxing THF gave a green compound, which was isolated as its BF_4^- salt by treatment with $AgBF_4$ (Scheme 2). The ^{1}H-NMR spectrum of this species showed a singlet due to a Cp ring and peaks consistent with a pyridyl carbene ligand. In particular, the distinctive peak at ca. □11 in $CDCl_3$ of the imidazolium precursor due to the C2-bound proton is no longer present, suggesting deprotonation had occurred. X-ray crystallography (Figure 2, page 18) confirmed the structure to consist of an 18 electron CpNi(carbene) cation, {CpNi-□^{2}-[Im(Bu, 2-Py)]}$^+$, featuring a bidentate pyridine-carbene ligand. The Ni–C bond length of 1.861(2) Å is somewhat shorter than that in $CpNi[Im(Mes_2)]Cl$ (1.917(9) Å)[5], presumably due to the cationic nickel center and the lack of sterically demanding mesityl groups. There is



Scheme 2

a significant difference between the two structures, however, which is that in the chelating complex described here, the planar carbene group is essentially perpendicular to the Cp ring, whereas in the monodentate carbene complex, the ring is tilted. The structure of the bromide analogue was not determined crystallographically, but in view of the fact that it has a very similar color and ^{1}H-NMR spectrum as the BF_4^- salt, it is believed to exist as a similar salt with an η^2 carbene ligand, rather than a neutral species with the Br coordinated to the metal. The complex $\{CpNi\text{-}\eta^2\text{-}[Im(Bu, 2\text{-}Py)]\}^+BF_4^-$ could also be prepared by first forming the BF_4^- salt of the imidazolium precursor, followed by reaction with nickelocene (Scheme 2).

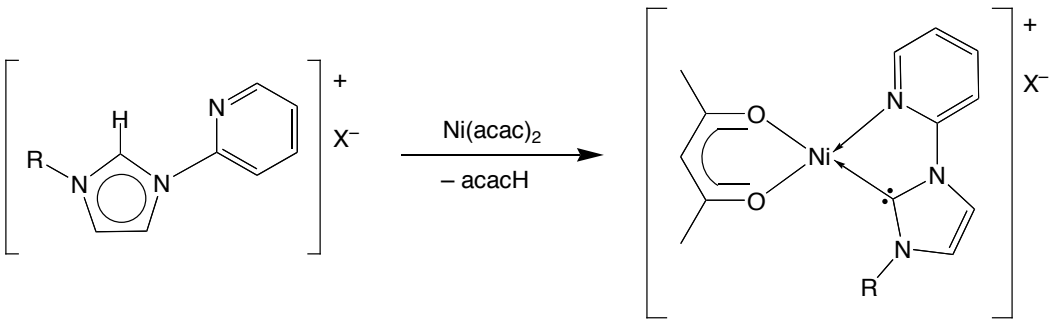
Treatment of Cp_2Ni with the ketone substituted imidazolium, $Im[Bu, CH_2COPh]^+Br^-$, gave a red complex, which was significantly more soluble in organic solvents than the pyridyl analogue (Scheme 3). X-ray crystallography (Figure 3, page 19) revealed the product to be a neutral species, with the Ni coordinated by Cp, monodentate carbene and bromide ligands, CpNi[Im(Bu, CH_2COPh)]Br. Unlike with the pyridyl functionalized ligand, the ketone donor group does not coordinate to the metal. This is demonstrated by a lack of a short Ni•••O separation, as well as by the IR data, which shows little difference in C–O stretching frequency between the imidazolium salt (1687 cm^{-1}) and the carbene complex



Scheme 3

(1699 cm^{-1}). Attempts to abstract the bromide to give a cationic species, using $AgBF_4$ in CH_3CN, gave a green oil with $\nu_{C=O}$ = 1701 cm^{-1}, again suggesting the carbonyl is still not bound to the metal. In the ^1H NMR spectrum of CpNi[Im(Bu, CH_2COPh)]Br, the protons of the CH_2 group a to the carbonyl are inequivalent, appearing as a pair of doublets with a separation by 1.2 ppm. The N-bound CH_2 protons of the *n*-butyl group are also slightly inequivalent. This suggests that, at room temperature, rotation of the carbene ligand around the Ni–C bond is hindered.

The above complexes, containing Cp ligands, are all 18 electron compounds. It was desired to prepare electronically unsaturated carbene complexes, which might be more effective as catalysts. It was attempted to deprotonate imidazolium salts with $Ni(acac)_2$. Catalysts have been previously prepared *in situ* from imidazolium salts and $Ni(acac)_2$[13-16] but apparently products of this reaction have not been isolated. Treatment of the pyridyl substituted imidazolium salt also containing either an *n*-butyl group, or the 3-propyl(triethoxysilane) group gave a yellow species, whose NMR was consistent with a (carbene)Ni(acac) species (Scheme 4). No evidence for the bis(carbene) species derived from protonation of both acac ligands was observed. The ketone functionalized imidazolium salt, Im[Bu, $CH_2COPh]^+Br^-$, did not react with $Ni(acac)_2$, suggesting that coordination of the pyridine is necessary prior to deprotonation to form the carbene complex. The structure of the silane-substituted species was determined by X-ray crystallography (Figure 4, page 19), revealing it to consist of a 16 electron cation featuring chelating carbene and acac ligands, with an iodide counterion. The nickel has a square planar geometry. The Ni–C and Ni–N bond lengths to the pyridylcarbene ligand (1.864(4) Å and 1.923(3) Å respectively) are very similar to those of the Cp substituted analogue. The acac ligand is bound essentially symmetrically to the nickel. This complex appears to be the first example of a structurally characterized transition metal complex containing both an NHC and an acac ligand.[17]



R = *n*-Bu, X = Br;
R = $(CH_2)_3Si(OEt)_3$, X = I

Scheme 4

Experimental

Experimental Details

Reactions were performed under an inert atmosphere of Ar, using Schlenk or drybox techniques, except where otherwise noted. Im(Bu, 2-Py)$^+Br^-H_2O$[8], $(EtO)_3Si(CH_2)_3I$[18], and N-(2-pyridyl)imidazole[19] were synthesized as described previously. NMR spectra were recorded

on Bruker AC250 and Bruker Avance 500 spectrometers. Chemical shifts (□) are reported in ppm relative to TMS (□ = 0) and are referenced relative to the residual protio solvent peak (^{1}H) or a ^{13}C resonance of the solvent. Coupling constants are reported in Hz.

Synthesis of {CpNi[Im(n-Bu, 2-Py)]}$^+$ BF_4^-

0.22 g $AgBF_4$ (1.1 mmol) was added to a solution of 0.32 g Im(n-Bu, 2-Py)$^+Br^-\cdot H_2O$ (1.1 mmol) in CH_2Cl_2 (ca. 10 mL). The resulting white suspension was stirred for 1 h, and then filtered. The solid residue was extracted with additional CH_2Cl_2 (ca. 10 mL). The filtrates were combined and the solvent removed under vacuum to give a brown oil of Im(n-Bu, 2-Py)$^+BF_4^-$. 0.21 g Cp_2Ni (1.1 mmol) and THF (20 mL) were added, and the resulting green suspension heated at 100 °C overnight in a thick-walled glass ampoule fitted with a Teflon stopper. After heating, a light green precipitate had formed, which was isolated by filtration and dried under vacuum, to give 0.18 g green solid. The filtrate was stored in the freezer at –20 °C, affording additional product (0.05 g, total yield 52 %). Crystals suitable for X-ray diffraction studies were obtained by layering diethyl ether onto a CH_2Cl_2 solution. Analysis calcd. for $C_{17}H_{20}N_3BF_4Ni$: C, 49.6 %; H, 4.9 %; N, 10.2 %. Found: C, 49.4 %; H, 4.8 %; N, 10.3 %. NMR data: ^{1}H (acetone-d_6): 0.98 (t, $J_{H–H}$ = 7, 3 H, $NCH_2CH_2CH_2\underline{CH_3}$), 1.45 (sextet, $J_{H–H}$ = 7, 2 H, $NCH_2CH_2\underline{CH_2}CH_3$), 1.87 (quintet, $J_{H–H}$ = 7, 2 H, $NCH_2\underline{CH_2}CH_2CH_3$), 4.11 (t, $J_{H–H}$ = 7, 2 H, $N\underline{CH_2}CH_2CH_2CH_3$), 5.91 (s, 5 H, C_5H_5), 7.30 (t, $J_{H–H}$ = 6, 1 H, C_5H_4N), 7.60 (d, $J_{H–H}$ = 2, 1 H, carbene CH), 8.2 (m, 2 H, C_5H_4N) 8.42 (d, $J_{H–H}$ = 2, 1 H, carbene CH), 8.60 (d, $J_{H–H}$ = 6, 1 H, C_5H_4N). ^{13}C (acetone-d_6): 13.9 ($NCH_2CH_2CH_2\underline{C}H_3$), 20.3 ($NCH_2CH_2\underline{C}H_2CH_3$), 33.4 ($NCH_2\underline{C}H_2CH_2CH_3$), 51.3 ($N\underline{C}H_2CH_2CH_2CH_3$), 94.2 ($C_5H_5$), 113.4, 118.1, 122.6, 125.8, 141.9, 158.8 (carbene CH or C_5H_4N). N–C(pyr) and Ni–C not observed.

Synthesis of [Im(Bu, CH_2COPh)]$^+Br^-$

This compound was prepared in a similar manner to the N-methyl analogue.[11] 4.0□g bromoacetophenone (20 mmol) was dissolved in THF (ca. 15 mL) and 2.6 mL N-*n*-butylimidazole (20 mmol) added via syringe. There was an exothermic reaction and an orange oil separated from the solution. Diethyl ether (ca. 10 mL) was added and the reaction stirred overnight, after which time a white precipitate had formed with a yellow supernatant. The solid was isolated by filtration and washed with diethyl ether until the washings were colorless (3 x ca. 50 mL). Drying under vacuum yielded an off-white solid lump that was broken up in the drybox. Yield: 6.1 g (94 %). Analysis calcd. For $C_{15}H_{19}BrN_2O$: C, 55.7 %; H, 5.9 %; N, 8.7 %. Found: C, 55.9 %; H, 5.7 %; N, 8.7 %. IR (KBr pellet): $\nu_{C=O}$: 1687 cm^{-1}. NMR data: ^{1}H ($CDCl_3$): □0.92 (t, $J_{H–H}$ = 7, 3 H, $NCH_2CH_2CH_2\underline{CH_3}$), 1.34 (sextet, $J_{H–H}$ = 7, 2 H, $NCH_2CH_2\underline{CH_2}CH_3$), 1.85 (quintet, $J_{H–H}$ = 7, 2 H, $NCH_2\underline{CH_2}CH_2CH_3$), 4.21 (t, $J_{H–H}$ = 7, 2 H, $N\underline{CH_2}CH_2CH_2CH_3$), 6.36 (s, 2 H, $N\underline{CH_2}COC_6H_5$), 7.42–7.46 (m, 3 H, $NCH_2COC_6\underline{H_5}$ and $C_3\underline{H_3}N_2$), 7.59 (t, $J_{H–H}$ = 8, 1 H, $NCH_2COC_6\underline{H_5}$), 7.68 (m, 1 H, $C_3\underline{H_3}N_2$), 8.00 (d, $J_{H–H}$ = 8, 2 H, $NCH_2COC_6\underline{H_5}$), 10.06 (s, 1 H, NCHN). ^{13}C ($CDCl_3$): □13.3 ($NCH_2CH_2CH_2\underline{C}H_3$), 19.3 ($NCH_2CH_2\underline{C}H_2CH_3$), 31.9 ($NCH_2\underline{C}H_2CH_2CH_3$), 49.9 ($N\underline{C}H_2CH_2CH_2CH_3$), 55.7 ($N\underline{C}H_2COC_6H_5$), 121.1 ($C_3H_3N_2$), 124.3 ($C_3H_3N_2$), 128.5 ($NCH_2CO\underline{C}_6H_5$), 129.0 ($NCH_2CO\underline{C}_6H_5$), 133.4 (*ipso*-$NCH_2CO\underline{C}_6H_5$), 134.6 ($NCH_2CO\underline{C}_6H_5$), 137.5 (NCHN), 190.6 ($NCH_2\underline{C}OC_6H_5$).

Synthesis of CpNi(Br)[Im(Bu, CH_2COPh)]

THF (20 mL) was added to a mixture of 0.31 g nickelocene (1.64 mmol) and 0.53 g [Im(Bu, CH_2COPh)]$^+Br^-$ (1.64 mmol) in a thick-walled glass ampoule fitted with a Teflon stopper, and the resulting green suspension was heated at 100 °C for 4 days. After this time a red solution had formed, with some dark insoluble residue. The solution was filtered and the volatiles removed from the filtrate under vacuum. The red residue was washed with diethyl ether (ca. 10 mL) and then extracted into a mixture of CH_2Cl_2 (5 mL) and diethyl ether (10 mL), giving a red solution with a brown oily residue. The solution was filtered and the solvent removed under reduced pressure to give a red solid, which was dried under vacuum. Yield: 0.38 g (52 %). Analysis calcd. For $C_{20}H_{23}BrN_2ONi$: C, 53.9 %; H, 5.2 %; N, 6.3 %. Found: C, 54.0 %; H, 5.0 %; N, 6.2 %. IR (KBr pellet): $\nu_{C=O}$: 1699 cm^{-1}. NMR data: ^1H (d_6–acetone): δ 1.02 (t, J_{H-H} = 7, 3 H, $NCH_2CH_2CH_2C\underline{H}_3$), 1.51 (sextet, J_{H-H} = 7, 2 H, $NCH_2CH_2C\underline{H}_2CH_3$), 2.06 (m, obscured by solvent, 2 H, $NCH_2C\underline{H}_2CH_2CH_3$), 4.71 (m, 2 H, $NC\underline{H}_2CH_2CH_2CH_3$), 5.04 (s, 5 H, Cp), 6.00 (d, J_{H-H} = 18, 1 H, $NC\underline{H}_2COC_6H_5$), 7.19 (d, J_{H-H} = 18, 1 H, $NC\underline{H}_2COC_6H_5$), 7.32–7.35 (m, 2 H, $C_3H_2N_2$), 7.65–7.76 (m, 3 H, $NCH_2COC_6\underline{H}_5$), 8.24–8.28 (m, 2 H, $NCH_2COC_6\underline{H}_5$). $^{13}C\{^1H\}$ (d_6–acetone): δ 10.0 (s, $NCH_2CH_2CH_2\underline{C}H_3$), 14.0 (s, $NCH_2CH_2\underline{C}H_2CH_3$), 33.5 (s, $NCH_2\underline{C}H_2CH_2CH_3$), 52.1 (s, $N\underline{C}H_2CH_2CH_2CH_3$), 58.7 (s, $N\underline{C}H_2COC_6H_5$), 91.9 (s, Cp), 123.0 (s, carbene C–H), 125.3 (s carbene C–H), 128.8 (s, $NCH_2CO\underline{C}_6H_5$), 129.9 (s, $NCH_2CO\underline{C}_6H_5$), 134.8 (s, $NCH_2CO\underline{C}_6H_5$), 136.0 (s, $NCH_2CO\underline{C}_6H_5$), 162.7 (s, Ni–C), 194.4 (s. $NCH_2\underline{C}OC_6H_5$).

Synthesis of {Ni(acac)[Im(*n*-Bu, 2-Py)]}$^+Br^-$

This reaction could be performed in air. A solution of 0.54 g $Ni(acac)_2$ (2.1 mmol) and 0.63 g Im(*n*-Bu, 2-Py)$^+Br^-H_2O$ (2.1 mmol) in acetone (ca. 30 mL) was stirred for 5 h, resulting in the formation of a yellow precipitate, which was isolated by filtration, washed with acetone (2 x ca. 10 mL) and dried under vacuum. Yield of yellow solid: 0.48 g (52 %). Analysis calcd. for $C_{17}H_{22}N_3O_2BrNi$: C, 46.5 %; H, 5.1 %; N, 9.6 %. Found: C, 46.7 %; H, 4.8 %; N, 9.6 %. NMR data: ^1H ($CDCl_3$): δ 0.98 (t, J_{H-H} = 7, 3 H, $NCH_2CH_2CH_2C\underline{H}_3$), 1.38 (sextet, J_{H-H} = 7, 2 H, $NCH_2CH_2C\underline{H}_2CH_3$), 1.78 (quintet, J_{H-H} = 7, 2 H, $NCH_2C\underline{H}_2CH_2CH_3$), 2.07 (s, 6 H, acac CH_3), 4.17 (t, J_{H-H} = 7, 2 H, $NC\underline{H}_2CH_2CH_2CH_3$), 5.65 (s, 1 H, acac CH), 7.04 (s, 1 H, $C_3H_2N_2$), 7.32 (m, 1 H, C_5H_4N), 8.18 (t, J_{H-H} = 8, 1 H, C_5H_4N), 8.27 (m, 1H, C_5H_4N), 9.16 (d, J_{H-H} = 8, 1 H, C_5H_4N), 9.51 (s, 1 H, $C_3H_2N_2$). ^{13}C NMR data was not obtained, due to insufficient solubility in all solvents tried.

Synthesis of {Im[2-Py, $(CH_2)_3Si(OEt)_3$]}$^+I^-$

2.3 g $(EtO)_3Si(CH_2)_3I$ (6.9 mmol) was added to a solution of 1.0 g N-(2-pyridyl)imidazole (6.9 mmol) in 30 mL toluene in a thick-walled glass ampoule fitted with a Teflon stopper, and the cloudy tan solution was heated overnight at 120 °C. On returning to room temperature, a dark oil separated out. The supernatant was decanted off, and the oil washed with toluene (10 mL), pentane (2 x 20 mL), and ether (2 x 10 mL), causing a tan solid to form, which was dried under vacuum. Yield: 0.63 g (19 %). NMR data: ^1H (d_6–acetone): δ 0.75 (m, 2 H, $NCH_2CH_2C\underline{H}_2Si$), 1.15 (t, J_{H-H} = 7, 9 H, $OCH_2C\underline{H}_3$), 2.15 (m, 2 H, $NCH_2C\underline{H}_2CH_2Si$), 3.79 (q, J_{H-H} = 7, 6 H, $OC\underline{H}_2CH_3$), 4.70 (t, J_{H-H} = 7, 2 H,

$NC\underline{H}_2CH_2CH_2Si$), 7.65 (m, 1 H, C_5H_4N), 8.16 (m, 1 H, C_5H_4N), 8.32 (s, 1 H, $C_3H_3N_2$), 8.41 (d, $J_{H–H}$ = 8, 1 H, C_5H_4N), 8.61 (m, 2 H, $C_5\underline{H}_4N$ and $C_3\underline{H}_3N_2$), 10.73 (s, 1 H, NCHN). ^{13}C (d_6–acetone): 7.4 (s, $NCH_2CH_2\underline{C}H_2Si$), 18.4 (s, $OCH_2\underline{C}H_3$), 24.7 (s, $NCH_2\underline{C}H_2CH_2Si$), 52.7 (s, $N\underline{C}H_2CH_2CH_2Si$), 58.6 (s, $O\underline{C}H_2CH_3$), 115.2 (s, C_5H_4N), 119.7 (s, C_5H_4N), 124.4 (s, $C_3H_3N_2$), 125.8 (s, C_5H_4N), 135.5 (s, NCHN), 140.9 (s, C_5H_4N), 147.0 (s, Quaternary C_5H_4N), 149.8 (s, $C_3H_3N_2$).

Synthesis of {Ni(acac)[Im(2-Py, $(CH_2)_3Si(OEt)_3$)]}$^+I^-$

0.28 g {Im[2-Py, $(CH_2)_3Si(OEt)_3$]}$^+I^-$ (0.59 mmol) and 0.16 g $Ni(acac)_2$ (0.62 mmol) were dissolved in THF (ca. 10 mL), giving a yellow/green solution. After stirring a few minutes, a yellow precipitate began to appear. The reaction was continued for 4 h, and then the yellow solid was isolated by filtration, washed with THF (ca. 20 mL) and dried under vacuum. Yield: 0.16 g (43 %). Analysis calcd. For $C_{22}H_{34}IN_3O_5NiSi$: C, 41.7 %; H, 5.4 %; N, 6.6 %. Found: C, 42.1 %; H, 5.3 %; N, 6.5 %. NMR data: ^1H ($CDCl_3$): 0.57 (m, 2 H, $NCH_2CH_2C\underline{H}_2Si$), 1.20 (t, $J_{H–H}$ = 7, 9 H, $OCH_2C\underline{H}_3$), 1.87 (m, 2 H, $NCH_2C\underline{H}_2CH_2Si$), 2.05 (s, 6 H, acac), 3.79 (q, $J_{H–H}$ = 7, 6 H, $OC\underline{H}_2CH_3$), 4.17 (t, $J_{H–H}$ = 7, 2 H, $NC\underline{H}_2CH_2CH_2Si$), 5.65 (s, 1 H, acac), 7.14 (s, 1 H, $C_3H_3N_2$), 7.39 (m, 1 H, C_5H_4N), 8.16 (m, 1 H, C_5H_4N), 8.21 (m, 1 H, C_5H_4N), 8.69 (m, 1 H, C_5H_4N), 8.86 (s, 1 H, $C_3H_3N_2$). ^{13}C ($CDCl_3$): 7.4 (s, $NCH_2CH_2\underline{C}H_2Si$), 18.2 (s, $OCH_2\underline{C}H_3$), 25.1 (s, $NCH_2\underline{C}H_2CH_2Si$), 26.0 (s, acac) 50.4 (s, $N\underline{C}H_2CH_2CH_2Si$), 58.5 (s, $O\underline{C}H_2CH_3$), 102.1 (s, acac) 114.0 (s, C_5H_4N), 118.7 (s, C_5H_4N), 122.5 (s, $C_3H_3N_2$), 125.9 (s, C_5H_4N), 143.8 (s, NCHN), 146.3 (s, C_5H_4N), 150.9 (s, Quaternary C_5H_4N), 187.5 (s, Ni–C).

Rh- and Pd-Based Complexes with Carbene Ligands

Discussion

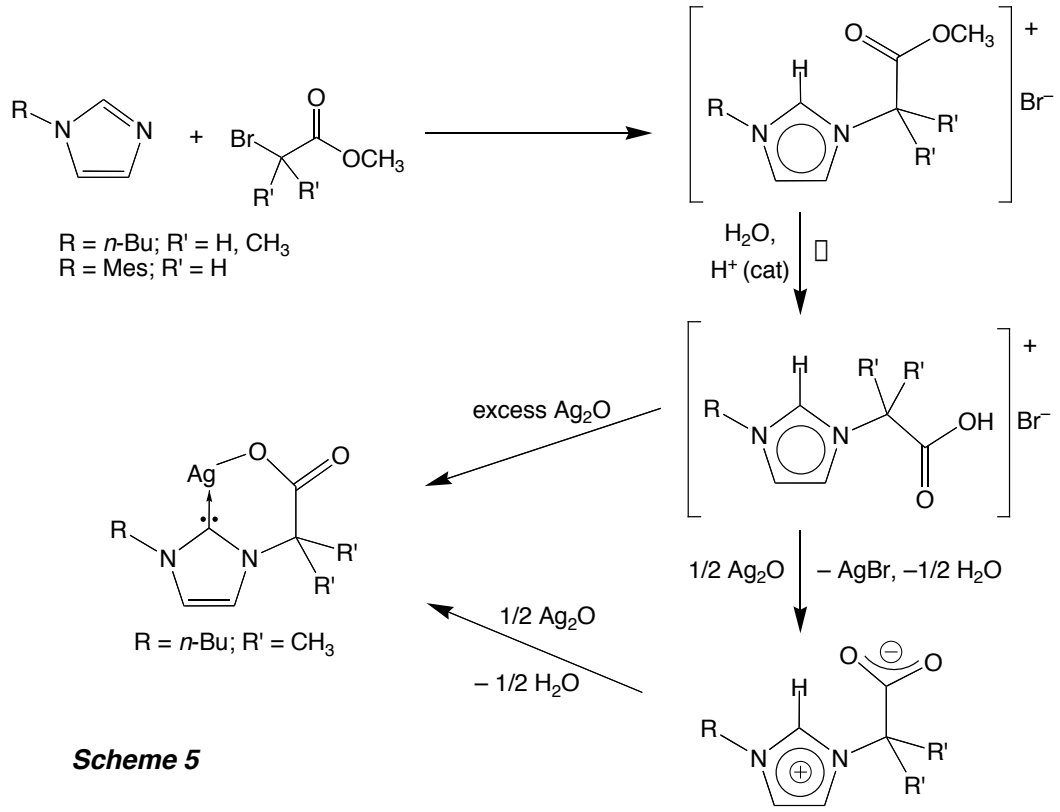
There has been much recent research into the use of N-heterocyclic carbene (NHC) complexes as catalysts, particularly as replacements for catalysts possessing phosphine ligands.[2,20,21] Synthetically, NHC-based catalysts have the advantage that imidazolium carbene precursors can be functionalized relatively easily with additional donor groups, which can potentially form chelating NHC ligands. We were interested in preparing carboxylate functionalized carbene ligands, which would form C–O chelating complexes, as analogs to the phosphine-carboxylate chelate complexes of Ni that are used as catalysts for the oligomerization of ethylene to a-olefins in the Shell Higher Olefins Process (SHOP).[22] There have been many reports of NHCs functionalized with neutral donors such as pyridine; examples of anionic functionalized NHC ligands are less common, but have begun to appear recently. Examples include chelating phenoxide-carbenes[23-26], bis-carbene alkoxides[27,28], and a carbene-enolate.[29]

It was first necessary to synthesize an imidazolium substituted carboxylic acid, which would be a precursor to a functionalized carbene ligand. It has been reported that imidazolyl esters can be hydrolyzed to imidazolyl acetic acid simply by heating in water[30,31], so it was reasoned that analogous cationic imidazolium species might be prepared in a similar manner. Methyl ester functionalized imidazolium salts were synthesized by treatment of an alkyl imidazole with methyl bromoacetate, as has been reported previously[11] (Scheme 5). Hydrolysis led to formation of the corresponding imidazolium carboxylic acid. As with the neutral imidazole-substituted species, the hydrolysis proceeded in refluxing water, but the reaction was quite slow, requiring several days to go to completion. Addition of a catalytic amount of acid increased the rate of reaction.

Having prepared the ligand precursor, it was then attempted to form carbene complexes. A frequently successful method for preparing complexes of functionalized NHCs is by deprotonation of an imidazolium salt with Ag_2O, leading to a silver carbene complex, followed by transmetallation using a halide of another metal.[32] Treatment of a CH_2Cl_2 suspension of the imidazolium carboxylic acids $[Im(R, CH_2CO_2H)]^+Br^-$ with Ag_2O led to the clean formation of new, CH_2Cl_2 soluble species. The ^1H NMR of these products, however, did not suggest a carbene complex had been formed. There was a resonance far downfield of the others (δ ca. 9.5 in $CDCl_3$), indicative of the C2 proton of an imidazolium species. It was believed therefore that the Ag_2O had only removed the carboxylic proton, and eliminated AgBr, to give a zwitterionic imidazolium carboxylate (Scheme 5).

Ohno has recently reported related imidazolium carboxylate zwitterions, synthesized by a slightly different method from imidazolium ethyl esters: In this case the bromide counterion was first ion-exchanged for OH^-, followed by heating to eliminate ethanol, giving a zwitterion.[33] Furthermore, imidazolium zwitterions with carboxylate groups bound to the 2-position (*i.e.* to carbon rather than nitrogen) have been prepared recently, either by treatment of an NHC with CO_2[34], or by the reaction of N-methylimidazole with dimethyl carbonate.[35] It

should also be noted that imidazolyl acetic acids have been in fact shown to exist as zwitterionic imidazolium acetates in solution and the solid state.[36]

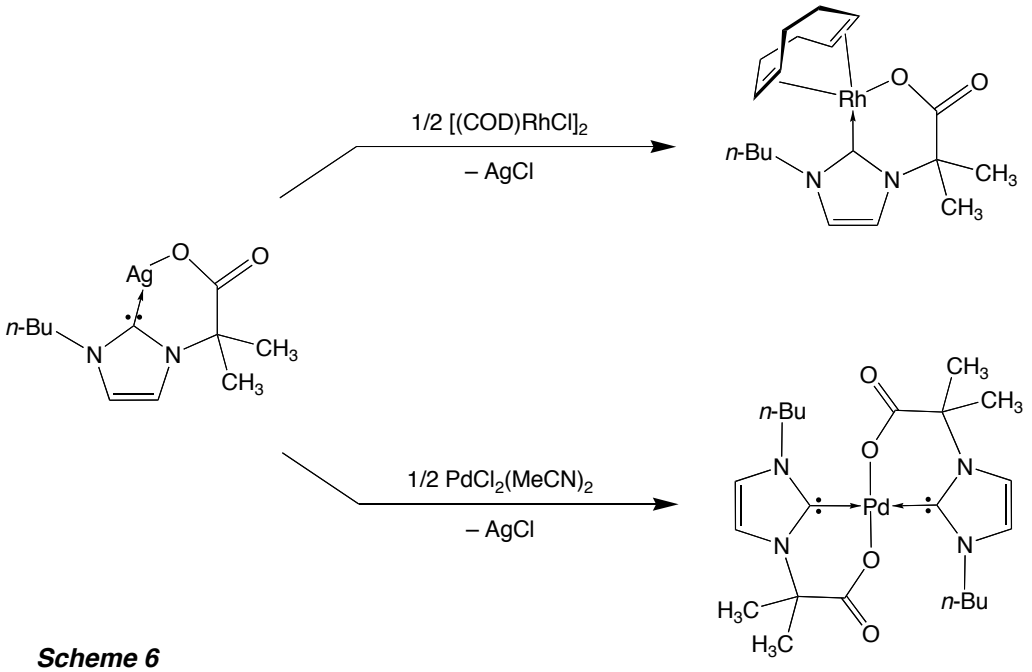


Scheme 5

It was attempted to react the imidazolium zwitterions with additional Ag_2O to form a silver carbene complex. While there did appear to be some reaction, clean products could not be isolated from this reaction. Likewise, attempts to deprotonate the imidazolium group with sterically hindered bases such as *t*-BuOK or $KN(SiMe_3)_2$ followed by reaction with transition metal salts were not successful. A potential problem with the imidazolium acetic acids is the presence of the protons a to the carboxylate group, which would be expected to be acidic, and may be deprotonated in preference to the imidazolium C2 proton, which would lead to complications in trying to synthesize carbenes. It was therefore attempted to synthesize the analogous compound with methyl groups in the position. Such a species has also been reported by Ohno[33]. An imidazolium ester was prepared by treating N-*n*-butylimidazole with methyl -bromoisobutyrate in refluxing CH_3CN. The reaction has been found to work best using 3 eq. of the imidazole. The ester could again be hydrolyzed to give the corresponding carboxylic acid, and a zwitterionic carboxylate could be isolated by reaction of the carboxylic acid with 0.5 eq. of Ag_2O. Treatment of the zwitterion with additional Ag_2O gave an orange complex, believed to be the silver carbene complex. The same species could be prepared directly from the carboxylic acid by treatment with excess Ag_2O (Scheme 5). The silver carbene complex is unstable in solution; solutions rapidly start to deposit silver. Although NMR data could be acquired, the compound could not be purified, nor X-ray quality crystals grown, due to decomposition. So while the complex has been formulated as shown in

Scheme 1, in reality the structure may be more complex. Silver carbene complexes have exhibited a variety of structures.[6,37,38] It has been shown that the complex of the NHC 1,3-dimesitylimidazol-2-ylidene with AgCl crystallizes from CH_2Cl_2 as a monomeric [carbene]AgCl species[39]. Other complexes have been found to exist as $\{[carbene]_2Ag\}^+[AgX_2]^-$ ion pairs, particularly in donor solvents. It is quite possible that the structure of [Im(Bu, CMe_2CO_2)]Ag is fluxional, since the carbene carbon was not observed by ^{13}C-NMR, presumably due to broadening. In a static structure, a doublet should be observed due to coupling to both ^{107}Ag and ^{109}Ag. Broadening of the carbene ^{13}C resonance has been observed previously in Ag NHC complexes and attributed to fluxionality in the structure.[28,40]

Treatment of a solution of the Ag carbene complex in CH_2Cl_2 with a solution of $[(COD)RhCl]_2$ leads to immediate precipitation of AgCl, and allows a bright yellow complex to be isolated (Scheme 6). NMR data reveals the presence of a COD ligand and the carbene ligand, suggesting that Cl has been substituted by the carbene-carboxylate group. Complexes of the type (COD)M[carbene]Cl have been reported previously by a related reaction involving treatment of $[(COD)MCl]_2$ (M = Rh, Ir) with a silver complex of a monodentate carbene.[41] Attempts to form a related Pd complex by reaction of [Im(Bu,CMe_2CO_2)]Ag with 1 eq. $(COD)PdCl_2$ gave a mixture of several compounds by NMR, as did reaction with 1 eq. $PdCl_2(MeCN)_2$. Treatment of $PdCl_2(MeCN)_2$ with 2 eq. of the Ag complex, however, gave a product whose NMR spectrum showed only the set of resonances expected for the carbene ligand. This species is thus presumably the bis(carbene) species $[Im(Bu, CMe_2CO_2)]_2Pd$.



Scheme 6

Experimental

Experimental Details

Reactions were performed under an inert atmosphere of Ar, using Schlenk or drybox techniques, except where otherwise noted. N-Mesitylimidazole was synthesized as described previously.[42,43] NMR spectra were recorded a Bruker Avance 500 spectrometer. ^{13}C NMR peaks were assigned with the aid of HMQC spectra. Coupling constants are reported in Hz.

Synthesis of [Im(Mes, CH_2CO_2H)]$^+Br^-$

The methyl ester of N-mesitylimidazolium acetate was first prepared in a similar manner to that reported for the N-methylimidazolium analogue[11]: 1.3 mL methyl bromoacetate (13.7 mmol) was added via syringe to a solution of 2.34 g N-mesitylimidazole (12.6 mmol) in THF (ca. 30 mL). On stirring, the imidazolium ester began to precipitate. After 2 days there was a thick suspension. The THF was removed under vacuum and the white solid residue washed with diethyl ether (2 x 20 mL) and dried. The solid was then dissolved in deionized water (ca. 30 mL) in a thick-walled glass ampoule fitted with a Teflon stopper, a few drops concentrated HCl (aq) added, and the solution heated at 100 °C for 2 days. After this time, the slightly brown solution was filtered to remove a small amount of insoluble material, and the volatiles removed via rotavap. The off-white solid residue was washed with acetone (2 x ca. 20 mL) and dried under vacuum. Yield: 2.75 g white solid (63 % based on N-mesitylimidazole). IR data (KBr pellet): $\nu_{C=O}$: 1720 cm^{-1}. NMR data: ^{1}H (D_2O): δ 2.05 (s, 6 H, Mes-C<u>H</u>$_3$), 2.32 (s, 3 H, Mes-C<u>H</u>$_3$), 5.24 (s, 2 H, NCH_2CO_2), 7.14 (s, 2 H, Mes-C<u>H</u>), 7.57 (s, 1 H, $C_3H_3N_2$), 7.78 (s, 1 H, $C_3H_3N_2$), 9.01 (s, 1 H, NCHN). ^{13}C (D_2O): δ 16.2 (Mes-<u>C</u>H$_3$), 20.1 (Mes-<u>C</u>H$_3$), 50.3 (N<u>C</u>H$_2$CO$_2$), 123.7 ($C_3H_3N_2$), 124.1 ($C_3H_3N_2$), 129.1 (Mes-<u>C</u>H), 130.6 (Mes quaternary C), 134.5 (Mes quaternary C), 137.8 (NCHN), 141.4 (Mes quaternary C), 169.7 (NCH$_2$<u>C</u>O$_2$).

Synthesis of Im$^+$(Mes, $CH_2CO_2^-$)

CH_2Cl_2 (ca. 30 mL) was added to a mixture of 2.54 g [Im(Mes, CH_2CO_2H)]$^+Br^-$ (7.8 mmol) and 0.90 g Ag_2O (3.9 mmol). After stirring for 1 h, there was a slightly green suspension. The mixture was filtered, and the solid residue extracted with more CH_2Cl_2 (ca. 10 mL). The filtrates were combined, the volatiles removed under vacuum, and the resulting solid washed with pentane (ca. 10 mL) and dried under vacuum. NMR spectroscopy revealed the presence of 0.5 eq. CH_2CH_2; residual amounts of CH_2CH_2 were invariably observed even after extended periods under vacuum. Yield: 2.12 g of white solid (95 % assuming Im$^+$(Mes, $CH_2CO_2^-$)(.0.5 CH_2Cl_2). Analysis calcd. for $C_{14}H_{16}N_2O_2$.0.7CH_2Cl_2: C, 58.1 %; H, 5.8 %; N 9.2 %. Found: C, 58.4 %; H, 5.4 %; N, 8.8 %. IR data (KBr pellet): $\nu_{C=O}$: 1628 cm^{-1}. NMR data: ^{1}H ($CDCl_3$): δ 2.06 (s, 6 H, Mes-C<u>H</u>$_3$), 2.32 (s, 3 H, Mes-C<u>H</u>$_3$), 5.00 (s, 2 H, NCH_2CO_2), 6.97 (s, 2 H, Mes-C<u>H</u>), 7.05 (s, 1 H, $C_3H_3N_2$), 7.73 (s, 1 H, $C_3H_3N_2$), 9.54 (s, 1 H, NCHN). ^{13}C ($CDCl_3$): δ 17.5 (Mes-<u>C</u>H$_3$), 21.0 (Mes-<u>C</u>H$_3$), 53.4 (N<u>C</u>H$_2$CO$_2$), 121.6 ($C_3H_3N_2$), 124.5 ($C_3H_3N_2$), 129.7 (Mes-<u>C</u>H), 131.0 (Mes quaternary C), 134.5 (Mes quaternary C), 138.6 (NCHN), 140.9 (Mes quaternary C), 167.5 (NCH$_2$<u>C</u>O$_2$).

Synthesis of [Im(Bu, CH_2CO_2H)]$^+Br^-$

This compound was prepared in a similar manner to the N-mesityl analogue described above, using 2.9 mL N-*n*-butylimidazole (22.1 mmol) and 2.1 mL methyl bromoacetate (22.2 mmol). After hydrolysis of the ester, 4.90 g of [Im(Bu, CH_2CO_2H)]$^+Br^-$ was isolated as an off-white solid (84 %). Analysis calcd. for $C_9H_{15}N_2O_2Br$: C, 41.1 %; H, 5.7 %; N, 10.6 %. Found: C, 40.5 %; H, 5.9 %; N, 10.4 %. NMR data: ^1H (D_2O): δ 0.93 (t, J_{H-H} = 7, 3 H, $NCH_2CH_2CH_2C\underline{H}_3$), 1.33 (sextet, J_{H-H} = 7, 2 H, $NCH_2CH_2C\underline{H}_2CH_3$), 1.88 (quintet, J_{H-H} = 7, 2 H, $NCH_2\underline{C}H_2CH_2CH_3$), 4.25 (t, J_{H-H} = 7, 2 H, $NC\underline{H}_2CH_2CH_2CH_3$), 5.09 (s, 2 H, NCH_2CO_2), 7.52 (s, 1 H, $C_3H_3N_2$), 7.56 (s, 1 H, $C_3H_3N_2$), 8.86 (s, 1 H, NCHN).

Synthesis of Im^+(Bu, $CH_2CO_2^-$)

A suspension of 0.44 g Ag_2O (1.9 mmol) and 1.02 g [Im(Bu, CH_2CO_2H)]$^+Br^-$ (3.9 mmol) in CH_2Cl_2 (ca. 20 mL) was stirred for 30 mins, after which time the fine grey precipitate was allowed to settle. The solution was filtered and the filtrate concentrated to ca. 10 mL. Storage in the freezer at –20 °C overnight caused a white solid to crystallize, which was isolated by filtration and pumped dry. Yield: 0.54 g (76 %). Analysis calcd. for $C_9H_{14}N_2O_2$: C, 59.3 %; H, 7.7 %; N, 15.4 %. Found: C, 59.2 %; H, 7.2 %; N, 14.7 %. NMR data: ^1H ($CDCl_3$): δ 0.93 (t, J_{H-H} = 7, 3 H, $NCH_2CH_2CH_2C\underline{H}_3$), 1.36 (sextet, J_{H-H} = 7, 2 H, $NCH_2CH_2C\underline{H}_2CH_3$), 1.84 (quintet, J_{H-H} = 7, 2 H, $NCH_2C\underline{H}_2CH_2CH_3$), 4.21 (t, J_{H-H} = 7, 2 H, $NC\underline{H}_2CH_2CH_2CH_3$), 4.71 (s, 2 H, NCH_2CO_2), 7.09 (s, 1 H, $C_3H_3N_2$), 7.33 (s, 1 H, $C_3H_3N_2$), 9.72 (s, 1 H, NCHN). $^{13}C\{^1H\}$ ($CDCl_3$): δ 13.4 (s, $NCH_2CH_2CH_2\underline{C}H_3$), 19.5 (s, $NCH_2CH_2\underline{C}H_2CH_3$), 32.0 (s, $NCH_2\underline{C}H_2CH_2CH_3$), 49.6 (s, $N\underline{C}H_2CH_2CH_2CH_3$), 53.4 (s, $N\underline{C}H_2CO_2$), 119.8 (s, $C_3H_3N_2$), 123.6 (s, $C_3H_3N_2$), 138.2 (s, NCHN), 167.5 (s, $NCH_2\underline{C}OC_6H_5$).

Synthesis of [Im(Bu, CMe_2CO_2H)]$^+Br^-$

Air sensitive conditions were not used. 5.4 mL N-n-butylimidazole (41 mmol) and 1.8 mL methyl bromoisobutyrate (14 mmol) were heated in 20 mL CH_3CN at 110 °C for 3 days. After this time, the solution was concentrated to ca. 15 mL, and 80 mL ether added, causing an orange oil to form. The oil was separated, and redissolved in ca. 10 mL acetone. 80 mL ether was added, again causing an oil to form, which was separated, and the thick, orange oil dried under vacuum. 20 mL deionized water and ca. 0.5 mL concentrated HCl (aq) were added, and the mixture heated at 100 °C. On heating, the oil dissolved to give an orange solution. After heating 2 days, the volatile components were removed, giving a yellow oil. Prolonged drying under vacuum, as well as washing with small amounts of THF, eventually resulted in the formation of a cream-colored solid. Yield: 3.05 g (75 % overall based on methyl bromoisobutyrate). IR data (KBr pellet): $\nu_{C=O}$: 1737 cm^{-1}. NMR data: ^1H (D_2O): δ 0.92 (t, J_{H-H} = 7, 3 H, $NCH_2CH_2CH_2C\underline{H}_3$), 1.32 (sextet, J_{H-H} = 7, 2 H, $NCH_2CH_2C\underline{H}_2CH_3$), 1.87 (quintet, 2 H, $NCH_2C\underline{H}_2CH_2CH_3$), 1.92 (s, 6 H, $NC(C\underline{H}_3)_2$), 4.24 (t, J_{H-H} = 7, 2 H, $NC\underline{H}_2CH_2CH_2CH_3$), 7.57 (s, 1 H, $C_3H_3N_2$), 7.68 (s, 1 H, $C_3H_3N_2$), 9.03 (s, 1 H, NCHN). $^{13}C\{^1H\}$ (D_2O): δ 12.6 (s, $NCH_2CH_2CH_2\underline{C}H_3$), 18.7 (s, $NCH_2CH_2\underline{C}H_2CH_3$), 24.7 (s, $NC(\underline{C}H_3)_2$), 31.1 (s, $NCH_2\underline{C}H_2CH_2CH_3$), 49.2 (s, $N\underline{C}H_2CH_2CH_2CH_3$), 64.4 (s, $N\underline{C}(CH_3)_2$), 121.3 (s, $C_3H_3N_2$), 122.1 (s, $C_3H_3N_2$), 134.9 (s, NCHN), 174.4 (s, $NCH_2\underline{C}OC_6H_5$).

Synthesis of $Im^{+}(Bu, CMe_2CO_2^{-})$

Air sensitive conditions were not used, except that the product was isolated and stored in the drybox. 1.35 g Ag_2O (5.8 mmol) was added to a suspension of 3.38 g $[Im(Bu, CMe_2CO_2H)]^{+}Br^{-}$ (11.6 mmol) in 20 mL CH_2Cl_2. After stirring 1 h, the resulting grey precipitate was allowed to settle. The yellow supernatant was filtered and the solvent removed under vacuum, to give a yellow oil, which was washed with ether (3 x 10 mL), giving a soft white solid, which was dried under vacuum. Yield: 2.1 g (86 %). IR data (KBr pellet): $\nu_{C=O}$: 1627 cm^{-1}. NMR data: ^1H ($CDCl_3$): δ 0.91 (t, J_{H-H} = 7, 3 H, $NCH_2CH_2CH_2C\underline{H}_3$), 1.34 (sextet, J_{H-H} = 7, 2 H, $NCH_2CH_2C\underline{H}_2CH_3$), 1.80 (m, obscured, 2 H, $NCH_2C\underline{H}_2CH_2CH_3$), 1.80 (s, 6 H, $NC(C\underline{H}_3)_2$), 4.30 (t, J_{H-H} = 7, 2 H, $NC\underline{H}_2CH_2CH_2CH_3$), 7.14 (s, 1 H, $C_3H_3N_2$), 7.38 (s, 1 H, $C_3H_3N_2$), 9.61 (s, 1 H, NCHN). $^{13}C\{^1H\}$ ($CDCl_3$): δ 13.4 (s, $NCH_2CH_2CH_2\underline{C}H_3$), 19.4 (s, $NCH_2CH_2\underline{C}H_2CH_3$), 27.1 (s, $NC(\underline{C}H_3)_2$), 32.2 (s, $NCH_2\underline{C}H_2CH_2CH_3$), 49.5 (s, $N\underline{C}H_2CH_2CH_2CH_3$), 67.2 (s, $N\underline{C}(CH_3)_2$), 119.5 (s, $C_3H_3N_2$), 120.8 (s, $C_3H_3N_2$), 136.9 (s, NCHN), 172.5 (s, $NCH_2\underline{C}OC_6H_5$).

Synthesis of $[Im(Bu, CMe_2CO_2)]Ag$

The reaction was performed under air, but the product was worked up under Ar and stored in the drybox. 1.23 g $[Im(Bu, CMe_2CO_2H)]^{+}Br^{-}$ (4.2 mmol) and excess Ag_2O (2.00 g, 8.6 mmol) were stirred in 40 mL CH_2Cl_2 overnight. The resulting black suspension was filtered and the solvent removed from the filtrate under vacuum to give $[Im(Bu, CMe_2CO_2H)]Ag$ as an orange solid. Yield: 1.01 g (76 % based on imidazolium salt). IR data (KBr pellet): $\nu_{C=O}$: 1603 cm-1. NMR data: ^1H ($CDCl_3$): δ 0.92 (t, J_{H-H} = 7, 3 H, $NCH_2CH_2CH_2C\underline{H}_3$), 1.34 (sextet, J_{H-H} = 7, 2 H, $NCH_2CH_2C\underline{H}_2CH_3$), 1.80 (m, obscured, 2 H, NCH2C<u>H</u>2CH2CH3), 1.84 (s, 6 H, $NC(C\underline{H}_3)_2$), 4.09 (t, J_{H-H} = 7, 2 H, $NC\underline{H}_2CH_2CH_2CH_3$), 6.88 (s, 1 H, $C_3H_2N_2$), 7.18 (s, 1 H, $C_3H_2N_2$). $^{13}C\{^1H\}$ ($CDCl_3$): δ 13.7 (s, $NCH_2CH_2CH_2\underline{C}H_3$), 19.8 (s, NCH2CH2<u>C</u>H2CH3), 28.6 (s, $NC(\underline{C}H_3)_2$), 33.4 (s, $NCH_2\underline{C}H_2CH_2CH_3$), 52.6 (s, $N\underline{C}H_2CH_2CH_2CH_3$), 66.0 (s, $N\underline{C}(CH_3)_2$), 118.5 (s, carbene C–H), 118.6 (s, carbene C–H), 177.3 (s, $NCH_2\underline{C}OC_6H_5$), (Ag–C not observed).

Synthesis of (COD)Rh[Im(Bu, CMe_2CO_2)]

A solution of 0.25 g $[(COD)RhCl]_2$ (1.0 mmol Rh) in ca. 3 mL CH_2Cl_2 was added to a solution of 0.33 g $[Im(Bu, CMe_2CO_2)]Ag$ (1.0 mmol) in 20 mL CH_2Cl_2. There was immediate formation of a tan precipitate, which was allowed to settle. The yellow supernatant was filtered and the solvent removed under vacuum. The resulting bubbly solid was washed with ether (ca. 5 mL) and dried under vacuum, yielding 0.36 g of a bright yellow powder (85 %). IR data (KBr pellet): $\nu_{C=O}$: 1616 cm^{-1}. NMR data: ^1H ($CDCl_3$): δ 0.99 (t, J_{H-H} = 8, 3 H, $NCH_2CH_2CH_2C\underline{H}_3$), 1.37 (sextet, J_{H-H} = 8, 2 H, $NCH_2CH_2C\underline{H}_2CH_3$), 1.79 (quintet, J_{H-H} = 8, 2 H, $NCH_2C\underline{H}_2CH_2CH_3$), 1.93 (m, 4 H, COD), 2.27 (s, 6 H, $NC(C\underline{H}_3)_2$), 2.39 (m, 4 H, COD), 3.83 (m, 2 H, COD), 3.91 (t, J_{H-H} = 8, 2 H, $NC\underline{H}_2CH_2CH_2CH_3$), 4.78 (m, 2 H, COD), 6.69 (d, J_{H-H} = 2, 1 H, $C_3H_2N_2$), 6.98 (d, J_{H-H} = 2, 1 H, $C_3H_2N_2$). $^{13}C\{^1H\}$ ($CDCl_3$): δ 13.7 (s, $NCH_2CH_2CH_2\underline{C}H_3$), 20.0 (s, $NCH_2CH_2\underline{C}H_2CH_3$), 28.2 (s, COD), 29.4 (s, $NC(\underline{C}H_3)_2$), 33.0 (s, COD), 34.2 (s, $NCH_2\underline{C}H_2CH_2CH_3$), 50.4 (s, $N\underline{C}H_2CH_2CH_2CH_3$), 64.8 (s, $N\underline{C}(CH_3)_2$),

66.7 (d, J_{Rh-C} = 14), 97.0 (d, J_{Rh-C} = 8), 118.2 (s, carbene C–H), 119.4 (s, carbene C–H), 174.7 (s, $NCH_2\underline{C}OC_6H_5$), ca. 174 (obscured, Rh–C).

Synthesis of [Im(Bu, CMe_2CO_2)]$_2$Pd

A solution of 0.23 g $PdCl_2(MeCN)_2$ (0.89 mmol) in 20 mL CH_2Cl_2 was added to a solution of 0.56 g [Im(Bu, CMe_2CO_2)]Ag (1.77 mmol) in 20 mL CH_2Cl_2. A grey suspension formed immediately. The reaction was stirred for 2 h, and then the grey solid allowed to settle. The pale yellow supernatant was filtered and the solvent removed under vacuum, to give 0.40 g [Im(Bu, CMe_2CO_2)]$_2$Pd as a light yellow solid (86 %). NMR data: ^{1}H ($CDCl_3$): 0.94 (t, J_{H-H} = 7, 6 H, $NCH_2CH_2CH_2C\underline{H}_3$), 1.40 (sextet, J_{H-H} = 7, 4 H, $NCH_2CH_2C\underline{H}_2CH_3$), 1.88 (quintet, J_{H-H} = 7, 4 H, $NCH_2C\underline{H}_2CH_2CH_3$), 2.14 (s, 12 H, $NC(C\underline{H}_3)_2$), 4.26 (t, J_{H-H} = 7, 4 H, $NC\underline{H}_2CH_2CH_2CH_3$), 6.82 (d, J_{H-H} = 2, 2 H, $C_3H_2N_2$), 7.01 (d, J_{H-H} = 2, 2 H, $C_3H_2N_2$). ^{13}C{^{1}H} ($CDCl_3$): 13.8 (s, $NCH_2CH_2CH_2\underline{C}H_3$), 20.0 (s, $NCH_2CH_2\underline{C}H_2CH_3$), 28.7 (s, $NC(\underline{C}H_3)_2$), 34.0 (s, $NCH_2\underline{C}H_2CH_2CH_3$), 49.3 (s, $N\underline{C}H_2CH_2CH_2CH_3$), 64.1 (s, $N\underline{C}(CH_3)_2$), 117.7 (s, carbene C–H), 119.8 (s, carbene C–H), 162.8 (s, Pd–C), 174.8 (s, $NCH_2OC_6H_5$).

X-ray Crystal Structure Thermal Ellipsoid Plots

Figure 2. X-ray structure of {CpNi-η^2-[Im(Bu,2-Py)]}$^+$ BF_4^-

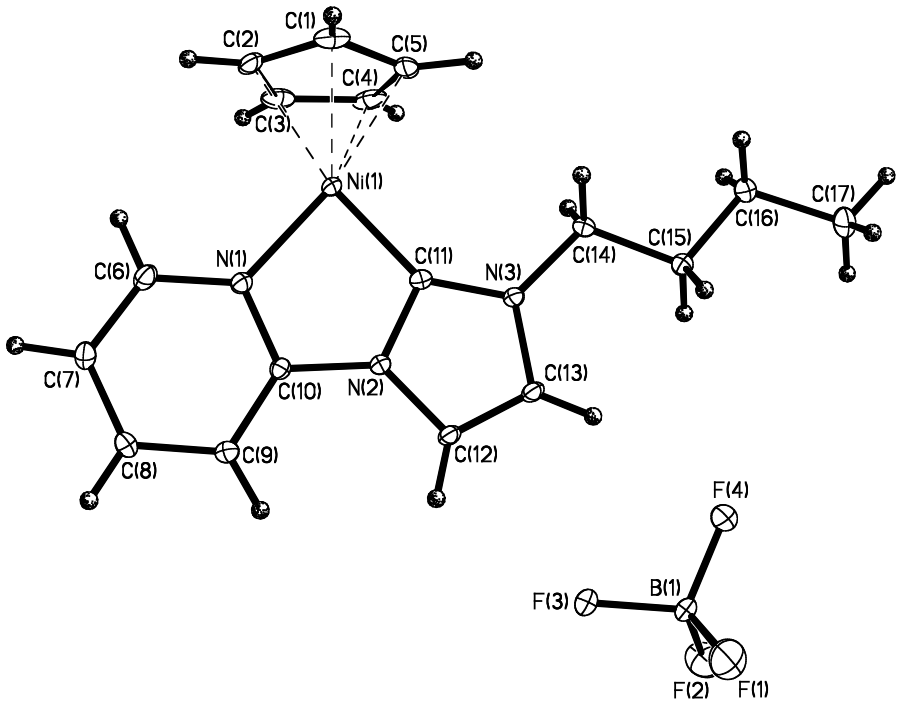


Figure 3. X-ray structure of CpNi[Im(Bu,CH_2COPh)]Br

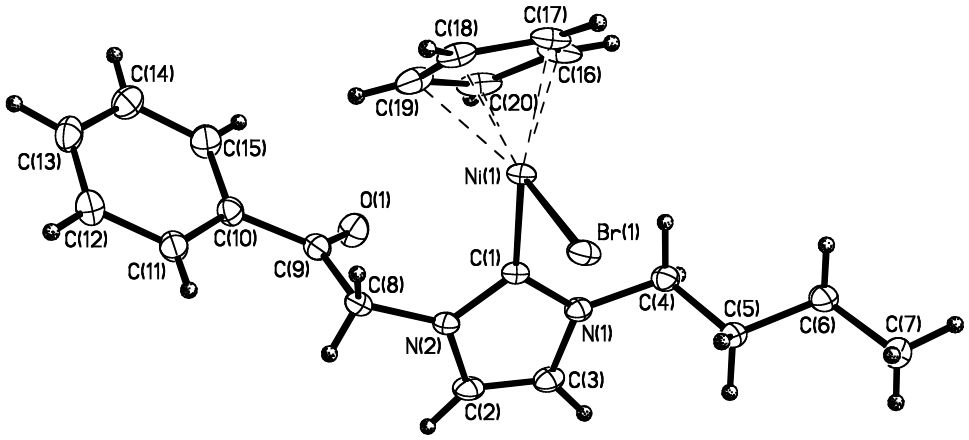
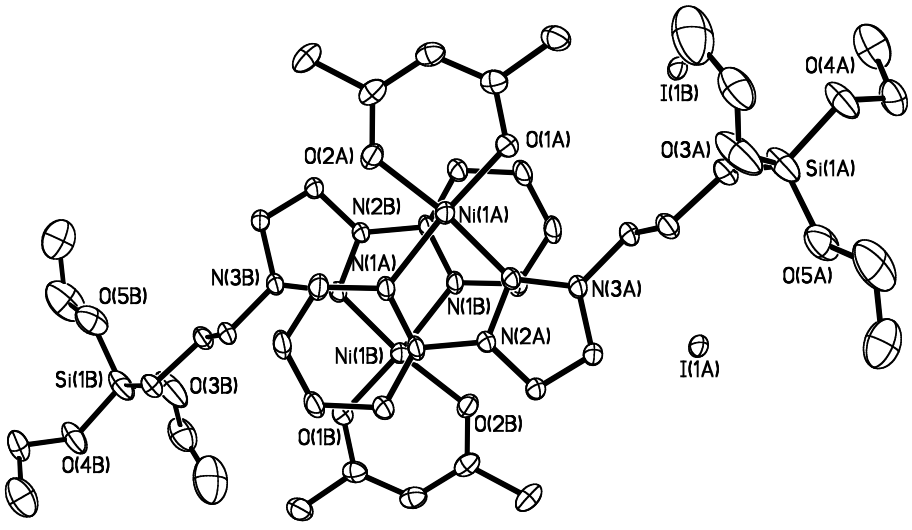


Figure 4. X-ray structure of {Ni(acac)[Im(2-Py,$(CH_2)_3Si(OEt)_3$)]}$^+$ I^-



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