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Notes

Indenylnickel(II) N-Heterocyclic Carbene Complexes: Synthesis via Indene Elimination and Catalytic Activity for Ethylene Dimerization

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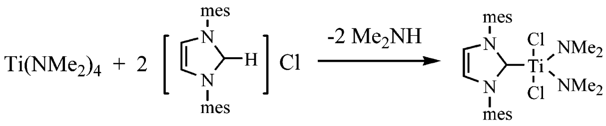
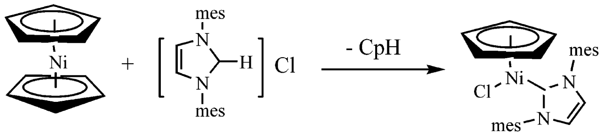
*Summary: The reaction of 1,3-diisopropylimidazolium salt with (Ind)$_2$Ni results in the synthesis of 1,3-diisopropylimidazol-2-ylidene complexes of (Ind)Ni(L)X [Ind = indenyl; L = 1,3-diisopropylimidazole-2-ylidene; X = Cl (**1**), Br (**2**)], which were characterized by elemental analysis, NMR, and X-ray crystal determination. The complexes in combination with MMAO can catalyze the dimerization of ethylene with a high selectivity.*

Introduction

N-Heterocyclic carbenes (NHCs), as alternatives to traditional phosphine ligands, have attracted great attention in organometallic chemistry over the past few years.[1] This is because their metal complexes, particularly palladium- or nickel-based ones, show remarkable catalytic activity and significant thermal stability in a variety of homogeneous reactions.[2] It is obviously that finding available and convenient routes to prepare these complexes is the key point for developing their chemistry. Therefore, the majority of research in this area is focused on the study of synthetic methodology of NHC complexes. To date, several routes to prepare NHC complexes have been explored, including (i) the reaction of transition metal precursors with free NHC in isolation or in situ generation;[3] (ii) transmetalation of the NHC usually from silver(I) and copper(I) complexes;[4] (iii) the reaction of metal precursors with electron-rich olefins;[5] and (iv) C−H activation of imidazolium salts by zerovalent metal.[6] Very recently, salt metathesis and elimination reactions of imidazolium salts are shown to occur for some transition metal complexes, involving amine elimination (eq 1)[7] and cyclopendiene elimination (eq 2).[8] Since the procedure needs no extra step and gives no byproduct, this direct synthesis provides an exciting opportunity for accessing new kinds of NHC complexes with variable co-ligands.



(1)



(2)

mes = 2,4,6-trimethylphenyl

It was noticed that few studies deal with the synthesis of indenyl NHC complexes,[9] although the indenyl ligand has potential for application in organometallic chemistry of transition metals.[10] Until now only one review mentioned briefly the synthesis of NHC complexes of indenylnickel(II) by the reaction of (1-Me-Ind)(PPh$_3$)-Ni−Cl (1-Me-Ind = 1-methylindenyl) with free carbene.[9] Exploring a convenient route for the synthesis of indenyl NHC complexes of transition metals is of interest. Herein we report a direct approach for the synthesis of the NHC complexes of indenylnickel(II) by indene elimination through the reaction of bis-indenyl nickel(II), (Ind)$_2$Ni, with 1,3-diisopropylimidazolium halide, thereby avoiding the isolation and purification of the corresponding N-heterocyclic carbene.

Results and Discussion

The treatment of bis-indenyl nickel(II) complex, (Ind)$_2$Ni, with 1 equiv of 1,3-diisopropylimidazolium chloride in THF/CH$_2$Cl$_2$ solution at 45 °C gives a dark

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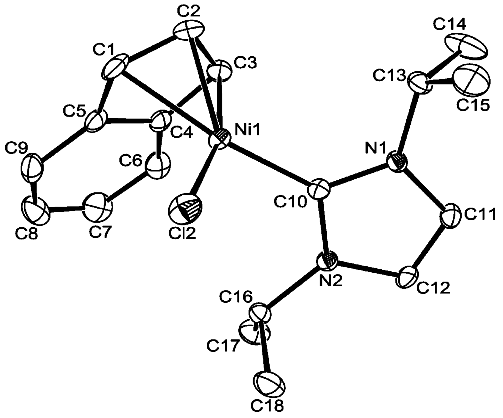
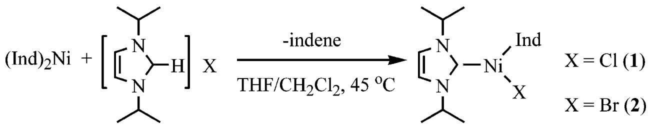


Figure 1. Crystal structure of complex **1**.

Scheme 1



red solution. After workup, the NHC complex (C_9H_7)-NiCl(1,3-diisopropylimidazol-2-ylidene) (**1**) was isolated as dark red crystals in ca. 73% yield (Scheme 1). The proposed structure for **1** was first supported by elemental analysis and NMR spectroscopy. The ^{1}H NMR and ^{13}C NMR data indicated the presence of one indenyl group and one carbene group, respectively. Further characterization of its molecular structure was obtained by X-ray analysis. The results obviously indicated that the indene elimination does occur smoothly to yield the corresponding NHC complex in good yield. To ascertain the versatility of the new synthetic approach, the same reaction with 1,3-diisopropylimidazolium bromide was also tested. The analogue bromide **2** was really isolated as black crystals in ca. 74% yield by a similar procedure (Scheme 1). The result demonstrated undoubtedly that the indene elimination should become a common synthetic route to indene–NHC complexes of late transition metals.

Complexes **1** and **2** are soluble in protic solvents CH_2Cl_2, DME, THF, diethyl ether, and even toluene, but are insoluble in hexane. They are thermally stable and will melt (or decompose) at 147 °C for **1** and at 125 °C for **2**, respectively. It is worth mentioning that both **1** and **2** are much less sensitive to air and moisture as compared to the corresponding triphenylphosphine halides $(Ind)(PPh_3)Ni-Cl$.[11a] The two complexes can even remain unchanged for a few minutes in open air, whereas $(Ind)(PPh_3)Ni-Cl$ will decompose immediately.

Crystals of **1** and **2** suitable for X-ray structure determination are grown from cold toluene solution. The molecular structures of **1** and **2** are analogous, although they crystallize in different space groups (orthorhombic for **1** and monoclinic for **2**). Accordingly, only the molecular structure of **1** was presented herein, as shown in Figure 1. The crystallographic data and selected bond lengths and angles for **1** and **2** are listed in Tables 1 and 2, respectively. The two complexes have monomeric structure. The nickel atom is bonded to the indenyl group in a highly unsymmetric bonding mode. The bond lengths of Ni–C1, Ni–C2, and Ni–C3 are equal to 2.097, 2.041, and 2.026 Å in **1** and 2.107, 2.051, and 2.031 Å in **2**, respectively, which are within normal bonding distance, while the other two carbon atoms of the five-ring of the indenyl group (C4 and C5) are considerably farther away [Ni–C4 = 2.363, Ni–C5 = 2.379 Å for **1** and Ni–C4 = 2.349, Ni–C5 = 2.377 Å for **2**]. Such a highly unsymmetric mode of the indenyl ligand is common in the family of the corresponding triphenylphosphine indenylnickel(II) complexes.[9]

Table 1. X-ray Crystallographic Data for 1 and 2

	1	**2**
empirical formula	$C_{18}H_{23}ClN_2Ni$	$C_{18}H_{23}BrN_2Ni$
fw	361.55	406.00
temperature (K)	193(2)	193(2)
λ(Mo Ka) (Å)	0.71070	0.71070
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	*P*21/*n*
unit cell dimens		
a (Å)	17.281(4)	11.250(2)
b (Å)	10.375(2)	10.887(2)
c (Å)	19.912(4)	14.630(2)
α (deg)	90.00	90.00
β (deg)	90.00	98.458(3)
γ (deg)	90.00	90.00
V (Å^3)	3570.3(13)	1772.5(5)
Z	8	4
D_{calcd} (g cm^{-3})	1.345	1.521
absorp coeff (mm^{-1})	1.234	3.354
F(000)	1520.00	832.00
cryst size (mm)	0.12 × 0.35 × 0.25	0.25 × 0.39 × 0.40
$2\theta_{max}$ (deg)	55.0	55.0
no. of reflns collected	81 066	352
no. of indep reflns	4579 ($R_{int} = 0.074$)	4053 ($R_{int} = 0.034$)
goodness-of-fit on F^2	1.000	1.001
final *R* indices [$I > 2\sigma(I)$]	0.035	0.042
R_w	0.049	0.098

Table 2. Select Bond Lengths (Å), Angles (deg), and Structural Parameters[a] for 1 and 2

param	**1**	**2**
Ni–X	2.2025(7)	2.3160(6)
Ni–C10	1.886(3)	1.888(4)
Ni–C1	2.097(3)	2.107(4)
Ni–C2	2.041(3)	2.051(4)
Ni–C3	2.026(3)	2.031(4)
Ni–C4	2.363(3)	2.349(4)
Ni–C5	2.379(3)	2.377(4)
C1–C2	1.405(4)	1.404(6)
C1–C5	1.449(4)	1.456(5)
C2–C3	1.405(4)	1.421(5)
C3–C4	1.454(4)	1.444(5)
C4–C5	1.424(4)	1.422(6)
C1–Ni–X	98.94(8)	97.9(1)
C1–Ni–C3	66.4(1)	66.7(2)
C3–Ni–C10	97.5(1)	98.8(2)
C10–Ni–X	97.12(8)	96.6(1)
ΔM–C (Å)[a]	0.31	0.30
HA (deg)[b]	12.06	12.33
FA (deg)[c]	9.08	9.52

[a] ΔM–C = 1/2[M–C_{av}(for C4, C5)] – 1/2[M–C_{av}(for C1, C3)]. [b] HA is the angle formed between the planes formed by the atoms C(1), C(2), C(3) and C(1), C(3), C(4), C(5). [c] FA is the angle formed between the planes formed by the atoms C(1), C(2), C(3) and C(4), C(5), C(6), C(7), C(8), C(9).

The Ni–Ind interaction could be quantitatively calculated by the main geometrical parameters such as (a) the slip value represented by ΔM–C {1/2[M–C_{av}(for C4, C5)] – 1/2[M–C_{av}(for C1, C3)]} and (b) hinge and fold angles (HA and FA) representing the bending of the

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indenyl ligand at C1/C3 and C4/C5, respectively.[11] For example, ΔM−C values close to zero indicate little distortion from η^5 hapticity, whereas the values above ca. 0.5 Å indicate nearly η^3 hapticity; HA values of about 14° or greater are associated with nearly trihapto cases.[12] Here, in complex **1**, ΔM−C = 0.31, HA = 12.1°, FA = 9.1°, and in complex **2**, ΔM−C = 0.30, HA = 12.3°, FA = 9.5° (Table 2). The data indicated that the two complexes have almost the same Ni−Ind interaction. These values also led us to propose that the Ni−Ind bonding fashion here can be described as an intermediate hapticity between η^5- and η^3-mode, which is similar to that found in $(ind)_2Ni$ (ΔM−C = 0.42, HA = 13.9°, FA = 13.1°).[9] Such a coordinated fashion can be mainly attributed to the tendency of Ni(II) to avoid forming 18-electron complexes and the unequal *trans* influences of the N-heterocyclic carbene and the halogen groups.[11b]

Thus, the nickel atom is bonded to a halide ligand (X), a carbene carbon (C10), C1, C2, and C3 of the indenyl group, to form either a highly distorted square pyramid with X, C10, C1, and C3 in the basal plane and C2 above it (complex **1**: C1−C2 = C2−C3, Table 2) or a highly distorted square plane with C1 = C2 occupying a single coordination site (complex **2**: C1−C2 < C2−C3, Table 2).

Because there are no structural data for the analogue NHC indenyl complex of Ni(II) reported in the literature, the comparison of their data can only be made with those of the corresponding phosphine complex. As compared with 0.26 (ΔM−C), 10.9° (HA), and 11.7° (FA) reported for $(Ind)(PPh_3)Ni-Cl$,[11a] the larger parameter values (ΔM−C, HA, and FA) for **1** and **2** indicated the presence of a more unsymmetric Ni−Ind interaction in **1** and **2**. This difference in these parameters between the NHC or PPh_3 co-supported indenylnickel(II) complexes should be attributed to the stronger σ-donor strength of 1,3-diisopropylimidazol-2-ylidene than that of PPh_3[13] and a more unequal *trans* influences between 1,3-diisopropylimidazol-2-ylidene and halogen groups. The $Ni-C_{carbene}$ bond distances are almost the same for the two complexes (1.886 Å in **1** and 1.888 Å in **2**), indicating the halogen atom has almost no effect on the $Ni-C_{carbene}$ interaction.

It is worth noticing that the $Ni-C_{carbene}$ bond distance is shorter than that of the Ni−P bond (2.184 Å) in $(Ind)(PPh_3)NiCl$.[11a] Meanwhile, the bond distance of Ni−Cl, 2.203 Å, in **1** is slightly longer than 2.183 Å in $(Ind)(PPh_3)NiCl$.[11a] These results demonstrate that 1,3-diisopropylimidazol-2-ylidene is a much stronger donor ligand than PPh_3, which stabilizes the center metal.

Finally, the catalytic activity of **1** and **2** for ethylene oligomerization was examined. **1** and **2** in combination with MMAO show a modest activity for ethylene oligomerization, respectively. For example, when the ethylene oligomerization was carried out under 1 atm pressure of ethylene at 60 °C with Al/Ni = 1000 (mol ratio), a catalytic activity of 12.9 g $mmol^{-1}$ h^{-1} for **1** and 15.1 g $mmol^{-1}$ h^{-1} for **2**, respectively, was obtained after 60 min (the oligomerization conditions were not optimized). GC/MS analysis of the final reaction solution showed the products to be 1-butene, indicating that β-H elimination from the putative Ni−Bu intermediate is too fast for chain propagation. We suggest that the high selectivity of the two NHC complexes for ethylene dimerization might be due to the facile reductive elimination of the alkyl group from Ni(II) N-heterocylic carbene complexes.[14]

Conclusions

The present work has provided a facile one-step synthetic route to Ni(II)-based indene−carbene complexes via imidazolium salt metathesis and indene elimination. Since a variety of indenyl complexes of transition metals are available, we reasoned that it might be possible to use this direct method for synthesizing Ind−NHC complexes with other transition metals. The research is under way in our laboratory.

Experimental Section

General Considerations. All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl under pure argon prior to use. Indene (Fluka) (dried over 4 Å molecular sieves) was distilled immediately before use. $(Ind)_2Ni$,[15] 1,3-diisopropylimidazolium chloride,[16] and 1,3-diisopropylimidazolium bromide[16] were prepared by published methods. Elemental analysis was performed by direct combustion on a Carlo-Erba EA-1110 instrument. NMR (C_6D_6) spectra were measured on a Unity Inova-400 spectrometer at 25 °C.

Structure Determination. For **1** or **2**, a suitable crystal was mounted in a thin-walled glass capillary for X-ray structural analysis. Diffraction data were collected on a Rigaku Mercury CCD area detector at 193(2) K. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures were solved and refined using SHELXS-97 and SHELXL-97 programs, respectively. Crystal data and collection and main refinement parameters are given in Table 1.

Synthesis of $(C_9H_7)NiCl$(1,3-diisopropylimidazol-2-ylidene) (1). A Schlenk flask was charged with 1,3-diisopropylimidazolium chloride (0.57 g, 3.00 mmol), CH_2Cl_2 (5 mL), and a stir bar. To this solution was added $(Ind)_2Ni$ (0.83 g, 2.87 mmol) in 20 mL of THF via syringe at 0 °C. The solution was stirred overnight at 45 °C, filtered, and evaporated to dryness. The residue was extracted with hot toluene and recrystallized from concentrated toluene at −10 °C, yielding crystals (0.76 g, 73%) suitable for X-ray diffraction studies and elemental analysis. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 166.3 (NCN, s). Anal. Calcd for $C_{18}H_{23}ClN_2Ni$: C, 59.80; H, 6.41; N, 7.75. Found: C, 60.23; H, 6.60; N, 7.99.

Synthesis of $(C_9H_7)NiBr$(1,3-diisopropylimidazol-2-ylidene) (2). Following a procedure similar to the synthesis of **1**, $(Ind)_2Ni$ (0.31 g, 1.07 mmol) in 25 mL of THF was added to a solution of 1,3-diisopropylimidazolium bromide (0.28 g, 1.20 mmol) in $CHCl_2$ (3 mL) at 0 °C. Crystals (0.32 g, 74%) suitable for X-ray diffraction studies and elemental analysis were obtained from concentrated toluene at −10 °C. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 166.8 (NCN, s). Anal. Calcd for

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$C_{18}H_{23}BrN_2Ni$: C, 53.25; H, 5.71; N, 6.90. Found: C, 53.99; H, 6.10; N, 7.08.

Ethylene Dimerization. In a typical run, a flame-dried Schlenk flask was charged with toluene [45 mL, saturated by ethylene (1 atm)] and MMAO (1000 equiv), and a toluene solution (5 mL) of complex **1** (5.5 μmol) was added via syringe under N_2 at 60 °C. After 60 min the ethylene was bled off and the reaction quenched with HCl (6 M) at −20 °C. The toluene phase was analyzed by GC/MS with *n*-heptane (0.8 mL) as an internal standard.

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Supporting Information Available: Crystallographic data, in CIF format, for the structure analyses of **1** and **2**, and a figure of the crystal structure of complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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