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Nickel and palladium complexes of enolate-functionalised N-heterocyclic carbenes

Invited Paper

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Abstract: The reaction of chloroethyltrimethylsilylether with 1-methylimidazole furnishes an ionic liquid that undergoes methanolysis to crystalline 2-hydroxyethylimidazolium chloride (crystal structure presented). Conversion to defined hydroxyethylimidazol-2-ylidene nickel complexes failed, but was accomplished with 1-methyl-3-acetophenyl-imidazolium bromide. The bis(NHC⌒O$^-$) nickel(II) chelate is formed, rather than a methallylnickel monochelate, but with nickelocene a monochelate NiCp complex was detected. The bulky 1-(2,6-diisopropylphenyl)-3-(2'-phenyl-enolato)-imidazol-2-ylidene allylpalladium chloride was obtained in pure form. Attempts to generate catalysts for ethylene oligomerization by *in situ* techniques have failed so far whereas P⌒O$^-$ ligands, comparable by the P-C diagonal relationship, provide active catalysts.

Keywords: *Functionalized imidazolium salt • N-heterocyclic carbenes • Nickel • Palladium complexes*

1. Introduction

Bidentate or polydentate hybrid ligands containing both hard and soft donor groups have found widespread use in coordination chemistry and homogeneous catalysis. Depending on the degree of binding to the metal, they can act either as spectator chelate ligands, stabilizing the catalyst backbone, or as hemilabile ligands, by reversible dissociation allowing uptake of substrate at the free coordination site after ring opening [1]. Examples include nickel catalysts with anionic P,O spectator ligands for the oligo- or polymerization of ethylene [2] or hemilabile rhodium complexes with neutral P,O ligands, successfully applied in asymmetric hydrogenation or hydroformylation [3]. With the development of easily accessible N-heterocyclic carbene ligands [4] and the awareness of the diagonal relationship of low-valent carbon and phosphorus [5], several types of O-donor functionalized N-heterocyclic carbenes NHC [6] have recently been synthesized for use as ligands in transition metal complexes and have been applied in catalysis. Our research interests in the chemistry of P, O [2d,7] and NHC [8] ligands motivated us to also conduct some investigations of C,O hybrid ligands based on NHC [9]. We selected hydroxyethyl- and phenacyl-functionalized NHC and their nickel and palladium complexes and note here some results not previously published by others [6,10,11].

2. Experimental Procedure

All reactions were carried out in carefully dried, freshly distilled solvents. Reactions with air- or moisture-sensitive compounds were conducted under an argon atmosphere using Schlenk techniques. NMR spectra were recorded on a multinuclear FT NMR spectrometer ARX300 (Bruker) at 300.1 (^{1}H), 75.5 (^{13}C), and 121.5

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(^{31}P) MHz. Tetramethylsilane was used as the shift reference for ^{1}H and ^{13}C, and H_3PO_4 (85%) was used as the shift reference for ^{31}P. Coupling constants refer to J_{HH} unless stated otherwise. Melting points (uncorrected) were determined with a Sanyo Gallenkamp melting point apparatus and elemental analyses were performed with a CHNS-932 analyzer from LECO using standard conditions.

2.1. 3-Methyl 1-(2-trimethylsilyloxy)ethyl-imidazolium chloride (1)

An autoclave was charged with *N*-methylimidazole (1.10 g, 13.4 mmol) and 2-chloroethoxy trimethylsilane (2.38 g, 15.6 mmol). It was heated to 150ºC for 24 hours. After cooling the oily viscous liquid was transferred into a beaker and washed with hexane. The insoluble viscous oily liquid was extracted with $CHCl_3$. The solvent was evaporated to give a dark oily liquid, yield 2.1g (53%). ^{1}H NMR ($CDCl_3$): δ = –0.03 (s, 9 H, $SiMe_3$), 3.83, 3.97 (2s br, 5 H, NMe, NCH_2), 4.38 (s br, 2 H, OCH_2), 7.54 (2s br, 2 H, 4-H, 5-H), 10.09 (s vbr, 1 H, H-2) ppm. ^{13}C NMR ($CDCl_3$, sample slowly decomposed forming an oil): δ = –0.94 ($SiMe_3$), 37.16, (NMe), 52.25 (NCH_2), 61.15 (OCH_2), 123.02, 123.19, (CH-4, CH-5), 137.46 (vbr, C-2) ppm. Calculated for $C_9H_{19}ClN_2OSi{\bullet}0.55\,CHCl_3$ (300.46) : C38.18, H 6.56; found: C 38.30, H 6.46.

2.2. 3-(2-Hydroxyethyl)-1-methylimidazolium chloride (2)

N-Methylimidazole (1.10 g, 13.4 mmol) along with 2-chloroethoxy trimethylsilane (2.38 g, 15.6 mmol) was heated as above in an autoclave, washed with hexane and then extracted with methanol. The solvent was evaporated and a dark sticky syrup collected (1.86 g, 81%), out of which large colourless single crystals deposited over a period of several months. NMR data and analysis refer to crystals. ^{1}H NMR (D_2O, ref. dioxane 4.72 ppm): δ = 3.87, 3.89 (s, t, ^{3}J = 5.2 Hz, 5 H, NMe, NCH_2), 4.29 (t, ^{3}J = 5.2 Hz, 2 H, OCH_2), 7.35, 7.55 (AB, ^{3}J = 16-18 Hz, 2 H, 4-H, 5-H) ppm; 2-C*H* exchanged against 2-CD. ^{13}C NMR (D_2O, ref. dioxane 66.3 ppm): δ = 35.44 (NMe), 51.24 (NCH_2), 59.50 (OCH_2), 122.13, 123.29 (CH-4, CH-5), 135.88 (t, $^{1}J_{CD}$ = 34 Hz, CD-2) ppm. Calculated for $C_6H_{11}ClN_2O{\bullet}0.55\,H_2O$ (172.53): C 41.77, H 7.07, N 16.24; found: C 41.47, H 6.82, N 16.00.

2.3. Detection of nickel-bis(3-methyl-imidazol-2-ylidene-1-(2-phenyl-ethen-2-olate)) (5)

$NiBr_2(THF)_2$ (212 mg, 0.58 mmol), KO*t*Bu (294 mg, 2.63 mmol), and compound **3** depicted in Scheme 2 (328 mg, 1.17 mmol) were combined at −78°C in a flask under argon in THF. The reaction mixture was allowed to warm up to room temperature and stirring continued for 16 h. After filtration the solvent was removed in vacuum. The residue was washed several times with diethyl ether and dried in vacuum to yield 160 mg (< 45%) of pale yellow powder (compound **5**), which still contained KBr and a small amount of THF. ^{1}H NMR ($CDCl_3$): δ = 3.10 (s, 3 H, NCH_3), 6.65 (s, 1 H, NCHC-O), 6.81, 6.82 (2 d, ^{3}J = 1.7 Hz, 2 H, 4,5- CH), 7.20-7.36 (m, 3 H, CH_{Ph}), 7.86-7.88 (m, 2 H, CH_{Ph}) ppm. ^{13}C NMR ($CDCl_3$): δ = 36.55 (NCH_3), 98.28 (N-CH=CO), 118.60, 122.37 (4,5-CH), 125.40 (2 *o*-CH), 127.31 (*p*-CH), 127.75 (2 *m*-CH), 138.67 (*i*-C_q), 154.75 (CO) ppm, C-2 at noise level. MS (EI, 70 eV): Calculated for $C_{24}H_{22}N_4NiO_2$ isotopic cluster : (rel. int.%) 458.1 (39) [M^+ for ^{60}Ni], 457.1 (27) [M^+ for ^{58}Ni, ^{13}C], 456.1 (100) [M^+ for ^{58}Ni]; found: *m/e* (rel. int.%) = 458 (12), 457 (9), 456 (30) [M^+ for ^{58}Ni].

2.4. Detection of putative η^5-(cyclopentadienyl) nickel(3-methyl-imidazol-2-ylidene-1-phenylacyl)(triethylamine) bromide (8)

3-Methyl-1-phenacylimidazolium bromide (220 mg, 0.783 mmol) and triethylamine (0.10 mL, 0.799 mmol) were stirred in THF (10 mL) at –78ºC for 30 min. A solution of nickelocene (148 mg, 0.783 mmol) was added, and the mixture was warmed up and refluxed overnight. During the first hour of reflux, the colour of the solution changed from dark green to dark red. After refluxing for 20 h, the mixture was filtered and the solvent removed in vacuum. The viscous semi-solid residue was washed with hexane (10 mL) and dried *in vacuo* to give 109 mg (28%) of a dark reddish brown powder. ^{1}H NMR (CD_3OD): δ = 1.15 (t, ^{3}J = 6.7 Hz, CCH_3), 2.80 (q, ^{3}J = 6.7 Hz, NCH_2), 3.77 (s, 3 H, NCH_3), 5.17 (s, 5 H, C_5H_5), 7.00, 7.11 (s, 2 H, 4-CH, 5-CH), 7.50-7.80 (m, 3 H, *m*-CH, *p*-CH), 7.99 (d, 2 H, *o*-CH) ppm. ^{13}C NMR (CD_3OD): δ = 10.26 (3 CCH_3), 41.01 (NCH_3), 47.26 (3 NCH_2), 92.25 (η^5-C_5H_5), 106.51 ($C_5H_5^-$), 125.79, 126.47 (4-CH, 5-CH), 128.38, 129.78 (2 *m*-CH, 2 *o*-CH), 133.73 (*i*-C), 135.11 (*p*-CH), 164.22 (NCN), 191.78 (C=O) ppm; [$NC(H/D)_2$ in noise]. MS (EI, 70 eV, 360ºC): *m/e* (%) = 256 (0.4) [Ni($\mathbf{3}_{cat.}$)-2H], 242 (0.4), 86 (5), 44 (100). $C_{23}H_{32}BrN_3NiO$ (505.12).

2.5. η^3-Allylpalladium-3-(2,6-diisopropylphenyl)-imidazol-2-ylidene-1-(2-phenyl-ethen-2-olate) (9)

Allyl palladium chloride dimer (141 mg, 0.385 mmol), KO*t*Bu (179 mg, 1.60 mmol), and compound **4** shown in Scheme 3 (329 mg, 0.77 mmol) were transferred to a Schlenk flask under argon. Diethyl ether (10 mL) was added followed by THF (20 mL) and the reaction mixture was stirred at –78ºC for 2 h and at 25ºC for 16 h. Ether

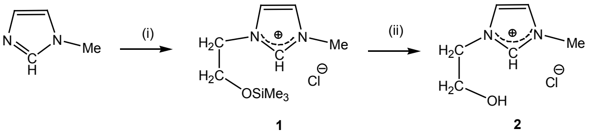
(20 mL) was added, the mixture was filtered, and the solvent was removed in vacuum to yield 344 mg (90%) of a pale yellow powder. ^{1}H NMR ($CDCl_3$): δ = 1.09 (d, ^3J = 7.0 Hz, 3 H, CH_3), 1.10 (d, ^3J = 7.0 Hz, 3 H, CH_3), 1.12 (d, ^3J = 7.0 Hz, 3 H, CH_3), 1.21 (d, ^3J =7.0 Hz, 3 H, CH_3), 1.65 (d, J = 0.9 Hz, 1 H, allyl), 1.68 (m, 1 H, allyl), 2.47 (sept, ^3J = 6.7 Hz, 1 H, CH), 2.71 (sept, ^3J = 6.7 Hz, 1 H, CH), 3.34 (dd, J = 13.2, 0.6 Hz, 1 H, *anti* allyl, *cis* to O), 4.10 (m, $J \approx$ 7.9 Hz, 1 H, *syn* allyl, *cis* to O), 5.11 (m, 1 H, allyl, central), 6.61 (s, 1 H, NCH=CO), 6.93 (d, ^3J = 1.8 Hz, 1 H, dipN-CH=C), 7.21 (d, ^3J = 1.8 Hz, 1 H, dipN-C=CH), 7.22-7.51 (m, 6 H, aryl), 7.23-7.83 (m, 2 H, aryl) ppm. ^{13}C NMR ($CDCl_3$): δ = 23.09, 23.56, 24.68, 25.36 (4 CH_3), 28.06, 28.21 (2 CH), 43.27 (allyl *cis* to carbene),71.56 (allyl *cis* to O), 98.19 (N-C=C-O), 115.58 (central allyl), 119.15, 121.67 (C=C), 123.70, 123.77 (2 m-CH_{dip}), 125.80 (2 o-CH_{Ph}), 127.31 (p-CH_{Ph}), 127.85 (2 m-CH_{Ph}), 129.93 (p-CH_{dip}), 137.52 (i-C_{Ph}), 141.17 (i-C_{dip}), 146.31, 146.35 (2 o-C_{dip}), 154.19 (C=C-O), 172.19 (NCN) ppm. Calculated for $C_{26}H_{31}N_2O$ Pd (493.96): C 63.22, H 6.33, N 5.67; found: C 63.03, H 6.80, N 5.28.

2.6. Crystal Structure Analysis

X-ray diffraction data for compound **2** (Scheme 1) were recorded on an Oxford Diffraction Nova A diffractometer using mirror-focussed CuK_α-radiation. The data were corrected for absorption effects. The structure was refined by full-matrix least-squares methods on F^2 (SHELXL-97) [12]. All non-hydrogen atoms were refined anisotropically. The OH and the carbene H atom were refined freely; other H-atoms were calculated assuming ideal geometries and refined using a riding model or rigid methyl groups. Crystallographic data are given in Table 1 and selected bond lengths and angles in Fig. 1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 760805. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

3. Results and Discussion

There are currently three established methods to synthesise an OH-functionalised NHC: 1) reaction of the imidazole with a halogeno alcohol [10], 2) reaction of an N-substituted imidazole with an epoxide [13], and 3) incorporation of the OH-functional group during the synthesis of the imidazole ring system [14]. We decided to attempt a variation of method 1) by reacting methylimidazole with 2-chloroethoxy-trimethylsilane, generating an imidazolium salt with a pendant silylether sidearm (Scheme 1). The reaction of methylimidazole with 2-chloroethoxy-trimethylsilane was carried out at 150°C for 24 h in an autoclave without added solvent, and produced (2-trimethylsilyloxy)ethyl-3-methylimidazolium chloride, compound **1**, as a viscous oil, which, after washing with hexane, was dissolved in chloroform. Slow evaporation did not yield a solid but an ionic liquid, containing residual $CHCl_3$. The compound was identified by its ^{1}H– and ^{13}C-NMR spectroscopic characteristics, such as the very broad signals for H-2 at δ = 10.09 ppm and C-2 at δ = 137.46 ppm. The silylether group is easily cleaved by polar protic solvents and 1-methylimidazolium-3-(2-ethanol) hydrochloride (compound **2**) from compound **1** by methanolysis. The identity was confirmed by validating the ^{1}H- and ^{13}C-NMR results against the values reported in the literature [10a], and also by an X-ray crystal structure analysis (Fig. 1). The H-2 proton could not be detected directly, which is likely due to the rapid exchange with the deuterium atoms of the solvent. Its presence is observed as a $^1J_{CD}$ coupling constant of 34 Hz towards C2 in the ^{13}C-



Scheme 1. Synthesis of functionalized imidazolium salts. Reagents and conditions: (i) 2-Chloroethoxytrimethylsilane, 150°C, 24 h; (ii) dry MeOH.

Table 1. Crystal data and structure refinement.

Empirical formula	$C_6H_{11}ClN_2O$	
Formula weight	162.62	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 7.3105(6) Å	α= 90°
	b = 6.9927(5) Å	β=111.047(9)°
	c = 8.4642(6) Å	γ = 90°
Volume	403.82(5) Å^3	
Z	2	
Density (calculated)	1.337 Mg m^{-3}	
Absorption coefficient	3.683 mm^{-1}	
F(000)	172	
Crystal size	0.20×0.20×0.05 mm^3	
Theta range for data collection	5.60 to 75.78°	
Index ranges	-9<=h<=9,-8<=k<=8,-10<=l<=10	
Reflections collected	5005	
Independent reflections	1567 [R(int) = 0.0310]	
Completeness to theta = 72.50°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.30607	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1567 / 1 / 100	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0248, wR2 = 0.0639	
R indices (all data)	R1 = 0.0250, wR2 = 0.0642	
Absolute structure parameter	0.013(13)	
Largest diff. peak and hole	0.148 and -0.208 e.Å^{-3}	

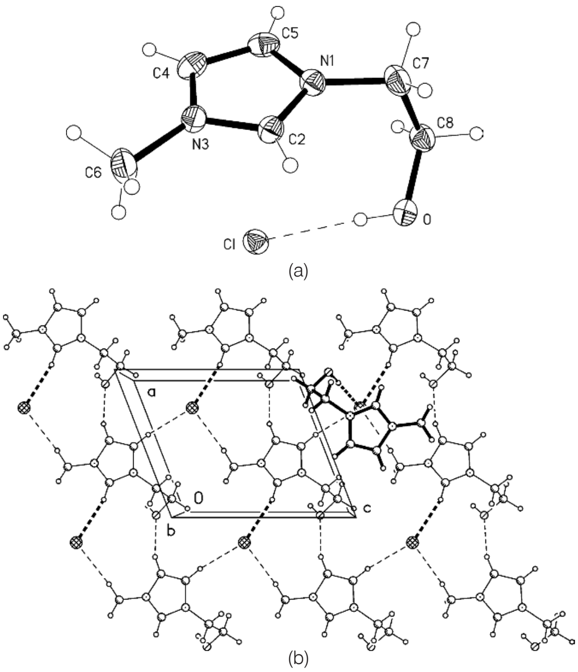
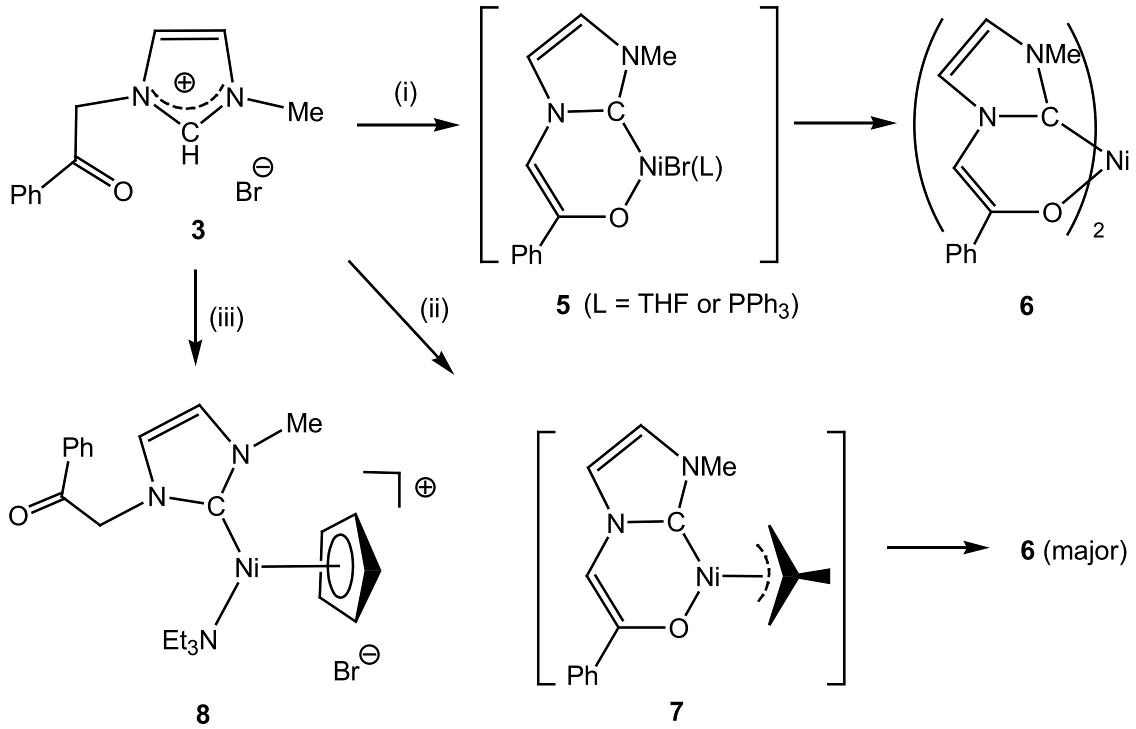


Figure 1. Molecular structure (a) and packing (b) of **2** in the crystal. Selected bond lengths and angles: N1-C2 1.3287(19), N3-C2 1.332(2), N1-C5 1.375(2), N3-C4 1.384(2), C4-C5 1.353(2); N1-C2-N3 108.27(14). The packing diagram shows the layer structure built up from the four "weak" hydrogen bonds; the classical H bond connects to adjacent layers (one cation of which is shown in bold, top right).

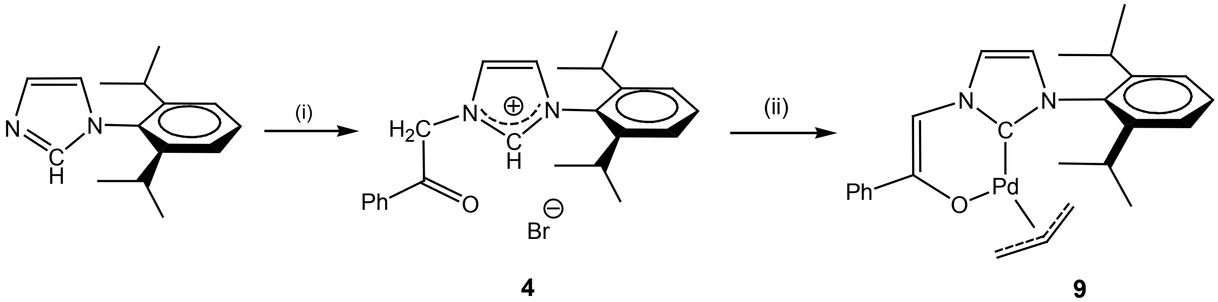
NMR spectrum. In the crystal, monoclinic with space group P2$_1$, the side arm is turned nearly perpendicular (C2-N1-C7-C8 87.8(3), C5-N1-C7-C8 −87.2(3)°) to the ring plane (mean deviation from the best plane 0.003 Å) with the hydroxyl group directed towards the chloride anion below the ring. Besides the O-H···Cl hydrogen bond (O-H 0.85(3), H···Cl 2.20(3), O···Cl 3.0449(14) Å, O-H···Cl 175(2)°) the packing involves four further "weak" hydrogen bonds, three Cl···H-C contacts to H2, H5 and a methyl H-atom of three different imidazolium cations, and one O···H-C contact from H4. The three C-H···Cl contacts connect the residues to form layers parallel to the *xz* plane; the classical H bond connects the layers in the y direction. The observed bond lengths and angles represent typical values.

Both compounds, **1** and **2**, are very hygroscopic, and various amounts of water were detected in the elemental analysis of **2**. Since attempts to obtain a nickel and palladium C,O complex for comparison with our recently reported Ni(II)- and Pd(II)-P,O$^-$-chelate complexes [2d] failed, the known keto-functionalised imidazolium salt 3-methyl-1-phenacylimidazolium bromide **3** [11a] and the bulky 3-(2,6-diisopropylphenyl)-1-phenacylimidazolium bromide **4** [11c] were used instead.

The reaction of the less bulky precursor, compound **3**, with two equivalents of KO*t*Bu as the base and subsequently with Ni(THF)$_2$Br$_2$ or Ni(PPh$_3$)$_2$Br$_2$ did not yield the expected mono-ligated complexes **5** with L = THF or PPh$_3$. Instead, this reaction led to the formation of the doubly substituted nickel(II) complex nickel-bis(3-methyl-imidazol-2-ylidene-1-(2-phenyl-ethen-2-olate), which we denote as compound **6**. The triphenylphosphine generated in the reaction was removed by washing with diethyl ether. This tendency to form symmetric bis(NHC,O) chelate complexes was also observed with the similar 1-(*o*-phenolato-methyl)-imidazol-2-ylidene [15] and o-phosphinophenolate [16] ligands. In addition, the reaction between NiPhCl(PPh$_3$)$_2$ and a bulky 1-(o-phenolato)-imidazol-2-ylidene also did not lead to the formation of a R(Ph$_3$P)Ni(NHC$^\cap$O) monochelate (R = Cl or Ph), even though NiPhCl(PPh$_3$)$_2$ is able to remove the acidic proton by the phenyl anion. Instead, this reaction seems to proceed via a ring opening followed by the insertion of nickel into a 6-membered ring. Only the stable NiMesBr(PPh$_3$)$_2$ allowed access to a Mes(Ph$_3$P)Ni(NHC$^\cap$O) monochelate complex [17]. We then tried the synthesis of a methallylnickel monochelate complex, which succeeded in the case of o-phosphinophenolates [18]. Generation of the carbene enolate with two equivalents of KOtBu as before and subsequent treatment with [Ni(methallyl)Br]$_2$ as an alternative starting material, however, led once again to the bis-ligated nickel carbene complex 6 as the main product (Scheme 2), possibly with the mono-ligated nickel carbene complex 7 among the impurities. Attempts to obtain suitable crystals for an X-ray crystal structure determination failed, leaving us with the difficult task of assigning the structure from spectroscopic evidence alone. Nickel(II) complexes are known for their variable structures, dark green to violet paramagnetic octahedral or tetrahedral complexes, and usually yellow to brown diamagnetic square planar complexes. The square planar bis(chelate) complexes can be either *cis* or *trans* with respect to the carbenes. Of these the *cis*-complexes are usually more stable by the push-pull effect, even in the case of some steric hindrance as shown *e.g.* for the nickel(II) *cis*-bis(chelate) complex with the bulky 6-*tert*-butyl-substituted 1-(2-phenolato-methyl)-imidazol-2-ylidene ligand [15]. Only in the presence of very strong steric hindrance, as in the case of branched dialkylphosphinophenolate ligands, are *trans*-bis(P,O-chelate) Ni complexes preferred [19]. Therefore we assume that the pale yellow diamagnetic nickel(II)-complex 6 is the *cis*-complex. The enolate, NHC chelate coordination follows from typical ^{1}H and particularly ^{13}C NMR data (NCN, C=C-O, δ = 154.6, 154.9 ppm), and the nature of the nickel bis(chelate) is deduced from the molar masses and typical isotopic pattern observed in the mass spectra.



Scheme 2. Synthesis of the nickel enolate NHC complexes. Reagents and conditions: 3 [11a]; (i) $Ni(THF)_2Br_2$ or $NiBr_2(PPh_3)_2$, 2 KOtBu, THF, –78 to 20°C, 16 h; (ii) $[Ni(methallyl)Br]_2$, 2 KOtBu, THF, –78 to 20°C, 16 h; (iii) nickelocene, Et_3N, THF, –78 to 70°C (20 h).



Scheme 3. Synthesis of the allyl Pd enolate NHC complex 9. Reagents and conditions: (i) 2-bromoacetophenone, THF, 25°C, 24 h (cf. [11c]); (ii) 2 KOtBu, $[Pd(allyl)Cl]_2$, Et_2O/THF, –78 to 25°C, 16 h.

From our experience with P,O hybrid ligands we know that reaction with nickelocene in toluene may produce monoligated nickel complexes [16]. Thus, the imidazolium salt **3** was reacted with nickelocene in the presence of NEt_3. Upon heating to reflux, the green color of the solution turned to dark red. A dark reddish brown solid was isolated. The NMR spectroscopic data show that not enolate, but a η^5Cp-Ni-NHC complex was formed. The ^{13}C=O signal (δ = 191.8 ppm) appears in the same region as for compound **3**, but new signals (δ^{13}C = 164.2, 92.3 ppm), characteristic for NCN and η^5-Cp of NHC-NiCp complexes [20,21], are observed. The lack of the NCH_2 signal can be attributed to H→D exchange in the solvent CD_3OD. The roughly equimolar ratio of NHC, Cp and downfield shifted NEt_3 group signals, estimated from proton NMR integration, fits best with the above presented formula **8**. A small amount of bromide is replaced by the cyclopentadienyl anion, indicated by a rather small CH-signal in the ^{13}C NMR spectrum (δ = 106.5 ppm) and known from the reaction of free NHC with nickelocene to $[(NHC)Ni(\eta^5Cp)(\eta^1Cp)]$ [20], whereas hints at η^1-CpNi (expected at δ= 113 ppm) are not observed. The above assignments are justified by spectroscopic data established for the cationic $[(NHC)_2Ni(\eta^5\text{-}Cp)]^+$ Cp^- and neutral $(NHC)Ni(\eta^5\text{-}Cp)(\eta^1\text{-}Cp)$ complexes. Furthermore, X-ray crystallography was also used as a means of characterization [20]. The yield of compound **8** was found to be low (28%), but was not optimized.

Allylpalladium phosphinophenolate complexes [22] proved much more stable than methallylnickel complexes [18]. This suggests that the chances of isolating stable allylpalladium NHC$^\cap$O$^-$ monochelate complexes are much greater than for nickelmethallyl NHC$^\cap$O$^-$ complexes. By reacting the more bulkily substituted phenacyl precursor **4** with two equivalents of KOtBu as base, followed by allyl palladium(II) chloride dimer $[C_3H_5PdCl]_2$, the stable and clean monoligated NHC$^\cap$O$^-$ -chelate complex **9** was obtained in 90% yield (Scheme 3). Compound **9** is structurally similar to the slightly less bulky 3-mesityl analogue [11b] and was identified by ^{1}H- and ^{13}C-NMR spectroscopy and elemental analysis. Characteristic features include a signal for the C-2 carbon at δ = 172.18 ppm in the expected region for a palladium coordinated NHC, and the signature of the enolate CH group at $\delta(^1H)$ = 6.60 ppm and $\delta(^{13}C)$ = 98.19 ppm.

Phenylnickel imidazol-2-ylidene-enolate complexes stabilized by pyridine were shown to catalyze the polymerization of ethylene [11c] without additives with productivites comparable to SHOP-type P$^\cap$O$^-$ nickel catalysts [2] whereas allylnickel complexes stabilized by the more bulky ligand **4** become active only after activation by diethylzinc [11d]. Screening tests to generate active NHC$^\cap$O$^-$ -nickel catalysts *in situ* from **3** or **4**, $Ni(COD)_2$ or $NiBr_2$•2THF and two equivalents of various bases (NaH 20ºC, or KOtBu or nBuLi at –70ºC) in toluene or THF (after 1 h pressurizing with ethylene and heating at 100ºC within 20 min) failed, whereas phosphinoketones in the presence of base and phosphinoacetic acids, phosphinoglycines, or phosphinoglycolates even in the absence of base [2,23] allow easy *in situ* access to active P$^\cap$O$^-$ -nickel catalysts with $Ni(COD)_2$ in a variety of solvents.

4. Conclusions

We have introduced a simple method to synthesise hydroxyalkyl functionalised imidazolium salts. Attempts to use them and the known keto-functionalised imidazolium salts in the synthesis of mono-ligated nickel complexes were successful in the case of nickelocene as the starting material. Nickel(II) halides yielded the bis-ligated nickel(II) complexes as major products. The mono-ligated complex could be obtained using the somewhat less reactive palladium-allyl chloride dimer as the starting material.

The keto-functionalised imidazolium salts are not suitable for *in situ* olefin polymerisation protocols, but catalytic reactions using defined precatalysts, as shown by other groups, are likely to be successful and deserve further experimental investigations.

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