

Communication

Reaction of nickelocene with 1,3-dimesitylimidazolium chloride

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Dedicated to Professor F.A. Cotton on the occasion of his 70th birthday.

Abstract

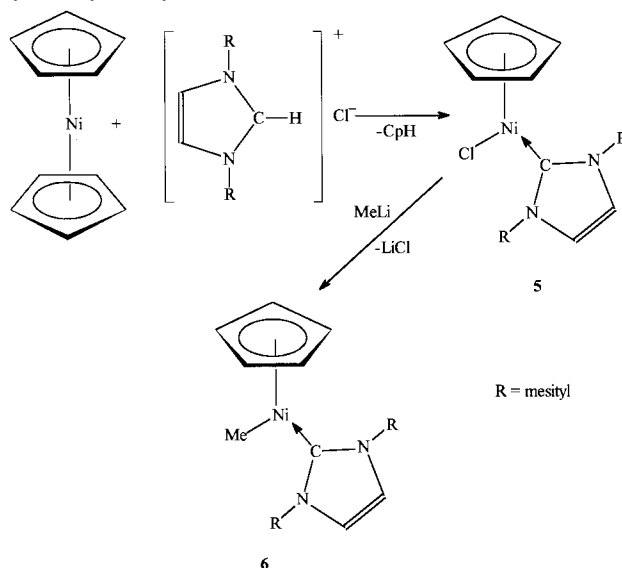
Treatment of nickelocene with 1,3-dimesitylimidazolium chloride affords the corresponding carbene complex,  $(\eta^5\text{-C}_5\text{H}_5)\text{NiCl}(\text{carbene})$  (**5**). The structure of **5** was determined by X-ray crystallography. The distorted trigonal planar nickel atom is attached to an  $\eta^5\text{-Cp}$ , a carbene, and a chloride ligand. Compound **5** reacts with MeLi to afford  $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{Me})(\text{carbene})$ . © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cyclopentadienyl; Nickel; Chlorine; Carbene complex; Imidazolium

Recently, we reported that nickelocene and chromocene will react with stable carbenes [1]. In the case of sterically encumbered carbenes it is possible to isolate 1:1 adducts of the type  $(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_5)\text{M}(\text{carbene})$  (**1**,  $\text{M} = \text{Ni}$ , carbene = 1,3-bis(2,6-dimethyl-4-bromophenyl)imidazol-2-ylidene; **2**,  $\text{M} = \text{Cr}$ , carbene = 1,3-dimesitylimidazol-2-ylidene). While this work was in progress, Tilset and co-workers [2] reported a similar type of compound, namely  $(\eta^5\text{-C}_5\text{H}_5)\text{CrPh}(\text{carbene})$  (**3**). However, their route involved the reaction of chromocene with 1,3-dimesitylimidazolium chloride to form the chloride complex,  $(\text{C}_5\text{H}_5)\text{CrCl}(\text{carbene})$  (**4**), which was treated with  $\text{PhMgCl}$  to produce **3**. Unfortunately, crystals of **4** were unsuitable for X-ray diffraction. We have found that nickelocene undergoes a similar type of reaction with imidazolium chlorides (Scheme 1). Moreover, we have been able to obtain X-ray crystallographic data for the synthetically useful chloride complex  $(\eta^5\text{-C}_5\text{H}_5)\text{NiCl}(1,3\text{-dimesitylimidazol-2-ylidene})$  (**5**).

Initial support for the proposed structure for **5** was derived from  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data, which showed

the presence of one  $\eta^5$ -bonded cyclopentadienyl group and one carbene ligand. Moreover, the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data for **5** are consistent with those anticipated for an 18-electron diamagnetic complex. The presence of a chloride ligand was evident in the mass spectrum of **5** (see below). Further structural insights were gained by X-ray analysis of **5**.



Scheme 1.

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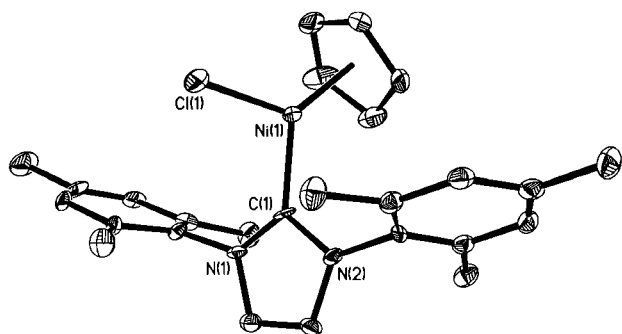


Fig. 1. View of the molecular structure of **5**. Important bond distances (Å) and angles (°): Ni(1)–C(1) 1.917(9), Ni(1)–Cl(1) 2.185(2), Ni(1)–Cp(c) 1.760(7), C(1)–Ni(1)–Cl(1) 98.4(2), C(1)–Ni(1)–Cp(c) 132.4(2), Cl(1)–Ni(1)–Cp(c) 129.2(2).

The X-ray analysis revealed that the crystalline state of **5** consists of two independent molecules in the asymmetric unit. There are no unusually short intermolecular contacts. The molecular structure of **5** features a three-coordinate nickel atom bonded to an  $\eta^5$ -Cp, a carbene, and a chloride ligand (Fig. 1). The geometry at nickel is trigonal planar (sum of bond angles using the Cp ring centroid = 360.0°); however, there are significant departures from the ideal angles (Fig. 1). The Ni–carbene bond distance of 1.917(9) Å is similar to those reported for **1** (1.885(4) Å) [1] and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{carbene})_2]^+$  (1.883(2) Å) [1], but somewhat shorter than that reported for the carbene complex  $(\eta^2\text{-C}_2\text{H}_4)_2\text{NiC}(\text{Ph})\text{NH-}i\text{-Bu}$  (2.008(1) Å) [3]. As in the case of **1**, the carbene mesityl rings are twisted (by 39.0°) in order to minimize steric interactions with the other ligands. Overall, the structure of **5** is very similar to those reported very recently [4] for ruthenium complexes of the type  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}(\text{carbene})$  that were prepared by direct reaction of stable carbenes with  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}]_4$ . Finally, we note that the Ni–Cl bond of **5** is reactive and, for example, treatment with MeLi affords a 55% yield of the methyl derivative  $(\eta^5\text{-C}_5\text{H}_5)\text{NiCH}_3(1,3\text{-dimesitylimidazol-2-ylidene})$  (**6**) (see Scheme 1).

In conclusion, **5** is readily prepared by the reaction of nickelocene with 1,3-dimesitylimidazolium chloride. In turn, **5** promises to be a useful intermediate for the preparation of a wide variety of derivatives by means of metathetical reactions.

## 1. Experimental

### 1.1. General procedures

All reactions were performed under a dry, oxygen-free argon atmosphere utilizing standard Schlenk manifold techniques or a Vacuum Atmospheres drybox. All solvents were dried and distilled under nitrogen imme-

diately prior to use. NMR spectra were recorded on a GE GE-300 spectrometer at 298 K ( $^1\text{H}$ , 300.16 MHz;  $^{13}\text{C}$ , 75.48 MHz), and chemical shifts are reported relative to  $\text{Si}(\text{CH}_3)_4$  ( $\delta = 0.00$ ). High-resolution mass spectra were obtained using a VG Analytical ZABZ-E mass spectrometer operating in the chemical ionization mode with isobutane as the ionizing gas. Melting points were obtained in capillaries sealed under argon (1 atm) and are uncorrected. Elemental analyses were obtained from Atlantic Microlab, Norcross, GA.

### 1.2. $(\eta^5\text{-C}_5\text{H}_5)\text{NiCl}(1,3\text{-dimesitylimidazol-2-ylidene})$

A solution of nickelocene (2.0 g, 10.6 mmol) in tetrahydrofuran (100 ml) was added to 1,3-dimesitylimidazolium chloride [**5**] (3.75 g, 11.0 mmol). The mixture was refluxed for 30 min. During the first 10 min of reflux, the color of the solution changed from dark green to bright red. The solvent was removed under vacuum and the resulting red residue was extracted with hot (100°C) toluene (100 ml). The solution was filtered and reduced in volume to 25 ml. On standing for 12 h at ambient temperature, large red crystals of **5** were formed. These were collected by filtration and washed with pentane (25 ml). The yield was 70%, m.p.: 240°C (dec). Elemental analysis for  $\text{C}_{26}\text{H}_{29}\text{N}_2\text{ClNi}$ : calc. C 67.35%, H 6.3%, N 6.0%, Cl 7.65%; found C 67.33%, H 6.28%, N 5.92%, Cl 7.62%. HRMS (CI<sup>+</sup>): calc. for  $\text{C}_{26}\text{H}_{29}\text{N}_2\text{ClNi}$  462.137274; found 462.137096.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (*o*-CH<sub>3</sub>): 2.21 (s, 12H);  $\delta$  (*p*-CH<sub>3</sub>): 2.48 (s, 6H);  $\delta$  ( $\eta^5\text{-C}_5\text{H}_5$ ): 4.61 (s, 5H);  $\delta$  (NCH): 7.11 (s, 2H);  $\delta$  (*m*-H): 7.16 (s, 4H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (*o*-CH<sub>3</sub>): 18.0 (s);  $\delta$  (*p*-CH<sub>3</sub>): 20.9 (s);  $\delta$  ( $\eta^5\text{-C}_5\text{H}_5$ ): 91.4 (s);  $\delta$  (NCH): 124.0 (s);  $\delta$  (MesC-3,5): 128.6 (s);  $\delta$  (MesC-2,6): 135.2 (s);  $\delta$  (MesC-4): 136.0 (s);  $\delta$  (MesC-1): 138.4;  $\delta$  (NCN): 165.9 (s).

*Crystal data*:  $\text{C}_{26}\text{H}_{29}\text{ClNi}_2\text{N}_2$ ,  $M = 463.67$ , orthorhombic, space group  $Pca2_1$  (No. 29),  $a = 16.8524(14)$ ,  $b = 12.022(8)$ ,  $c = 22.911(2)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 4634.2$  (6) Å<sup>3</sup>,  $D_{\text{calc.}} = 1.329$  g cm<sup>-3</sup>,  $Z = 8$ ,  $\lambda(\text{Mo-K}\alpha) = 0.71073$  Å,  $\mu(\text{Mo-K}\alpha) = 9.67$  cm<sup>-1</sup>. A total of 7226 independent reflections (one octant of data) was collected on a Siemens P4 diffractometer at 178(2) K with  $2\theta$  between 3.4 and 60.0° using the  $\theta$ – $2\theta$  scan mode and a graphite monochromator. The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  to  $R$  and  $wR_2$  values of 0.0493 and 0.1153, respectively.

### 1.3. $(\eta^5\text{-C}_5\text{H}_5)\text{NiCH}_3(1,3\text{-dimesitylimidazol-2-ylidene})$

Methyl lithium (3.1 ml of 1.4 M solution in Et<sub>2</sub>O, 4.34 mmol) was added dropwise to a stirred solution of **5** (2.0 g, 4.31 mmol) in tetrahydrofuran (100 ml) at –78°C. The reaction mixture was allowed to warm slowly to ambient temperature, during which time the

solution changed color from dark red to yellow. The solvent and volatiles were removed under reduced pressure and the resulting yellow residue was extracted with 50 ml of hexane. Lithium chloride was removed by filtration and the filtrate was reduced in volume to 10 ml. After storage for 2 days at  $-30^{\circ}\text{C}$ , a yellow powder formed which was collected by filtration and dried in vacuo.

Yield 55%. m.p.:  $136\text{--}139^{\circ}\text{C}$ . Elemental analysis for  $\text{C}_{27}\text{H}_{32}\text{N}_2\text{Ni}$ : calc. C, 73.16; H, 7.28; N, 6.32; found: C, 72.91; H, 7.36; N, 6.22%. HRMS (CI+): calc. for  $\text{C}_{27}\text{H}_{32}\text{N}_2\text{Ni}$  442.191896; found 442.190943.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  (Ni- $\text{CH}_3$ ):  $-0.62$  (s, 3H);  $\delta$  (*o*- $\text{CH}_3$ ): 2.13 (s, 12H);  $\delta$  (*p*- $\text{CH}_3$ ): 2.21 (s, 6H);  $\delta$  ( $\eta^5\text{-C}_5\text{H}_5$ ): 4.94 (s, 5H);  $\delta$  (NCH): 6.17 (s, 2H);  $\delta$  (*m*-H): 6.83 (s, 4H).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  (*o*- $\text{CH}_3$ ): 18.9 (s);  $\delta$  (*p*- $\text{CH}_3$ ): 20.8;  $\delta$  ( $\eta^5\text{-C}_5\text{H}_5$ ):  $\delta$  90.3 (s);  $\delta$  (NCH): 120.1 (s);  $\delta$  (MesC-3,5): 128.2 (s);  $\delta$  (MesC-2,6) 135.4(s);  $\delta$  (MesC-4); 136.4 (s);  $\delta$  (MesC-1): 138.7 (s);  $\delta$  (NCN): 187.4 (s); Ni- $\text{CH}_3$  not observed.

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