trans-BIS[1,3-BIS(2,4,6-TRIMETHYLPHENYL)IMIDAZOLIDIN-2-YLIDENE]DICHLORONICKEL(II): SYNTHESIS AND STRUCTURE

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Dedicated to Dr Karel Mach on the occasion of his 70th birthday in recognition of his outstanding contributions to organometallic chemistry and homogeneous catalysis.

trans-Bis[1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]dichloronickel(II), [$NiCl_2(SIMes)_2$], was synthesized in a one-pot reaction of fluorenyllithium with nickel(II) bromide followed by the addition of 1,3-bis(2,4,6-trimethylphenyl)imidazolidinium chloride. Labile difluorenylnickel, formed in the course of the reaction, behaves differently than nickelocene and indenocene in analogous reactions. It exchanges both fluorenyl ligands giving the title compound. The crystal and molecular structure of this compound have been determined by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic crystal system with square-planar geometry around the central nickel atom.

Keywords: Nickel; N-heterocyclic carbenes; Carbene complexes; Imidazolium salts; Fluorene; Crystal structure determination; X-ray diffraction.

Although metal carbene complexes have been known for over 40 years, an interest in them has rapidly grown when Arduengo et al.[1] prepared a stable crystalline carbene. N-heterocyclic carbenes (NHC) have found many applications as ligands in the fields of organometallic chemistry and catalysis (for recent reviews, see refs[2–5]). Several papers dealing with stable Ni(0) and Ni(II) complexes with N-heterocyclic carbenes have been published recently[6–11]. Bis(carbene)nickel complexes of Ni(0) as well as of Ni(II) have been also prepared. The first such complex of Ni(0) was obtained by Arduengo et al.[12] in the reaction of an NHC with [$Ni(cod)_2$]. The first bis(carbene) complex of Ni(II) was synthesized by Herrmann et al.[13] in the reaction of an NHC with [NiX_2L_2] (X = Cl, Br; L = PPh_3) in THF solution.

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They determined also the crystal and molecular structure of this complex. Baird et al.[14] used Herrmann's method to prepare bis(carbene) complex [$NiCl_2(IPr)_2$] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene). Syntheses of several other nickel complexes bearing two or three N-heterocyclic carbene ligands have also been reported[15–26]. The most common method of preparation of bis(carbene)nickel(II) complexes is the replacement of weaker donor ligands in [NiX_2L_2] complexes (X = Cl, Br; L = PPh_3, thf, cod, etc.) by a stable N-heterocyclic carbene[13]. Herrmann et al.[13] demonstrated also preparation of bis(1,3-dimethylimidazolidin-2-ylidene)diiodonickel(II) in the reaction of nickel(II) acetate with 1,3-dimethylimidazolium iodide. The deprotonation of the imidazolium salt requires quite drastic conditions (150 °C, vacuum, no solvent).

In this paper we present a convenient method of preparation of bis[1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]dichloronickel(II) in the reaction of difluorenylnickel with 1,3-bis(2,4,6-trimethylphenyl)imidazolidinium chloride. The reaction proceeds at room temperature and shows the unexpected behavior of difluorenylnickel(II).

EXPERIMENTAL

Techniques and Materials

All manipulations were carried out under an atmosphere of purified argon using standard Schlenk techniques. Solvents were dried and distilled under argon employing standard drying agents. Fluorene (Aldrich) was recrystallized from hexane, butyllithium as 2.5 M solution in hexane was purchased from Aldrich. 1,3-Bis(2,4,6-trimethylphenyl)imidazolidinium chloride, $[SIMesH]^+Cl^-$, was prepared according to the literature method[27]. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra (δ, ppm; J, Hz) were recorded on a Mercury-400BB spectrometer in C_6D_6 or THF-d_8 at ambient temperature. Mass spectra (EI, 70 eV) were measured on an AMD-604 mass spectrometer.

Synthesis of Fluorenyllithium [LiFlu]

A solution of butyllithium in hexane (2.7 cm^3, 6.8 mmol) was added at once to a solution of fluorene (1.13 g, 6.8 mmol) in 40 cm^3 of hexane at room temperature. The mixture was stirred for three days. The yellow solid was filtered off, washed four times with 30 cm^3 of hexane and dried under reduced pressure. Yield 1.12 g (6.4 mmol, 96%). ^1H NMR (THF-d_8, 25 °C): 7.79 (d, 2 H, $^3J_{HH}$ = 7.6, H-4,5); 7.18 (d, 2 H, $^3J_{HH}$ = 7.6, H-1,8); 6.67 (t, 2 H, $^3J_{HH}$ = 6.8, H-2,7); 6.29 (t, 2 H, $^3J_{HH}$ = 6.8, H-3,6); 5.81 (s, 1 H, H-9).

Synthesis of *trans*-Bis[1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]dichloronickel(II) (**1**)

A solution of LiFlu in THF (1.2 cm^3, 1.22 mmol) was added at once to a suspension of $[NiBr_2(dme)_2]$ (0.188 g, 0.61 mmol) in THF at –78 °C. The reaction mixture was slowly heated to room temperature. The resulting brown solution was stirred for 30 min and then 1,3-bis(2,4,6-trimethylphenyl)imidazolidinium chloride $[SIMesH]^+Cl^-$ (0.21 g, 0.61 mmol) was added in one portion. The orange reaction mixture was stirred for another 24 h. The solvent was removed under reduced pressure. The crude product was extracted with toluene (3 × 20 cm^3). The extract was concentrated and left standing for crystallization at 0 °C, affording 0.27 g (0.366 mmol, 60%) of **1**. ^1H NMR (C_6D_6, 25 °C): 6.96 (s, 8 H, arom. H); 2.86 (s, 8 H, NCH_2); 2.43 (s, 12 H, *p*-CH_3); 2.26 (s, 24 H, *o*-CH_3). ^{13}C NMR: 19.48, *o*-CH; 21.3, *p*-CH_3; 50.39, NCH_2; 129.76, C-3,5; 136.15, C-2,6; 137.09, C-4; 137.53, C-1; 200.12, NCN. EI-MS, *m/z* (rel.%) (^{58}Ni): 740 (M^+, 8), 341 ($[Cl(NHC) - H]^+$, 91), 305 ($[NHC]^+$, 22), 277 ($[C_{19}H_{21}N_2]^+$, 1), 158 ($[C_{10}H_{10}N_2]^+$, 2), 146 ($[C_9H_{10}N_2]^+$, 5), 119 ($[C_9H_{11}]^+$, 1), 91 ($[C_7H_7]^+$, 1). HRMS: calculated for $C_{42}H_{52}{}^{35}Cl_2N_4{}^{58}Ni$: 740.29225; found: 740.29125. Crystals suitable for X-ray diffraction measurements were grown from a toluene solution at 0 °C.

Reaction of $[Ni(Flu)_2]$ with PPh_3 and CCl_4

Solution of LiFlu in THF (2 cm^3, 0.35 mmol) was added at once to the suspension of $[NiBr_2(dme)_2]$ (0.055 g, 0.178 mmol) in 4 cm^3 THF at room temperature. To a brown solution formed, triphenylphosphine (0.046 g, 0.178 mmol) and CCl_4 (0.1 cm^3, 0.16 g, 1.04 mmol) were added after 5 min. The reaction has been carried out for 1 h and then the solvent was removed under reduced pressure. The solid was washed with hexane (3 × 20 cm^3) and then extracted with toluene. 0.07 g of $[NiCl_2(PPh_3)_2]$ (5.6 mmol, 53%) was obtained. M.p. 245–246 °C (dec.); lit.[28] gives 247–250 °C (dec.). Broad signals appeared in ^1H NMR spectrum owing to paramagnetism of the compound. The spectrum is in good agreement with the literature data[29]. ^1H NMR (C_6D_6, 25 °C): 18.36 (broad s, 2 H, H-2,6); –0.88 (broad s, 2 H, H-3,5); –6.12 (broad s, 1 H, H-4).

Crystal Structure Determination of **1**

Crystal data, data collection and refinement parameters for *trans*-$[NiCl_2(SIMes)_2]$ (**1**) are given in Table I. The molecular structure of this compound is presented in Fig. 1. Selected bond lengths and angles are shown in the figure.

CCDC 639131 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via 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 336033; or deposit@ccdc.cam.ac.uk).

The crystal was mounted onto a glass fiber and then flash-frozen to 100 K (Oxford Cryosystem–Cryostream Cooler). Preliminary examination and intensity data collection were carried out on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromatized MoKα radiation. The data were corrected for Lorentz, polarization and absorption effects. Data reduction and analysis were carried out with the Kuma diffraction (Wrocław, Poland) programs[30]. The structures were solved by direct methods and refined by the full-matrix least-squares method on all F^2 data using the SHELXTL program[31]. The carbon-bonded hydrogen atoms were included in the calculated positions and refined using a riding model.

TABLE I
Crystal data and structure refinement for *trans*-[$NiCl_2(SIMes)_2$] (**1**)

Empirical formula	$C_{42}H_{52}Cl_2N_4Ni\ C_6H_5CH_3$
Crystal size, mm	0.23 × 0.10 × 0.04
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
Unit cell dimensions:	
a, Å	10.612(5)
b, Å	16.201(5)
c, Å	26.710(5)
β, °	99.30(1)
V, $Å^3$	4532(3)
Z	4
M, g mol^{-1}	834.62
D_{calc}, g cm^{-3}	1.223
Temperature, K	100(2)
Absorption coefficient, mm^{-1}	0.583
$F(000)$	1776
Radiation	MoKα (λ = 0.71073 Å, graphite monochromator)
θ range, °	2.64–25.00
Scan type	ω
Absorption correction:	
T_{min}, T_{max}	0.851, 0.953
Index ranges	$-7 \le h \le 12$; $-19 \le k \le 19$; $-31 \le l \le 31$
Reflections collected	26279
Unique data	7971, $R_{int} = 0.0660$
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	4524/0/518
GOF[a] on F^2	0.811
Final R indices [$I > 2\sigma(I)$][b]	$R_1 = 0.0397$
	$wR_2 = 0.0701$
R indices (all data)	$R_1 = 0.0844$
	$wR_2 = 0.0747$
Largest diff. peak and hole, e $Å^{-3}$	0.354/–0.279
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2]$, where $P = [2F_c^2 + \max(F_o^2,0)]/3$

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[a] GOF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

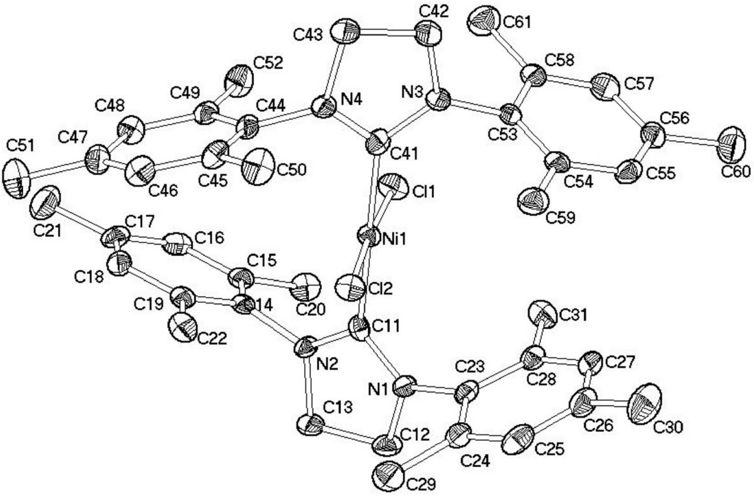


FIG. 1

ORTEP drawing of the molecular structure of *trans*-[$NiCl_2(SIMes)_2$] (**1**) with the atom numbering scheme. Hydrogen atoms and toluene molecule have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (in Å) and angles (in °): Ni1–Cl1 2.180(1), Ni1–Cl2 2.191(1), Ni1–C11 1.910(3), Ni1–C41 1.920(3), N1–C11 1.348(3), N1–C12 1.486(3), N1–C23 1.440(3), N2–C11 1.348(3), N2–C13 1.478(3), N2–C14 1.437(3), N3–C41 1.343(3), N3–C42 1.484(3), N3–C53 1.442(3), N4–C41 1.357(3), N4–C43 1.484(3), N4–C44 1.436(3), C12–C13 1.515(3), C42–C43 1.525(3); C11–Ni1–C41 179.13(11), Cl1–Ni1–Cl2 177.21(3), C11–Ni1–Cl1 88.42(8), C41–Ni1–Cl1 91.04(8), C11–Ni1–Cl2 90.50(8), C41–Ni1–Cl2 90.06(8), N1–C11–Ni1 126.82(18), N2–C11–Ni1 126.18(19), N3–C41–Ni1 127.70(19), N4–C41–Ni1 125.11(19), C11–N1–C23 125.8(2), C11–N2–C14 128.3(2), C11–N1–C12 112.8(2), C11–N2–C13 112.9(2), C41–N3–C53 127.4(2), C41–N4–C44 125.6(2), C41–N3–C42 113.3(2), C41–N4–C43 112.8(2), N2–C11–N1 107.0(2), N3–C41–N4 107.2(2)

RESULTS AND DISCUSSION

1,2-Dimethoxyethane complex of nickel(II) bromide, [$NiBr_2(dme)_2$], reacts with fluorenyllithium in THF forming labile [$Ni(Flu)_2$]. A one-pot reaction of [$Ni(Flu)_2$] with 1,3-bis(2,4,6-trimethylphenyl)imidazolidinium chloride at room temperature affords dark orange crystals of **1** in 60% yield (Eq. (*1*)).

$$\begin{tikzcd} {[\mathrm{NiBr_2(dme)}] + 2\,\mathrm{LiFlu}} \arrow[r, "\mathrm{THF}"] & {[\mathrm{Ni(Flu)_2}] + 2\,\mathrm{LiBr}} \arrow[d, "\mathrm{THF}"', "{[\mathrm{SIMesH}]^+\mathrm{Cl}^-}"] \\ & {\mathrm{NiCl_2(SIMes)_2} + 2\,\mathrm{FluH}} \\ & \mathbf{1} \end{tikzcd} \tag{1}$$

The molecular structure of difluorenylnickel(II) has not been determined so far, but our current studies indicate that the two fluorenyl ligands are bonded η^5-Flu and η^1-Flu, forming 16VE complex [(η^5-Flu)Ni(η^1-Flu)] (Fig. 2). We presume that lability of difluorenylnickel is caused by high stability of fluorenyl anion or radical.

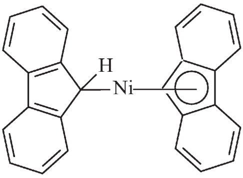
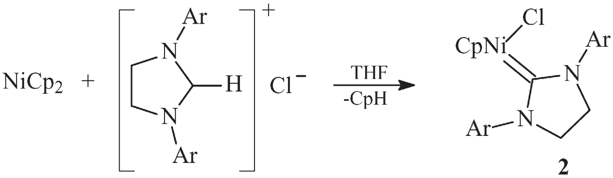


FIG. 2
Presumed bonding mode in difluorenylnickel(II)

The proposed course of the reaction is depicted in Scheme 1. An attack of the chloride anion on the nickel atom of difluorenylnickel(II) leads to the formation of a Ni–Cl bond with simultaneous dissociation of the fluorenyl anion. This anion reacts with imidazolidinium cation to form fluorene and the stable carbene. The carbene forms a complex with fluorenylnickel chloride. A rearrangement of the fluorenyl ligand η^5-fluorenyl → η^1-fluorenyl is followed by the reaction with the second molecule of 1,3-bis(2,4,6-trimethylphenyl)imidazolidinium chloride leading to the formation of **1** and fluorene.

In contrary to difluorenylnickel(II), nickelocene and nickel indenocene react differently with imidazolium salt. The reaction stops after substitution of one cyclopentadienyl or indenyl group[32] (Eq. (*2*)) forming complex **2**.

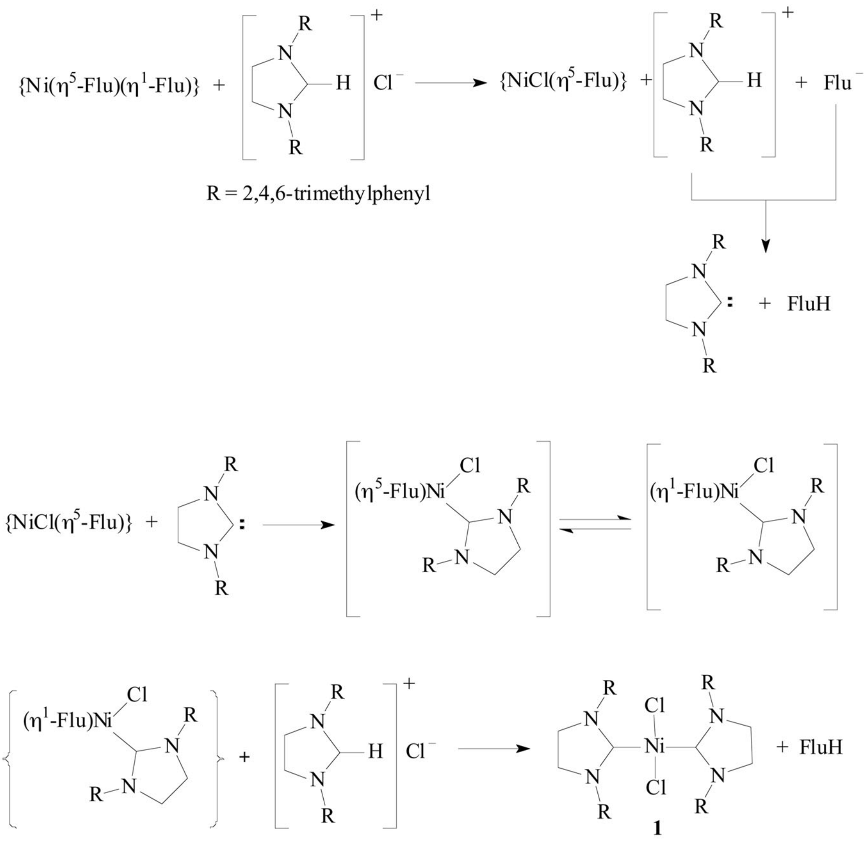


2

(*2*)

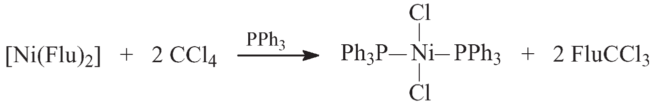
Ar = 2,4,6-trimethylphenyl, 2,6-diisopropylphenyl

The second cyclopentadienyl or indenyl groups are not substituted owing to high stability of their η^5 bonds with nickel atom; therefore $\eta^5 \rightarrow \eta^1$ rearrangement, shown in Scheme 1, is not possible, which prevents further reactions.



SCHEME 1

The same differences in behavior of fluorenyl and cyclopentadienyl ligands were observed in the reactions of difluorenylnickel(II) and nickelocene with CCl_4 and triphenylphosphine. In the case of difluorenylnickel(II), both the fluorenyl ligands are substituted and the known complex $[NiCl_2(PPh_3)_2]$ is formed (Eq. (*3*)).

 (*3*)

$$[Ni(Flu)_2] + 2\,CCl_4 \xrightarrow{PPh_3} Ph_3P{-}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{Ni}}{-}PPh_3 + 2\,FluCCl_3 \tag{3}$$

Nickelocene, on the other hand, exchanges only one cyclopentadienyl ligand forming $[NiCl(\eta^5\text{-}Cp)(PPh_3)]$ [33].

Crystals of **1** suitable for X-ray diffraction structure determination were obtained by slow crystallization from a toluene solution at 0 °C. One molecule of toluene per one molecule of **1** was included in the crystal and it was successfully refined. The compound crystallizes in the monoclinic crystal system with square-planar coordination sphere of the central nickel atom. The carbene ligands are situated trans to each other and at angles close to 90° to the chloride ligands which is a common feature of bis(imidazolin-2-ylidene)metal complexes[13,14,24]. Carbene–nickel bond lengths in **1** (1.910(3) and 1.920(3) Å) are very close to those exhibited by *trans*-[$NiCl_2$(1,3-dicyclohexylimidazolidin-2-ylidene)$_2$] [13] and by *trans*-[$NiCl_2$(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene)$_2$] [14,24]. On the other hand, carbene–nickel distances in **1** are about 0.05 Å longer than those exhibited by other nickel(II) complexes with imidazolidin-2-ylidenes, reported by Sellmann et al.[34,35]. These observations indicate that C–C saturation has not a substantial influence on carbene σ donor abilities. Shorter Ni–C distances reported in refs[34,35] can probably be explained by the chelating character of the carbene ligands used. The carbene rings in **1** are twisted against the square-planar coordination sphere by 70.1(1) and 66.7(1)°. These values are lower by about 7° than reported in refs[13,14], which is probably due to steric requirements of bulky substituents on nitrogen atoms.

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