Homoleptic Nickel(0) Phenyl Isocyanide Complexes

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The tetrakis(phenyl isocyanide)nickel(0) complexes $[Ni(CNR)_4](R = C_6H_5, 1; R = C_6H_3-2, 6-Me_2, 2; R = C_6H_4-2-NO_2, 3)$ have been synthesized from $[Ni(COD)_2]$ and the corresponding phenyl isocyanides in toluene. Complexes 1-3 were characterized by X-ray diffraction. All three complexes contain a nickel atom which is coordinated in a slightly distorted tetrahedral fashion.

Key words: Phenyl Isocyanide Complexes, Nickel(0), Crystal Structures

Introduction

Carbene complexes with benzannulated N-heterocyclic carbene ligands can be obtained from 2functionalized phenyl isocyanides. 2-(Trimethylsiloxy)phenyl isocyanide, for example, reacts after cleavage of the Si-O bond under formation of the NH,Ostabilized carbene complex **A** [1], which can be Nalkylated giving **B** (Scheme 1) [2]. This cyclization reaction can also be used to generate complexes **C** with NH,NH-stabilized carbene ligands [3]. Dialkylation of complexes of type **C** leads to complexes **D** with NR,NR-stabilized benzannulated carbene ligands (Scheme 1) [3]. Such carbene ligands are stable in the free state and can also be generated in a metal



Scheme 1. Cyclization of 2-functionalized phenyl isocyanides.



Scheme 2. Preparation of tetrakis(phenyl isocyanide)nickel(0) complexes.

template free reaction sequence from benzimidazol-2-thiones [4].

We tried to prepare nickel(II) carbene complexes by cyclization of coordinated 2-functionalized phenyl isocyanides. However, nickel(II) is a catalyst for the polymerization of isocyanides [5] and the preparation of nickel(II) isocyanide complexes is hampered by this polymerization. We have therefore studied the reaction of phenyl isocyanides with nickel(0) to obtain homoleptic nickel(0) phenyl isocyanide complexes. It was intended to oxidize these complexes later to the nickel(II) derivatives, which should then undergo the cyclization reaction to give the carbene complexes. In this contribution we describe the reaction of [Ni(COD)₂] with three differently substituted phenyl isocyanides and the molecular structures of three homoleptic tetrakis(phenyl isocyanide)nickel(0) complexes 1 - 3 (Scheme 2).

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Fig. 1. Molecular structures of **1** and **3** (hydrogen atoms omitted for clarity). Both molecules reside on special positions (site symmetry $\overline{4}$, * and ** denotes symmetry equivalent positions) in the unit cell. Selected bond lengths [Å] and angles [°] for **1** [**3**]: Ni-C1 1.828(3) [1.835(3)], C1-N1 1.162(4) [1.167(3)], N1-C2 1.388(5) [1.388(3)]; C1-Ni-C1* 111.4(1) [114.40(15)], C1-Ni-C1** 106.6(2) [107.07(7)], Ni-C1-N1 176.9(3) [174.3(2)], C1-N1-C2 168.4(4) [168.9(3)].

Results and Discussion

Homoleptic tetraisocyanide complexes of nickel(0) complexes have been described as early as 1950 [6,7]. Tetrakis(phenyl isocyanide)nickel(0) complexes were prepared by substitution of the CO ligands in [Ni(CO)₄]. Nicolocene is reported to react with phenyl isocyanide to give [Ni(CN-C₆H₅)₄] [8] and tetrakis(isocyanide)nickel(0) complexes were also obtained by disproportionation of K₄[Ni₂(CN)₆] in the presence of alkyl and aryl isocyanides [9]. Most known tetrakis(aryl isocyanide)nickel(0) complexes were characterized only by microanalytical data. The ¹³C NMR spectrum of [Ni(CN-C₆H₅)₄] has bee reported [10]. IR spectra of some complexes have been recorded showing one $C \equiv N$ stretching mode slightly above 2000 cm^{-1} , which is indicative of the expected tetrahedral coordination geometry [9, 11]. It has been noted that sometimes more than one $C \equiv N$ stretching vibration was observed in the IR spectra of complexes [Ni(CNR)₄] [9, 12]. It was proposed that $M \rightarrow C$ backbonding causes loss of linearity of the coordinated isocyanide ligand and thus leads to a coordination geometry less symmetrical than T_d for these complexes. However, to date no structural data for any homoleptic tetrakis(isocyanide)nickel(0) complex have been reported.

In our preparation of homoleptic nickel(0) isocyanide complexes we have substituted the toxic [Ni(CO)₄] or the other reported Ni^{II} starting materials by stable and easy to handle [Ni(COD)₂]. [Ni(COD₂] reacts with phenyl isocyanide, 2,6-dimethylphenyl



Fig. 2. Molecular structure of **2** (hydrogen atoms omitted for clarity). The molecule resides on a general position in the unit cell. Selected bond lengths [Å] and angles [°]: Ni-C11 1.822(4), Ni-C21 1.839(3), Ni-C31 1.839(4), Ni-C41 1.841(3), C11-N11 1.177(4), N11-C12 1.389(4), C21-N21 1.161(4), N21-C22 1.388(4), C31-N31 1.173(4), N31-C32 1.387(4), C41-N41 1.168(4), N41-C42 1.193(4); C11-Ni-C21 109.45(14), C11-Ni-C31 101.69(14), C11-Ni-C41 111.60(15), C21-Ni-C31 112.28(14), C21-Ni-C41 110.13(14), C31-Ni-C41 111.43(14), Ni-C11-N11 172.7(3), C11-N11-C12 161.5(3), Ni-C21-N21 179.3(3), C21-N21-C22 175.0(3), Ni-C31-N31 172.9(3), C31-N31-C32 169.9(3), Ni-C41-N41 175.9(3), C41-N41-C42 173.4(3).

isocyanide or 2-nitrophenyl isocyanide to give the tetrakis(phenyl isocyanide)nickel(0) complexes 1-3 in good (around 80%) yield (Scheme 2). All three complexes are stable in air. Complexes 1 and 2 are yellow solids which are soluble in almost all organic solvents with the exception of aliphatic hydrocarbons. Complex 3 is a dark purple solid which is less soluble in chlorinated organic solvents but is freely soluble in THF.

¹H and ¹³C NMR spectra were recorded for 1–3. The chemical shifts for the isocyanide carbon atoms fall in the narrow range of $\delta = 169.0 - 176.1$ ppm taking into account that the spectra were recorded in three different solvents. The chemical shift for the isocyanide carbon atom in 1 has been reported (15.1 MHz in CHCl₃) at $\delta = 165.6$ ppm [10]. The substitution pattern of the isocyanide ligand appears to have no influence on the chemical shift of the isocyanide carbon atom.

IR spectra of 1-3 were measured in KBr. Two C=N absorptions (one vs around 2030 cm⁻¹ and one s around 2000 cm⁻¹) were detected for each complex confirming earlier observations [9, 12] that the complexes possess less than ideal T_d symmetry of the spectral symmetr

	1	2	3	Table 1. Crystal and data col-
Crystal habit	yellow needle	yellow cube	black needle	lection details for $1-3$.
Crystal size [mm]	0.50 imes 0.07 imes 0.7	0.20 imes 0.15 imes 0.10	$0.15 \times 0.05 \times 0.05$	
Formula	C ₂₈ H ₂₀ N ₄ Ni	C ₃₆ H ₃₆ N ₄ Ni	C ₂₈ H ₁₆ N ₈ NiO ₈	
fw [amu]	471.19	583.40	651.20	
a [Å]	12.575(2)	11.537(1)	9.671(1)	
<i>b</i> [Å]	12.575(2)	11.803(1)	9.671(1)	
<i>c</i> [Å]	7.266(1)	12.549(1)	14.559(1)	
α [deg]	90	106.44(1)	90	
β [deg]	90	106.70(1)	90	
γ[deg]	90	98.65(1)	90	
V [Å ³]	1149.0(3)	1524.5(2)	1361.7(2)	
space group	<i>P</i> 4̄ (no. 82)	<i>P</i> 1̄ (no. 2)	$P4_2/n$ (no. 86)	
Z	2	2	2	
$\mu [mm^{-1}]$	0.867	0.667	0.781	
Abs. corr.	empirical	empirical	empirical	
	$0.671 \le T \le 0.942$	$0.878 \le T \le 0.936$	$0.892 \le T \le 0.962$	
2θ Range [deg]	4.6 to 55.1	3.6 to 52.5	5.1 to 55.0	
Unique data	1316	6133	1566	
Obsvd. data $(I > 2\sigma(I))$	1071	4308	1115	
R(observed)[%]	$5.13, R_{\rm w} = 9.09$	$5.47, R_{\rm w} = 10.17$	$4.76, R_{\rm w} = 11.12$	
<i>R</i> (all), [%]	$6.90, R_{\rm w} = 9.75$	$9.51, R_{\rm w} = 12.41$	$7.57, R_{\rm w} = 12.30$	
GOF	1.024	1.020	1.036	
BASF	0.5	_	-	
No. of variables	75	378	102	
Res. el. dens. [e/Å ³]	0.607/-0.356	0.354/-0.459	0.513/-0.635	

try. Free 2-functionalized phenyl isocyanides exhibit a C \equiv N stretching frequency around 2120 cm⁻¹ [13]. The lower frequency absorptions observed in complexes 1-3 indicate significant d $\rightarrow \pi^*$ backbonding to the isocyanide ligands as would be expected for electron-rich nickel(0) centers. No significant differences for the C \equiv N absorptions in 1-3 depending on the substituents of the isocyanide ligand were observed. It should be noted that C \equiv N stretching frequencies for 1-3 are observed around the value found for [Ni(CO)₄], and are much lower than observed for the less electron-rich complexes of type [Ni(X₂)(CNR)₂] [14].

Complexes 1-3 can be crystallized from toluene and crystals suitable for X-ray diffraction studies were obtained this way. The molecular structures of 1 and 3 are depicted in Fig. 1 and the molecular structure of 2 is shown in Fig. 2. The nickel atom in 1 and 3 resides on a special position in the tetragonal unit cell (site symmetry $\overline{4}$) and the asymmetric unit contains only 1/4 of the complex. Complex 2 is located on a general position in the unit cell. All three complexes show a slightly distorted tetrahedral coordination environment (range of C-Ni-C angles $101.69(14)^\circ - 114.40(15)^\circ$). The unique C \equiv N-C angles in 1 and 3 deviate from linearity (C1-N1-C2 $168.4(4)^\circ$ for 1 and $168.9(3)^\circ$ for 3). However, in 2 four different C \equiv N-C angles ranging from $161.5(3)^{\circ}$ to $175.0(3)^{\circ}$ are found for isocyanides coordinated to the same metal center. We therefore assume, that the non-linearity of the C=N-C moieties in 1-3 is not only determined by electronic effects but also by the packing of the molecules in the crystal.

The Ni-C bond lengths in 1-3 fall in the narrow range of 1.822(4) to 1.841(3) Å. These values are very similar compared to those of the only other homoleptic, albeit nickel(II) tetraisocyanide complex [Ni(CN- $C_6H_3-2,6-CH_3)_4]^{2+}$ [15]. As we have noticed with alkyl isocyanides, enhanced backbonding from a metal center to the isocyanide, which manifests itself by a reduction of the wave number for the $C \equiv N$ vibration, is not necessarily reflected in the M-CN bond length [16]. Backbonding from Ni⁰ to the isocyanide ligands in 1-3 is stronger than in the Ni^{II} phenyl isocyanide complexes but significant differences in the M-CN bond lengths are not observed. This holds also for the $C \equiv N$ bond lengths in 1-3, which are not significantly longer than in Ni^{II} phenyl isocyanide complexes. The bond parameters of the Ni(C \equiv N)₄ core can be compared to the molecular structure of [Ni(CO)₄] [17], where the Ni-C and C \equiv O separations are 1.817(2) and 1.127(3) Å, respectively.

We have developed a new synthetic procedure for the preparation of homoleptic Ni^0 phenyl isocyanide complexes 1-3 starting from [Ni(COD)₂]. The complexes 1-3 are air stable and easy to handle compounds, which will be useful starting materials for the preparation of other Ni⁰ complexes.

Experimental Section

All experiments were carried out in an argon atmosphere using standard Schlenk techniques. All solvents were dried by standard methods and distilled prior to use. NMR spectra were recorded on a Bruker AC 200 spectrometer. The isocyanide ligands were prepared by dehydration of formamides according to the procedure described by Ugi *et al.* [18].

Preparation of tetrakis(phenyl isocyanide)nickel(0) complexes 1-3: An almost identical procedure was employed for the preparation of 1-3. The synthesis of 1 is described as an example. A sample of bis(cyclooctadiene)nickel(0) (100 mg, 0.37 mmol) was dissolved in 150 ml of toluene. Phenyl isocyanide (200 mg, 1.94 mmol) dissolved in 10 ml of toluene was added to this solution over a period of 1 h at room temperature. Subsequently the reaction mixture was concentrated to 30 ml and cooled to -10 °C. After 24 h at -10 °C yellow crystals of 1 were collected by filtration. Yield 142 mg (30.1 mmol, 81%). Suitable crystals for the X-ray structure determination were obtained by recrystallization from toluene at -10 °C. -1 H NMR (200.1 MHz, CD₂Cl₂, ppm): $\delta = 7.32$ (m, br, 20 H, Ar-H). – ¹³C NMR (50.3 MHz, CD₂Cl₂, ppm): $\delta = 169.0$ (CN-Ph), 130.1, 129.3, 126.2, 124.1 (Ar-C). IR (KBr): $\tilde{v} = 2031$ (vs, CN), 1986 (s, CN). – C₂₈H₂₀N₄Ni (471.19): calcd. C 71.38, H 4.28, N 11.89; found C 71.33, H 4.19, N 11.77.

Analytical data for 2: Yellow crystals (89% yield). – ¹H NMR (200.1 MHz, [D₆]benzene, ppm): $\delta = 6.78$ (m, br,

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12 H, Ar-*H*), 2.39 (s, 24 H, C*H*₃). – ¹³C NMR (50.3 MHz, [D₆]benzene, ppm): δ = 176.1 (*C*N-Ph), 134.3, 131.6, 126.9, 125.2 (Ar-*C*). IR (KBr): \tilde{v} = 2029 (vs, CN), 1999 (s, CN). – C₃₆H₃₆N₄Ni (583.40): calcd. C 74.12, H 6.22, N 9.60; found C 73.26, H 6.10, N 9.40.

Analytical data for **3**: Purple crystals (83% yield). – ¹H NMR (200.1 MHz, CDCl₃, ppm): $\delta = 8.0$ (m, 4 H, Ar-*H*), 7.7 (m, 8 H, Ar-*H*), 7.5 (m, 4 H, Ar-H). – ¹³C NMR (50.3 MHz, [D₈]THF, ppm): $\delta = 173.4$ (br, *CN*-Ph), 134.1, 130.3, 127.2, 123.8 (Ar-*C*), only 4 of the expected 6 Ar-C resonances were detected. – IR (KBr): $\tilde{\nu} = 2037$ (vs, CN), 2003 (s, CN). – C₂₈H₁₆N₈NiO₈ (651.20): calcd. C 51.65, H 2.48, N 17.21; found C 52.67, H 2.75, N 16.96.

X-ray structure determination of **1-3** [19]: Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591 at 198(2) K. The data for **1** were refined as a racemic twin with a ratio of 0.5 to 0.5. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom were placed on calculated positions and were refined as riding atoms. The nickel atoms in **1** and **3** reside on special positions (site symmetry $\bar{4}$) with 1/4 of the molecule per asymmetric unit. Additional data collection and refinement details are listed in Table 1. Programs used: data collection COLLECT [20], data reduction Denzo-SMN [21], absorption correction SORTAV [22], structure solution SHELXS-97 [23], structure refinement SHELXL-97 [24], graphics ORTEP [25].

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