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Synthesis, spectroscopy and molecular structures of new salicylketiminato nickel(II) complexes

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Abstract

A series of salicylketimines (2-[(2,6-diisopropylphenylimino)ethyl]phenol, 2-[(2,6-diisopropylphenylimino)ethyl]naphthol and 2-[(2,6-diisopropylphenylimino)(phenyl)-methyl]phenol), and their nickel complexes of general forms [(salicylketiminato)-Ni(PPh_3)(Ph)] and [(salicylketiminato)$_2$Ni] were synthesized and characterized. The formation of monophenyl-nickel(II) complexes versus the corresponding bis(sal)Ni(II) complexes depends on the fine tuning of the reaction work up and is affected by the substituent at the ketimine. Salicylketimines were thus found to form more readily the bis(sal)Ni(II) complexes than salicylaldimines. The molecular structures of the complexes were determined by X-ray crystallography and in all of them Ni has a nearly ideal square-planar coordination sphere.

Keywords: Nickel(II) complexes; Schiff bases; Salicylketimine ligands; X-ray crystallography

1. Introduction

Until middle of 1990s, only few reports were introduced utilizing late transition metal complexes as catalyst precursors for polymerization of α-olefins [1]. This could be due to the fact that these catalysts generally exhibited low activities for olefin polyinsertion. In addition, β-hydride elimination steadily competed with the chain growth resulting in the formation of oligomers [2]. However, in 1995 new nickel(II)- and palladium(II)-based catalysts bearing bulky diimine ligands were reported for ethene polymerization, and few years later also iron(II) was successfully applied as a metal centre with bis(imino)pyridine ligands [3]. These complexes, after methylaluminoxane (MAO) activation, produced high molecular weight polymers with a high activity. Moreover, due to their tolerance towards polar functionalities, these systems are viewed as promising alternatives to Ziegler-Natta and metallocene catalysts. By now, late transition metals as olefin polymerization catalysts have been extensively reviewed, and possibilities to apply them even in acrylate polymerization have been demonstrated [4].

The MAO-activated cationic catalysts are, anyhow, electrophilic and hence sensitive to protic solvents and polar monomers. For this reason, there has been a substantial interest in developing new, less oxophilic, catalysts for olefin polymerization [5]. Shell higher olefin process (SHOP) offers an intriguing insight for catalytic activity of neutral nickel catalysts used for ethylene oligomerization [6] and recently novel salicylaldimine based Ni(II) complexes as catalysts for homo and co-polymerization of olefins were described by DuPont [7] and Grubbs and co-workers [8]. The most active systems contain either electron-withdrawing nitro substituents on the aromatic ring or bulky substituents at C-3, a 9-anthracenyl group being the most effective [activity of

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1.3×10^5 mol ethylene/(mol Ni h)]. It has been reported that the neutral salicylaldiminato nickel(II) complexes work as a single component catalysts or require only a phosphine scavenger such as [Ni(COD)$_2$] (COD: 1,5-cyclooctadiene) to act as catalysts for homo- and copolymerization of ethylene [8]. However, MAO as activator surprisingly turned out to be essential to initiate the homopolymerization of norbornene [9].

Recently, we and other research groups have found that penta-coordinated iron(II) complexes with tridentate ketimine ligands (2,6-bis(imino)pyridyl derivatives) are an order of magnitude more active, as ethylene polymerization catalysts, than their aldimine analogues [3,10]. As an augmentation to our studies upon both the coordination chemistry of heteroatom-containing ligands [11,12] and their catalytic application [4f,10a,13], we now report the synthesis of new nickel(II) complexes with salicylketimine Schiff base ligands. The new compounds were characterized by methods of elemental analysis, IR-, MS-, ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy. Furthermore, the complexes were subjects to X-ray structure analysis.

2. Experimental

2.1. Materials

All reactions were carried out under argon by using standard Schlenk techniques. Reagent grade chemicals were purchased from commercial suppliers and used as received unless otherwise stated. *trans*-[(PPh$_3$)$_2$Ni((Ph)Cl] was prepared according to literature [14]. The hydrocarbon and ether solvents were purified by distillation over LiAlH$_4$.

2.2. Physical measurements

Elemental analyses were performed at the Departments of Chemistry of the Universities of Konstanz and Ulm or at the Department of Pharmacy at University of Helsinki with an EA 1110 CHNS-O CE instrument. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded using a Varian Gemini 200 or a Bruker AMX 400 spectrometer. Infrared spectra were measured on a Perkin–Elmer Spectrum One spectrometer using ATR sampling assessor. Mass spectra were acquired using a JEOL JMS-SX102 mass spectrometer (EI) or Bruker ion trap 3000+ MS equipped with Agilent's AP-MALDI ion source (proto 3).

2.3. Synthesis of ligands

2.3.1. 2-[(2,6-Diisopropylphenylimino)ethyl]phenol (**4**)

A solution of 2-hydroxyacetophenone (3.2 g, 23.9 mmol), 2,6-diisopropylaniline (4.7 g, 23.9 mmol) and five drops of HCOOH in methanol were stirred together with ca. 5 g of Na_2SO_4 at 200 °C in a closed steel autoclave for 24 h. The reaction mixture was then cooled, filtered and the filtrate was evaporated to dryness. The residue was purified with column chromatography on silica with 1:5 mixture of diethylether/hexane as eluent. Yield: 46%. *Anal.* Calc. for $C_{20}H_{25}NO$: C, 81.31; H, 8.53; N, 4.74. Found: C, 81.22; H, 8.54; N, 4.75%. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.15$ (dd, 12H, $J_{HH} = 1.8$ Hz, $^3J_{HH} = 7.0$ Hz, CHCH_3), 2.19 (s, 3H, N=CCH$_3$), 2.78 (sept, 2H, $^3J = 7.0$ Hz, CHMe$_2$), 6.91 (m, 1H, H–Ar), 7.05 (m, 1H, H–Ar), 7.18 (b, 3H, H–Ar), 7.41 (m, 1H, H–Ar), 7.65 (m, 1H, H–Ar), 14.95 (s, 1H, OH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 17.6$, 23.1, 23.6, 28.3, 118.0, 118.3, 119.1, 123.2, 125.1, 128.9, 133.1, 138.0, 142.3, 162.4, 172.1 ppm. IR: $\nu = 1608$ cm^{-1} (C=N).

2.3.2. 2-[(2,6-diisopropylphenylimino)ethyl]naphthol (**5**)

The compound was prepared and purified as described above (Section 2.3.1). Yield: 48%. *Anal.* Calc. for $C_{24}H_{27}ON$: C, 83.44; H, 7.87; N, 4.05. Found: C, 83.39; H, 7.88; N, 4.03%. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.17$ (d, 12H, $^3J_{HH} = 7.0$ Hz, CHCH_3), 2.28 (s, 3H, CCH$_3$), 2.89 (sept, 2H, $^3J = 7.0$ Hz, CHMe$_2$), 7.14 (m, 1H, H–Ar), 7.24 (m, 3H, H–Ar), 7.52 (m, 3H, H–Ar), 7.73 (m, 1H, H–Ar), 8.53 (m, 1H, H–Ar), 17.08 (s, 1H, OH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 17.2$, 22.8, 23.9, 28.5, 110.56, 115.8, 123.5, 124.7, 126.4, 127.2, 129.1, 136.5, 139.1, 140.6, 167.4, 172.3 ppm. IR: $\nu = 1596$ cm^{-1} (C=N).

2.3.3. 2-[(2,6-diisopropylphenylimino)(phenyl)methyl]-phenol (**6**)

The compound was prepared as described for **4** (Section 2.3.1). The isolated residue was purified with column chromatography using petroleum ether/ethylacetate (8:1) solvent mixture as eluent. Isolated yield: 6%. *Anal.* Calc. for $C_{25}H_{27}ON$: C, 83.99; H, 7.61; N, 3.92. Found: C, 82.29; H, 7.66 N, 3.86%. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.08$ (d, 6H, $^3J_{HH} = 8.0$ Hz, CHCH_3), 1.17 (d, 6H, $^3J_{HH} = 8.0$ Hz, CHCH_3), 2.97 (sept, 2H, $^3J = 8.0$ Hz, CH Me$_2$), 6.81 (m, 1H, H–Ar), 7.03 (m, 2H, H–Ar), 7.16 (b, 5H, H–Ar), 7.30 (m, 3H, H–Ar), 7.43 (m, 1H, H–Ar), 14.76 (s, 1H, OH). IR: $\nu = 1605$ cm^{-1} (C=N). MS(EI): 357 (M$^+$), 280 (M$^+$ − Ph).

2.4. Synthesis of complexes

2.4.1. {Phenyl)(triphenylphosphine)(2-[(2,6-diisopropylphenylimino) ethyl]phenoxy)}-nickel(II) (**7**)

A solution of ligand **4** (0.65 g, 2.2 mmol) in THF was added to excess amount of NaH (0.18 g, 7.5 mol) at 0 °C. The mixture was stirred for 1 h at room temperature, filtered and evaporated. The pale yellow residue was washed with *n*-pentane and dried. Yield of the sodium salt Na-**4** was 98%. To a solid mixture of

Na-**4** (0.30 g, 0.94 mmol) and *trans*-[$(PPh_3)_2$Ni((Ph)Cl] (0.62 g, 0.90 mmol), 20 ml of benzene was added at 0 °C. The mixture was stirred at room temperature for 6 h and then filtered. After concentrating the filtrate to ca. 3 ml, the product was precipitated as orange powder upon addition of *n*-pentane (30 ml). The solid was isolated by cannula filtration, then washed with pentane and dried. Isolated yield: 30%. *Anal.* Calc. for $C_{44}H_{44}NNiOP$: C, 76.31; H, 6.40; N, 2.02. Found: C, 76.86; H, 6.41; N, 2.04%. ^{1}H NMR (200 MHz, C_6D_6): $\delta = 1.05$ (d, 6H, $^3J_{HH} = 6.8$ Hz, *i*Pr–CH_3), 1.21 (d, 6H, $^3J_{HH} = 6.8$ Hz, *i*Pr–CH_3), 1.83 (s, 3H, N=CCH_3), 3.84 (sept, 2H, $^3J_{HH} = 6.8$ Hz, *i*Pr–CH), 6.29–7.70 (m, 27H, Ar–H). ^{31}P NMR (200 MHz, C_6D_6): $\delta = 23.8$ ppm. IR: $\nu = 1598$ cm^{-1} (C=N).

2.4.2. {Phenyl)(triphenylphosphine)(2-[(2,6-diisopropylphenylimino)ethyl]naphthoxy)}-nickel(II) (*8*)

The sodium salt of the ligand (Na-**5**) and the corresponding complex were prepared following the same procedure used above (Section 2.4.1). The product was purified by recrystallization from 1:5 benzene/*n*-pentane solvent mixture at −20 °C and collected as orange crystals. Isolated yield: 39%. *Anal*. Calc. for $C_{48}H_{46}NNiOP$: C, 77.63; H, 6.24; N, 1.89. Found: C, 77.64; H, 5.90; N, 1.54%. ^{1}H NMR (200 MHz, C_6D_6): $\delta = 1.10$ (d, 6H, $^3J_{HH} = 7.0$ Hz, *i*Pr–CH_3), 1.24 (d, 6H, $^3J_{HH} = 7.0$ Hz, *i*Pr–CH_3), 1.97 (s, 3H, N=CCH_3), 3.89 (sept, 2H, $^3J_{HH} = 7.0$ Hz, *i*Pr–CH), 6.25–7.69 (m, 29H, Ar–H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 23.6$, 24.7, 25.1, 29.4, 114.2, 116.7, 121.8, 124.0, 124.5, 125.8, 126.4, 127.1, 127.3, 127.8, 128.3, 128.5, 128.7, 130.2, 131.7, 131.9, 132.2, 135.0, 135.1, 137.4, 138.7, 140.8, 147.9, 164.2, 169.5 ppm. ^{31}P NMR (200 MHz, C_6D_6): $\delta = 24.3$ ppm. IR: $\nu = 1597$ cm^{-1} (C=N).

2.4.3. Bis[{2-(2,6-diisopropylphenylimino)(phenyl)methyl}phenoxy]nickel(II) (*9*)

The sodium salt of the ligand **6** was prepared as described above (Section 2.4.1). A solution of Na-**6** (0.53 g, 1.40 mmol) in benzene (30 ml) was added to a suspension of *trans*-[$(PPh_3)_2$Ni((Ph)Cl] (0.88 g, 1.27 mmol) in the same solvent (20 ml). The reaction took soon a deep red color and was stirred at room temperature for 6 h and then filtered. After concentrating the filtrate to ca. 3 ml, the product was precipitated upon addition of *n*-pentane (30 ml). The solid was isolated by cannula filtration then washed with *n*-pentane and dried. The isolated product was crystallized from toluene/*n*-hexane 1:5 mixture to give orange crystals suitable for X-ray structure analysis. Isolated yield was 32%. ^{1}H NMR (200 MHz, C_6D_6): $\delta = 1.24$ (d, 12H, $^3J_{HH} = 6.6$ Hz, *i*Pr–CH_3), 2.13 (d, 12H, $^3J_{HH} = 6.6$ Hz, *i*Pr–CH_3), 3.87 (sept, 4H, $^3J_{HH} = 6.6$ Hz, *i*Pr–CH), 5.68 (m, 2H, H–Ar), 6.11 (m, 2H, H–Ar), 6.56–7.20 (m, 10H, H–Ar) ppm. IR: $\nu = 1599$ cm^{-1} (C=N).

2.4.4. Bis[(2-(2,6-diisopropylphenylimino)ethyl)phenoxy]nickel(II) (*10*)

The compound was prepared as described in Section 2.4.3. Crystals suitable for single crystal X-ray analysis were formed upon recrystallization from benzene/*n*-pentane (1:5) solvent mixture. ^{1}H NMR (200 MHz, C_6D_6): $\delta = 1.13$ (d, 12H, $^3J_{HH} = 7.0$ Hz, *i*Pr–CH_3), 1.73 (m, 18H, *i*Pr–CH_3, N=CCH_3), 4.08 (sept, 4H, $^3J_{HH} = 7.0$ Hz, *i*Pr–CH), 5.77 (m, 2H, Ar–H), 6.33 (m, 2H, Ar–H), 6.83–7.25 (m, 10H, Ar–H) ppm. MS(EI): 647 (M^+), 358 ($M^+ - (N \cap O)$). IR: $\nu = 1602$ cm^{-1} (C=N).

2.4.5. Bis[(2-(2,6-diisopropylphenylimino)ethyl)naphtoxy]nickel(II) (*11*)

A solution of Na-**5** (0.52 g, 1.42 mmol) in benzene (30 ml) was added to a suspension of *trans*-[$(PPh_3)_2$Ni((Ph)Cl] (0.88 g, 1.27 mmol) in the same solvent (20 ml). The reaction took soon a deep red color and was stirred at room temperature for 6 h, after which it was treated as in Section 2.4.3. Yield 86%. *Anal.* Calc. for $C_{48}H_{52}N_2O_2Ni$: C, 77.11; H, 7.01; N, 3.74. Found: C, 75.02; H, 6.93; N, 3.65%. ^{1}H NMR (200 MHz, C_6D_6): $\delta = 1.13$ (d, 12H, $^3J_{HH} = 7.0$ Hz, *i*Pr–CH_3), 1.39 (d, 12H, $^3J_{HH} = 7.0$ Hz, *i*Pr–CH_3), 1.72 (s, 3H, N=CCH_3), 4.60 (sept, 2H, $^3J_{HH} = 7.0$ Hz, *i*Pr–CH), 6.14 (m, 2H, H–Ar), 6.76–7.46 (m, 16H, H–Ar) ppm. MS(AP-MALDI): 746 (M^+). IR: $\nu = 1591$ cm^{-1} (C=N).

2.5. X-ray crystal structure determination for the complexes 7–*10*

Single crystals of the compounds were selected for the X-ray measurements and mounted on the glass fibre using the oil drop method [15a]. Data were collected at 120(2) (**7**, **10**) and 173(2) (**8**, **9**) K using Nonius KappaCCD diffractometer. The intensity data were corrected for Lorentz and polarization [15b] effects and for absorption by multi-scan method [16]. The structures were solved by direct methods (SHELXS 97). The refinements and graphics were done using SHELXL 97 and SHELXTL/PC program package, respectively. All non-hydrogen atoms were refined anisotropically. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. The cell parameters and the specific data collections parameters are summarized in Table 1.

3. Results and discussion

3.1. Ligand and complex synthesis

The synthesis of the ligands (**4**–**6**) and their nickel complexes (**7**–**11**) are shown in Scheme 1. Preparation of the desired salicylketimines turned out to proceed with

Table 1
Crystal data and structure refinement for **7**–**10**

	7	**8**	**9**	**10**
Formula	$C_{44}H_{44}NNiOP$	$C_{48}H_{46}NNiOP$	$C_{50}H_{52}N_2NiO_2$	$C_{40}H_{48}N_2NiO_2$
Formula weight	692.48	742.54	771.65	647.51
T (K)	120(2)	173(2)	173(2)	120(2)
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P21/c$	$P21/c$	$P\bar{1}$
Unit cell dimensions				
a (Å)	11.6450(1)	14.1440(11)	10.3310(19)	8.36340(10)
b (Å)	11.7285(1)	13.681(2)	11.577(3)	9.9331(2)
c (Å)	14.1484(2)	22.128(4)	19.815(3)	11.5502(2)
α (°)	99.491(1)	90.000(11)	90.000(16)	112.6720(1)
β (°)	96.400(1)	114.726(9)	121.123(15)	100.1010(10)
γ (°)	109.777(1)	90.000(8)	90.000(16)	99.0720(10)
V (Å^3)	1764.13(3)	3889.3(10)	2028.8(8)	844.43(2)
Z	2	4	2	1
D_{calc} (Mg m^{-3})	1.304	1.268	1.263	1.273
Absorption coefficient (mm^{-1})	0.631	0.577	0.521	0.612
Crystal dimensions (mm)	$0.30 \times 0.30 \times 0.10$	$0.25 \times 0.20 \times 0.15$	$0.20 \times 0.20 \times 0.06$	$0.20 \times 0.15 \times 0.05$
θ range (°)	2.13–27.48	5.02–27.50	3.52–27.52	3.96–27.45
Number of data collected	31 239	47 797	139 71	10 310
Number of unique data	8063 [$R_{int} = 0.0437$]	8855 [$R_{int} = 0.0759$]	4622 [$R_{int} = 0.0775$]	3838 [$R_{int} = 0.0293$]
Number of data refined	8063	8855	4622	3838
Number of parameters	438	469	250	210
$R^a[I > 2\sigma(I)]$	0.0366	0.0436	0.0533	0.0317
$wR_2{}^b$	0.0789	0.0828	0.1023	0.0710
Residual density (e A^{-3})	0.369 and −0.437	0.328 and −0.397	0.439 and −0.476	0.282 and −0.313

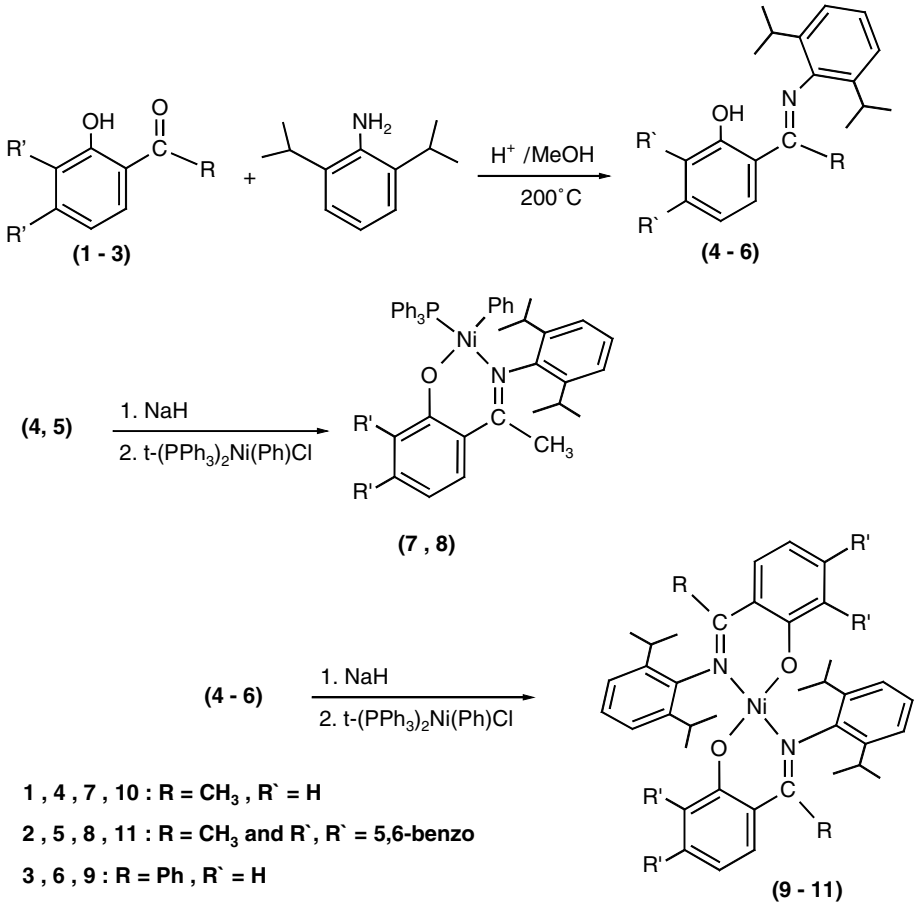
[a] $R = \sum \|F_o| - |F_c\| / \sum |F_o|$.
[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.

negligible yields, even with extended refluxing periods. Therefore, ligands **4**, **5** and **6** were prepared in methanol at 200 °C in a closed steel autoclave in the presence of Na_2SO_4 and a catalytic amount of formic acid. After purification by column chromatography, ligands **4** and **5** were isolated with nearly 50% yields, but with only 6% yield for ligand **6**. After deprotonation of the ligands with an excess of NaH in THF, the corresponding sodium salts were allowed to react with *trans*-[$(PPh_3)_2$-Ni((Ph)Cl], either by addition of the reaction solvent (benzene) to a solid mixture of the two reactants at low temperature or by addition of a solution of the corresponding sodium salt to a suspension of the nickel precursor. The former method favours the formation of monophenyl-nickel(II) complexes **7** and **8**, while the latter method leads to the formation of the bis(sal)Ni(II) complexes **9**–**11**.

^{1}H NMR spectra of the ligands are similar to those of the corresponding salicylaldimines [8], except for a singlet (**4** and **5**) which appears at 2.19–2.28 ppm that can be attributed to the ketimine methyl group. Upon complexation, this singlet is shifted upfield to 1.83–1.97 ppm. The septet which is due to CH protons of the isopropyl groups is shifted down field (from that in the spectra of ligands **4** and **5** (2.78 and 2.89 ppm)) to 3.84–3.89 ppm as observed for **7** and **8**. In the case of the bis(sal) complexes, this septet is further shifted to 3.87, 4.08 and 4.60 ppm for **9**, **10** and **11**, respectively. The signals of the triphenylphosphine ligand in the ^{31}P NMR spectra of complexes **7** and **8** are observed at 23.8–24.3 ppm. The IR spectra of **4**, **5** and **6** show bands at 1608, 1596 and 1605 cm^{-1}, respectively, which are ascribed to C=N group. After complexation, these bands are correspondingly found at 1598 and 1597 cm^{-1} for the monophenyl complexes (**7** and **8**) and 1599, 1602 and 1591 cm^{-1} for the bis(sal)-Ni(II) complexes (**9**–**11**), respectively. The IR spectra of all the studied complexes are in good agreement with previous reports of analogous compounds [9].

The reaction of Na-**5** with *trans*-[$(PPh_3)_2$Ni((Ph)Cl] was monitored by ^{1}H NMR. When benzene was added to a solid mixture of the reacting materials, only the monophenyl complex **8** was detected. This complex was purified by recrystallization from 1:5 benzene/*n*-pentane solvent mixture at −20 °C which gave orange crystals. However, when a slight excess of a solution of the sodium salt of **5** in benzene was added to a suspension of nickel precursor at ambient temperature, the bis(sal)-Ni(II) complex **11** was obtained as a major product and only a trace amount of **8** was observed in ^{1}H NMR. Ligand **4** behaved similarly upon complexation, both the monophenyl complex (**7**) and the bis(sal)Ni(II) (**10**) could be isolated.

In its isolated form complex **8** was found to be quite stable in solution at room temperature. According to ^{1}H NMR, no decomposition or transformation to the corresponding bis(sal)–Ni(II) species was detected even after 8 h room temperature and after 50 h the molar ratio of **11**:**8** was found to be 1:15. In the case of the



Scheme 1. Synthesis of ligands (**4**–**6**) and complexes (**7**–**11**).

salicylaldimines, the formation of bis(sal)Ni(II) complexes usually require more harsh reaction conditions [17]. In order to form the desired bis(sal)Ni(II) complex [17b], the neutral phenyl substituted salicylaldiminato Ni(II) complex had to be stirred at 50 °C first with vinyl chloride (VC) for four days in toluene and then to continue stirring for another four days in *n*-hexane at 50 °C. The complexation occurred via tetrahedral Ni complex bearing a Cl instead of the Ph ligand, where Cl–Ni bond was formed by 1,2-insertion of VC into Ni–Ph bond followed by β-Cl elimination.

With the salicylketimine ligands, the formation of the bis(sal) complexes can take place spontaneously. Moreover, in the reaction of Na-**6** with *trans*-[$(PPh_3)_2$-Ni((Ph)Cl], the bis(sal)Ni(II) complex (**11**) was the predominant product. It seems that the presence of the phenyl group on the ketimine carbon of the ligand increased the tendency to form a bis(sal) complex. The reason for this particular behaviour remains unclear but it could be due to *trans* influence of the ketimine site, thus allowing a faster dissociation of the second PPh_3 ligand. So, in addition to fine tuning of the reaction conditions, also different substituents on the ketimine carbon may affect on the complexation behaviour of these salicylketimine ligands.

Surprisingly, the monophenyl salicylketiminato based Ni(II) complexes **7** and **8** turned out to be catalytically inactive in homopolymerization of ethene or norbornene when [$Ni(COD)_2$] or BF_3 were applied as phosphine scavengers, even at elevated temperatures (up to 60 °C) and pressures (up to 40 bar).

3.2. Crystal structures of the complexes

For further investigation of structural features of the complexes, crystals of complexes **7** and **8**, suitable for X-ray structure determination, were grown from 1:5 benzene/*n*-pentane mixture at −20 °C and crystals of complexes **9** and **10** were obtained at ambient temperature. The coordination sphere of complex **8** was found to be similar to that of **7**. Also, the coordination spheres of bis(sal)Ni(II) complexes **9** and **10** were found to be alike. Data collection and the refinement of data of **7**–**10** (Figs. 1–4) are summarized in Table 1. [1]

In the solid state, complex **7** has a square-planar geometry. The Ni atom is approximately 0.01 Å out of the

[1] The molecular structure of **11** was also determined. It was found similar to that of **10** and is thus left from discussion here but the data is included in the supplementary material.

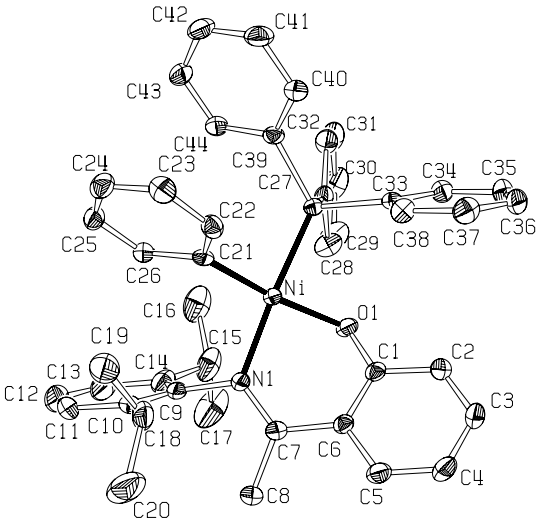


Fig. 1. ORTEP plot of the molecular structure of compound **7**. Displacement ellipsoids are drawn at 50% probability level.

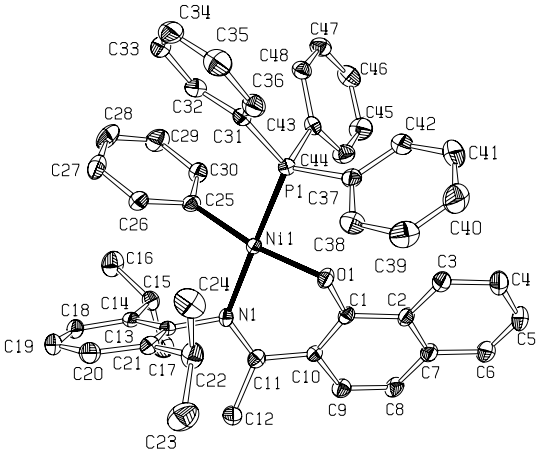


Fig. 2. ORTEP plot of the molecular structure of compound **8**. Displacement ellipsoids are drawn at 50% probability level.

plane of the donor atoms. The bulky 2,6-diisopropylphenylimine occupies the *trans* position to the triphenylphosphine ligand with almost a linear N1–Ni–P1 angle (172.17(5)°) (Table 2). The phenyl group attached to Ni lies in *trans* position to O1 with an O1–Ni–C21 angle of 171.73(7)°. The Ni–O1, Ni–N1 and Ni–C21 bond distances in complex **7** are similar to those for known nickel complexes [18].

The Ni–P1 bond distance (2.185(1) Å) is only a bit longer than those in Grubbs' nickel-based complex (2.172(2) Å) and in Cavell's [Ni(PPh_3)(*o*-tolyl)(N–O)] complexes with N–O bidentate pyridinecarboxylate ligands (*d*(Ni–P) 2.1653(2) Å) [18d]. But, it is clearly shorter than that in nickel(II) salicylaldiminato complexes bearing naphthyl instead of phenyl group *cis* to PPh_3 (2.200(1) and 2.198(2) Å) [9].

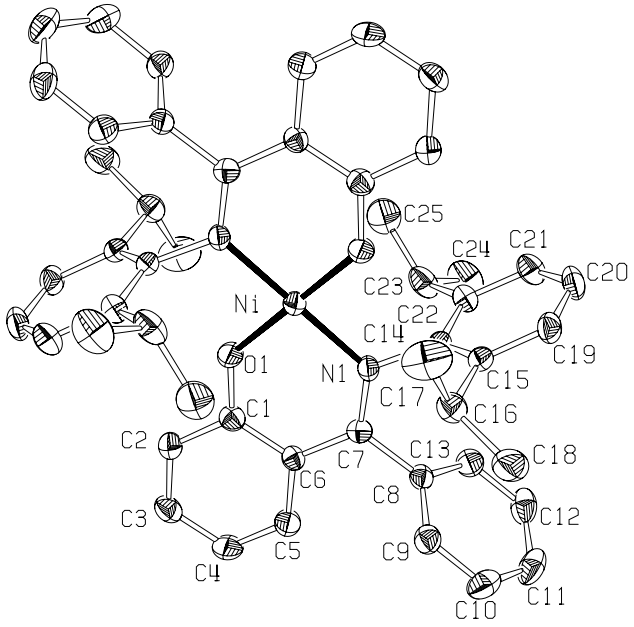


Fig. 3. ORTEP plot of the molecular structure of compound **9**. Displacement ellipsoids are drawn at 50% probability level.

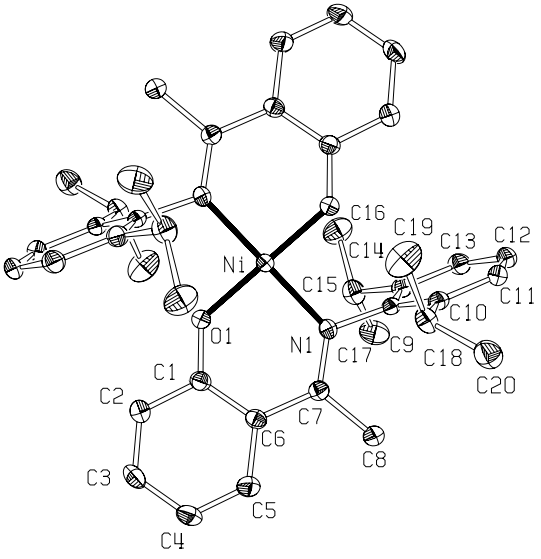


Fig. 4. ORTEP plot of the molecular structure of compound **10**. Displacement ellipsoids are drawn at 50% probability level.

Complex **9** forms a square planar complex, at which nickel lays in the symmetry centre of the molecule and thus in the plane of the four donor atoms (Table 1, Fig. 3). The bond angles and distances are similar to those found for **10** (Table 1, Fig. 4), where the average Ni–O distance (1.808 Å) is somewhat shorter, and the Ni–N distance (1.926) is somewhat longer than those in the bis(salicylaldiminato) complexes which were reported by Jordan and co-workers (Ni–O 1.846 Å, Ni–N 1.899 Å) [17b] and Knoch et al. (1.856, 1.899 Å) [17a].

Table 2
Selected bond lengths (Å) and angles (°) for **7**–**10** (symmetry transformations were used to generate equivalent atoms)

	7 ($x = 21$)	**8** ($x = 26$)	**9**	**10**
Bond lengths				
Ni–C(x)	1.8957(18)	1.905(2)		
Ni–O(1)	1.9050(12)	1.8890(14)	1.809(2)	1.8081(10)
Ni–N(1)	1.9582(15)	1.9498(16)	1.933(2)	1.9262(11)
Ni–P(1)	2.1845(5)	2.1907(7)		
Bond angles				
C(x)–Ni–O(1)	171.73(7)	167.92(8)		
C(x)–Ni–N(1)	95.96(7)	97.00(8)		
O(1)–Ni–N(1)	89.75(6)	90.07(6)	92.04(9)	91.88(5)
O(1)–Ni–P(1)	84.19(4)	87.71(4)		
N(1)–Ni–P(1)	172.17(5)	173.27(5)		
C(x)–Ni–P(1)	90.60(5)	86.31(6)		
O(1A)–Ni–O(1)			180.00(13)	180.00(10)
O(1)–Ni–N(1A)			87.96(9)	88.12(5)
N(1A)–Ni–N(1)			180.000(1)	180.00(10)

4. Conclusions

A method for the synthesis of salicylketimine ligands was developed by condensation of a ketone with an amine in methanol at 200 °C in a closed steel-autoclave. The complexation behaviour of these ligands towards *trans*-[$(PPh_3)_2$Ni((Ph)Cl] was investigated. Two types of Ni(II) complexes could be isolated and characterized, the monophenyl(salicylketimine)Ni(II) complexes and the corresponding bis(salicylketimine) Ni(II) complexes. It was found that salicylketimine ligands form readily the bis(sal)Ni(II) complexes.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 230868 (**7**), CCDC 230869 (**8**), CCDC 230871 (**9**), CCDC 230870 (**10**) and CCDC 230872 (**11**). Copies of the data can be obtained on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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