Short communication

Synthesis and structural characterisation of aluminium imino-amide and pyridyl-amide complexes: bulky monoanionic N,N chelate ligands via methyl group transfer [1]

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Abstract

Treatment of the imines [ArN=CH-CH=NAr] and [ArN=CH-2-py] (Ar = 2,6-Pr$_2^i$C$_6$H$_3$) with AlMe$_3$ in toluene affords the highly crystalline complexes [AlMe$_2$\{ArN-CH$_2$-C(Me)=NAr\}] (**1**) and [AlMe$_2$\{ArN-CH(Me)-2-py\}] (**2**); the molecular structures of **1** and **2** show that the aluminiums are bonded to imino-amide and pyridyl-amide ligands respectively arising from methyl group transfer from the aluminium centre to the backbone carbon of the imine ligand. © 1998 Elsevier Science S.A.

Keywords: Pyridyl-amide complexes; Imino-amide ligands; Methyl group transfer; Aluminium

The ability of α-diimine ligands to bind to transition metal centres is well-documented [1]. Recently, such complexes have been shown to be of technological significance with the discovery by Brookhart and coworkers [2–4] that certain nickel and palladium derivatives are highly efficient α-olefin polymerisation catalysts. It is the steric properties in particular of these diimine ligands that allow control over the molecular weight and microstructure of the resultant polymers.

Efficient preparations of new ligand systems are crucial to the design and development of new catalyst systems. We became interested in mono-anionic imino-derived ligands with a view to stabilising active catalysts based on other transition metals. We were attracted by the earlier observations of Vrieze and coworkers [5], that α-diimine ligands react with aluminium alkyls to give complexes that contain mono-anionic imino-amide ligands. We report here an extension of this methodology to the synthesis of related bulky imino-amide [ArN-CH$_2$-C(Me)=NAr] and pyridyl-amide [ArN-CH(Me)-2-py] (Ar = 2,6-Pr$_2^i$C$_6$H$_3$) ligand systems. The structures of two aluminium complexes are described.

Treatment of [ArN=CH-CH=NAr] with trimethylaluminium in toluene affords, after work-up, the monomeric complex [AlMe$_2$\{ArN-CH$_2$-C(Me)=NAr\}] (**1**). [2] Complex **1** is presumed to form via intramolecular methyl transfer to an imine carbon atom followed by hydrogen migration as proposed previously by Klerks et al. [5] for aluminium diazabutadiene (DAB) com-

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[2] ArN=CH-CH=NAr (3.0 g, 7.88 mmol) and AlMe$_3$ (7.9 cm^3, 2.0 M solution in toluene, 15.80 mmol) were refluxed in toluene (40 cm^3) for 12 h. The yellow solution was evaporated to dryness in vacuo, and the residue was extracted with hot acetonitrile (30 cm^3) to give pale-yellow needles of **1** (ca. 2 g) on prolonged standing (12 h) at ambient temperature. Further crops can be obtained by concentration and cooling of the mother-liquor. Overall yield 2.7 g, ca. 76%. Selected spectroscopic data for **1**: ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ: -0.39 (s, 6H, AlMe_2), 0.90 (d, 6H, $^3J_{HH}$ 6.8 Hz, CHMe_2), 1.23 (s, 3H, N=CMe), 1.26 (d, 6H, $^3J_{HH}$ 6.8 Hz, CHMe_2), 1.37 (d(bd), 6H, $^3J_{HH}$ 6.8 Hz, CHMe_2), 1.39 (d(bd), 6H, $^3J_{HH}$ 6.8 Hz, CHMe_2), 3.01 (spt, 2H, $^3J_{HH}$ 6.8 Hz, CHMe$_2$), 3.86 (spt, 2H, $^3J_{HH}$ 6.8 Hz, CHMe$_2$), 4.16 (s, 2H, NCH_2), 7.00–7.25 (3× m, 6H, arylH). ^{13}C NMR (C$_6$D$_6$, 100.6 MHz) δ: -8.03 (s, AlMe_2). M.S. (E.I.): 392 (M$^+$-AlMe$_2$).
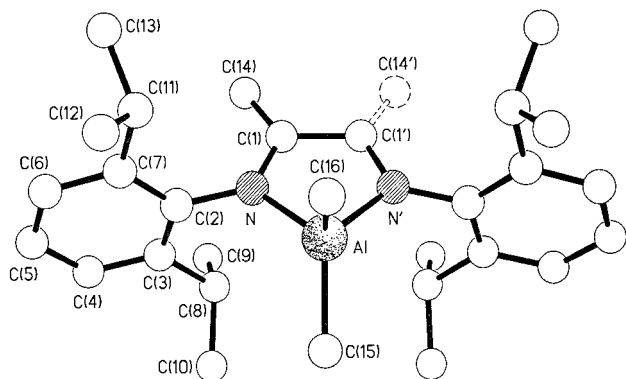

Fig. 1. The molecular structure of **1**. Key bond distances (Å) and angles (°): Al–N 1.919(2), Al–C(15) 1.958(4), Al–C(16) 1.970(5), N–C(1) 1.362(4), N–C(2) 1.442(3); N–Al–N′ 84.3(2), C(15)–Al–C(16) 113.4(2).
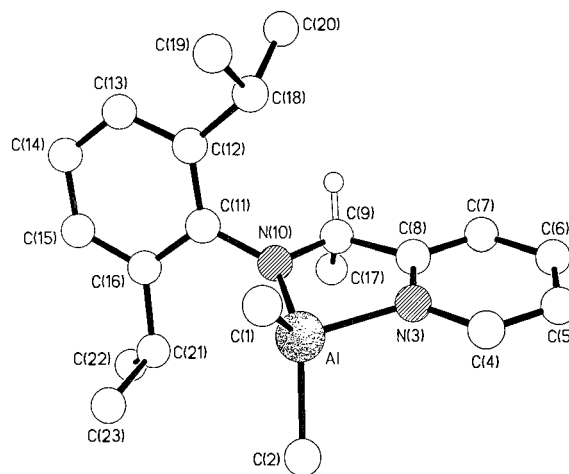
Fig. 2. The molecular structure of **2**. Key bond distances (Å) and angles (°): Al–N(3) 1.983(2), Al–N(10) 1.837(2), Al–C(1) 1.960(2), Al–C(2) 1.970(2), N(3)–C(8) 1.344(2), N(10)–C(9) 1.458(2), C(8)–C(9) 1.512(2); N(3)–Al–N(10) 84.48(6), C(1)–Al–C(2) 114.41(10).

plexes. Crystals of **1** suitable for an X-ray crystal structure determination [3] were grown from acetonitrile at room temperature. The asymmetric complex crystallises in the centrosymmetric space group *Pnma* with four molecules in the unit cell, thus requiring the molecule to have C_s symmetry about a plane passing through the aluminium and its two methyl substituents (Fig. 1). As a consequence the position of the 'transferred' methyl group [C(14)] is indeterminate, being either on C(1) or C(1′). [4] The coordination geometry at aluminium is distorted tetrahedral with angles ranging between 84.3(2) and 114.8(1)°, the former being due to the bite of the chelating imino-amide ligand. The heterometallocyclic ring has a slightly folded geometry with the aluminium atom lying 0.32 Å out of the plane of the other four atoms. The 2,6-diisopropylphenyl rings are each rotated by ca. 85° out of the metallocyclic ring plane, in contrast to derivatives containing sterically unhindered phenyl substituents in which one phenyl group is virtually coplanar with the AlN_2C_2 ring [6]. There is nothing noteworthy in the packing of the molecules.

A potentially powerful development of this approach is its extension to hybrid mono-anionic ligand systems. For example, treatment of the pyridyl-imine [ArN=CH-2-py] with trimethylaluminium affords a racemic mixture of the two enantiomers of the pyridyl-amide complex [AlMe₂{ArN-CH(Me)-2-py}] (**2**) [5] via a rearrangement process that is presumed to be analogous to that operating in the formation of **1**. Crystals of **2** suitable for an X-ray structure determination [6] were readily grown from acetonitrile at room temperature (Tables 1–5). The asymmetric unit contains four molecules of the metal complex. The molecular structure is shown in Fig. 2 and reveals the chiral nature of the ligand, though

[3] *Crystal data for* **1**: $C_{29}H_{44}N_2Al$, $M = 447.6$, orthorhombic, space group *Pnma* (no. 62), $a = 12.516(1)$, $b = 21.403(2)$, $c = 10.541(1)$ Å, $V = 2823.7(4)$ Å³, $Z = 4$ (the molecule has crystallographic C_s symmetry), $D_c = 1.053$ g cm⁻³, $\mu(Cu-K_\alpha) = 7.37$ cm⁻¹, $F(000) = 980$. A yellow prism of dimensions $0.33 \times 0.27 \times 0.20$ mm was used. 2153 independent reflections respectively were measured on a Siemens P4 rotating anode diffractometer at 213 K with Cu–K_α radiation (graphite monochromator) using ω-scans. The structure was solved by the heavy atom method and all the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give $R_1 = 0.064$, $wR_2 = 0.157$ for 1657 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$] and 155 parameters respectively.

[4] Analysis of the thermal vibration parameters of this atom clearly indicate that its occupancy should be 0.5, and hence the molecular image we observe is a consequence of the space group symmetry and the true structure has only one of the ring carbon atoms substituted.

[5] An analogous procedure to that described for the synthesis of compound **1** was employed, affording pale-yellow cubes of **2** in ca. 70% isolated yield. Selected spectroscopic data for **2**: ¹H NMR (C_6D_6, 500 MHz) δ: −0.34 (s, 3H, Al*Me*), −0.18 (s, 3H, Al*Me*), 1.18 (d, 3H, $^3J_{HH}$ 6.6 Hz, CH*Me*), 1.24 (d, 3H, $^3J_{HH}$ 6.8 Hz, CH*Me₂*), 1.29 (d, 3H, $^3J_{HH}$ 6.8 Hz, CH*Me₂*), 1.39 (d, 3H, $^3J_{HH}$ 6.9 Hz, CH*Me₂*), 1.42 (d, 3H, $^3J_{HH}$ 6.8 Hz, CH*Me₂*), 3.27 (spt, 1H, $^3J_{HH}$ 6.8 Hz, C*H*Me₂), 4.28 (spt, 1H, $^3J_{HH}$ 6.9 Hz, C*H*Me₂), 4.51 (q, 1H, $^3J_{HH}$ 6.6 Hz, C*H*Me), 6.25 (m, 1H, pyH), 6.48 (d, 1H, $^3J_{HH}$ 8.2 Hz, pyH), 6.74 (m, 1H, pyH), 7.23 (m, 2H, aryl), 7.29 (m, 1H, aryl), 7.58 (m, 1H, pyH). ¹³C NMR (C_6D_6, 100.6 MHz) δ: −9.23 (s, Al*Me*), −6.17 (s, Al*Me*). M.S. (E.I.): 338 (M⁺).

[6] *Crystal data for* **2**: $C_{21}H_{31}N_2Al$, $M = 338.5$, monoclinic, space group $P2_1/n$ (no. 14), $a = 14.420(2)$, $b = 9.296(1)$, $c = 16.879(2)$ Å, $\beta = 112.69(1)°$, $V = 2087.5(3)$ Å³, $Z = 4$, $D_c = 1.077$ g cm⁻³, $\mu(Cu-K_\alpha) = 8.57$ cm⁻¹, $F(000) = 736$. A yellow prism of dimensions $0.83 \times 0.67 \times 0.67$ mm was used. 3373 independent reflections respectively were measured on a Siemens P4 rotating anode diffractometer at 203 K with Cu–K_α radiation (graphite monochromator) using ω-scans. The structure was solved by the heavy atom method and all the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give $R_1 = 0.046$, $wR_2 = 0.116$ for 2923 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 128°$] and 218 parameters respectively.

Table 1
Crystal data and structure refinement for **1**

Identification code	VG9705
Empirical formula	$C_{21}H_{31}N_2Al$
Formula weight	338.46
Temperature	203(2) K
Diffractometer used	Siemens P4/RA
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 14.420(2)$ Å alpha $= 90°$
	$b = 9.2956(6)$ Å beta $= 112.688(8)°$
	$c = 16.879(2)$ Å gamma $= 90°$
Volume, Z	2087.5(3) Å^3, 4
Density (calculated)	1.077 Mg/m^3
Absorption coefficient	0.857 mm^{-1}
$F(000)$	736
Crystal morphology/size	Yellow prisms, $0.83 \times 0.67 \times 0.67$ mm
θ range for data collection	3.44 to 64.00°
Limiting indices	$-16 \leq h \leq 15$, $-4 \leq k \leq 10$,
	$-19 \leq 1 \leq 19$
Reflections collected	3512
Independent reflections	3373 ($R_{int} = 0.0406$)
Observed reflections	2923 $[F > 4\sigma(F)]$
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3372/0/218
Goodness-of-fit on F^2	1.060
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0456$, $wR_2 = 0.1159$
R indices (all data)	$R_1 = 0.0538$, $wR_2 = 0.1266$
Extinction coefficient	0.013(3)
Largest diff. peak and hole	0.208 and -0.196 eÅ^{-3}

Table 2
Atomic coordinates $[\times 10^4]$ and equivalent isotropic displacement parameters $[\text{Å}^2 \times 10^3]$ for **1**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
A1	4881(1)	2715(1)	1599(1)	33(1)
C(1)	5345(2)	3888(2)	2645(1)	47(1)
C(2)	5748(2)	2809(3)	940(1)	54(1)
N(3)	3567(1)	3342(2)	731(1)	34(1)
C(4)	3345(2)	4630(2)	335(1)	43(1)
C(5)	2423(2)	4920(2)	−290(1)	49(1)
C(6)	1701(2)	3858(2)	−523(1)	51(1)
C(7)	1923(2)	2530(2)	−124(1)	44(1)
C(8)	2873(1)	2292(2)	509(1)	35(1)
C(9)	3203(1)	880(2)	978(1)	35(1)
N(10)	4202(1)	1067(2)	1647(1)	32(1)
C(11)	4474(1)	32(2)	2321(1)	33(1)
C(12)	4011(1)	54(2)	2925(1)	39(1)
C(13)	4283(2)	−992(2)	3569(1)	50(1)
C(14)	5006(2)	−2015(2)	3640(1)	53(1)
C(15)	5484(2)	−1996(2)	3076(1)	46(1)
C(16)	5232(1)	−995(2)	2410(1)	37(1)
C(17)	3164(2)	−323(2)	341(1)	54(1)
C(18)	3270(2)	1216(2)	2928(1)	45(1)
C(19)	3655(2)	2050(3)	3781(1)	61(1)
C(20)	2226(2)	606(3)	2753(2)	64(1)
C(21)	5806(2)	−983(2)	1821(1)	44(1)
C(22)	5943(2)	−2479(3)	1504(2)	74(1)
C(23)	6830(2)	−255(3)	2269(2)	67(1)

Table 3
Bond lengths [Å] and angles [°] for **1**

Al–N(10)	1.837(2)	Al–C(1)	1.960(2)
Al–C(2)	1.970(2)	Al–N(3)	1.983(2)
N(3)–C(8)	1.344(2)	N(3)–C(4)	1.348(2)
C(4)–C(5)	1.368(3)	C(5)–C(6)	1.377(3)
C(6)–C(7)	1.384(3)	C(7)–C(8)	1.392(3)
C(8)–C(9)	1.512(2)	C(9)–N(10)	1.458(2)
C(9)–C(17)	1.538(3)	N(10)–C(11)	1.426(2)
C(11)–C(16)	1.415(3)	C(11)–C(12)	1.417(2)
C(12)–C(13)	1.397(3)	C(12)–C(18)	1.522(3)
C(13)–C(14)	1.382(3)	C(14)–C(15)	1.374(3)
C(15)–C(16)	1.395(3)	C(16)–C(21)	1.521(3)
C(18)–C(20)	1.527(3)	C(18)–C(19)	1.539(3)
C(21)–C(22)	1.529(3)	C(21)–C(23)	1.533(3)
N(10)–Al–C(1)	115.27(8)	N(10)–Al–C(2)	121.82(9)
C(1)–Al–C(2)	114.41(10)	N(10)–Al–N(3)	84.48(6)
C(1)–Al–N(3)	113.48(8)	C(2)–Al–N(3)	101.78(8)
C(8)–N(3)–C(4)	119.9(2)	C(8)–N(3)–Al	112.91(12)
C(4)–N(3)–Al	127.13(13)	N(3)–C(4)–C(5)	122.1(2)
C(4)–C(5)–C(6)	118.8(2)	C(5)–C(6)–C(7)	119.5(2)
C(6)–C(7)–C(8)	119.4(2)	N(3)–C(8)–C(7)	120.3(2)
N(3)–C(8)–C(9)	115.8(2)	C(7)–C(8)–C(9)	123.9(2)
N(10)–C(9)–C(8)	108.59(14)	N(10)–C(9)–C(17)	112.8(2)
C(8)–C(9)–C(17)	110.29(14)	C(11)–N(10)–C(9)	115.05(13)
C(11)–N(10)–Al	127.65(11)	C(9)–N(10)–Al	116.75(11)
C(16)–C(11)–C(12)	119.5(2)	C(16)–C(11)–N(10)	120.2(2)
C(12)–C(11)–N(10)	120.3(2)	C(13)–C(12)–C(11)	118.8(2)
C(13)–C(12)–C(18)	118.5(2)	C(11)–C(12)–C(18)	122.6(2)
C(14)–C(13)–C(12)	121.5(2)	C(15)–C(14)–C(13)	119.6(2)
C(14)–C(15)–C(16)	121.5(2)	C(15)–C(16)–C(11)	119.1(2)
C(15)–C(16)–C(21)	119.6(2)	C(11)–C(16)–C(21)	121.3(2)
C(12)–C(18)–C(20)	112.2(2)	C(12)–C(18)–C(19)	111.1(2)
C(20)–C(18)–C(19)	110.0(2)	C(16)–C(21)–C(22)	113.4(2)
C(16)–C(21)–C(23)	110.2(2)	C(22)–C(21)–C(23)	110.1(2)

Table 4
Anisotropic displacement parameters $[\text{Å}^2 \times 10^3]$ for **1**. The anisotropic displacement factor exponent takes the form:

$$-2\pi^2\left[(ha^*)^2 U_{11} + \ldots + 2hka^*b^*U_{12}\right]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
A1	32(1)	38(1)	30(1)	1(1)	14(1)	−3(1)
C(1)	52(1)	46(1)	41(1)	−2(1)	15(1)	−8(1)
C(2)	50(1)	68(2)	54(1)	−1(1)	30(1)	−7(1)
N(3)	39(1)	39(1)	27(1)	3(1)	16(1)	0(1)
C(4)	50(1)	44(1)	36(1)	7(1)	18(1)	1(1)
C(5)	57(1)	51(1)	39(1)	13(1)	18(1)	11(1)
C(6)	46(1)	66(1)	35(1)	9(1)	11(1)	11(1)
C(7)	37(1)	57(1)	34(1)	2(1)	9(1)	1(1)
C(8)	36(1)	44(1)	26(1)	−1(1)	15(1)	1(1)
C(9)	33(1)	40(1)	30(1)	0(1)	11(1)	−3(1)
N(10)	31(1)	36(1)	27(1)	3(1)	9(1)	−1(1)
C(11)	35(1)	33(1)	28(1)	0(1)	9(1)	−5(1)
C(12)	42(1)	41(1)	33(1)	1(1)	14(1)	−7(1)
C(13)	63(1)	52(1)	39(1)	7(1)	22(1)	−9(1)
C(14)	70(1)	42(1)	40(1)	11(1)	12(1)	−4(1)
C(15)	54(1)	35(1)	39(1)	1(1)	5(1)	2(1)
C(16)	39(1)	35(1)	31(1)	−3(1)	7(1)	−2(1)
C(17)	57(1)	48(1)	45(1)	−12(1)	8(1)	−1(1)
C(18)	50(1)	52(1)	42(1)	3(1)	27(1)	−2(1)
C(19)	76(2)	65(2)	51(1)	−5(1)	35(1)	1(1)
C(20)	51(1)	86(2)	63(1)	5(1)	32(1)	−3(1)
C(21)	44(1)	48(1)	38(1)	−1(1)	13(1)	9(1)
C(22)	102(2)	61(2)	66(2)	−5(1)	40(2)	22(1)
C(23)	43(1)	98(2)	59(1)	2(1)	18(1)	−3(1)

Table 5
Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1**

	x	y	z	U_{eq}
H(1A)	4881(2)	3786(2)	2932(1)	70
H(1B)	5375(2)	4890(2)	2495(1)	70
H(1C)	6008(2)	3570(2)	3025(1)	70
H(2A)	5470(2)	2203(3)	435(1)	81
H(2B)	6417(2)	2474(3)	1296(1)	81
H(2C)	5784(2)	3794(3)	766(1)	81
H(4A)	3840(2)	5352(2)	494(1)	51
H(5A)	2285(2)	5827(2)	−556(1)	59
H(6A)	1062(2)	4034(2)	−951(1)	61
H(7A)	1438(2)	1796(2)	−278(1)	53
H(9A)	2731(1)	632(2)	1255(1)	42
H(13A)	3966(2)	−999(2)	3963(1)	61
H(14A)	5170(2)	−2719(2)	4072(1)	64
H(15A)	5992(2)	−2673(2)	3140(1)	56
H(17A)	3377(2)	−1223(2)	649(1)	81
H(17B)	3609(2)	−85(2)	51(1)	81
H(17C)	2482(2)	−422(2)	−80(1)	81
H(18A)	3208(2)	1906(2)	2463(1)	54
H(19A)	3170(2)	2783(3)	3767(1)	91
H(19B)	4292(2)	2502(3)	3865(1)	91
H(19C)	3746(2)	1391(3)	4251(1)	91
H(20A)	1778(2)	1380(3)	2760(2)	96
H(20B)	2269(2)	−93(3)	3193(2)	96
H(20C)	1967(2)	143(3)	2195(2)	96
H(21A)	5417(2)	−398(2)	1310(1)	53
H(22A)	6314(2)	−2399(3)	1133(2)	111
H(22B)	5290(2)	−2902(3)	1187(2)	111
H(22C)	6313(2)	−3084(3)	1993(2)	111
H(23A)	7190(2)	−253(3)	1888(2)	101
H(23B)	7217(2)	−778(3)	2789(2)	101
H(23C)	6732(2)	728(3)	2414(2)	101

in this instance crystallisation has occurred in a centrosymmetric space group [$P2_1/n$] and thus there are equal numbers of D and L forms. Clearly, in this structure the transfer of the methyl group to the C(9) position is definitive. The geometry at aluminium is distorted tetrahedral with angles in the range 84.5(1) to 121.8(1)°, the former angle, as in **1**, corresponding to the bite of the chelating ligand. The two Al–N bonds are noticeably asymmetric with that to the pyridine nitrogen atom [1.983(3) Å] being typical while that to the amido nitrogen [N(10)] is appreciably shorter at 1.837(2) Å. The five-membered metallocyclic ring has a slightly folded geometry with the aluminium atom lying 0.24 Å out of the plane of the other four ring atoms. As observed in **1**, the 2,6-diisopropylphenyl ring is orientated almost orthogonally [75°] with respect to the metallocyclic ring plane. The molecules are loosely packed ($D_c = 1.08$ g cm^{-3}) and there are no notable strong intermolecular interactions.

Hydrolysis of **1** and **2** readily and quantitatively releases the free imino-amine [ArNH-CH$_2$-C(Me)=NAr] and pyridyl-amine [ArNH-CH(Me)-2-py] respectively. The use of these bulky monoanionic ligands in transition metal chemistry will be published elsewhere.

References

[1] G. van Koten, K. Vrieze, Adv. Organomet. Chem. 21 (1982) 151.
[2] L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414.
[3] L.K. Johnson, S. Mecking, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 267.
[4] C.M. Killian, D.J. Tempel, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 11994.
[5] J.M. Klerks, D.J. Stufkens, G. van Koten, K. Vrieze, J. Organomet. Chem. 181 (1979) 271.
[6] J.A. Kanters, G.P.M. van Mier, R.L.L.M. Nijs, F. van der Steen, G. van Koten, Acta Cryst. C44 (1988) 1391.