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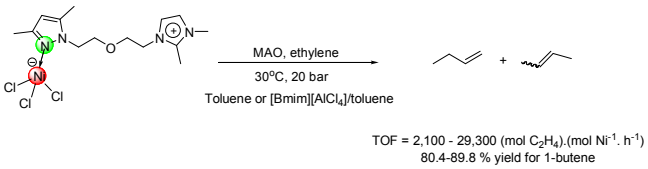

Nickel complexes bearing pyrazolyl-ether-imidazolium monodentate ligands have been synthesized and their catalytic behavior in ethylene oligomerization has been investigated in homogeneous and biphasic phase.

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ARTICLE

Zwitterionic Ni(II) Complexes Bearing Pyrazolyl-Ether-Imidazolium Ligands: Synthesis, Structural Characterization and use in Ethylene Oligomerization

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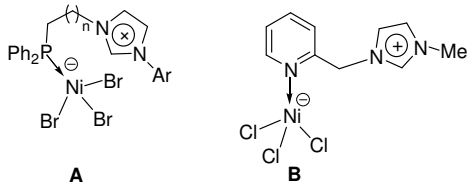
A series of new tetracoordinated Ni(II) complexes of general formula $NiCl_3(L)$ (**Ni1**, L = 1-(2-(2-methylimidazole-ethoxy)ethyl)-3,5-dimethylpyrazole; **Ni2**, L = 1-(2-(1,2-dimethylimizadole-ethoxy)ethyl)-pyrazole; **Ni3**, L = 1-(2-(1,2-dimethylimizadole-ethoxy)ethyl)-3,5-dimethyllpyrazole; **Ni4**, L= 1-(2-(2-*n*-butylimizadole-ethoxy)ethyl)-3,5-dimethylpyrazole) were prepared in high yields. All these complexes were characterized by elemental analysis, and X-ray crystallography was performed for **Ni1**, **Ni2**, and **Ni3**. In the solid state, these nickel complexes are monomeric with the pyrazolyl-ether-imidazolium acting as a monodentate ligand. The positive charge on the imidazolium unit is cancelled out by the negative charge that is provided by the third chloride ion linked to Ni(II), forming a zwitterionic structure. Upon activation with methylaluminoxane (MAO) or ethylaluminum sesquichloride (EASC), these complexes show moderate activity in ethylene oligomerization (TOF = 2,100-29,300 (mol C_2H_4)·(mol Ni^{-1} h^{-1}] with good selectivities for 1-butene (80.4–89.8 wt% of total products), which vary according to the ligand environment. Under biphasic conditions, the **Ni3**/[Bmim]·[$AlCl_4$]/toluene catalytic system proved to be active for ethylene oligomerization with TOF of 10,700 (mol C_2H_4)·(mol Ni^{-1} h^{-1}) and highly selective towards production of 1-butene (90.9 wt%).

Introduction

The oligomerization of ethylene is one of the most important industrial processes to obtain linear α-olefins (LAOs).[1] These substrates have been extensively used for preparing detergents, lubricants, plasticizers, and oil field chemicals or as monomers for copolymers, etc.[2] Many efforts are still devoted to the development of highly selective ethylene oligomerization catalysts, and among classes of catalysts used for production of α-olefins, nickel complexes containing bidentate[3] and tridentate[4] chelating ligands are the most frequently studied. However, while several classes of Ni(II) complexes bearing heterobi- and tridentate *N*-heterocyclic carbene ligands have been described in the literature,[5] just a very few examples have been used in ethylene oligomerization.[6] Especially, Ni(II) compounds of general formula $[NiX_3L]$ (X = Br, Cl; L = functionalized-imidazolium ligand) have been restrictedly used in Grignard cross-coupling,[7] and ethylene polymerization reactions.[8] In this case, the functionalized-imidazolium acts as a monodentate ligand promoting the formation of zwitterionic complexes that feature formal charge separation between an anionic nickel fragment and a positively charged imidazolium moiety within an overall neutral molecular framework. Thus, Poli *et al.* showed that zwitterionic Ni(II) complexes containing a monodentate phosphine–imidazolium ligand (**A**) were very active catalysts for the cross-coupling of aryl Grignard reagents with aryl chlorides.[7b,c] Jin *et al.* described a catalytic system, based on pyridyl-imidazolium nickel(II) complex (**B**) capable to polymerize ethylene in presence of MAO producing high-density polyethylene.[8]



A **B**

Chart 1. Examples of structurally characterized nickel complexes bearing functionalized-imidazolium ligands.[7b-c,8]

In the last years, several classes of functionalized-imidazolium ligands bearing kinetically inert coordination groups, such as pyridyl,[8,9] bipyridyl,[10] pyrazolyl,[11] phenantroline,[12] phosphine,[7,13] furan,[14] phthalimido,[15] thioether,[16] and oxazolyl,[17] have been synthesized and used in coordination chemistry,[18] homogeneous and biphasic phase catalytic processes. In this latter case, the use of

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† Electronic Supplementary Information (ESI) available: Crystallographic data for **L1**^{PF6}, **L3**^{PF6}, **Ni1**, **Ni2** and **Ni3**. See DOI: 10.1039/x0xx00000x

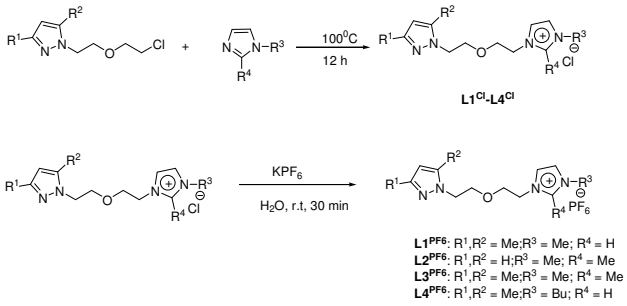
functionalized-imidazolium ligands is especially suitable to avoid catalyst leaching from the ionic liquid (IL) layer.[19] Moreover, the resulting ionic catalyst should be completely soluble in IL and would allow the ethylene oligomerization to be carried out under standard homogeneous conditions.

Over the past few years, pyrazolyl-based ligand metal complexes have attracted attention as efficient catalysts for oligo- and polymerization of ethylene.[20] Our group has been interested in exploring the potential applications of such pyrazolyl-based ligands in the oligomerization catalysis field.[21] Herein, we report the synthesis and structural characterization of several new zwitterionic Ni(II) complexes bearing pyrazolyl-ether-imidazolium ligands. Their catalytic behavior for ethylene oligomerization upon activation with MAO has been investigated. We discuss the performance of these catalysts, evaluating the role of the ligand, and the experimental parameters on the activity and selectivity towards the production of 1-butene.

Results and discussion

Synthesis and Characterization of the Pyrazolyl-ether-imidazolium ligands and Nickel Complexes

The pyrazolyl-ether-imidazolium ligands **L1^{Cl}-L4^{Cl}** were prepared by reaction of 1-(2-(2-chloroethoxy)ethyl)-3,5-dimethyl-1-pyrazole with the appropriate imidazole in moderate to good yields (60–95%) as shown in Scheme 1. The chloride counterion can be exchanged for hexafluorophosphate using KPF_6 in water to afford the hexafluorophosphate salts **L1^{PF6}-L4^{PF6}** in good yields (typically 68–85%, Scheme 1). The identity of this class of ligands was established by IR and NMR spectroscopy, elemental analysis, and by an X-ray diffraction study for ligands **L1^{PF6}** and **L3^{PF6}**.



Scheme 1

Single crystals of **L1^{PF6} and L3^{PF6}** suitable for an X-ray diffraction analysis were obtained by recrystallization from CH_2Cl_2/pentane solutions at room temperature. The molecular geometry and atom-labeling scheme are shown in Figures 1 and 2. Crystallographic data are summarized in Table S1.

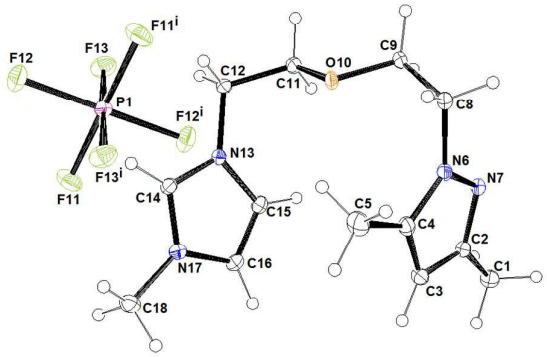


Fig. 1 ORTEP drawing of **L1^{PF6}**. Ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): N6–N7 = 1.3628(17), C9–O10 = 1.4300(15), O10–C11 = 1.4179(16), N13–C14 = 1.3291(18), C14–N17 = 1.3260(18), N13–C15 = 1.3773(19), C16–N17 = 1.3775(19), C15–C16 = 1.348(2), N17–C18 = 1.4730(18). C11–O10–C9 = 112.70(10), N6–C8–C9 = 111.18(11), N13–C12–C11= 111.88(11).

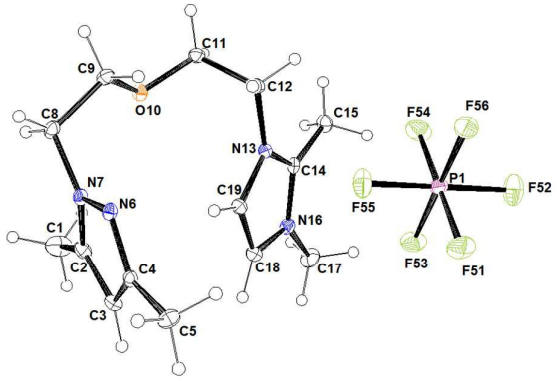
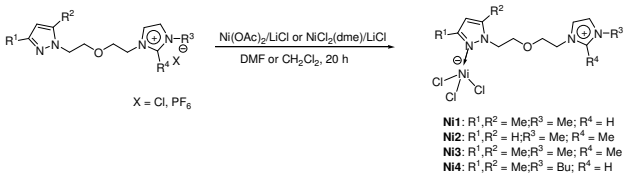


Fig 2 ORTEP drawing of **L3^{PF6}**. Ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): N6–N7 = 1.3695(17), C9–O10 = 1.4287(18), O10–C11 = 1.4262(18), C14–N16 = 1.335(2), N13–C14 = 1.338(2), N13–C19 = 1.3759(19), N16–C18 = 1.379(2), C18–C19 = 1.345(2). C11–O10–C9 = 113.58(12), N7–C8–C9 = 112.57(13), N13–C12–C11 = 110.86(13).

The reaction of $Ni(OAc)_2$ with the pyrazolyl-ether-imidazolium salt was initially chosen in an attempt to prepare carbene-Ni(II) complexes and to study the coordination behavior of pyrazolyl-ether-functionalized NHC ligands. However, reacting $Ni(OAc)_2$/LiCl (2 equiv) with **L1^{Cl}–L4^{Cl}** (1 equiv) in DMF at room temperature leads to the corresponding pyrazole-coordinated nickel complexes (**Ni1–Ni4**), which were isolated as blue solids in high yields (typically 81–88%) (Scheme 2). Alternatively, **Ni1–Ni4** can be obtained by reaction of $NiCl_2$(dme)/LiCl (1 equiv) with **L1–L4^{PF6}** in CH_2Cl_2 at room temperature.



Scheme 2

Single crystals of **Ni1, Ni2** and **Ni3** suitable for X-ray diffraction were grown from a concentrated acetonitrile/ether solution (80:20) at room temperature. In the solid state, these three complexes are monomeric with a four-coordinated nickel center in a slightly distorted tetrahedral geometry with the pyrazolyl-ether-imidazolium acting as a monodentate ligand (Figures 3-5). Two independent molecules were found in the asymmetric unit of **Ni1**, but the two molecules are quite similar so that only the distances and the angles for one of them are listed in Figure 3. The nickel center is coordinated by the nitrogen atom of the pyrazolyl group and by three chloride atoms. The positive charge on the imidazolium unit is cancelled out by the negative charge that is provided by the third chloride ion linked to Ni(II), forming a zwitterionic structure. The Ni–N bond distance [2.0131(13) Å for **Ni1**, 1.9968(16) Å for **Ni2** and 2.0133(13) Å for **Ni3**] are close to the values previously reported for Ni(II) complexes having pyrazole ligands.[21a-d,22] The average Ni–Cl_{av} bond distances are 2.2508 Å for **Ni1**, 2.2605 Å for **Ni2**, and 2.2543 Å for **Ni3**. These values are unexceptional and lie within the ranges found for other complexes containing $[Ni(L)X_3]^-$ anions.[7,8] The three Cl–Ni–Cl angles show a significant deviation from their mean values, 112.8(1) °, with two values greater than the ideal tetrahedral angle. In particular, for **Ni3**, the Cl(1)–Ni–Cl(3) angle is significantly wider [122.49(4) °] than the other two Cl–Ni–Cl angles. This could be attributed to the establishment of a hydrogen bonding interaction between the C(20) and C(6) hydrogen atoms and the chloride atoms Cl(1) and Cl(3), respectively. In this case, the Cl(1)–H(20) and Cl(3)–H(6) distances are 2.838 Å and 2.737 Å, which are shorter than the sum of the van der Waals radii of H and Cl. The internal bond distances and angles of the imidazolium ring are unexceptional and lie within the expected range.[23]

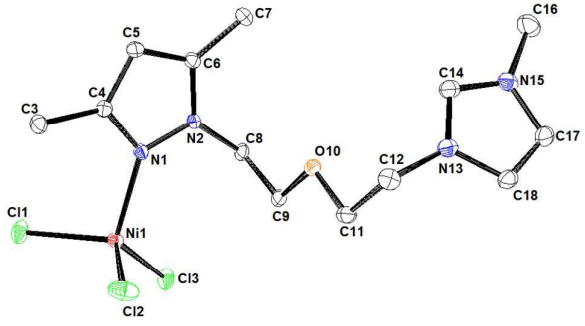


Fig. 3 ORTEP drawing of **Ni1**. Ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni1–Cl1 = 2.2438(5), Ni1–Cl2 = 2.2398(5), Ni1–Cl3= 2.2687(4), Ni1–N1 = 2.013(1), C12–N13 = 1.472(2), N2–C8 = 1.463(2), O10–C11 = 1.429(2), C9–O10 = 1.426(2), N13–C18 = 1.380(2), N1–N2 = 1.368(2), N15–C17 = 1.365(2), C17–C18 = 1.344(2), C14–N15 =1.341(2), N13–C14 = 1.320(2). N1–Ni1–Cl2 = 101,75(4). N1–Ni1–Cl3 = 114.34(4), N2–N1–Ni1 = 129.73(9), Cl2–Ni1–Cl1 = 115.19(2), Cl1–Ni1–Cl3 = 102.99(2), Cl2–Ni1–Cl3 = 117.64(2).

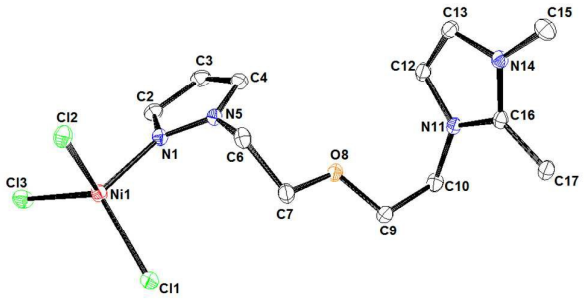


Fig. 4 ORTEP drawing of **Ni2**. Ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni1–N1 = 2.0039(16), Ni1–Cl1 = 2.2493(6), Ni1–Cl2 = 2.2665(6), Ni1–Cl3 = 2.2755(6), C10–N11 = 1.470(3), N5–C6 = 1.463(3), C7–O8 = 1.422(2), O8–C9 = 1.426(2), N11–C16 = 1.345(2), N11–C12 = 1.383(3), N14–C16 = 1.342(3), N14–C15 = 1.463(3), C13–N14 = 1.389(3), C12–C13 = 1.345(3), N1–N5 = 1.361(2). N1–Ni1–Cl1 = 108.77(5), N1–Ni1–Cl2 = 103.47(5), Cl1–Ni1–Cl2 = 108.78(2), N1–Ni1–Cl3 = 104.66(5), Cl1–Ni1–Cl3 = 120.82(2), Cl2–Ni1–Cl3 = 108.93(2).

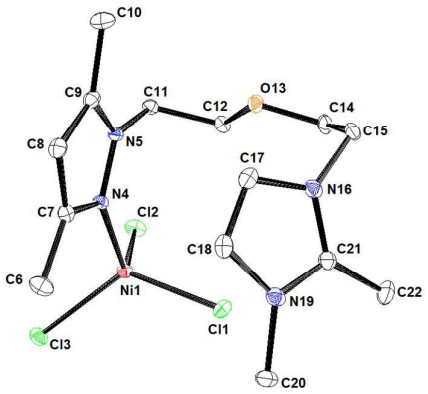


Fig. 5 ORTEP drawing of **Ni3**. Ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni1–N4 = 2.0133(13), Ni1–Cl1 = 2.2408(4), Ni1–Cl2 = 2.2537(5), Ni1–Cl3 = 2.2685(4), C15–N16 = 1.461(2), N5–C11 = 1.459(2), C12–O13 = 1.4194(19), O13–C14 = 1.419(2), C21–C22 = 1.475(2), N16–C21 = 1.337(2), N19–C21 = 1.330(2), C18–N19 = 1.392(2), N16–C17 = 1.392(2), C17–C18 = 1.329(3), N4–N5 = 1.3684(18). N4–Ni1–Cl1 = 100.90(4),

N4–Ni1–Cl2 = 112.10(4), Cl1–Ni1– Cl2 = 111.659(18), N4–Ni1–Cl3 = 109.30(4), Cl1–Ni1–Cl3 = 122.493(18), Cl2–Ni1–Cl3 = 100.687(17)

Ethylene Oligomerization Studies

Nickel complexes **Ni1**–**Ni4** were evaluated in ethylene oligomerization at 30 °C, 20 bar constant ethylene pressure, and using methylaluminoxane (MAO) as cocatalyst. Table 1 summarizes the results of reactions carried out using 10 µmol of precatalyst in 40 mL of a toluene. All experiments were at least duplicated, yielding reproducible results within ±10%.

Table 1 Ethylene Oligomerization with **Ni1–Ni4** catalytic systems.[a]

entry	cat	Olig. (g)	TOF[b] (x10^3)	selectivity(wt%)	
				C_4 (α-C_4)	C_6 (α-C_6)
1	**Ni1**	0.30	3.20	94.1 (93)	5.9 (59)
2	**Ni2**	0.56	6.00	94.6 (85)	5.4 (27)
3	**Ni3**	0.72	7.80	97.6 (92)	2.4 (50)
4	**Ni4**	0.20	2.10	95.3 (84)	4.7 (30)
5[d]	**Ni3**	0.17	1.82	95.4 (88.5)	4.6 (41)
6[e]	**Ni3**	0.32	3.42	97.2 (91)	2.8 (51)
8[f]	**Ni3**	2.74	29.3	98.1 (81.1)	1.9 51
7[g]	**Ni3**	9.71	104.0	85.2 (49.3)	14.8 (11.9)
9[h]	**Ni3**	1.00	10.7	95.7 (95)	4.3 (53)

[a] Reaction conditions: toluene = 40 mL, [Ni] = 10 µmol, oligomerization time = 20 min, P(ethylene) = 20 bar (kept constant), T = 30 °C, MAO(Al)/[Ni] = 300. The results shown are representative of at least duplicated experiments. [b] Mol of ethylene converted (mol of Ni)$^{-1}$·h^{-1} as determined by quantitative GLC. [d] T = 50 °C. [e] [Al]/[Ni] = 1,000. [f] EASC as cocatalyst, [Al]/[Ni] = 50. [g] CH_2Cl_2 as solvent. [h] oligomerization reaction performed in ionic liquid [Bmim]·[$AlCl_4$].

All the nickel complexes investigated have been found to generate active systems for the production of short-chain olefins in the C_4–C_6 range. The oligomerization results showed that the substituent at the C2 position of the imidazolium group influenced the catalytic performance of the nickel catalysts on ethylene oligomerization. Thus, the catalytic systems based on **Ni1/Ni4** were found to give lower activities [TOF = 2,100–3,200 (mol C_2H_4)·(mol Ni^{-1} h^{-1})] as compared to the performance of **Ni2/Ni3** [TOF = 6,000–7,800 (mol C_2H_4)·(mol Ni^{-1} h^{-1})]. This can be tentatively attributed to the reaction of acidic proton at the C2 position of the imidazolium cation in **Ni1/Ni4** with methylaluminoxane. Overall, this class of catalysts showed lower activities than other classes of nickel precatalysts bearing bi- and tridentate pyrazolyl ligands. We surmise that this can be tentatively associated to the lower stability of **Ni1–Ni4** as a consequence of the monodentate coordination mode of the pyrazolyl-ether-imidazolium ligands.

For all nickel complexes (**Ni1–Ni4**), the selectivity for butenes and especially 1-butene were similar (80.4–89.8 wt%) indicating that the variation of steric hindrance on the pyrazolyl group (H, Me) had little influence on the product distribution. This observation is in agreement with previous ethylene oligomerization results using MAO-activated nickel complexes bearing pyrazolyl ligands.[21a,21c,21e] In all cases, minimal amounts of hexenes (2.4–5.9 wt%) were detected with poor selectivity for 1-hexene (1.2–3.4 wt%).

The preliminary study was extended to investigate the effect of temperature, [Al]/[Ni] molar ratio, cocatalyst type, and solvent on the catalytic performance of the **Ni3**/MAO (Table 1, entries 5–9). Elevating the temperature from 30 °C to 50 °C led to a reduction in activity [TOF = 1,820 (mol C_2H_4)·(mol Ni^{-1} h^{-1})], suggesting that a partial decomposition of the active catalytic species took place. However, upon elevating the temperature from 30 to 50 °C, the 1-butene selectivity remained at the same level (84.4 wt%).

Increasing the [Al]/[Ni] molar ratio from 300 to 1,000 negatively affected the catalytic performance of nickel precatalyst. Thus, with 1,000 equiv of MAO, a lower activity [TOF = 3,420 (mol C_2H_4)·(mol Ni^{-1} h^{-1}), entry 6] was observed. On the other hand, the use of higher amounts of MAO had little impact on the selectivity for α-C_4 that remained in the same level (88.4 wt%) as compared to that one obtained using 300 equiv of MAO. Quite interestingly, activation of nickel precatalyst **Ni3** with 50 equiv of ethylaluminum sesquichloride ($Et_3Al_2Cl_3$, EASC) instead of MAO produced a much more active system [29,300 (mol C_2H_4)·(mol Ni^{-1} h^{-1}], along with a high, although lower selectivity for 1-butene (79.5 wt%). It is worth noting that, even upon using a lower amount of EASC (50 equiv), **Ni3** led to a much more active system than that based on $NiCl_2${3,5-dimethyl-1-(3-phenoxypropyl)-1H-pyrazole} [EASC = 100 equiv, TOF = 5500 (mol C_2H_4)·(mol Ni^{-1} h^{-1}] under identical oligomerization conditions.[21g]

Performing the oligomerization reaction in a more polar solvent, such as dichloromethane, led to a much higher TOF [104,000 (mol C_2H_4)·(mol Ni^{-1} h^{-1}]. This high activity generated significant exothermicity, so that the reaction with **Ni3**/MAO performed at an initial temperature of 30 °C (entry 7) rapidly rose to 45–50 °C, despite the thermostating fluid around the reactor. Although the catalyst activity was improved by approximately 13-fold, the selectivity for 1-butene was drastically reduced, attaining only 42 wt% with a concomitant production of larger amounts of internal butenes (43.2 wt%) and hexenes (14.8 wt%). We assume that, in polar solvents, dissociation of cationic active Ni-complex ion pairs is made easier, which may favour chain transfer reactions and isomerization, accounting for the lower selectivity.[24]

In order to investigate the catalytic behaviour of this nickel(II) zwitterionic complex under biphasic conditions, we carried out an oligomerization reaction using **Ni3** in an organoaluminate ionic liquid/toluene solvent system. Chloroaluminate 1-*n*-butyl-3-methylimidazolium ionic liquid ([Bmim]·[$AlCl_4$]) was chosen because of it renown good dissolution abilities for metal complexes and its convenient preparation.[25] Thus, the ethylene oligomerization was performed using a solution of the nickel precatalyst **Ni3** dissolved in [Bmim]·[$AlCl_4$] (3 mL), toluene (40 mL) and MAO (250 equiv) at 30 °C and 20 bar constant ethylene pressure. Under these reaction conditions, ethylene oligomerization proceeded with a TOF slightly higher than in homogeneous phase [10,700 (mol C_2H_4)·(mol Ni^{-1} h^{-1}), entry 9]. This activity is comparable to previously reported

biphasic oligomerization systems using nickel complexes; however, the **Ni3**/[Bmim]·[$AlCl_4$]/toluene catalytic system showed a higher selectivity towards production of 1-butene (90.9 wt%) as compared to similar biphasic nickel-catalyzed ethylene oligomerization (21-83 wt%).[25, 25a-c]

Conclusions

Zwitterionic nickel complexes bearing pyrazolyl-ether-imidazolium ligands have been synthesized and structurally characterized. Upon activation with MAO or EASC co-catalysts, these Ni(II) complexes show moderate to high catalytic activity for ethylene oligomerization with good selectivity for 1-butene. The substituent at the C2 position of the imidazolium group influenced the catalytic performance of the nickel precatalysts; lower activities were found using **Ni1** and **Ni4**, suggesting a possible reaction between the acidic proton at the C2 position of the imidazolium cation and methylaluminoxane. Preliminary results using **Ni3** under biphasic conditions showed that this catalyst was able to oligomerize ethylene with good activity and improved selectivitys for 1-butene. Further studies are underway in our laboratories to investigate the recyclability and reuse of this catalytic system as well as the influence of oligomerization parameters on the activity and selectivity towards production of 1-butene.

Experimental

General Procedures

All manipulations involving air- and/or moisture-sensitive compounds were carried out in an MBraun glovebox or under dry argon using standard Schlenk techniques. Solvents were dried from the appropriate drying agents under argon before use. $Ni(OAc)_2$, $NiCl_2$(dme) bis-(2-chloroethyl)ether, 1-methylimidazole, 1-*n*-butylimidazole, and 1,2-dimethylimidazole were purchased from Sigma-Aldrich and used as received. Ethylene (White Martins Co.) and argon were deoxygenated and dried through BTS columns (BASF) and activated molecular sieves prior to use. 1-(2-(2-Chloroethoxy)ethyl)-3,5-dimethyl-1H-pyrazole was prepared by following literature procedures.[26] The ionic liquid [Bmim]·[$AlCl_4$] was obtained by reacting 1-*n*-butyl-3-methylimidazolium chloride ([Bmim]Cl) with aluminum chloride, as described in the literature.[27] MAO (AXION® CA 1310, 10 wt.-% solution in toluene) was used as received. EASC (Akzo Nobel) was used with the previous dilution (2.1 wt.% Al solution in toluene). Infrared spectra were performed using neat products in KBr pellets on a FT-IR Bruker Alpha Spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 25 °C on a Varian Inova 300 spectrometer operating at 300 MHz. Chemical shifts are reported in ppm vs. $SiMe_4$ and were determined by reference to the residual solvent peaks. Elemental analyses were performed by the Analytical Central Service of the Institute of Chemistry-USP (Brazil) and is the average of two independent determinations. Quantitative gas chromatographic analysis of ethylene oligomerization products was performed on a Agilent 7890A instrument equipped with a Petrocol HD capillary column (methyl silicone, 100 m length, 0.25 mm i.d. and film thickness of 0.5 µm) (36 °C for 15 min, then heating at 5 °C·min^{-1} until 250 °C); cyclohexane was used as internal standard.

Synthesis of the pyrazolyl-ether-imidazolium ligands

[1-(2-(2-methylimidazole-ethoxy)ethyl)-3,5-dimethylpyrazole]$^+$Cl$^-$ (**L1^{Cl}**)

A reaction vessel was charged with 1-(2-(2-chloroethoxy)ethyl)-3,5-dimethyl-1-pyrazole (1.23 g, 6.1 mmol), and 1-methylimidazole (1.15 g, 14.0 mmol). The vessel was closed and stirred overnight at 100 °C. The crude product was extracted with toluene (3 x 10 mL) and the solvent was removed under vacuo to afford a beige solid. Recrystallization from THF yielded a white solid (1.14 g, 65%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ 2.19 (3H, s), 2.22 (3H, s), 3.81 (4H, m), 4.05 (3H, s), 4.14 (2H, t, $^3J_{HH}$ = 5.2 Hz), 4.56 (2H, t, $^3J_{HH}$ = 4.6 Hz), 5.80 (1H, s), 7.34 (1H, t, $^3J_{HH}$ = 1.8 Hz), 7.42 (1H, t, $^3J_{HH}$ = 1.6 Hz), 10.30 (1H, s). ^{13}C{^{1}H} NMR (75 MHz, 298 K, $CDCl_3$): 10.8 (Pz 5-CH_3), 13.3 (Pz 3-CH_3), 35.9 (Im 3-CH_3), 47.9 (CH_2), 49.4 (CH_2), 68.2 (O-CH_2), 69.5 (O-CH_2), 104.9 (Pz 4-C), 122.9 (Im 2-C), 122.9 (Im 3-C), 135.9 (Im 2-C), 139.9 (Pz 5-C), 147.4 (Pz 3-C). Anal. calcd. for $C_{13}H_{21}ClN_4O$: C, 53.83; H, 7.43; N, 19.67%. Found: C, 53.24; H, 7.08; N, 19.31%.

[1-(2-(2-methylimidazole-ethoxy)ethyl)-3,5-dimethylpyrazole]$^+$$PF_6^-$ (**L1^{PF6}**)

To a solution of **L1^{Cl}** (0.44 g, 1.5 mmol) in distilled water (20 mL) was added potassium hexafluorophosphate (0.33 g, 1.8 mmol). The resulting mixture was stirred for 30 min at room temperature, and the resulting pale yellow solid extracted with dichloromethane (3 x 10 mL). The solution was dried on $MgSO_4$ and the solvent removed in vacuo to yield a pale yellow solid (0.59 g, 85%). Recrystallization from a concentrated CH_2Cl_2/pentane solution (90:10) at room temperature afforded **L1^{PF6}** as white crystals, some of which proved suitable for X-ray diffraction studies. ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ 2.19 (3H, s), 2.20 (3H, s), 3.72 (2H, t, $^3J_{HH}$ = 4.6 Hz), 3.80 (2H, t, $^3J_{HH}$ = 5.2 Hz), 3.84 (3H, s), 4.12 (2H, t, $^3J_{HH}$ = 5.3 Hz), 4.24 (2H, t, $^3J_{HH}$ = 4.5 Hz), 5.81 (1H, s), 7.17 (1H, t, $^3J_{HH}$ = 1.8 Hz), 7.19 (1H, s), 8.30 (1H, s). ^{13}C{^{1}H} NMR (75 MHz, 298 K, $CDCl_3$): 10.6 (Pz 5-*C*H_3), 13.1 (Pz 3-*C*H_3), 35.8 (Im 3-*C*H_3), 47.6 (*C*H_2), 49.8 (*C*H_2), 67.8 (O-*C*H_2), 69.1 (O-*C*H_2), 104.7 (Pz 4-C), 122.4 (Im 2-C), 122.8 (Im 3-C), 140.1 (Im 2-C), 140.1 (Pz 5-C), 147.2 (Pz 3-C). IR (neat, cm^{-1}): 3178 (m), 3161 (m), 3124 (w), 2958 (m), 29033 (m), 2881 (w), 1614 (w), 1566 (m), 1552 (m), 1461 (m), 1431 (m), 1387 (w), 1303 (w), 1172 (s), 1134 (s), 1066 (m), 840 (s), 752 (m), 646 (m), 622 (m), 557 (s). Anal. calcd. for $C_{13}H_{20}F_6N_4OP$: C, 39.70; H, 5.13; N, 14.25%. Found: C, 39.46; H, 5.15; N, 14.01%. Mp: 76.2 °C

[1-(2-(1,2-dimethylimizadole-ethoxy)ethyl)-pyrazole]$^+$Cl$^-$ (**L2^{Cl}**)

This ligand was prepared according to the method described above for **L1** using 1-(2-(2-chloroethoxy)ethyl)-3,5-dimethyl-1-pyrazole (2.89 g, 16.0 mmol), and 1,2-dimethylimidazole (1.59 g, 16.0 mmol). **L2^{Cl}** was obtained as a yellow oil (4.13 g, 92%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ 2.60 (3H, s), 3.82 (4H, m), 3.92 (3H, s), 4.26 (2H, t; $^3J_{HH}$ = 5.2 Hz), 4.45 (2H, t; $^3J_{HH}$ = 4.6 Hz), 6.22 (1H, t; $^3J_{HH}$ = 2.1 Hz), 7.42 (1H, d; $^3J_{HH}$ = 2.1 Hz), 7.44 (1H, d; $^3J_{HH}$ = 1.5 Hz), 7,60 (1H, d; $^3J_{HH}$ = 2.1 Hz), 7.67 (1H, d; $^3J_{HH}$ = 2.1 Hz). ^{13}C{^{1}H} NMR (75 MHz, 298 K, $CDCl_3$): 10.2 (Im 2-CH_3), 35.5 (Im 3-CH_3), 48.5 (CH_2), 51.3 (CH_2), 690 (O-CH_2), 69.2 (O-CH_2), 105.3 (Pz 4-C), 121.7 (Im 2-C), 122.4 (Im 3-C), 129.7 (Im 2-C), 139.1 (Pz 5-C), 144.4 (Pz 2-C). Anal. calcd. for $C_{14}H_{23}ClN_4O$: C, 52.27; H, 7.76; N, 18.75%. Found: C, 52.15; H, 7.54; N, 18.66%.

[1-(2-(1,2-dimethylimizadole-ethoxy)ethyl)-pyrazole]$^{+}PF_6^{-}$ (**L2^{PF6}**)

This ligand was prepared according to the method described above for **L1^{PF6}** using **L2^{Cl}** (3.70 g, 12.0 mmol), and KPF_6 (2.70 g, 14.0 mmol). **L2^{PF6}** was obtained as a white solid (3.10 g, 68%). Recrystallization from a concentrated CH_2Cl_2/pentane solution (90:10) at room temperature afforded **L2^{PF6}** as white crystals. ^{1}H NMR (300 MHz, 298 K, CD_2Cl_2): δ 2.45 (3H, s), 3.70 (2H, t, $^3J_{HH}$ = 4.8 Hz), 3.73 (3H, s), 3.82 (2H, t, $^3J_{HH}$ = 5.1 Hz), 4.16 (2H, t, $^3J_{HH}$ = 4.8 Hz), 4.23 (2H, t, $^3J_{HH}$ = 5.2 Hz), 6.22 (1H, t, $^3J_{HH}$ = 2.0 Hz), 7.09 (1H, d, $^3J_{HH}$ = 2.2 Hz), 7.11 (1H, d, $^3J_{HH}$ = 2.2 Hz), 7.36 (1H, d, $^3J_{HH}$ = 2.2 Hz), 7.42 (1H, d, $^3J_{HH}$ = 1.3). $^{13}C\{^1H\}$ NMR (75 MHz, 298 K, CD_2Cl_2): 9.7 (Im 2-CH_3), 35.4 (Im 3-CH_3), 48.8 (CH_2), 51.7 (CH_2), 68.9 (O-CH_2), 69.8 (O-CH_2), 105.5 (Pz 4-C), 121.5 (Im 2-C), 122.4 (Im 3-C), 130.0 (Im 2-C), 139.3 (Pz 5-C), 145.0 (Pz 3-C). IR (neat, cm^{-1}), ν: 3157 (w), 3125 (w), 1593 (w), 1542 (w), 1417(w), 1180(w), 1057 (m), 826 (s), 753 (m), 669 (m), 649 (w), 614 (m), 556 (s). Anal. calcd. for $C_{12}H_{19}F_6N_4OP$: C, 37.90; H, 5.04; N, 14.73%. Found: C, 37.74; H, 4.85; N, 14.53%. Mp: 77.7 °C.

[1-(2-(1,2-dimethylimizadole-ethoxy)ethyl)-3,5-dimethylpyrazole]$^{+}Cl^{-}$ (**L3^{Cl}**)

This ligand was prepared according to the method described above for **L1** using 1-(2-(2-chloroethoxy)ethyl)-3,5-dimethyl-1-pyrazole (1.79 g, 8.9 mmol) and 1,2-dimethylimidazole (1.66 g, 17.0 mmol). **L3^{Cl}** was obtained as an orange oil (2.53 g, 95%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ 2.18 (6H, s), 2.68 (3H, s), 3.80 (4H, m), 3.97 (3H, s), 4.07 (2H, t, $^3J_{HH}$ = 5.3 Hz), 4.48 (2H, t, $^3J_{HH}$ = 4.6 Hz), 5.78 (1H, s), 7.65 (1H, s), 7.67 (1H, s). $^{13}C\{^1H\}$ NMR (75 MHz, 298 K, $CDCl_3$): 10.0 (Pz 5-CH_3), 10.8 (Im 2-CH_3), 13.2 (Pz 3-CH_3), 35.4 (Im 3-CH_3), 47.6 (CH_2), 48.4 (CH_2), 69.0 (O-CH_2), 69.3 (O-CH_2), 104.6 (Pz 4-C), 121.5 (Im 2-C), 122.3 (Im 3-C), 139.1 (Im 2-C), 144.1 (Pz 5-C), 147.0 (Pz 3-C). Anal. calcd. for $C_{14}H_{23}ClN_4O$: C, 52.27; H, 7.76; N, 18.75%. Found: C, 52.15; H, 7.54; N, 18.66%.

[1-(2-(1,2-dimethylimizadole-ethoxy)ethyl)-3,5-dimethyllpyrazole]$^{+}PF_6^{-}$ (**L3^{PF6}**)

This ligand was prepared according to the method described above for **L1^{PF6}** using **L3^{Cl}** (1.79 g, 6.0 mmol) and KPF_6 (1.32 g, 7.2 mmol). **L3^{PF6}** was obtained as a white solid (2.83 g, 68%). Recrystallization from a concentrated CH_2Cl_2/pentane solution (90:10) at room temperature afforded **L3^{PF6}** as white crystals, some of which proved suitable for X-ray diffraction studies. ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ 2.17 (3H, s), 2.18 (3H, s), 2.49 (3H, s), 3.70-3.78 (7H, m), 4.07 (2H, t, $^3J_{HH}$ = 5.1 Hz), 4.17 (2H, t, $^3J_{HH}$ = 4.4 Hz), 5.78 (1H, s), 7.12 (1H, s), 7.13 (1H, s). $^{13}C\{^1H\}$ NMR (75 MHz, 298 K, $CDCl_3$): 9.3 (Pz 5-CH_3), 10.9 (Im 2-CH_3), 13.4 (Pz 3-CH_3), 35.0 (Im 3-CH_3), 47.9 (CH_2), 48.4 (CH_2), 68.8 (O-CH_2), 69.6 (O-CH_2), 105.0 (Pz 4-C), 121.3 (Im 2-C), 122.0 (Im 3-C), 139.6 (Im 2-C), 144.6 (Pz 5-C), 147.5 (Pz 3-C). IR (neat, cm^{-1}), ν: 3152 (m), 2903 (w), 2876 (w), 1592 (w), 1540 (w), 1517 (w), 1464 (w), 1420 (w), 1398 (w), 1354 (w), 1332 (w), 1256 (w), 1180(w), 1123 (m), 1087 (m),1064 (w), 1041 (w), 997 (w), 947 (w), 915 (w), 828 (s), 753 (s), 717 (s), 667 (m), 649 (m), 616 (m), 556 (s), 501 (m), 468 (w). Anal. calcd. for $C_{14}H_{22}F_6N_4OP$: C, 41.28; H, 5.44; N, 13.76%. Found: C, 40.74; H, 5.91; N, 13.42%. Mp: 91.8 °C.

[1-(2-(2-butylimizadole-ethoxy)ethyl)-3,5-dimethylpyrazole]$^{+}Cl^{-}$ (**L4^{Cl}**)

This ligand was prepared according to the method described above for **L1^{Cl}**, using 1-(2-(2-chloroethoxy)ethyl)-3,5-dimethyl-1-pyrazole (1.62 g, 8.0 mmol) and 1-*n*-butyllimidazole (1.01 g, 8.0 mmol). **L4^{Cl}** was obtained as a yellow oil (2.48 g, 95%).^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ 0.97 (3H, t; $^3J_{HH}$ = 7.3 Hz), 1.39 (2H, m), 1.89 (2H, m), 2.20 (3H, s), 2.22 (3H, s), 3.82 (4H, m), 4.14 (2H, t; $^3J_{HH}$ = 5.1 Hz), 4.29 (2H, t; $^3J_{HH}$ = 7.5 Hz), 4.60 (2H, t; $^3J_{HH}$ = 4.6 Hz), 5.80 (1H, s) 7.37-7.38 (2H, m), 10.37 (1H, s). $^{13}C\{^1H\}$ NMR (75 MHz, 298 K, $CDCl_3$): 10.9 (Pz 5-CH_3), 13.2 (Pz 3-CH_3), 13.3 (CH_2CH_3), 19.2 (CH_2), 31.9 (Im N-CH_2CH_2), 47.9 (Im N-CH_2), 49.2 (CH_2), 49.5 (CH_2), 68.9 (O-CH_2), 69.4 (O-CH_2), 104.8 (Pz 4-C), 121.0 (Im 2-C), 123.0 (Im 3-C), 137.0 (Im 2-C), 139.4 (Pz 5-C), 147.2 (Pz 3-C). Anal. calcd. for $C_{16}H_{27}ClN_4O$: C, 58.79; H, 8.33; N, 17.14%. Found: C, 58.35; H, 7.97; N, 17.01%.

[1-(2-(2-butylimizadole-ethoxy)ethyl)-3,5-dimethylpyrazole]$^{+}Cl^{-}$ (**L4^{PF6}**)

This ligand was prepared according to the method described above for **L1^{PF6}** using **L4^{Cl}** (0.49 g, 1.5 mmol) and KPF_6 (0.33 g, 1.8 mmol). **L4^{PF6}** was obtained as a yellow oil (0.57g, 87%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ 0.94 (3H, t; $^3J_{HH}$ = 7.3 Hz), 1.35 (2H, m), 1.82 (2H, m), 2.18 (s, 3H), 2.20 (s, 3H), 3.72 (2H, $^3J_{HH}$ = 4.5 Hz), 3.80 (2H, t; $^3J_{HH}$ = 5.2 Hz), 4.11 (4H, m), 4.27 (2H, t; $^3J_{HH}$ = 4.6 Hz), 5.79 (1H, s) 7.21 (1H, s), 7.25 (1H, s), 8.38 (1H, s). $^{13}C\{^1H\}$ NMR (75 MHz, 298 K, $CDCl_3$): 10.7 (Pz 5-CH_3), 13.1 (Pz 3-CH_3), 13.3 (CH_2CH_3), 19.2 (CH_2), 31.6 (Im N-CH_2CH_2), 47.9 (Im N-CH_2), 49.5 (CH_2), 49.5 (CH_2), 68.3 (O-CH_2), 69.5 (O-CH_2), 104.9 (Pz 4-C), 121.6 (Im 2-C), 123.1 (Im 3-C), 135.1 (Im 2-C), 139.7 (Pz 5-C), 147.3 (Pz 3-C). IR (neat, cm^{-1}), ν: 3640 (w), 3161 (w), 3117 (w), 2962 (w), 2932 (w), 2876 (w), 1563 (m), 1460 (m), 1421 (w), 1377 (w), 1302 (w), 1223 (w), 1163 (m), 1123 (m), 1066 (w), 1027 (w), 825 (s), 749 (s), 642 (m), 554 (s). Anal. calcd. for $C_{16}H_{27}F_6N_4OP$: C, 44.04; H, 6.24; N, 12.84%. Found: C, 43.70; H, 6.05; N, 12.78%.

Synthesis of the Zwitterionic Ni(II) Complexes

[L1][$NiCl_3$] (**Ni1**)

Method A: To a solution of $Ni(OAc)_2$ (0.11 g, 0.62 mmol) and LiCl (0.054 g, 1.30 mmol) in DMF (4 mL) was added a solution of **L1^{Cl}** (0.20 g, 0.71 mmol) in DMF (6 mL), and the resulting solution was stirred for 20 h at room temperature. The solvent was removed under vacuum, and the resulting blue solid residue was washed with Et_2O (3 x 10 mL). Complex **Ni1** was obtained as a blue solid (0.24 g, 88%). **Method B**: To a solution of $NiCl_2$(dme) (0.10 g, 0.46 mmol) and LiCl (0.019 g, 0.46 mmol) in CH_2Cl_2 (5 mL) was added a solution of **L1^{PF6}** (0.20 g, 0.51 mmol) in CH_2Cl_2 (4 mL), and the resulting solution was stirred for 20 h at room temperature. The solvent was removed under vacuum, and the resulting blue solid residue was washed with Et_2O (3 x 10 mL). Complex **Ni1** was obtained as a blue solid (0.080 g, 40%). Anal. calcd. for $C_{13}H_{21}Cl_3N_4NiO$: C, 37.68; H, 5.11; N, 13.52%. Found: C, 37.13; H, 4.87; N, 13.31%.

[L2][$NiCl_3$] (**Ni2**)

This compound was prepared according to the method described above for **Ni1** using $Ni(OAc)_2$ (0.16 g, 0.90 mmol), LiCl (0.076 g, 1.80 mmol) and **L2^{Cl}** (0.27 g, 0.99 mmol). Complex **Ni2** was obtained as a blue solid (0.27 g, 87%). Anal. calcd. for $C_{12}H_{19}Cl_3N_4NiO$: C, 36.00; H, 4.78; N, 13.99%. Found: C, 35.77; H, 4.23; N, 13.32%.

[L3][$NiCl_3$] (**Ni3**)

This compound was prepared according to the method described above for **Ni1** using $Ni(OAc)_2$ (0.14 g, 0.79 mmol), LiCl (0.066 g, 1.58 mmol) and **L3^{Cl}** (0.295 g, 0.99 mmol). Complex **Ni3** was obtained as a blue solid (0.29 g, 87%). Anal. calcd. for $C_{14}H_{23}Cl_3N_4NiO$: C, 39.25; H, 5.41; N, 13.08%. Found: C, 38.75; H, 5.05; N, 12.89%.

[L4][$NiCl_3$] (**Ni4**)

This compound was prepared according to the method described above for **Ni1** using $Ni(OAc)_2$ (0.13 g, 0.73 mmol), LiCl (0.062 g, 1.46 mmol), and **L4^{Cl}** (0.26 g, 0.80 mmol). Complex **Ni4** was obtained as a blue solid (0.27 g, 81%). Anal. calcd. for $C_{16}H_{27}Cl_3N_4NiO$: C, 42.10; H, 5.96; N, 12.27%. Found: C, 42.01; H, 5.87; N, 12.08%.

General oligomerization procedure

Ethylene oligomerization was performed in a 100 mL double-walled stainless Parr reactor equipped with mechanical stirring, internal temperature control and continuous feed of ethylene. The Parr reactor was dried in an oven at 120 °C for 5 h prior to each run, and then cooled under vacuum for 30 min. A typical reaction was performed by introducing toluene (30 mL) and the proper amount of co-catalyst (MAO or EASC) into the reactor under an ethylene atmosphere. After 20 min, the toluene catalyst solution (10 mL, [Ni] = 10 µmol) was injected into the reactor under a stream of ethylene and then the reactor was immediately pressurized. Ethylene was continuously fed in order to maintain the desired ethylene pressure. After 20 min, the reaction was stopped by cooling the system to −60 °C and depressurizing. An exact amount of cyclohexane was introduced (as an internal standard) and the mixture was analyzed by quantitative GLC.

X-ray Diffraction Analyses

Suitable single-crystals of **L1^{PF6}**, **L3^{PF6}**, **Ni1**, **Ni2** and **Ni3** were mounted onto a glass fiber using the ''oil-drop'' method. Selected bond lengths and angles are given in the Figure captions. Diffraction data were collected at 150(2) K using an APEXII Bruker-AXS diffractometer with graphite-monochromatized MoKα radiation (λ = 0.71073 Å). A combination of ω and ϕ scans was carried out to obtain at least a unique data set. The crystal structures were solved by direct methods, remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F2 (programs SIR97 and SHELXL-97) with the aid of the WINGX program. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. Crystal data and details of data collection and structure refinement can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CCDC 1055620, 1055623, 1055629, 1055632, and 1406895).

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