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# Synthesis of nickel(II) complexes containing neutral $N,N^$ and anionic $N,O^-$ bidentate ligands, and their behaviour as chain-growth catalysts; structural characterisation of complexes containing (mim)<sub>2</sub>CO, mimCO<sub>2</sub><sup>-</sup>, and mimCPh<sub>2</sub>O<sup>-</sup> (mim = 1-methylimidazol-2-yl)

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Dedicated to Professor Gerard van Koten.

## Abstract

The complexes NiBr<sub>2</sub>(L<sub>2</sub>) [L<sub>2</sub> = (mim)<sub>2</sub>CO (7a), (bim)<sub>2</sub>CO (7b), py(mim)CO (8), PhN=CHbim (9)], NiBr(*o*-Tol){(mim)<sub>2</sub>CO} (10), Ni(L<sub>2</sub>)(*o*-Tol)(PPh<sub>3</sub>) [L<sub>2</sub> = mimCO<sub>2</sub><sup>-</sup> (11a), bmCO<sub>2</sub><sup>-</sup> (11b), mimCPh<sub>2</sub>O<sup>-</sup> (12), mimC<sub>6</sub>H<sub>4</sub>O<sup>-</sup> (13)], and [Ni{(mim)<sub>2</sub>CO}<sub>3</sub>][B-F<sub>4</sub>]<sub>2</sub> · 0.25H<sub>2</sub>O (16) have been synthesised from nickel(II) salts (7–9, 16) or NiBr(*o*-Tol)(PPh<sub>3</sub>)<sub>2</sub> [10–13], where mim = 1-methylimidazol-2-yl, bim = 1-benzylimidazol-2-yl, and py = pyridin-2-yl. The square-planar complexes (11a, 12) and octahedral 16 have been characterised by X-ray diffraction studies, together with octahedral *cis*-[Ni{(mim)<sub>2</sub>CO}<sub>2</sub>Br(OH<sub>2</sub>)]Br · CD<sub>3</sub>CN (14) and *cis*-[Ni{(mim)<sub>2</sub>CO}<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]Br<sub>2</sub> · 3CD<sub>3</sub>CN (15). Preliminary catalytic studies have been undertaken with a number of the nickel complexes. Complexes 11–13 form single component catalysts for the oligomerization or polymerization of ethylene and the bromo-complexes (7–9) form active catalysts for the oligomerization or polymerization of ethylene when activated with MMAO. © 2004 Elsevier B.V. All rights reserved.

Keywords: Nickel; Catalysis; Imidazole; Structure; X-ray; Bidentate

#### 1. Introduction

Following the pioneering work by Reppe, Wilke and Keim [1], nickel complexes have found widespread application in industrial catalysis [1–6]. Notably, the shell higher olefins process (SHOP) is one of the most

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prominent applications of nickel in homogeneous catalysis [2]. The SHOP catalysts contain a bidentate  $[P-O]^$ ligand coordinated to nickel(II) and show exceptionally high selectivities for linear  $\alpha$ -olefins. Interest in nickel based catalysts has been renewed by Brookhart and co-worker's [3–6] discovery that bulky  $\alpha$ -diimine–Ni(II) [and Pd(II)] complexes are capable of oligomerising or polymerising ethylene and higher olefins. In these systems the molecular weight of the polymer formed is dependent on the steric bulk of the ligand, since increas-

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ing bulk hinders associative displacement ( $\beta$  elimination) of the growing polymer chain. Another important feature of this class of nickel catalysts is their tolerance for heteroatoms, which allows copolymerisation of olefins with substrates such as acrylate, vinylacetate and pyrimidone functionalised olefins [7]. In contrast, early transition metal catalysts tend to be limited to non-polar olefins due to the oxophilic nature of these metals.

The transition metal organometallic chemistry of Nheterocyclic, and in particular imidazole containing ligands has been developed more recently [8–22]. In view of the close relationship between the imidazole group and  $\alpha$ -diimine and related ligands, we have commenced studies on the coordination chemistry and of the potential application in catalysis of such ligands. We recently reported preliminary studies of Pd(II) and Cr(III) systems [16,17,21], and have now extended our investigations to Ni(II) and included a wider range of ligand systems (Scheme 1). The ligands were selected to contain two imidazole groups (1), an imidazole and a pyridine group (2), or an imidazole and an imine group (3) allowing comparison with diimine chemistry; or an imidazole and anionic oxygen donor groups (4–6) to provide comparisons with the SHOP system and the more recently reported pyridine-2-carboxylate [18], pyrazine-2-carboxylate [19] and salicylaldimine systems [23]. We report here nickel imidazole-carboxylate complexes that are inert to atmospheric moisture and are stable in ethanol.



Scheme 1. Bidentate ligands containing imidazole groups and four-coordinate nickel complexes.

Preliminary catalytic studies on examples of Ni(II) complexes containing imidazole-based ligands illustrate their ability to oligomerise and polymerise lower olefins.

# 2. Experimental

All manipulations were carried out using Schlenk techniques and dry nitrogen as an inert atmosphere unless specifically noted. Celite was stirred with concentrated hydrochloric acid for 12 h and washed with deionised water until the washings were neutral and free of chloride ions, then washed consecutively with methanol and dichloromethane, dried at 100°C in vacuo and degassed with nitrogen. Solvents were purified and dried in the usual manner [24]. Sodium tetraphenylborate, nickel(II) tetrafluoroborate solution and 1-benzylimidazole were purchased from Aldrich and used without further purification. Ethylene (polymer grade) was supplied by Matheson. MAO was obtained as a 10% w/w toluene solution from Schering and MMAO was supplied as a 1.82 M heptane solution from Akzo Nobel. Bis(1-methylimidazol-2-yl)methanone [25], bis(1-benzylimidazol-2-yl)methanone [26], (pyridin-2-yl)(1-methylimidazol-2-yl)methanone [9,27], 1-methylimidazol-2diphenylmethanol [28], 1-methylimidazol-2-ylphenol [29], potassium 1-benzylimidazole-2-carboxylate.2/3hydrate [30] trans-[NiBr(o-tolyl)(PPh<sub>3</sub>)<sub>2</sub>] [18], dibromo-(dimethoxyethane)nickel(II) [31], dibromo(bipyridine)nickel(II) [5], dibromo(dioxane)nickel(II) [32], and bis(1-methylimidazole-2-carboxylato)(1-methylimidazole) zinc(II) [33] were prepared as reported.

Electronic spectra were recorded using a Cary 5E UV-Vis double beam spectrophotometer fitted with a low temperature platform. Solid state spectra were obtained from KBr discs using a diffraction grating as reference; CH<sub>2</sub>Cl<sub>2</sub> solutions were made up in oven dried volumetric flasks under a nitrogen atmosphere, and a Dewar flask fitted with a vacuum chamber, thermocouple and quartz windows was used for variable temperature solution phase experiments. Quartz cells were oven dried, cooled in a vacuum, and filled and sealed under nitrogen. IR spectra were measured on a Bruker IFS 66 FT-IR spectrometer as KBr mulls prepared in a glove box or in air. Polymer IR spectra were measured using the same instrument, as films or on an FT-IR microscopy stage. Polymer melting points were measured using a Settaram DSC-92 using a temperature program suitable for polyethylene samples. NMR spectra were recorded on a Varian Gemini-200 spectrometer at 199.98 MHz (<sup>1</sup>H), 161.80 MHz (<sup>31</sup>P) or 50.00 MHz (<sup>13</sup>C); variable temperature experiments were performed on a Varian Unity Inova 400 WB spectrometer at the Central Science Laboratory, University of Tasmania, and chemical shifts are given in ppm relative to internal SiMe<sub>4</sub>  $(^{1}H, ^{13}C)$ , or external 85% H<sub>3</sub>PO<sub>4</sub>  $(^{31}P)$ . Magnetic moments were measured by Prof. K.S. Murray at Monash University. GC-FID was carried out using an HP 5890 series II GC fitted with a 25 m SGE 50QC3/BP1 column. GC-MS were measured on an HP 5890 GC fitted with a 25, HP1 capillary column and an HP 5970 mass selective detector. Electrospray ionisation mass spectrometry (ESMS) were recorded on a Finnigan MAT LCQ mass spectrometer using continuous infusion of the sample. Electron impact (EI) and liquid secondary ion (LSI) mass spectra were recorded at the Central Science Laboratory, University of Tasmania on a Kratos Concept ISQ. Microanalyses were performed by Dr. Graham Rowbottom at the Central Science Laboratory, University of Tasmania, using a Carlo Erba EA1108 Elemental Analyser.

The synthesis of 1-benzyl-2-hydroxymethylimidazole is presented here as it involves significant improvement on the published report [34] and provides full characterisation data.

## 2.1. Synthesis of reagents

#### 2.1.1. 1-Benzyl-2-hydroxymethylimidazole

1-Benzylimidazole (5.97 g, 37.8 mmol) and paraformaldehyde (4.42 g, 150 mmol) were placed in an autoclave and heated at 120 °C for 18 h. The resulting clear syrup was distilled, the product being collected at 250 °C and 0.2 mm. Yield: 6.70 g, 94%. <sup>1</sup>H NMR (CDC1<sub>3</sub>):  $\delta$  7.38–7.27 (2H, m, H3'5'), 7.17–7.13 (2H, m, H2'6'), 6.80 (1H, s, H4'), 6.56 (1H, s, H5), 5.23 (1H, s, CH<sub>2</sub>OH), 4.63 (1H, s, CH<sub>2</sub>Ph). <sup>13</sup>C NMR (CDC1<sub>3</sub>):  $\delta$  148.6 (C2), 136.8, 129.4, 128.5, 127.8, 127.1, 121.1, 56.1 (CH<sub>2</sub>OH), 50.2 (CH<sub>2</sub>Ph).

## 2.1.2. 1-Benzyl-2-1-phenylaldiminoimidazole, PhN= CHbim (3)

1-Benzyl-2-hydroxymethylimidazole (1.88 g, 10 mmol) was dissolved in chloroform (50 mL) and stirred with activated manganese dioxide (8.5 g). After 48 h the suspension was filtered and the solvent removed in a vacuum. The residue was distilled, giving 1-benzyl-2formylimidazole (1.50 g) at 135 °C and 0.2 mm. 1-Benzyl-2-formylimidazole (0.50 g, 2.7 mmol) was stirred with aniline (1.02 g, 11.0 mmol) for 15 min, toluene (42 mL) was added resulting in a cream solid that dissolved as toluene addition was completed. The solution was stirred (15 min) before being distilled to give the product at >250 °C and at 0.2 mm. Yield: 0.70 g, quantitative. <sup>1</sup>H NMR (CDC1<sub>3</sub>):  $\delta$  8.58 (1H, s, H C=N), 7.44-7.19 (11H, m, Ph), 7.08 (1H, s, H4), 5.88 (2H, s, CH<sub>2</sub>Ph). <sup>13</sup>C NMR (CDC1<sub>3</sub>):  $\delta$  151.7, 151.4, 143.6, 137.6, 131.1, 129.8, 129.3, 128.4, 128.1, 127.0, 125.2, 121.4, 51.6 (CH<sub>2</sub>Ph). EI-MS m/z: 261(M<sup>+</sup>, 30%), 245(12), 193(14), 169(100), 157(20), 91(52), 77(25) (C<sub>17</sub>H<sub>15</sub>N<sub>3</sub> requires C, 78.14; H, 5.79; N, 16.08. Found: C, 78.20; H, 5.52; N, 16.09%).

#### 2.2. Synthesis of complexes

# 2.2.1. Dibromo {bis(1-methylimidazol-2yl)methanone}nickel(II), NiBr<sub>2</sub> {(mim)<sub>2</sub>CO} (7a)

A solution of bis(1-methylimidazol-2-yl)methanone (0.500 g, 2.63 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (9 mL) was added to a stirred suspension of dibromo(dimethoxyethane)nickel(II) (0.812 g, 2.63 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (13 mL). After 25 min the suspension was filtered, the solid washed with  $CH_2Cl_2$  (3 × 4 mL) and dried in a vacuum to give the product as a green solid. Yield: 1.075 g, quantitative. Insufficiently soluble for NMR spectroscopy. LSI-MS in mnba m/z: 519 [Ni{(mim)<sub>2</sub>CO}<sub>2</sub>Br, 47%], 438 [Ni{(mim)<sub>2</sub>CO}<sub>2</sub>, 52%], 329 (MH<sup>+</sup> – HBr, 45), 248  $[\{(\min)_2 CO\}Ni, 100]$ . EI-MS: m/z 408 (M<sup>+</sup>-distorted isotope pattern, 2%), 329 (100), 248 (50), 190 (14). Electronic spectrum, KBr disc  $-180 \degree C$ ,  $\lambda$ : 511, 683 (sh), 716, 759, 1404. IR (KBr disc): 3107 (w,b), 2360 (w,b), 1641 (1632 free ligand, m), 1487 (w), 1421 (s), 1292 (w), 1169 (w), 952 (w), 900 (s), 790 (w), 653 (w), 607 (w) cm<sup>-1</sup>. Magnetic moment 3.00 BM (C<sub>9</sub>H<sub>10</sub>N<sub>4</sub>NiBr<sub>2</sub> requires C, 26.45; H, 2.47; N, 13.71. Found: C, 26.50; H, 2.65; N, 13.58%).

# 2.2.2. Dibromo {bis(1-benzylimidazol-2yl)methanone }nickel(II), NiBr<sub>2</sub>{(bim)<sub>2</sub>CO} (7b)

A solution of bis(1-benzylimidazol-2-yl)methanone (0.226 g, 0.661 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added to a stirred suspension of dibromo(dioxane)nickel(II) (0.203 g, 0.661 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). After 18 hr the red-brown suspension was collected and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was treated with diethyl ether (15 mL) to precipitate a green solid that was collected, washed with diethyl ether  $(3 \times 5 \text{ mL})$  and dried in a vacuum to give a green solid. Yield: 0.292 g, 79%. ESMS in CH<sub>3</sub>CN m/z: 1041(20%), 823(100), 521(M + 1-Br with coordinated MeCN 58). Electronic spectrum (KBr disc):  $\lambda$  662(sh), 705, 760, 942; (CH<sub>2</sub>Cl<sub>2</sub> solution at 18 °C):  $\lambda$ 510, 644, 864, 976; (CH<sub>2</sub>Cl<sub>2</sub> solution 0 °C): λ 510, 655, 821(sh), 976. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C): δ 7.41 and 6.98 (12H, m, Ph+H4,5), 6.3 (2H, s, CH<sub>2</sub>Ph); (CD<sub>2</sub>Cl<sub>2</sub>, -10 °C) δ 7.42, 7.07, 6.99, 6.36 (s, CH<sub>2</sub>Ph). IR (KBr disc): 1653 (s, br), 1436 (s, br), 1296 (m), 1180 (s), 901 (s), 798 (m), 775 (m), 668 (m), 647 (m), 612 (w), 592 (w) cm<sup>-1</sup>. Magnetic moment 2.48 BM ( $C_{21}H_{18}N_4O_{-1}$ NiBr<sub>2</sub> requires C, 44.97; H, 3.23; N, 9.99. Found: C, 44.87; H, 3.23; N, 10.05%).

# 2.2.3. Dibromo {(pyridin-2-yl)(1-methylimidazol-2-yl) methanone }nickel(II), NiBr<sub>2</sub> {py(mim)CO} (8)

A solution of 1-methylimidazol-2-yl(pyridin-2-yl) methanone (0.173 g, 0.925 mmol) in  $CH_2Cl_2$  (15 mL) was added to a stirred suspension of dibromo(dimeth-oxyethane)nickel(II) (0.286 g, 0.926 mmol) in  $CH_2Cl_2$  (15 mL). The brown suspension was filtered and the solids extracted with  $CH_2Cl_2$  (20 × 5 mL). The filtered ex-

tracts were evaporated in a vacuum to give a pale yellow powder. Yield: 0.311 g, 83%. Insufficiently soluble for NMR spectroscopy. LSI-MS in *mnba m/z*: 326 (MH<sup>+</sup> – HBr, 100%), 245 (48), 188 (LH<sup>+</sup>, 17). Electronic spectrum (KBr disc):  $\lambda$  703, 749, 1167 nm. IR (KBr disk): 1623 (m), 1581 (m), 1533 (m), 1443 (w), 1484 (m), 1453 (m, sh), 1437 (s), 1385 (w), 1359 (w), 1329 (w), 1207 (w), 1134 (w), 969 (m), 916 (w), 895 (m), 769 (m), 718 (m), 696 (m), 599 (w), 555 (w) cm<sup>-1</sup>. Magnetic moment 2.53 BM (C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>OBr<sub>2</sub>Ni requires C, 29.60; H, 2.36; N, 10.36. Found: C, 29.72; H, 2.27; N, 10.25%).

# 2.2.4. Dibromo {1-benzylimidazol-2-yl(1-phenylaldimine) } nickel(II), NiBr<sub>2</sub>(PhN=CHbim) (9)

1-Benzylimidazol-2-yl(1-phenylaldimine) (0.157 g, 0.602 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) was added to a stirred of dibromo(dimethoxyethane)nickel(II) suspension (0.185 g, 0.599 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). After 1.5 h the olive green mixture was filtered and the solid product washed with  $CH_2Cl_2$  (3 × 5 mL) and light petroleum (bp 40–60 °C) ( $2 \times 5$  mL), and dried to give a pale green powder. Yield: 0.202 g, 70%. Insufficiently soluble for NMR spectroscopy. LSI-MS in mnba m/z: 661(100%), 580(26), 400(M - Br,100), 319(70), 260(35). Electronic spectrum (KBr disc):  $\lambda$  679(sh), 707, 757, 1001 nm. IR (KBr disk): 1607 (m, sh), 1584 (m), 1531 (w), 1484 (s), 1454 (sh), 1437 (s), 1386 (w), 1357 (w), 1329 (w), 1207 (w), 1134 (w), 969 (m), 916 (w), 895 (m), 717 (s), 697 (s), 600 (w), 555 (w) cm<sup>-1</sup>. Magnetic moment 3.21 BM (C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>NiBr<sub>2</sub> requires C, 42.55; H, 3.15; N, 8.76. Found: C, 42.36; H, 3.32; N, 8.68%).

# 2.2.5. Bromo(ortho-tolyl) {bis(1-methylimidazol-2-yl) methanone}nickel(II), NiBr(o-Tol) {(mim)<sub>2</sub>CO} (10)

A solution of bis(1-methylimidazol-2-yl)methanone (0.042 g, 0.221 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4.2 mL) was added to a well stirred solution of *trans*-[NiBr(o-Tol)(PPh<sub>3</sub>)<sub>2</sub>] (0.167 g, 0.221 mmol) in CH<sub>2</sub>Cl<sub>2</sub> at -14 °C. After 45 min the blood red solution had warmed to 4 °C, it was frozen and petroleum ether (8 mL) added. The mixture was allowed to melt and diffuse with the aid of gentle stirring, further diethyl ether/petroleum ether  $(3 \times 5)$ mL) were then added and the precipitated red solid dried in vacuo. Yield: 0.71 g, 80%. Electronic spectrum (KBr disc)  $\lambda$  : 508; (CH<sub>2</sub>Cl<sub>2</sub> solution at 18 °C)  $\lambda(\varepsilon)$  : 508 (1550). LSI-MS of an MeCN solution in mnba m/ z: 519(7%), 473(14), 438(33), 339(M - Br, 12), 327(M-Tol), 283(M-Br<sub>2</sub> + Cl, 18), 248(100). EI-MS in CH<sub>2</sub>Cl<sub>2</sub> m/z: 329(M-Tol, 7%), 283(12), 248(5), 190(29), 162(44), 109(54), 82(100). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  at 18<sup>o</sup>C: 8.00 (1H,s (br), mim), 7.47 (1H, m, H5-Tol). 7.17 (1H, s (br), mim), 6.85 (1H, s (br), mim), 6.70 (3H, m, H2,3-Tol), 5.88 (1H, mim), 4.02 (6H, m, mim-CH<sub>3</sub>), 3.03 (3H, s, Tol-CH<sub>3</sub>);  $\delta$  at  $-50^{\circ}$ C: 7.90 (1H, s, mim), 7.44 (1H, m, H5-Tol), 7.19 (1H, s, mim), 6.86 (1H, s, mim), 6.69 (3H, m, H2,3-Tol), 5.78 (1H, s, mim), 4.02 (3H, s,

mim-CH<sub>3</sub>), 3.95 (1H, s, mim-CH<sub>3</sub>), 3.03 (3H, s, Tol-CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  204.8, 156.0, 149.1, 145.0, 140.5, 134.3, 133.3, 131.7, 127.5, 43.2, 29.6 (C<sub>16</sub>H<sub>17</sub>N<sub>4</sub>OBrNi requires C, 45.76; H, 4.08; N, 13.34. Found: C, 46.16; H, 4.17; N, 13.71%).

# 2.2.6. (ortho-Tolyl)(1-methylimidazol-2-carboxylato) (triphenylphosphine)nickel(II), Ni(mimCO<sub>2</sub>)(o-Tol) (PPh<sub>3</sub>) (11a)

A solution of bis(1-methylimidazol-2-carboxylato)(1methylimidazole)zinc(II) (0.13 g, 0.33 mmol) in tetrahydrofuran (10 mL) was added to a stirred solution of trans-[NiBr(o-Tol)(PPh<sub>3</sub>)<sub>2</sub>] (0.57 g, 0.76 mmol) in tetrahydrofuran (10 mL). After 7 h the dark orange suspension had faded to pale yellow, the solvent was removed in a vacuum at 40 °C to give a solid that was taken up in dichloromethane (10 mL), filtered through celite and washed with further dichloromethane  $(3 \times 5 \text{ mL})$ . Diethyl ether (60 mL) was added to the filtrate, the precipitated solid removed by filtration through celite and the pale yellow solution was evaporated in vacuo. The resulting solid was recrystallised from dichloromethane/pentane to give the product as a yellow microcrystalline solid. Yield: 0.163 g, 91%. LSI-MS of an acetonitrile solution in mnba m/z: 537 (MH+, 7%), 445 (6), 353 (100). IR (KBr disk): 1655 (s), 1570 (w), 1495 (m), 1434 (s), 1309 (m), 1287 (m), 1183 (m), 1097 (m), 1022 (w), 827 (w), 802 (w), 744 (m), 694 (m), 650 (w), 624 (w), 532 (m), 506 (m), 435 (w)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.57–7.36 (18H, m, H3,4,5-Tol and mim), 6.78-6.52 (3H, H3,4,5-Tol and mim), 3.97 (3H, s, mim-CH<sub>3</sub>), 2.65 (3H, s, Tol-CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 238.7, 164.3, 149.7, 143.7, 138.1, 136.7, 135.5, 135.4, 135.1, 134.9, 134.8, 134.4, 132.9, 132.7, 131.6, 131.1, 130.6, 130.5, 129.7, 129.4, 129.0, 128.7, 128.6, 128.3, 125.3, 124.9, 123.7, 123.4, 34.3, 26.3. <sup>31</sup>P-{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>) & 29.3. (C<sub>50</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub>NiP requires C, 67.07; H, 5.07; N, 5.21. Found: C, 67.17; H, 5.06; N, 5.19%.) LSI-MS of acetonitrile solution in mnba m/z: 537(MH<sup>+</sup>, 7%), 445(6), 353 (100).

# 2.2.7. (ortho-Tolyl)(l-benzylimidazol-2-carboxylato) (triphenylphosphine)nickel(II), Ni(bimCO<sub>2</sub>)(o-Tol) (PPh<sub>3</sub>) (11b)

*trans*-[NiBr(o-Tol)(PPh<sub>3</sub>)<sub>2</sub>] (0.88 g, 1.17 mmol) in tetrahydrofuran (30 mL) was added to potassium 1-methylimidazol-2-carboxylate.2/3hydrate (0.24 g, 1.19 mmol) and the red-brown mixture stirred at 26 °C for 5 h. The solvent was removed in a vacuum and the solid residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered through Celite and the solvent removed in a vacuum to give a yellow solid. The crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and diethyl ether added to precipitate a pale yellow solid. The filtrate was concentrated and hexanes added to afford a second crop of pale yellow solid. Yield: 0.40 g, 85%. LSI-MS in *m/z*: 613 (MH<sup>+</sup>, 100%), 521 (20), 353 (53). IR (KBr disk): 1667 (s), 1634 (s), 1591 (m), 1488 (m), 1443 (m), 1412 (s), 1384 (m), 1276 (w), 1251 (w), 1173 (w), 1161 (w), 1060 (w), 1020 (w), 927 (s), 777 (m), 723 (w), 703 (m), 656 (m), 642 (w), 623 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.51–7.26 (21H, m), 7.18–7.15 (1H, m), 6.77 (1H, m), 6.61–6.48 (3H, m), 5.62 (2H, s, CH<sub>2</sub>Ph), 2.53 (3H, s, Tol-CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  143.0, 136.2, 135.9, 134.4, 134.3, 130.6, 130.4, 130.1, 129.1, 128.5, 128.3, 128.2, 127.6, 125.1, 122.9, 122.6. <sup>31</sup>P–{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  29.2 (C<sub>36</sub>H<sub>31</sub>N<sub>2</sub>O<sub>2</sub>PNi requires C, 70.50; H, 5.09; N, 4.57. Found: C, 70.68; H, 5.08; N, 4.75%).

# 2.2.8. (ortho-Tolyl)(1-methylimidazol-2-diphenylmet hanolato)(triphenylphosphine)nickel(II), Ni(mim-CPh<sub>2</sub>O) (o-Tol)(PPh<sub>3</sub>) (12)

1-Methylimidazol-2-diphenylmethanol (2.11 g, 7.54 mmol) in tetrahydrofuran (20 mL) was added to solid potassium methoxide (0.437 g, 7.52 mmol) and the suspension stirred for 12 h. The solvent was evaporated in a vacuum to give a white solid. A solution of trans-[Ni- $Br(o-Tol)(PPh_3)_2$  (0.83 g, 1.10 mmol) in tetrahydrofuran (25 mL) was added to the white solid (0.349 g) and stirred to form a red-brown suspension. After 24 h the suspension had faded to yellow and a fine precipitate had formed. The suspension was filtered and the solvent removed in vacuo, the remaining solid dissolved in dichloromethane (5 mL), filtered through celite and the celite washed with solvent  $(2 \times 2 \text{ mL})$ . Pentane was added and the orange crystals that formed were collected and washed with pentane  $(2 \times 2.5 \text{ mL})$  and dried in a vacuum. Yield: 0.59 g, 79%. LSI-MS acetonitrile solution in mnba m/z: 675 (MH<sup>+</sup>, 30%), 583 (MH<sup>+</sup> - toluene, 53), 353 (100), 305 (58), 247 (42). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.50–7.07 (27H, m), 6.66–6.39 (4H, m), 3.09 (3H, s, mim-CH<sub>3</sub>), 2.51 (3H, 3,Tol-CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 147.8, 144.1, 137.2, 134.7, 134.6, 132.4, 132.0, 129.4, 128.5, 128.3, 127.8, 127.6, 127.5, 126.6, 123.8, 122.3, 121.8, 121.6, 34.6, 25.6.  ${}^{31}P - {}^{1}H$ NMR (CD<sub>2</sub>Cl<sub>2</sub>) & 30.2 (C<sub>42</sub>H<sub>37</sub>N<sub>2</sub>OPNi requires C, 74.69; H, 5.52; N, 4.15. Found: C, 74.39; H, 5.63; N, 4.07%).

# 2.2.9. (ortho-Tolyl)(1-methylimidazol-2-phenoxo) (triphenylphosphine)nickel(II), Ni(mimC<sub>6</sub>H<sub>4</sub>O)(o-Tol) (PPh<sub>3</sub>) (13)

1-Methylimidazol-2-phenol (0.046 g, 0.264 mmol) in tetrahydrofuran (4 mL) was treated with potassium methoxide (1.2 mL of 0.219 M solution, 0.26 mmol) in methanol and stirred for 2 h. The solvent was evaporated in a vacuum to give a white solid. A solution of *trans*-[NiBr(o-Tol)(PPh<sub>3</sub>)<sub>2</sub>] (0.199 g, 0.264 mmol) in tetrahydrofuran (75 mL) was added, and the suspension stirred for 12 h and the solvent removed to give an amber solid. The solid was dissolved in dichloromethane (7 mL), filtered, diethyl ether added and the resulting sus-

pension filtered and the filtrate evaporated in a vacuum to give a yellow solid which was recrystallised from diethyl ether/light petroleum. Yield: 0.075 g, 48%. LSI-MS in *mnba m*/*z*: 584 (M<sup>+</sup>, 7%), 493 (M<sup>+</sup> – C<sub>7</sub>H<sub>7</sub>, 17), 353 (M<sup>+</sup> – PPh<sub>3</sub>, 100), 322 (10), 263 (PPh<sub>3</sub>, 5) 231 [Ni-(mimC<sub>6</sub>H<sub>4</sub>O)<sup>+</sup>, 12]. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.00 (7H, m), 6.89 (5H, m), 6.77 (7H, m), 6.42 (1H, m), 6.16 (1H, m), 6.10–5.95 (4H), 3.13 (3H, s, mim-CH<sub>3</sub>), 2.10(3H, s, Tol-CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  144.1, 137.1, 134.5, 134.4, 131.7, 131.3, 130.0, 129.7, 128.0, 127.9, 127.2, 127.0, 126.6, 122.8, 122.7, 122.2, 121.4, 115.2, 112.5, 37.5, 25.8. <sup>31</sup>P–{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ 27.9 (C<sub>35</sub>H<sub>31</sub>N<sub>2</sub>OPNi requires C, 71.82; H, 5.34; N, 4.79. Found: C, 71.91; H, 5.28; N, 4.89%).

# 2.2.10. cis-Di {bis(1-methylimidazol-2-yl)methanone} (bromo)aquanickel(II) bromide.acetonitrile, [Ni ${(mim)_2CO}_2Br(OH_2)$ ]Br · MeCN (14)

A solution of bis(1-methylimidazol-2-yl)methanone (0.251 g, 1.32 mmol) in MeCN (21 mL) was added to a solution of NiBr<sub>2</sub>.3H<sub>2</sub>O (0.367 g, 1.34 mmol) in MeCN (20 mL), and a blue precipitate rapidly formed. The solution was decanted and a second equivalent of solid ligand was added to the solution. The solution changed from blue to blue-green and a blue crystalline solid deposited. Yield: 0.152 g, 17%. Electronic spectrum (KBr disc):  $\lambda$  561 nm. IR (KBr disc): 3700–2750 (b), 1647 (m), 1489 (m), 1424 (s), 1176 (w), 1090 (w), 957 (w), 901 (s), 798 (w), 653 (w), 604 (w) cm<sup>-1</sup>. Magnetic moment 3.09 BM.

# 2.2.11. Di {bis(1-methylimidazol-2-yl)methanone} diaquanickel(II) bromide tris(acetonitrile), [Ni{(mim)<sub>2</sub>CO}<sub>2</sub> (OH<sub>2</sub>)<sub>2</sub>]Br<sub>2</sub>·3MeCN (15)

A solution of bis(1-methylimidazol-2-yl)methanone (0.188 g, 0.989 mmol) in MeCN (8 mL) was added to a solution of NiBr<sub>2</sub>.3H<sub>2</sub>O (0.135 g, 0.495 mmol) in MeCN (10 mL). A blue precipitate rapidly formed, and after 19 d the solution had become green. The solution was decanted and the solids washed with  $CH_2Cl_2$  (4 mL). The combined solvents were allowed to stand for a week, and a single green crystal of the product was isolated.

# 2.2.12. Tri {bis(1-methylimidazol-2-yl)methanone}nickel (II) tetrafluoroborate quadrantishydrate, [Ni{(mim)<sub>2</sub>-CO}<sub>3</sub>] [ $BF_4$ ]<sub>2</sub> · 0.25 $H_2O$ (16)

A solution of nickel(II) tetrafluoroborate (0.34 mL, 50% wt, 0.74 mmol) was added to a solution of bis(1methylimidazol-2-yl)methanone (0.43 g, 2.3 mmol) in water (5.6 mL). A thick pink suspension immediately formed, acetone (10 mL) was added and the resulting purple solution gave purple crystals on standing for 6 days. Yield: 0.60 g, quantitative. Electronic spectrum (single crystal):  $\lambda$  541, 768 (sh), 876 nm. IR (KBr disc): 3416 (m, br), 1643 (s), 1487 (m), 1463 (m), 1419 (s), 1294 (w), 1168 (w), 1051 (m, br), 953 (w), 900 (s), 771 (w), 724 (w), 656 (w), 606 (w) cm<sup>-1</sup>. Magnetic moment 3.09 BM ( $C_{27}H_{30.5}B_2F_8N_{12}NiO_{3.25}$  requires C, 40.16; H, 3.81; N, 20.82. Found: C, 40.08; H, 3.83; N, 20.84%).

# 2.3. X-ray structure determinations

Full spheres of low-temperature CCD area-detector diffractometer data were measured (Bruker AXS instrument,  $\omega$ -scans, monochromatic Mo K $\alpha$  radiation,  $\lambda = 0.7107$  Å; T ca. 153 K) yielding N<sub>t</sub> reflections, merging to N unique ( $R_{int}$  quoted) after 'empirical'/multiscan absorption correction (proprietary software),  $N_0$  with  $F > 4\sigma(F)$  being considered 'observed' and used in the full matrix least squares refinements, refining anisotropic displacement parameter forms for the non-hydrogen atoms,  $(x, y, z, U_{iso})_{H}$  being refined for the hydrogen atoms. Conventional residuals R,  $R_w$  (weights:  $((\sigma^2 F) + 0.0004F^2)^{-1})$  are quoted on |F| at convergence, neutral atom complex scattering factors being employed within the XTAL-3.7 program system [35]. Pertinent results are given below and in Tables 1-3 and Figs. 1-3, the latter displaying 50% probability displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Individual difficulties, variations in procedure, abnormalities, etc., are cited as Variata.

# 2.3.1. Crystallrefinement data

Complex 11a. Ni(mimCO<sub>2</sub>)(o-Tol)(PPh<sub>3</sub>) · 1/3CH<sub>2</sub>Cl<sub>2</sub>  $\equiv$ C<sub>30</sub>H<sub>27</sub>N<sub>2</sub>NiO<sub>2</sub>P · 1/3CH<sub>2</sub>Cl<sub>2</sub>, M = 565.5, triclinic, space group  $P\bar{1}$ , a = 11.291(1) Å, b = 19.375(2) Å, c = 20.051(2) Å,  $\alpha = 82.311(3)^{\circ}$ ,  $\beta = 85.098(3)^{\circ}$ ,  $\gamma = 75.897(3)^{\circ}$ , V = 4210 Å<sup>3</sup>,  $D_{c}$  (Z = 6) = 1.33<sub>8</sub> g cm<sup>-3</sup>,  $\mu_{Mo} = 8.4$  cm<sup>-1</sup>, specimen:  $0.45 \times 0.13 \times 0.10$  mm,  $T_{min,max} = 0.71$ , 0.86,  $2\theta_{max} = 50^{\circ}$ ,  $N_{t} = 47025$ , N = 14482 ( $R_{int} = 0.069$ ),  $N_{o} = 8538$ , R = 0.049,  $R_{w} = 0.048$ ,  $|\Delta \rho_{max}| = 0.80(7)$  e Å<sup>-3</sup>.

*Variata.*  $(x, y, z, U_{iso})_{H}$  were included in the refinement, constrained at estimated values. The dichloromethane solvent molecule was modelled as disordered over two sets of sites, occupancies refining, within a total constraint set at unity after trial refinement, to x = 0.608(3), 1 - x. Similarly, each *o*-tolyl ring was modelled as disordered over two sets of sites, occupancies 0.848(7), 0.77(1), 0.65(1) and complements.

Complex 12. Ni(mimCPh<sub>2</sub>O)(o-Tol)(PPh<sub>3</sub>)=C<sub>42</sub>H<sub>37</sub> N<sub>2</sub>NiOP, M = 675.4, monoclinic, space group  $P2_1$ , a = 8.884(1) Å, b = 15.201(3) Å, c = 12.918(2) Å,  $\beta = 104.115(4)^\circ$ , V = 1692 Å<sup>3</sup>,  $D_c$  (Z = 2) = 1.33<sub>5</sub> g cm<sup>-3</sup>,  $\mu_{Mo} = 6.6$  cm<sup>-1</sup>, specimen:  $0.32 \times 0.27 \times 0.14$  mm,  $T_{min,max} = 0.73$ , 0.86,  $2\theta_{max} = 75^\circ$ ,  $N_t = 34564$ , N = 8351 ( $R_{int} = 0.031$ ),  $N_o = 7168$ , R = 0.033,  $R_w = 0.039$ ,  $|\Delta \rho_{max}| = 0.64(6)$  e Å<sup>-3</sup>. Table 1

(a) Selected geometries for Ni(L-*N*,*O*)(*o*-Tol)(PPh<sub>3</sub>) (**11a**, **12**)  $L = L' = mimCO_2^{-}$  (**11a**),  $L = L'' = mimCPh_2O^{-}$  (**12**)

L/molecule	L'/1	L′/2	L'/3	L"(/1) <sup>a</sup>
Distances (Å)				
Ni–N(1)	1.907(4)	1.910(4)	1.894(4)	1.895(2)
Ni-O(21)	1.961(3)	1.964(3)	1.960(3)	1.923(2)
Ni–P	2.150(1)	2.152(2)	2.152(2)	2.1536(6)
$Ni-C(01)^{b}$	1.861(7)	1.87(1)	1.93(1)	1.896(2)
C(20)–O(21)	1.294(6)	1.284(7)	1.281(6)	1.408(2)
C(2)–C(20)	1.502(7)	1.491(7)	1.497(7)	1.509(3)
C(01) - C(01')	0.73(4)	0.48(3)	0.69(2)	
$N(1) \cdots O(21)$	2.581(5)	2.586(5)	2.583(5)	2.568(3)
Angles (°)				
N(1)-Ni-O(21)	83.7(2)	83.8(2)	84.2(1)	84.55(8)
N(1)–Ni–P	173.7(1)	174.8(1)	173.7(1)	178.56(6)
N(1)-Ni-C(01)	91.4(2)	91.6(4)	91.4(4)	89.18(9)
O(21)–Ni–P	92.79(9)	93.7(1)	91.8(1)	96.19(5)
O(21)-Ni-C(01)	170.7(2)	172.0(4)	174.6(3)	168.49(9)
P-Ni-C(01)	92.8(2)	91.4(3)	92.3(3)	90.30(7)
Ni-N(1)-C(2)	111.5(3)	111.5(3)	111.4(3)	113.2(2)
Ni-O(21)-C(20)	115.3(3)	114.9(3)	115.1(3)	115.9(1)
N(1)-C(2)-C(20)	118.1(4)	118.2(5)	118.0(4)	118.5(2)
C(2)-C(20)-O(21)	110.7(5)	111.6(4)	111.1(4)	107.1(2)
Interplanar dihedral angles (°	) ('PCNO' is the coordination en	vironment of the nickel)		
PCNO/C <sub>3</sub> N <sub>2</sub>	13.5(2)	5.4(1)	5.5(1)	12.06(7)
PCNO/CCO(2)	19.86(8)	17.57(8)	15.4(1)	2.5(2)
PCNO/C <sub>6</sub>	87.3(2)	87.6(3)	88.6(3)	82.93(9)
C <sub>3</sub> N <sub>2</sub> /CCO	6.3(2)	12.2(1)	10.8(2)	10.0(1)
Out-of-plane deviations, $\delta$ (Å	.)			
$\delta$ Ni/PCNO	0.035(2)	0.056(2)	0.084(7)	0.047(1)
$\delta \text{ Ni/C}_3 \text{N}_2$	0.305(8)	0.062(7)	0.080(7)	0.421(4)
$\delta$ Ni/CCO <sub>(2)</sub>	0.469(5)	0.517(5)	0.233(5)	0.039(6)
$\delta$ Ni/C <sub>6</sub>	0.249(10)	0.16(2)	0.03(2)	0.331(4)
Torsion angles (°)				
O(21)-Ni-O-C(11)	159.8(2)	157.8(2)	169.0(2)	169.9(1)
C(01)-Ni-P-C(11)	-27.7(3)	-28.5(4)	-7.4(4)	-19.7(1)
Ni-P-C(11)-C(16)	65.7(4)	77.7(4)	68.1(5)	80.3(2)
Ni-P-C(21)-C(26)	19.4(5)	23.5(4)	20.8(5)	23.2(2)
Ni-P-C(31)-C(36)	40.8(4)	35.0(5)	34.2(4)	-5.2(2)

(b) Comparative [Ni(ar-*N*,*O*)R (phosphine)] arrays "py" = pyridine, 'quin' = quinoline

Ligands				Distances (Å)				
Chelate	Phosphine	Hydrocarbyl	Ref.	Ni–N	Ni–O	Ni–P	Ni–C	
2-СО <sub>2</sub> -ру	PPh <sub>3</sub>	<i>o</i> -tolyl	c	1.945(4)	1.919(3)	2.163(2)	1.884(5)	
	PPhMe <sub>2</sub>	mesityl	d	1.926(6)	1.911(5)	2.148(2)	1.865(8)	
4NO <sub>2</sub> -2-CO <sub>2</sub> -py	$PPh_3$	<i>o</i> -tolyl	c	1.940(4)	1.931(3)	2.163(2)	1.851(7) <sup>e</sup>	
8- <i>O</i> -quin	$PMe_3$	Me	f	1.953(3)	1.924(3)	2.125(1)	1.917(5)	
2-O <sub>2</sub> CCH <sub>2</sub> -py	$PPh_2Me$	mesityl	d	1.951(6)	1.932(3)	2.162(2)	1.890(4)	

<sup>a</sup> In the chelate ring, torsions successively in the bonds Ni–N(1), N(1)–C(2), et seq. are  $7.0(2)^\circ$ ,  $-10.0(3)^\circ$ ,  $7.4(3)^\circ$ , -1.3(2),  $-2.9(2)^\circ$ .

<sup>b</sup> Major component, where appropriate.

<sup>c</sup> From [19].

<sup>d</sup> From [18].

<sup>e</sup> Disordered, as in the present arrays.

<sup>f</sup> From [36].

*Variata.*  $(x, y, z, U_{iso})_{H}$  were included in the refinement, constrained at estimated values. 'Friedel pair' data were retained distinct, ' $x_{abs}$ ' refining to -0.006(8).

Complex 14. cis-[Ni{(mim)<sub>2</sub>CO}<sub>2</sub>Br(OH<sub>2</sub>)]Br · CD<sub>3</sub>CN $\equiv$ C<sub>18</sub>H<sub>22</sub>Br<sub>2</sub>N<sub>8</sub>NiO<sub>3</sub> · CD<sub>3</sub>CN, M = 661.0, monoclinic, space group  $P2_1/c$ , a = 14.484(1) Å, b = 13.296(1) Å,  $\begin{array}{ll} c = 13.091(1) \quad \text{\AA}, \quad \beta = 94.615(2)^{\circ}, \quad V = 2513 \quad \text{\AA}^{3}, \quad D_{\rm c}\\ (Z = 4) = 1.74_{7} \quad {\rm g} \quad {\rm cm}^{-3}, \quad \mu_{\rm Mo} = 39.9 \quad {\rm cm}^{-1},\\ {\rm specimen:} \quad 0.40 \times 0.08 \times 0.08 \ {\rm mm}, \quad T_{\rm min,max} = 0.54, \quad 0.86,\\ 2\theta_{\rm max} = 65^{\circ}, \quad N_{\rm t} = 38716, \quad N = 9986 \quad (R_{\rm int} = 0.073),\\ N_{\rm o} = 6202, \quad R = 0.041, \quad R_{\rm w} = 0.041, \quad |\Delta\rho_{\rm max}| = 1.4(1) \quad {\rm e}\\ \text{\AA}^{-3}. \end{array}$ 

Table 2

Selected geometries, for *cis*-[Ni{(min)<sub>2</sub>CO}<sub>2</sub>XY] in 14 (X = Br, Y = OH<sub>2</sub>) and 15 (X = Y = OH<sub>2</sub>); r (Å) are the nickel–donor distances, the other entries in the matrix being the angles (°) subtended by the relevant atoms at the head of the row and column values for 15 are given below those for 14

Atom	r	N(121)	N(211)	N(221)	X	Y
N(111)	2.074(2)	87.3(1)	177.3(1)	91.8(1)	87.55(7)	87.6(1)
	2.061(2)	87.22(6)	178.7(1)	93.91(6)	92.17(6)	87.25(6)
N(121)	2.055(3)		95.5(1)	91.7(1)	93.01(8)	173.6(1)
	2.084(2)		92.93(6)	98.87(6)	89.29(6)	171.67(6)
N(211)	2.082(2)			88.2(1)	92.24(7)	89.6(1)
	2.060(2)			87.37(6)	86.51(6)	92.46(6)
N(221)	2.056(3)				175.23(8)	92.4(1)
	2.076(1)				170.04(6)	87.72(6)
X(Br)	2.6479(5)					82.89(8)
(O(2))	2.101(2)					84.70(6)
Y(=O(1))	2.146(2)					
(both)	2.101(2)					

 $C_2$ CO/im dihedral angles are 19.1(1)°, 16.1(1)°; 14.2(1)°, 16.8(1)° (14), 6.58(9)°, 1.95(9)°; 7.98(8)°, 3.31(8)° (15); im/im dihedral angles are 21.6(1)°, 12.5(1)° (14), 8.53(9)°, 11.20(8)° (15). Ni deviations from the  $C_3N_2$  im planes are 0.031(5), 0.258(5); 0.067(5), 0.069(5) (14), 0.045(3), 0.370(3); 0.134(3), 0.414(3) Å (15).

Table 3 The  $[Ni{(mim)_2CO_3}]^{2+}$  cation geometry of **16** 

Atom	r	N(121)	N(211)	N(221)	N(311)	N(321)
N(111)	2.078(3)	87.5(1)	93.3(1)	89.4(1)	89.9(1)	175.1(1)
N(121)	2.099(3)		177.4(1)	91.4(1)	90.6(1)	88.9(1)
N(211)	2.089(2)			86.1(1)	91.9(1)	90.4(1)
N(221)	2.115(2)				177.87(9)	94.0(1)
N(311)	2.106(2)					86.8(1)
N(321)	2.081(2)					

Metal atom environment; r (Å) are the nickel–donor distances, the other entries in the matrix being the angles (°) subtended by the relevant atoms at the head of the row and column.

Within the three ligands,  $C_2CO/im$  dihedral angles are:  $1.5(1)^\circ$ ,  $4.3(1)^\circ$ ;  $9.0(1)^\circ$ ,  $4.9(1)^\circ$ ;  $5.3(1)^\circ$ ; im/im angles are:  $3.6(2)^\circ$ ,  $10.6(1)^\circ$ ,  $11.7(1)^\circ$ ; Ni deviate from the im  $C_3N_2$  planes by 0.118(5), 0.013(5); 0.077(5), 0.275(5); 0.032(5), 0.556(5) Å.

Complex 15. cis-[Ni{(mim)<sub>2</sub>CO}<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]Br<sub>2</sub> · 3CD<sub>3</sub>CN C<sub>18</sub>H<sub>24</sub>Br<sub>2</sub>N<sub>8</sub>NiO<sub>3</sub> · 3CD<sub>3</sub>CN, M = 767.2, monoclinic, space group  $P2_1/n$ , a = 8.5382(7) Å, b = 24.308(2) Å, c = 15.766(1) Å,  $\beta = 92.256(2)^{\circ}$ , V = 3270 Å<sup>3</sup>,  $D_c$ (Z = 4) = 1.55<sub>8</sub> g cm<sup>-3</sup>,  $\mu_{Mo} = 30.8$  cm<sup>-1</sup>, specimen: 0.45 × 0.40 × 0.35 mm,  $T_{min,max} = 0.42$ , 0.70,  $2\theta_{max} = 68^{\circ}$ ;  $N_t = 49317$ , N = 12774 ( $R_{int} = 0.042$ ),  $N_o = 8322$ , R = 0.033,  $R_w = 0.034$ ,  $|\Delta \rho_{max}| = 0.84(8)$  e Å<sup>-3</sup>.

Complex 16.  $[Ni\{(\min)_2CO\}_3][BF_4]_2 \cdot 0.236-H_2O = C_{27}H_{30}B_2F_8N_{12}NiO_3 \cdot 0.236H_2O$ , M = 807.4, orthorhombic, space group *Pbca*, a = 15.240(1) Å, b = 11.728(2) Å, c = 37.283(4) Å, V = 6664 Å<sup>3</sup>,  $D_c$  $(Z = 8) = 1.60_9$  g cm<sup>-3</sup>,  $\mu_{Mo} = 6.8$  cm<sup>-1</sup>, specimen:  $0.1 \times 0.1 \times 0.05$  mm,  $T_{\min,max} = 0.68$ , 0.82,  $2\theta_{max} = 58^\circ$ ,  $N_t = 77863$ , N = 8908 ( $R_{int} = 0.016$ ),  $N_o = 4473$ , R = 0.043,  $R_w = 0.034$ ,  $|\Delta \rho_{max}| = 0.64(9)$  e Å<sup>-3</sup>.

*Variata.*  $BF_4(2)$  was modelled as disordered over two sets of sites, occupancies 0.736(4) and complement, the water molecule oxygen fragment concerted with the latter, associated hydrogen atoms not being located.

#### 2.4. Catalysis

#### 2.4.1. Dibromonickel precatalysts

In a typical procedure the precatalyst (0.02-0.03 mmol) was suspended in toluene (25 mL) at 50 °C in a dry 75 mL autoclave. The autoclave was purged with ethylene and MMAO in heptane (0.4–0.6 mmol, 20 eq.) was injected. After stirring for 3 min, ethylene (40 bar) was added, and after 1 h the autoclave was rapidly cooled to approximately -25 °C, brought to 1 bar and nonane (0.1 g) added. The autoclave was sealed, the contents mixed, brought to 1 bar and a liquid sample taken. The contents of the autoclave were treated with methanol (200 mL) and allowed to stand for 2 h. The solids were collected by filtration, washed with methanol, acetone, cyclohexane, and treated with conc. HCl ( $4 \times 150$  mL), where each treatment with solvent or acid involved standing for 30 min. The material remaining after acid leaching was washed with water, methanol, and acetone and dried to give a white polymer.



Fig. 1. Projections of single molecules of (a) Ni(mimCO<sub>2</sub>)(o-Tol)(PPh<sub>3</sub>) (11a, molecule 1) and (b) Ni(mimCPh<sub>2</sub>O)(o-Tol)(PPh<sub>3</sub>) (12) normal to their coordination planes.

## 2.4.2. Single component, cationic catalyst

In a typical procedure,  $[Ni\{(\min)_2CO\}\{o-tolyl\}Br]$ (0.018 g, 0.043 mmol) was suspended in toluene (16 mL) at 50 °C in a dry, 75 mL autoclave. The autoclave was purged with ethylene and a suspension of NaBAF [BAF = tetra(3,5-di(trifluoromethyl)phenyl)borate] (0.038 g, 0.043 mmol, 1 eq.) in toluene (9 mL) was added. After stirring for 5 min, ethylene (40 bar) was added, and after 1 h the autoclave was rapidly cooled to approximately -25 °C and the reaction solution worked up as described in Section 2.1.

# 2.4.3. Neutral, single component catalyst

In a typical procedure, the precatalyst (0.02-0.08 mmol) was dissolved in the solvent (40 mL) and placed in a dry, N<sub>2</sub>-purged 75 mL autoclave. The autoclave was



Fig. 2. Projections of the cations (a) cis-[Ni{(mim)<sub>2</sub>CO}<sub>2</sub>Br(OH<sub>2</sub>)]<sup>+</sup> and (b) cis-[Ni{(mim)<sub>2</sub>CO}<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> in **14** and **15**, respectively, normal to their *quasi 2* axes, showing close contacts to associated anions (see text).

equilibrated with ethylene (40 bar), sealed and heated to 80 °C for 15 hours, timed from thermal equilibrium. On completion the autoclave was rapidly cooled to approximately -25 °C and the reaction solution worked up as described in Section 2.1.

# 3. Results and discussion

# 3.1. Synthesis and characterisation of reagents and complexes

The square-planar nickel(II) complexes (Scheme 1) were obtained by substitution reactions in dichloro-

methane involving displacement of dimethoxyethane (DME) or dioxane (Eq. (1)), or triphenylphosphine (Eq. (2)). The complex Ni(mimCO<sub>2</sub>)(*o*-Tol)(PPh<sub>3</sub>)<sub>2</sub> (**11a**) was obtained from the reaction of NiBr(*o*-Tol)(PPh<sub>3</sub>)<sub>2</sub> with Zn(mimCO<sub>2</sub>)<sub>2</sub>(mimH), and related complexes **11b–13** were obtained, using the potassium salts of the [N–O]<sup>-</sup> ligands (Eq. (3)).

$$Ni(L)Br_2 + L^2 \rightarrow NiBr_2(L^2) + L$$
(1)

7a  $L^2 = (mim)_2 CO, L = DME$ 

**7b**  $L^2 = (bim)_2 CO$ , L = dioxane

8  $L^2 = py(mim)CO, L = DME$ 



Fig. 3. Projection of the cation of  $[Ni\{(mim)_2CO\}_3]^{2+}$  in 16, down its putative 3-axis.

# 9 $L^2 = PhN = CHbim, L = DME$

$$NiBr(o-Tol)(PPh_3)_2 + (mim)_2CO(1a)$$
  

$$\rightarrow NiBr(o-Tol)\{(mim)_2CO\}(10) + 2PPh_3$$
(2)

$$NiBr(o-Tol)(PPh_3)_2 + [L^2]^-$$
  

$$\rightarrow Ni(L^2)(o-Tol)(PPh_3) + Br^- + PPh_3$$
(3)

 $\label{eq:L2} \begin{array}{ll} \mbox{11b} \ L^2 = \mbox{bim}CO_2^-, & \mbox{12} \ L^2 = \mbox{mim}CPh_2O^-, \\ \mbox{13} \ L^2 = \mbox{mim}C_6H_4O^- \end{array}$ 

Although initial studies of the reactivity of nickel(II) bromide toward  $(mim)_2CO$  in acetonitrile in attempts to synthesize **7a** were unsuccessful, the reactions did give small quantities of blue (14) and green crystals (15) depending upon the stoichiometry used in the reactions. The crystals were characterised by X-ray diffraction as *cis*-[Ni{(mim)\_2CO}\_2Br(OH\_2)]Br · MeCN (14) and *cis*-[Ni{(mim)\_2CO}\_2(OH\_2)\_2]Br\_2 · 3MeCN (15) (Scheme 2), but reliable syntheses for these complexes could not be developed. A high yield synthesis of [Ni{(mim)\_2CO}\_3]-[BF\_4]\_2 · 0.25H\_2O (16) was subsequently developed from the reaction of nickel(II) tetrafluoroborate with the ligand in water and the complex characterised by

X-ray diffraction, but we were unable to exploit this synthetic method to devise improved routes to complexes **14** and **15**, e.g. reactions of Ni(II) tetrafluoroborate with ligand and NaBr in water or acetonitrile.

All of the complexes, except 14 and 15, were characterised by microanalysis. Mass spectra of complexes 7a, 11a, 11b, 12 and 13 are readily interpreted as showing parent ions as the highest m/z value; complexes 8 and 10 show the highest ion as  $[MH - HBr]^+$  and  $[M - o-Tol]^+$ ; and complex 9 shows higher ions together with  $[M - Br]^+$ . <sup>1</sup>H NMR spectra of *o*-tolylnickel(II) complexes exhibit spectra with integration consistent with the formulations presented, and of the dibromonickel(II) complexes only 7b was sufficiently soluble for <sup>1</sup>H NMR spectroscopy. Complexes 11–13 in CD<sub>2</sub>Cl<sub>2</sub> exhibit <sup>31</sup>P resonances within the range 27–30 ppm, similar to that reported for related pyridine-2-carboxylate and pyrazine-2-carboxylate complexes Ni(N–O)(*o*-Tol)(PPh<sub>3</sub>) in C<sub>6</sub>D<sub>6</sub> (24–27 ppm) [18].

#### 3.2. X-ray structural studies

The complexes  $Ni(mimCO_2)(o-Tol)(PPh_3)$  (11a) and  $Ni(mimCPh_2O)(o-Tol)(PPh_3)$  (12) have similar structures involving square-planar geometry with the *o*-Tol



Scheme 2. Octahedral nickel(II) cations containing bis(1-methylimidazol-2-yl)methanone (1a). Both enantiomers are present in crystal structures

determined for 14–16 (Figs. 1 and 2).

group trans to the oxygen donor atom of the bidentate ligands (Fig. 1). Three molecules of 11a comprise its asymmetric unit, there being no evidence of a superlattice in the structure. The o-tolyl group is rotationally disordered in both structures, the component occupancies being ca. 0.5 in **12** and 0.85, 0.77, 0.65 in **11a** where the latter may be in concert with solvent disorder. There is almost no significant difference in the 'bite' of the chelate rings, although the ring is puckered in 12; there is a van der Waals contact of  $2.3_5$  Å between H(216) and H(3a). Counterpart geometries of other 'Ni(aryl-N,O)R(P trans to N)' square planar Ni(II) arrays are tabulated in Table 1(b) for comparison, the chelate rings being five-membered with the exception of the six-membered pyridylacetate complex. The present Ni-N(im) distances, closely ranged at 1.902(8) Å, are appreciably shorter than those of the N-N(py) systems [1.926(6)-1.953(3) Å]. It is of interest to note the occurrence of aryl substituent disorder similar to 11a and 12 in the 4-nitro-2-picolinate complex [19].

Complexes 14 and 15, isolated from similar preparative procedures and crystallised in NMR tubes from solution in CD<sub>3</sub>CN, involve six-coordinate Ni(II) in the pair of isomers cis-[Ni{(mim)<sub>2</sub>CO}<sub>2</sub>Br(OH<sub>2</sub>)]-Br  $\cdot$  CD<sub>3</sub>CN (14) and *cis*-[Ni{(mim)<sub>2</sub>CO}<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]- $Br_2 \cdot 3CD_3CN$  (15) (Table 2 and Fig. 2). In both complexes one formula unit devoid of crystallographic symmetry comprises the asymmetric unit; hydrogen bonding is limited but significant involving short contacts (Br $\cdots$ H < 2.6 Å) between bromide ions and water molecules.  $Br(2) \cdot \cdot \cdot H(1a)$ 2.31(6)Á in 14.  $Br(1) \cdots H(2a, 1b) \quad 2.36(3), \quad 2.38(2) \quad A, \quad Br(2) \cdots H(2b),$ H(1a) (1/2 - x, 1/2 - y, 1/2 - z) 2.42(3), 2.34(3) Å in 15. The cation of 15 has quasi 2 symmetry (Table 2). Nickel-nitrogen distances trans to the water molecules are slightly elongated within each ligand, with the nickel atom lying considerably out of the associated imidazole planes. Nickel-O(H<sub>2</sub>) distances in the complexes [2.101(2), 2.146(2)] Å] are longer than the diverse values found in  $[Ni(OH_2)_6]^{2+}$  arrays, typically ca. 2.05 Å, while Ni-N trans to each other are generally shorter than in  $[Ni{(mim)_2CO}_3]^{2+}$  (see below). Replacement of one of the water molecules in 15 by a bromine atom impacts little by way of any 'trans' effect. Interplanar dihedral angles within the ligands in 14 are greater than in 15, while a considerable difference between the two is found in the interligand angle N(121)–Ni–N(221) *trans* to the unidentate ligands, and in the (*cis*-)X(1)–Ni–N(n11) angles.

The cation  $[Ni\{(mim)_2CO\}_3]^{2+}$  in 16 (Fig. 3) is the first structurally characterised example of a tris-{(mim)<sub>2</sub>-CO} complex, and the quasi-threefold axes of the cation are approximately directed along the crystallographic bdirection. Each ligand is non-planar, the overall array having significant perturbations from ideal 32 geometry (Table 3), perhaps most evident in departures of the metal atom from coplanarity with various ligand planes. There is a dearth of structural data available for tris(symmetrical N, N'-bidentate)nickel(II) arrays, the only accessible values (ca. 2.14 Å) for six-membered chelate systems being tris(propane-1,3-diamine)nickel(II) complexes [37,38], while data available for tris(symmetrical N, N'-biimidazolyl)nickel(II) species involve five-membered chelates, Ni-N varying widely around 2.1 Å [39].

#### 3.3. Catalytic studies

When activated with MMAO in the presence of moderate pressures of ethylene the four-coordinate nickel complexes, 7–10, give moderate to low yields of mainly polyethylene along with some oligomers. The polymers generated are, in general, high melting (118–120 °C) with a high degree of branching, as indicated by FT-IR (polymer samples were too insoluble for NMR studies), which is in contrast with the relatively linear products generated by the Ni–diimine type catalysts reported by Feldman et al. [40]. The oligomers generated by these catalysts show high linearity, as demonstrated in Table 4 by the analysis of the C6 fraction.

The catalyst generated from 10/NaBAF (BAF = tetra(3,5-di(trifluoromethyl)phenyl)borate) produced only oligomers (mainly linear), no nickel black being observed. Precatalyst 9 produced oligomers with very small amounts of linear polymer, similar to the behaviour previously noted for the bipyridine–Ni catalyst and low steric bulk  $\alpha$ -diimine–Ni systems [3–6]. Bipyridine–Ni catalysts were reported, by Brookhart and co-workers [3–6] to produce oligomers and by Pakkanen and

				-			
Precatalyst	Cocatalyst	Polymer productivity (gmmol $Ni^{-1} h^{-1}$ )	Tm	Oligomer productivity (gmmol Ni <sup>-1</sup> h <sup>-1</sup> )	Oligomer dist. C6 fraction		TON
					Linear C6 (%)	α (%)	
Bipy-NiBr <sub>2</sub>	MMAO	trace		6.3	91	38	230
9	MMAO	trace		5.3	>99	82	193
8	MMAO	2.3	126	0.82	>99	62	107
7b	MMAO	4.5	122	1.7	87	56	223
7a	MMAO	10	132	33	>99	56	1550
10	NaBArF	trace	92	32	>99	66	1140

Table 4 Ethylene oligomerisation/polymerisation [Ni-complex/MMAO] catalyst systems

co-workers [41] to produce HDPE in small quantities. In comparative studies, we also found that the bipyridine-Ni catalyst produces both oligomers as well as traces of linear polymer. For the catalyst systems reported here, the overall shape of the ligand appears to exert a major influence on both activity and product distribution. Ligands forming five-membered chelates generate catalysts that behave like typical low steric bulk  $\alpha$ -diimine systems and yield predominantly oligomeric products. The bis(heterocyle)methanone catalysts, which possess stronger  $\sigma$ -donor ligands, form six-membered chelates and generate a mixture of oligomers and significant amounts of high polymer. Within the series of bis(heterocyle)methanone precatalysts overall activity appears to decrease while the ratio of polymer to oligomer increases with increasing  $\pi$ -acidity of the chelating ligand.

The neutral organometallic complexes 11–13 react with ethylene under moderate pressures, without the need for cocatalyst, to form oligomers or polymer (Table 5). Catalysts formed from 11a/b generate a mixture of oligomer and polymer with 11b having a slightly lower selectivity for polymer. This follows the behaviour of previously reported substituted pyridine, pyrazine and salicylaldimine ligated catalysts in that the stronger donor 1-methylimidazole function results in a greater proportion of lower molecular weight products when the reaction is performed in chlorobenzene. The oligomers are predominantly linear with a high-content (see analysis of C6 fraction, Table 5). The robust nature of neutral Ni(II) catalysts is demonstrated by complex **11a** which retains activity in neat ethanol, the product distribution is shifted to oligomers. Changing the carboxylate group of **11a/b** to alkoxy (**12**) or phenoxy (**13**) groups lowers the activity of the catalysts and changes the product distribution to oligomer (**12**) and polymer (**13**), respectively.

Interestingly, a linear inverse relationship is observed between the <sup>31</sup>P chemical shifts of the catalyst precursors and the percentage of polymer product generated, and a reasonably linear positive correlation exists between <sup>31</sup>P chemical shifts and the linearity of the C6 oligomer fraction (Fig. 4). The <sup>31</sup>P chemical shift of the phosphine ligand may reflect the properties of the N–O ligands in these systems. Very recently two further reports on Nibased systems in olefin polymerisation reactions have appeared, which also demonstrate the significance of chelate ring size and ligand bulk on catalytic performance [42,43].

	1 7 0	· · ·				
Precatalyst	Solvent	Polymer (%)	Tm	Oligomer dist. C6 fraction		TON
				Linear C6 (%)	α (%)	
11a	Toluene	53	83	96	56	3160
11a <sup>b</sup>	Toluene	54	85	98	70	142
11a	Chlorobenzene	44	73	87	58	2980
11a <sup>c</sup>	Ethanol	0		99 <sup>d</sup>	85	914
11b	Toluene	40	84	97	55	3930
11b	Chlorobenzene	45	78	91	56	1950
12	Toluene	2	85 <sup>e</sup>	99	41	417
13	Toluene	96	113	90 <sup>f</sup>	57	168

Table 5 Ethylene oligomerisation/polymerisation single component catalysts<sup>a</sup>

<sup>a</sup> Catalytic runs were carried out at 80 °C unless otherwise indicated.

<sup>b</sup> 30 °C.

° 60 °C.

<sup>d</sup> No branched C<sub>6</sub> materials observed.

<sup>e</sup> Melting point, insufficient material for DSC.

<sup>f</sup> Traces of branched materials observed.



Fig. 4. Relationship between <sup>31</sup>P chemical shifts of catalyst precursors and (a) percentage of polymer product, and (b) linearity of the C6 oligomer fraction.

#### 4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 224050–224054. Copies of this information may be obtained free of charge from 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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