

Probing the Effect of Binding Site and Metal Centre Variation in Pentadentate Oligopyridylimine-Bearing Bimetallic (Fe₂, Co₂, Ni₂) Ethylene Oligomerisation Catalysts

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The symmetrical and unsymmetrical pentaaza 2,6-oligopyridylimines, 6,6'-[(2,6-*i*Pr₂C₆H₃)N=CMe]₂-2,2':6',2''-C₁₅H₉N₃ (L1) and 6-[(2,6-*i*Pr₂C₆H₃)N=CMe]-2,2':6',2''':6'',2'''-C₂₀H₁₃N₄ (L2), have been prepared in good yield using a combination of palladium(0)-mediated cross-coupling and condensation strategies. Treatment of L1 or L2 with two equivalents of MX₂ in *n*BuOH at elevated temperatures affords the paramagnetic bimetallic complexes [(L1)-M₂X₄] [M = Fe, X = Cl (**1**); M = Co, X = Cl (**2a**); M = Co, X = Br (**2b**); M = Ni, X = Br (**3**)] and [(L2)M₂X₄] [M = Fe, X = Cl (**4**); M = Co, X = Cl (**5a**); M = Co, X = Br (**5b**); M = Ni, X = Br (**6**)] in high yield, respectively. The molecular structures of **2a** along with the acetonitrile adduct of **5b**, [**5b**(NCMe)], have been determined and reveal that L1 and L2 compartmentalise the MX₂ units into mixed pyridylimine/dipyridylimine (**2a**) and pyridylimine/terpyridine [**5b**(NCMe)] binding sites.

Unexpectedly during crystallisation of **6** from acetonitrile, the salt [(L2)Ni₂Br₂(μ -Br)(NCMe)₂][NiBr₄] (**7**) was obtained as the only crystalline product. On activation with MAO (methylaluminoxane), **4**–**6** show only low activities for ethylene oligomerisation (**6**/MAO > **5**/MAO) or are inactive (**4**/MAO). On the other hand, **1**–**3** are considerably more active (**3**/MAO > **2**/MAO > **1**/MAO) with the most productive system, dinickel-based **3**/MAO (450 gmmol⁻¹h⁻¹bar⁻¹), yielding methyl-branched waxes composed of mostly internal unsaturation along with lower levels of α -olefins; conversely the diiron (**1**/MAO) and dicobalt (**2**/MAO) systems give uniquely linear α -olefins. For purposes of comparison the synthesis, structure and catalytic activity of mono-nickel [(6-[(2,6-*i*Pr₂C₆H₃)N=CMe]-2,2'-C₁₀H₇N₂)NiBr₂] (**8**) are also reported. (  Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2008)

Introduction

The application of metal-based oligomerisation catalysts to promote the conversion of ethylene- to olefinic-containing short/medium chain hydrocarbons continues to be the subject of considerable interest to both the academic and industrial communities.^[1] In particular, the production of α -olefins (range: C₄–C₂₀) represents an important industrial process due, in large measure, to the use that the resultant oligomers have in the manufacture of detergents, plasticisers and linear low-density polyethylene (LLDPE). A variety of different catalysts are currently used commercially to mediate this transformation but arguably the most well-known within the late-transition-metal arena is the SHOP catalyst, a neutral nickel(II)-based catalyst bearing a monoanionic P,O-chelate.^[2,3] More recently, cationic nickel catalysts based on a variety of neutral N,N-ligands such as 2-pyridylimines (A in Figure 1) have afforded highly active oligomerisation catalysts that can operate at more modest temperatures and pressures than their SHOP-type predecessors.^[4] 2-Pyridylimines and their more extended relatives,

e.g., 2,6-bis(imino)pyridines and 2,2'-dipyridyl-6-imines (B, in Figure 1), have also started to emerge as compatible supports for iron(II)- and cobalt(II)-mediated oligomerisation.

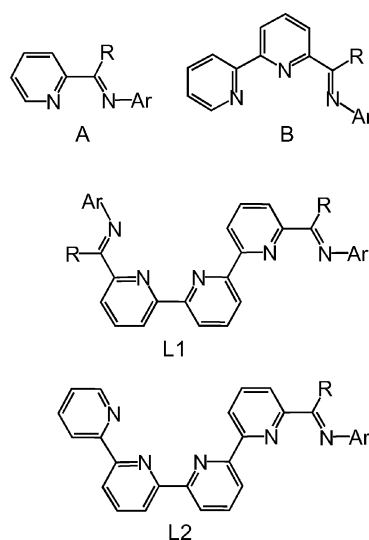


Figure 1. Pyridylimine (A), dipyridylimine (B), bis(imino)terpyridine (L1) and iminoquaterpyridine (L2).

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tions.^[5–8] For example, the [(B)FeCl₂]/MAO catalyst is highly active for the conversion of ethylene to 1-hexene and 1-octene.^[8] A general feature of these pyridylimine-based family of catalysts is the presence of a bulky *N*-aryl group (e.g., 2,6-*i*Pr₂C₆H₃), this is considered important in influencing the activity of the catalyst and in some cases the Schulz–Flory parameter α .^[7]

In recent years we have been interested in developing even more extended pyridylimine ligands and have reported a straightforward synthetic route to generate a range of symmetrical and unsymmetrical 2,6-oligopyridylimines, ArN=RC(C₅H₃N)_{*m*}CR=NAr or C₅H₄(C₅H₃N)_{*n*}CR=NAr (*m* = 2–5 or *n* = 2,3; R = H or Me; Ar = 2,6-*i*Pr₂C₆H₃).^[9] Depending on a variety of properties including the chain length, these ligand frames are capable of housing one or two metal centres furnishing complexes of general composition [(oligopyridylimine)M_{*x*}X_{*y*}] (*x* = 1, 2; *y* = 2, 4).^[10] Herein we are concerned with exploring the ethylene oligomerisation potential of diiron(II), dicobalt(II) and dinickel(II) catalysts bearing an oligopyridylimine that is capable of accommodating the closely located metals in two distinct binding sites (e.g., N,N-bidentate and N,N,N-tridentate). To this end we have targeted the pentaaza members as potential supports for two MX₂ units (X = Cl, Br); see Figure 1, bis(imino)terpyridine L1 and iminoquaterpyridine L2. In a previous study we have shown that only the diketimine (R = Me) derivative of L1 (with Ar = 2,6-*i*Pr₂C₆H₃) can readily facilitate the assembly of the two metal centres

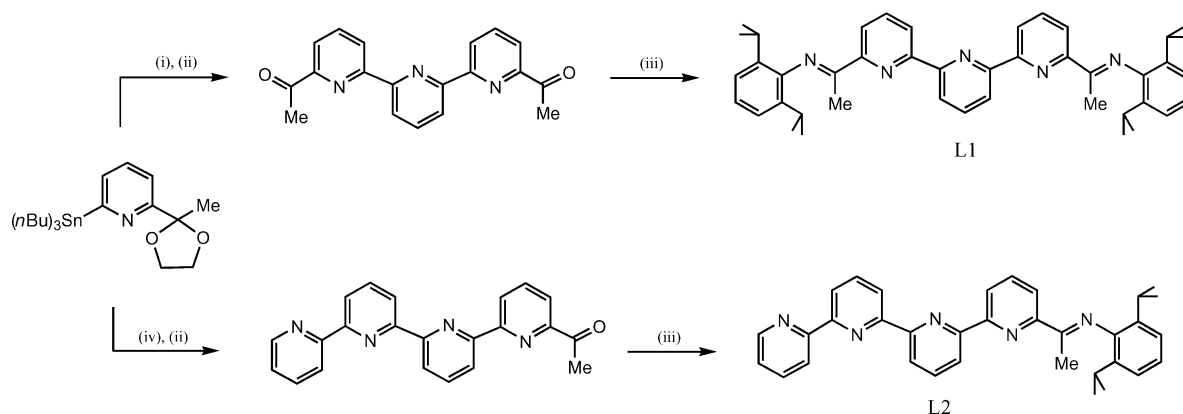
(metal = Fe, Ni, Zn) in the manner desired.^[10a] This work therefore begins by extending the range of L1_{ketimine}-supported complexes to include dicobalt species and then explores the potential of L2 (R = Me, Ar = 2,6-*i*Pr₂C₆H₃) to promote bimetallic assembly. Full details of MAO-activated oligomerisations are reported for bimetallic precatalysts based on L1 and L2.

Results and Discussion

1. Ligand Synthesis

Both ligands 6,6'-[(2,6-*i*Pr₂C₆H₃)N=CMe]₂-2,2':6',2''-C₁₅H₉N₃ (L1) and 6-[(2,6-*i*Pr₂C₆H₃)N=CMe]-2,2':6',2'':6'',2'''-C₂₀H₁₃N₄ (L2) can be prepared in good yield by the acid-catalysed condensation reaction of the corresponding carbonyl compound with 2,6-diisopropylaniline (as reagent and solvent) at 160–200 °C for 30 min. The carbonyl precursors have been prepared in a series of steps from 2-(2-methyl-1,3-dioxolan-2-yl)-6-tributylstannyl-pyridine (Scheme 1) using literature (L1)^[9] or slightly modified procedures (L2).

Crystals of L2 suitable for an X-ray determination were grown from a concentrated nitromethane solution. A view of L2 is shown in Figure 2; selected bond lengths and angles are given in Table 1. The molecular structure consists of a chain of four 2,6-linked pyridine rings containing one 2,6-diisopropylphenyl-substituted imino group as a chain-end.



Scheme 1. Reagents and conditions: (i) 6,6'-dibromo-2,2':6',2''-terpyridine (0.5 equiv.), Pd(PPh₃)₄ (8 mol-%), toluene, 90 °C, 72 h; (ii) HCl (4 M), 60 °C, 12 h; (iii) 2,6-*i*Pr₂C₆H₃NH₂ (xs.), 160–200 °C, cat. H⁺; (iv) 6-bromo-2,2':6',2''-terpyridine (1 equiv.), Pd(PPh₃)₄ (6 mol-%), toluene, 90 °C, 72 h.

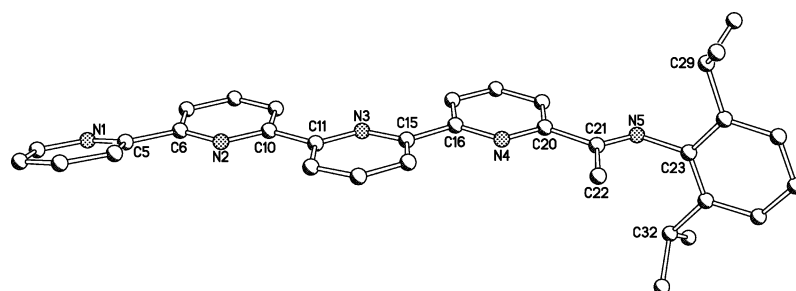


Figure 2. Molecular structure of L2 including a partial atom numbering scheme. All hydrogen atoms have been omitted for clarity.

A mutually *transoid* conformation of the nitrogen atoms is observed throughout the pyridine backbone which is also extended to the imino unit in a fashion akin to that observed for other 2,6-oligopyridylimines^[9,10] as well as 2,6-oligopyridines.^[11] Some twisting is evident within the backbone of L2 which is most notable with regard to the chain-end pyridine and its nearest neighbour [torsion angle N(1)–C(5)–C(6)–N(2) 167.80°]. The C(21)–N(5) bond length of the chain-end imine group [1.277(2) Å] is consistent with double bond character while the *N*_{imine}-aryl group is inclined essentially perpendicularly to this unit [torsion angle C(21)–N(5)–C(23)–C(24) 92.3°]. Some intermolecular π – π stacking of the pyridine groups (closest contact: 3.708 Å) is also evident.

Table 1. Selected bond lengths [Å] and angles [°] for L2.

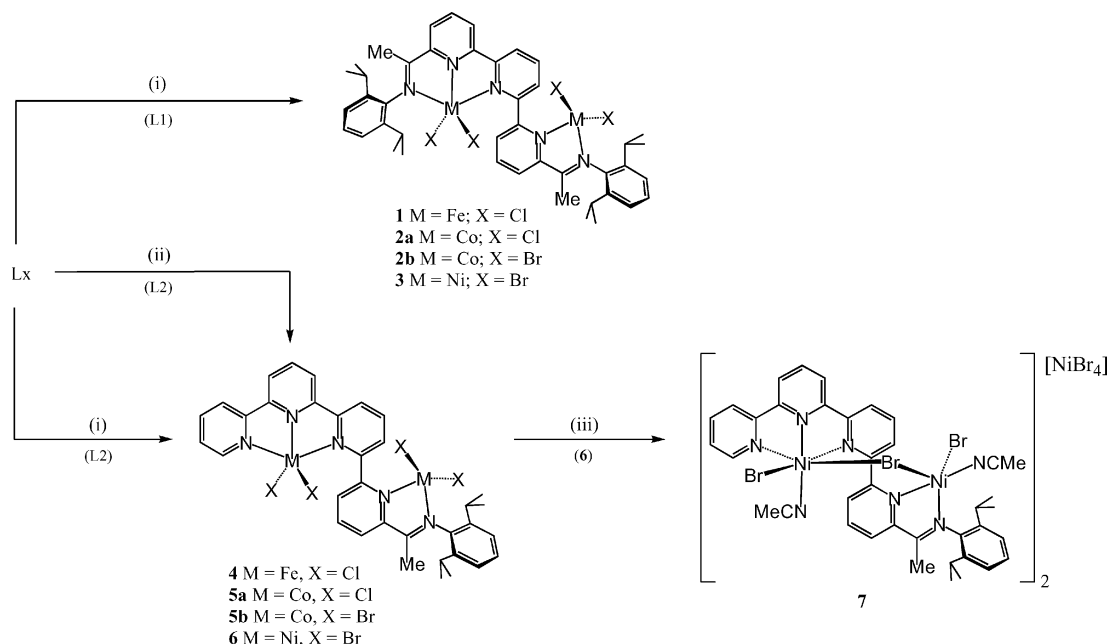
Bond lengths			
C(5)–C(6)	1.493(2)	C(21)–N(5)	1.277(2)
C(10)–C(11)	1.490(2)	C(21)–C(22)	1.501(3)
C(15)–C(16)	1.491(2)	N(5)–C(23)	1.426(2)
C(20)–C(21)	1.495(2)		
Bond angles			
C(22)–C(21)–N(5)	124.88(17)	C(20)–C(21)–N(5)	117.34(17)
C(21)–N(5)–C(23)	120.55(16)		

As with L1,^[9,10a] the spectroscopic properties of L2 support its formulation. In the ES mass spectrum of L2 a peak corresponding to the protonated form of the molecular ion is evident while in its IR spectrum a $\nu(\text{C}=\text{N})_{\text{imine}}$ band at 1634 cm^{−1} is clearly visible. The ¹H NMR spectrum reveals a singlet for the imino methyl group at δ = 2.28; the imino carbon is seen at δ = 166.1 in the ¹³C NMR spectrum.

2. Synthesis of Complexes

Complexes [(L1)Co₂X₄] (X = Cl **2a**; X = Br **2b**) and [(L2)M₂X₄] (M = Fe, X = Cl **4**; M = Co, X = Cl **5a**; M = Co, X = Br **5b**; M = Ni, X = Br **6**) have been prepared in high yield from the reaction of L1 or L2 with two equivalents of MX₂ in *n*BuOH using conditions previously employed for the formation of [(L1)M₂X₄] (M = Fe, X = Cl **1**; M = Ni, X = Br **3**) (Scheme 2).^[10a] Complex **6** has also been prepared by treating L2 with (DME)NiBr₂ in a 1:2 molar ratio in dichloromethane at room temperature. The new complexes **2a**, **2b** and **4–6** have been characterised by a combination of FAB mass spectrometry, IR spectroscopy, elemental analysis and by magnetic measurements (see Table 2 and experimental section). In addition, crystals of **2a** and the acetonitrile adduct of **5b** have been the subject of single-crystal X-ray diffraction studies.

Crystals of **2a** suitable for the X-ray determination were grown from a concentrated acetonitrile solution. A view of **2a** is shown in Figure 3; selected bond lengths and angles are listed in Table 3. The molecular structure reveals a bimetallic complex in which the two metal centres are supported on the same L1 ligand frame and each bound terminally by two chloride ligands. One of the metal centres [Co(2)] occupies a bidentate pyridylimine pocket while the other [Co(1)] a tridentate dipyridylimine cavity so as to generate a tetrahedral geometry at Co(2) and a distorted trigonal bipyramidal geometry at Co(1) [τ = 0.67].^[12] Within the ligand frame the chelating pyridylimine and dipyridylimine moieties are both nearly planar, with each of the planes being disposed orthogonally to one another [torsion angle N(3)–C(18)–C(19)–N(4) 90.1°] with the result that the metal centres are located 5.336 Å apart. For Co(1) the two Co(1)–



Scheme 2. Reagents and conditions: (i) MX₂ (2 equiv.) [MX₂ = FeCl₂, CoCl₂, CoBr₂, (DME)NiBr₂], *n*BuOH, 110 °C, 20 min; (ii) (DME)NiBr₂ (2 equiv.), CH₂Cl₂, room temp., 12 h; (iii) MeCN, heat.

Table 2. Selected data for the new complexes **2**, **4**–**6**.

Complex	Colour	$\nu(\text{C}=\text{N})$ [cm ⁻¹] ^[a]	μ_{eff} [μ_{B}] ^[b]	FAB mass spectrum	Microanalysis (%) ^[c]		
					C	H	N
2a	blue	1594	5.7	860 [M – Cl] ⁺ , 824 [M – 2Cl] ⁺	57.75 (57.67)	5.35 (5.51)	7.78 (7.82)
2b	blue	1595	5.6	993 [M – Br] ⁺ , 913 [M – 2Br] ⁺	48.22 (48.11)	4.36 (4.57)	6.41 (6.53)
4	dark purple	1596	6.8	731 [M – Cl] ⁺ , 696 [M – 2Cl] ⁺	53.11 (53.35)	4.29 (4.31)	9.46 (9.15)
5a	blue	1598	5.3	736 [M – Cl] ⁺ , 699 [M – 2Cl] ⁺	52.20 (52.33) ^[d]	4.34 (4.39) ^[d]	9.04 (8.97) ^[d]
5b	blue	1595	5.7	870 [M – Br] ⁺ , 789 [M – 2Br] ⁺	42.88 (43.02)	3.30 (3.50)	7.14 (7.38)
6	pale orange	1599	4.3	867 [M – Br] ⁺ , 786 [M – 2Br] ⁺	41.58 (41.70) ^[e]	3.42 (3.40) ^[e]	7.31 (7.08) ^[e]

[a] Recorded with a Perkin–Elmer Spectrum One FT-IR spectrometer on solid samples. [b] Recorded with an Evans Balance at room temperature. [c] Calculated values shown in parentheses. [d] Value calculated with 0.5 H₂O. [e] Value calculated with 1/3 CHCl₃.

Cl bond lengths are alike [2.2558(19) vs. 2.268(2) Å], while the Co(1)–N distances vary appreciably with the interior Co(1)–N(2)_{pyridyl} distance [2.027(5) Å] being shorter than the exterior Co(1)–N(1)_{imine} [2.219(6) Å] and Co(1)–N(3)_{pyridyl} [2.219(6) Å] ones. At Co(2), the two cobalt–nitrogen and two cobalt–chloride distances show little variation within each pair. On comparison with the free ligand L1,^[10a] there is no marked variation in the C=N bond lengths on coordination with the average value [1.284(8) Å] in **2a** consistent with double bond character being maintained. The structure of **2a** closely resembles the diiron (**1**) and dizinc analogues previously reported.^[10a]

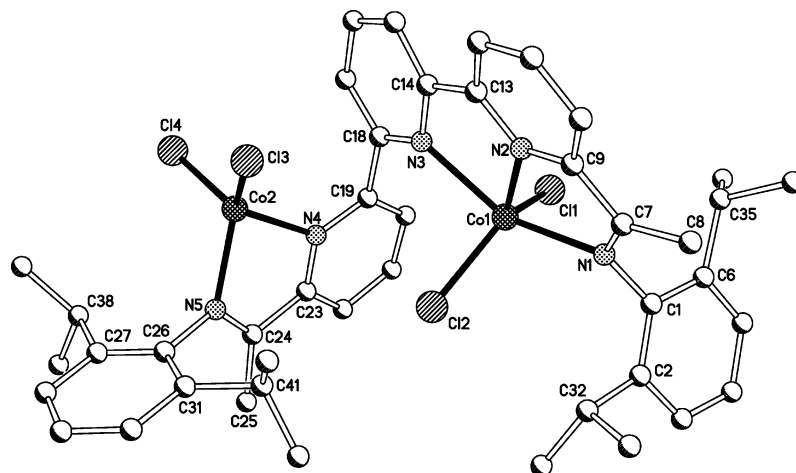
The FAB mass spectra for **2a** and **2b** show fragmentation peaks corresponding to the loss of one or two halide groups from the corresponding molecular ion peak. In their IR spectra, the $\nu(\text{C}=\text{N})_{\text{imine}}$ bands are seen at ca. 1595 cm⁻¹ and shifted to lower wavenumber by ca. 47 cm⁻¹ in comparison with the free ligand L1 and thus support the coordination of both imine groups. Complexes **2a** and **2b** are paramagnetic and display magnetic moments of ca. 5.7 μ_{B} (Evans Balance at ambient temperature) which are consistent with non-spin coupled Co^{II} ($S = 3/2$)–Co^{II} ($S = 3/2$) systems (using $\mu^2 = \sum \mu_i^2$, where μ_i is the magnetic moment

Table 3. Selected bond lengths [Å] and angles [°] for **2a**.

Bond lengths			
Co(1)–N(1)	2.219(6)	Co(2)–N(5)	2.052(5)
Co(1)–N(2)	2.027(5)	Co(2)–Cl(3)	2.212(2)
Co(1)–N(3)	2.219(6)	Co(2)–Cl(4)	2.229(2)
Co(1)–Cl(1)	2.2558(19)	C(7)–N(1)	1.281(8)
Co(1)–Cl(2)	2.268(2)	C(24)–N(5)	1.286(7)
Co(2)–N(4)	2.038(6)	Co(1)···Co(2)	5.336(5)
Bond angles			
N(1)–Co(1)–N(2)	75.2(2)	Cl(1)–Co(1)–N(2)	115.44(17)
N(1)–Co(1)–N(3)	151.8(2)	N(4)–Co(2)–N(5)	77.0(2)
Cl(1)–Co(1)–N(1)	96.78(15)	N(4)–Co(2)–Cl(3)	119.75(18)
Cl(2)–Co(1)–N(1)	101.44(15)	N(4)–Co(2)–Cl(4)	103.73(17)
Cl(1)–Co(1)–Cl(2)	127.10(8)	Cl(3)–Co(2)–Cl(4)	118.76(9)

of the individual metal centres).^[13] A similar pair of non-interacting high-spin configurations has also been seen for the diiron(II) and dinickel(II) counterparts.^[10a]

Crystals of **5b**(NCMe) were grown by slow cooling of a warm acetonitrile solution containing the complex. A view of **5b**(NCMe) is depicted in Figure 4; selected bond lengths and angles are collected in Table 4. The molecular structure of **5b**(NCMe) reveals a bimetallic neutral cobalt complex in

Figure 3. Molecular structure of **2a** including a partial atom-numbering scheme. All hydrogen atoms have been omitted for clarity.

which one metal centre occupies the tridentate terpyridyl pocket in L2 while the other one a bidentate pyridylimine cavity. The coordination spheres at both metal centres are completed by two terminal bromide ligands with an additional *N*-bound molecule of acetonitrile at Co(2). The geometries at Co(1) and Co(2) can be best described as distorted trigonal bipyramidal with the deviation from ideality being most significant at Co(1) [$\tau = 0.51$ (Co(1)) vs. 0.65 (Co(2))].^[12] Within the ligand frame the chelating terpyridyl [torsion angle N(1)–C(5)–C(6)–N(2) 1.2°, N(2)–C(10)–C(11)–N(3) 3.4°] and pyridylimine [torsion angle N(4)–C(20)–C(21)–N(5) 5.8°] units are almost planar with the respective planes inclined at an angle of 107.9° to one another [torsion angle N(3)–C(15)–C(16)–N(4)]; the *N*-substituted aryl group is oriented at 111.8° [torsion angle C(21)–N(5)–C(23)–C(24)] with respect to the pyridylimine plane. With regard to the Co(1) centre, the Co–Br distances are asymmetric [Co(1)–Br(1) 2.4196(18) Å vs. Co(1)–Br(2) 2.4505(19) Å] as are the three Co(1)–N_{pyridyl} distances with the one involving the central pyridine, the shortest [Co(1)–N(2) 2.035(8) Å vs. Co(1)–N(1) 2.153(9) and Co(1)–N(3) 2.197(9) Å]. At Co(2), the three Co–N bond lengths are also inequivalent with the Co–N_{acetonitrile} bond being the longest [Co(2)–N(6) 2.180(11) Å] while the Co–Br bond lengths again show some slight variation [Co(2)–Br(3) 2.4334(18) Å, Co(2)–Br(4) 2.4135(19) Å]. The C(21)–N(5)_{imine} distance of 1.271(13) Å is comparable with the corresponding length found in L2 [1.277(2) Å]. No intermolecular interactions of note are apparent.

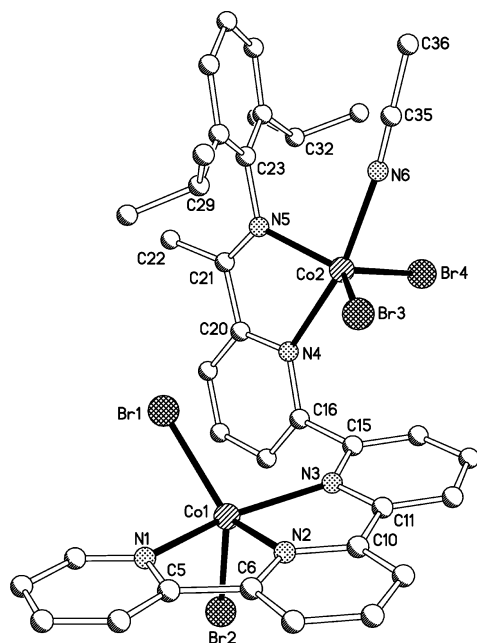


Figure 4. Molecular structure of **5b**(NCMe) including a partial atom numbering scheme. All hydrogen atoms have been omitted for clarity.

In the FAB mass spectra of **4–6**, fragmentation peaks corresponding to the loss of one or two halide ions from the corresponding molecular ion peak are evident. Their IR spectra show bands at ca. 1595 cm^{−1} corresponding to the

Table 4. Selected bond lengths [Å] and angles [°] for **5b**(NCMe).

Bond lengths			
Co(1)–Br(1)	2.4196(18)	Co(2)–N(5)	2.080(8)
Co(1)–Br(2)	2.4505(19)	Co(2)–N(6)	2.180(11)
Co(1)–N(1)	2.153(9)	C(5)–C(6)	1.489(16)
Co(1)–N(2)	2.035(8)	C(10)–C(11)	1.450(15)
Co(1)–N(3)	2.197(9)	C(15)–C(16)	1.525(13)
Co(2)–Br(3)	2.4334(18)	C(21)–N(5)	1.271(13)
Co(2)–Br(4)	2.4135(19)	C(35)–N(6)	1.147(14)
Co(2)–N(4)	2.176(9)	Co(1)···Co(2)	5.556(9)
Bond angles			
N(1)–Co(1)–N(2)	76.9(4)	N(4)–Co(2)–N(6)	167.1(3)
N(1)–Co(1)–N(3)	152.7(3)	N(4)–Co(2)–Br(3)	99.5(2)
N(1)–Co(1)–Br(1)	91.8(3)	N(4)–Co(2)–Br(4)	91.8(2)
N(1)–Co(1)–Br(2)	94.8(3)	N(5)–Co(2)–Br(3)	128.4(2)
Br(1)–Co(1)–Br(2)	122.16(7)	Br(3)–Co(2)–Br(4)	124.90(7)
N(4)–Co(2)–N(5)	76.1(3)		

$\nu(\text{C}=\text{N})_{\text{imine}}$ stretches and corroborate imino group coordination in each case. All the complexes are paramagnetic and exhibit magnetic moments of 6.8 μ_{B} (**4**), 5.3 μ_{B} (**5a**), 5.7 μ_{B} (**5b**) and 4.3 μ_{B} (**6**), their magnitudes being consistent with non-spin coupled Fe^{II} ($S = 2$)–Fe^{II} ($S = 2$), Co^{II} ($S = 3/2$)–Co^{II} ($S = 3/2$) and Ni^{II} ($S = 1$)–Ni^{II} ($S = 1$) systems, respectively.

Unlike with **2a** and **5**, recrystallisation of **6** from warm acetonitrile gave on prolonged standing a few crystals of salt [(L2)Ni₂Br₂(μ -Br)(NCMe)₂]₂[NiBr₄] (**7**) as green blocks. The molecular structure of **7** reveals two independent dinickel cationic units (cations A and B) that are charge balanced by a tetrahedral nickel tetrabromide dianion. The cations A and B are similar and show only minor structural differences; only the structure of cation A will be discussed in any detail. A perspective view of A is depicted in Figure 5 while selected bond lengths and angles for both cations are

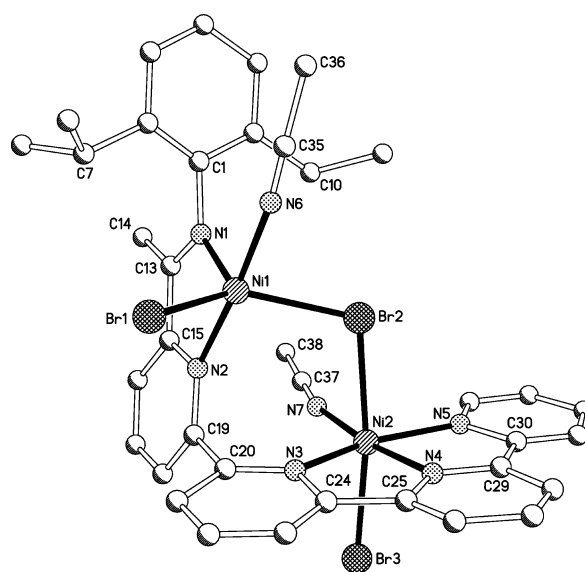


Figure 5. Molecular structure of one of the cationic units (A) in **7** including a partial atom numbering scheme. All hydrogen atoms have been omitted for clarity.

listed in Table 5. The structure of the cationic unit comprises a Ni(1)(μ -Br)Ni(2) core in which Ni(1) fills the pyridylimine pocket in L2 and Ni(2) the terpyridine pocket. Each nickel centre is further coordinated by a monodentate bromide and a molecule of acetonitrile to complete a distorted trigonal bipyramidal geometry [$\tau = 0.59$]^[12] at Ni(1) and an octahedral geometry at Ni(2). At Ni(2) the two bromide ligands are disposed *trans* to one another while at Ni(1) they fill the equatorial belt of the trigonal bipyramid.

Table 5. Selected bond lengths [Å] and angles [°] for **7**.

Bond lengths	Cation A	Cation B
Ni(1)–N(1)	2.034(5)	2.029(5)
Ni(1)–N(2)	2.099(5)	2.109(5)
Ni(1)–N(6)	2.043(6)	2.050(6)
Ni(1)–Br(1)	2.4093(13)	2.4130(13)
Ni(1)–Br(2)	2.4839(12)	2.5208(12)
Ni(2)–N(3)	2.135(5)	2.151(5)
Ni(2)–N(4)	2.002(5)	2.000(5)
Ni(2)–N(5)	2.105(5)	2.116(5)
Ni(2)–N(7)	2.061(5)	2.050(5)
Ni(2)–Br(2)	2.5868(12)	2.6251(13)
Ni(2)–Br(3)	2.5359(12)	2.5291(12)
Ni(1)···Ni(2)	4.134(5)	4.149(5)
range Ni–Br (dianion)	2.3745(13)–2.3956(14)	
Bond angles		
N(1)–Ni(1)–N(2)	79.6(2)	79.0(2)
N(1)–Ni(1)–N(6)	91.1(2)	92.2(2)
N(1)–Ni(1)–Br(1)	115.43(16)	113.71(15)
N(1)–Ni(1)–Br(2)	109.41(16)	112.04(15)
N(2)–Ni(1)–N(6)	170.7(2)	171.1(2)
N(2)–Ni(1)–Br(1)	93.26(14)	92.72(14)
N(2)–Ni(1)–Br(2)	95.57(14)	96.76(14)
Br(1)–Ni(1)–Br(2)	135.15(4)	134.24(4)
N(3)–Ni(2)–N(4)	78.2(2)	77.6(2)
N(3)–Ni(2)–N(5)	156.64(19)	155.74(19)
N(3)–Ni(2)–N(7)	110.12(19)	110.1(2)
N(3)–Ni(2)–Br(2)	85.56(13)	91.92(14)
N(3)–Ni(2)–Br(3)	89.35(13)	91.92(14)
N(4)–Ni(2)–N(5)	78.6(2)	78.2(2)
N(4)–Ni(2)–N(7)	171.2(2)	171.0(2)
N(4)–Ni(2)–Br(2)	91.71(14)	91.15(15)
N(4)–Ni(2)–Br(3)	93.46(14)	96.69(15)
N(5)–Ni(2)–N(7)	93.0(2)	93.95(19)
N(5)–Ni(2)–Br(2)	93.08(15)	95.59(14)
N(5)–Ni(2)–Br(3)	94.11(15)	91.63(14)
Br(2)–Ni(2)–Br(3)	171.85(4)	170.28(4)

Table 6. Catalytic evaluation of **1–6** for ethylene oligomerisation.^[a]

Entry	Pre-catalyst	Mass of oligomer ^[b] [g]	Activity [g mmol ^{−1} h ^{−1} bar ^{−1}]	Olefinic product ^[c] (%)				α ^[d]
				α -olefin	internal	vinylidene	tri-substituted	
1	1	0.05	10	99.0	1.0	–	–	0.58
2	2a	1.05	210	98.8	1.2	–	–	0.78
3	3	2.25	450	22.4	52.1	4.5	21.0	^[e]
4	4	0	0	–	–	–	–	^[e]
5	5a	0.04	8	24.5	63.2	3.9	8.4	^[e]
6	6	0.26	52	50.9	34.6	4.7	9.8	^[e]

[a] General conditions: 1 bar ethylene Schlenk test carried out in toluene (40 mL) at ambient temperature using 6.0 mmol MAO (Al/M = 300:1), 0.01 mmol precatalyst, over 30 min. Reactions were terminated by addition of dilute HCl. [b] Mass of oligomer based on GC using a C₁₇ standard. [c] Product percentages calculated via integration of their ¹H NMR spectra. [d] Determined from GC; α = (rate of propagation)/[(rate of propagation) + (rate of chain transfer)] = (mol of C_{n+2})/(mol of C_n). [e] Not measured.

At each metal centre the Ni–Br(2)_{bridging} distance is longer than the corresponding Ni–Br_{terminal} one [Ni(1)–Br(2) 2.4839(12) vs. Ni(1)–Br(1) 2.4093(13) Å; Ni(2)–Br(2) 2.5868(12) vs. Ni(2)–Br(3) 2.5359(12) Å] while, in general, the Ni(1)–Br distances are shorter than the Ni(2)–Br ones. Both acetonitrile molecules adopt sites *trans* to a pyridine nitrogen atom [N(7)–Ni(2)–N(4) 171.2(2)°, N(6)–Ni(1)–N(2) 170.7(2)°]. In comparison with **5b**(NCMe) the effect of the bridging bromide ligand is to compress the metal–metal distance [4.134(5) (**7**) vs. 5.556(9) Å (**5b**(NCMe))] and also to reduce the inclination between adjacent terpyridine and pyridylimine planes [torsion angle N(3)–C(20)–C(19)–N(2) 71.5° vs. 107.9° (**5b**(NCMe))]. No significant inter anion-cation interactions are evident.

The isolation of **7** during the attempted crystallisation of **6** was unexpected. It is uncertain whether **7** arises through partial decomposition of **6** during thermal treatment with acetonitrile or is a minor impurity in samples of **6**. Nevertheless, crystalline **7** could only be obtained in low yield.

3. Ethylene Oligomerisation

The bimetallic complexes **1–6** have all been screened as precatalysts for oligomerisation (or polymerisation) of ethylene; the results are collected in Table 6 (Entries 1–6). Typically, a complex in toluene was activated with 600 equiv. (300 per metal centre) of methylaluminoxane (MAO) at room temperature and ethylene (1 bar) gas then introduced over a period of 30 min. All the systems, except for iron-containing **4**/MAO (Entry 4; which was inactive), showed low to high activities for ethylene oligomerisation affording hydrocarbon-based materials that were readily soluble in toluene (and chloroform). No evidence for higher molecular weight polymeric materials could be detected under these experimental conditions.

The most active systems were found using L1 as the supporting ligand with dinickel-based **3**/MAO (Entry 3) giving the highest productivity (450 g mmol^{−1} h^{−1} bar^{−1}). Inspection of the vinylic region of the ¹H NMR spectrum of the resulting wax reveals the presence of a mixture of alkene-containing compounds composed of mostly internal olefins (63%), α -olefins (25%), along with lower levels of tri-substituted (8%) and vinylidenes (4%) (Figure 6). In addition, the

^{13}C NMR spectrum of these oligomeric products indicates the presence of mainly methyl branches, along with very low levels of longer chain branches (e.g., ethyl and propyl).^[13] Examination of the GC spectrum confirms the broad product distribution with multiple peaks found in addition to those corresponding to the linear α -olefins (in the range C8–C26). The observed production of methyl-branched materials is similar to that obtained using the highly active monometallic pyridylimine-nickel family of catalysts (e.g., [(2-{(2,6-*i*Pr₂C₆H₃)N=CMe}C₅H₄N)NiBr₂]/MAO), in which a chain-walking mechanism has been used to account for the observed isomerisation/branching,^[1g,1h,15] although the material obtained here is of lower molecular weight. In order to additionally compare the performance of **3**/MAO against a potential monometallic dipyridylimine-nickel catalyst (see B in Figure 1), we have prepared (see experimental section) and screened a genuine sample of [(6-{(2,6-*i*Pr₂C₆H₃)N=CMe}-2,2'-C₁₀H₇N₂)NiBr₂] (**8**). The molecular structure of **8** is shown in Figure 7; selected bond lengths and angles are collected in Table 7. The structure reveals the expected features with the single nickel centre bound by a tridentate dipyridylimine ligand and two bromide ligands to complete a distorted trigonal-bipyramidal geometry ($\tau = 0.63$;^[12] cf. 0.67 for the dipyridylimine-CoCl₂ moiety in **2a**). Solutions of **8**/MAO in toluene, however, show only low activity for ethylene oligomerisation with an olefinic product distribution comparable to that seen with **3**/MAO. It would, therefore, be possible to conclude based on the evidence above that the main propagation/termination pathway is occurring at the pyridylimine-Ni centre within L1 in **3**/MAO. However, this conclusion should be viewed with some caution as 6-organyl-substituted pyridylimine-nickel catalysts^[16] in general show much lower activities than their unsubstituted counterparts.^[4] Moreover, we have reported that dinickel catalysts in which the central pyridine ring in L1 has been replaced by 1,3-phenyl group displays an order of magnitude drop in activity.^[17]

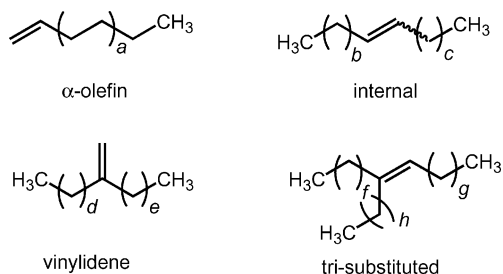


Figure 6. Types of olefinic products accessible in Entries 1–6.

In contrast to **3**/MAO, dicobalt and diiron systems bearing L1, **2a**/MAO (Entry 2) and **1**/MAO (Entry 1), are more selective and generate even-numbered linear α -olefins [$> 98\%$; range: C₆–C₂₀, $\geq \text{C}_{20}$ 0.28% (Entry 1), range: C₆–C₂₈, $\geq \text{C}_{20}$ 29% (Entry 2)] with the dicobalt system giving the higher of the activities (210 gmmol⁻¹ h⁻¹ bar⁻¹ vs. 10 gmmol⁻¹ h⁻¹ bar⁻¹). Both catalysts afford Schulz–Flory distributions for the α -olefins, with the α value [rate of

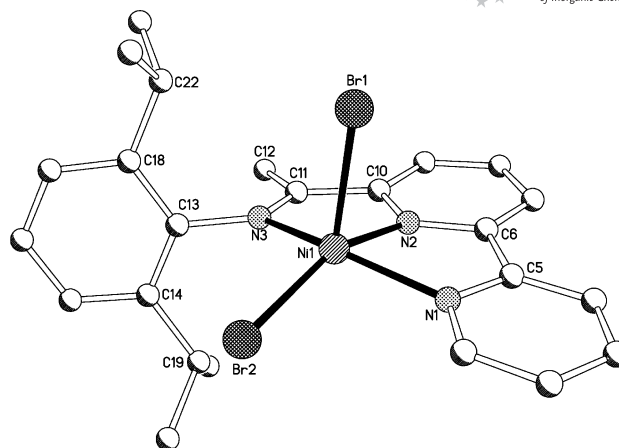


Figure 7. Molecular structure of **8** including a partial atom-numbering scheme. All hydrogen atoms have been omitted for clarity.

Table 7. Selected bond lengths [Å] and angles [°] for **8**.

Ni(1)–Br(1)	2.4555(6)	Ni(1)–N(2)	1.978(3)
Ni(1)–Br(2)	2.3520(6)	Ni(1)–N(3)	2.147(3)
Ni(1)–N(1)	2.103(3)	C(11)–N(3)	1.286(4)
N(1)–Ni(1)–N(2)	77.71(12)	N(1)–Ni(1)–Br(2)	96.72(8)
N(1)–Ni(1)–N(3)	151.12(11)	Br(1)–Ni(1)–Br(2)	113.21(2)
N(1)–Ni(1)–Br(1)	94.81(8)		

propagation/(rate of propagation + rate of chain transfer) = (mol of C_{n+2})/(mol of C_n)^[18] for Entry 2 being higher (0.78) than for Entry 1 (0.58) consistent with a higher probability of chain propagation and the observed broader range of α -olefins. No saturated hydrocarbon was produced in either Entry, which indicates the absence of chain transfer to aluminium as a termination mechanism.^[19] Interestingly, catalytic evaluation of the monometallic pyridylimine and dipyridylimine precursors [(2-{(2,6-*i*Pr₂C₆H₃)N=CMe}C₅H₄N)CoCl₂] and [(6-{(2,6-*i*Pr₂C₆H₃)N=CMe}-2,2'-C₁₀H₇N₂)CoCl₂] using MAO as co-catalyst have been previously reported to be inactive for ethylene oligomerisation using conditions similar to those employed in this work.^[4a,4b,4c] The explanation for the significant activity of **2a**/MAO for α -olefin production is unclear but it may be connected to the observation made by Bianchini and co-workers that the presence of a 6-substituted organyl group (with hemilabile donor properties) in monometallic pyridylimine-Co catalysts is important for oligomerisation activity.^[5b] Significantly, we have shown previously that the central pyridine ligand in the dizinc analogue of **2a**, [(L1)-Zn₂Cl₄], is labile and can interchange between metal centre coordination on the NMR timescale.^[10a] It is therefore possible that a similar hemilability of the central pyridine in the **2a**/MAO is operational and contributes to the performance characteristics observed.

Catalysts systems based on L2 display much lower activities than their L1 counterparts with dinickel-containing **6**/MAO (Entry 6) displaying the highest activity (52 gmmol⁻¹ h⁻¹ bar⁻¹) of the series followed by **5a**/MAO (Entry 5). As with **3**/MAO, **6**/MAO affords a mixture of α -olefins and internal olefins as the major oligomeric prod-

ucts. The superior catalytic activities of L1-based systems over the L2 systems is likely due to the presence of steric bulk at both ends of the pyridyl chain rather than one end, thereby limiting more effectively β -hydrogen elimination during termination. Notably, monometallic iron, cobalt and nickel catalysts bearing terpyridine ligands also show either very low catalytic activities or are inactive.^[20–22]

Conclusions

The pentaaza 2,6-oligopyridylimine-type ligands, bis-(imino)terpyridine (L1) and iminoquaterpyridine (L2), have been synthesised and successfully employed as scaffolds for supporting two metal(II) centres [metal = iron (**1,4**), cobalt (**2,5**) and nickel (**3,6**)]. As representative examples, the molecular structures of dicobalt complexes of both ligand types have been determined and indicate that the metal centres occupy inequivalent binding domains with the metal centres separated by 5.336(5)–5.556(9) Å. Upon activation with MAO, the L1-supported precatalysts (**1,2,3**) display modest to good activities for the oligomerisation of ethylene with the dinickel system, **3**/MAO, displaying the highest. On the other hand, the less sterically bulky L2-supported precatalysts (**4,5,6**) show significantly lower activities. In general the nickel systems afford a broad range of methyl-branched materials containing a variety of olefinic end groups, while the cobalt systems form either linear α -olefins (with L1) or a mixture of olefinic types (with L2); the only active iron system, **1**/MAO, displays low activity and yields uniquely linear α -olefins.

Experimental Section

General Remarks: All reactions, unless otherwise stated, were carried out under dry, oxygen-free nitrogen, using standard Schlenk techniques or in a nitrogen-purged glove box. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use.^[23] The infrared spectra were recorded with a Perkin–Elmer Spectrum One FT-IR spectrometer on solid samples. The ES (Electrospray) and the FAB (Fast atom bombardment) mass spectra were recorded using a micromass Quattro LC mass spectrometer and a Kratos Concept spectrometer with dichloromethane or NBA as the matrix, respectively. High-resolution FAB mass spectra were recorded with Kratos Concept spectrometer (xenon gas, 7 kV) with NBA as the matrix. Oligomer products were analysed by GC, using a Perkin–Elmer Autosystem XL chromatograph equipped with a flame ionisation detector and 30 m PE-5 column (0.25 mm thickness), injector temperature 45 °C and the following temperature programme: 45 °C/7 min, 45–195 °C/10 °C min^{–1}, 195 °C/5 min, 195–225 °C/10 °C min^{–1}, 225 °C/5 min, 225–250 °C/10 °C min^{–1}, 250 °C/22 min. ¹H and ¹³C NMR spectra were recorded with a Bruker ARX spectrometer (300 MHz) at ambient temperature unless otherwise stated; chemical shifts (ppm) are referred to the residual protic solvent peaks and chemical shifts are in Hertz [Hz]. Magnetic susceptibility studies were performed using an Evans Balance (Johnson Matthey) at room temperature. The magnetic moment data were calculated following standard methods^[24] and corrections for underlying diamagnetism were applied to the data.^[25] Elemental analyses were performed at the Science Technical Support Unit, London Metropolitan University.

The metal dihalides, MAO (10 wt.-% in toluene) and (DME)NiBr₂ (DME = 1,2-dimethoxyethane) were purchased from Aldrich Chemical Co. and used without further purification while 2,6-diisopropylaniline was distilled prior to use. The compounds tetrakis-(triphenylphosphane)palladium(0),^[26] 2-(2-methyl-1,3-dioxolan-2-yl)-6-(tributylstannyl)pyridine,^[9] 6-bromo-2,2':6'',2'''-terpyridine,^[27] L1,^[9,10a] **1**,^[10a] **3**^[10a] and 6-[(2,6-*i*Pr₂C₆H₃)N=CMe]-2,2'-C₁₀H₇N₂^[5b] were prepared according to previously reported procedures. All other chemicals were obtained commercially and used without further purification.

Synthesis of L2 (two-step procedure). (a) Preparation of 6-Acetyl-2,2':6'',2'''-quaterpyridine: 6-Bromo-2,2':6'',2'''-terpyridine (1.50 g, 4.82 mmol), 2-(*n*Bu₃Sn)-6-[C(Me)CH₂CH₂O]-C₅H₃N (2.410 g, 5.30 mmol, 1.1 equiv.) and tetrakis(triphenylphosphane)palladium(0) (0.334 g, 0.29 mmol, 0.06 equiv.) were loaded in a Schlenk vessel under nitrogen and the contents stirred in dry toluene (30 mL) for 72 h at 90 °C. After removal of the solvent under reduced pressure, ethanol was introduced to precipitate the acetal protected form of 6-acetyl-2,2':6'',2'''-quaterpyridine which was then filtered and dried. The collected solid was then treated with 4 M HCl (20 mL), stirred overnight at 60 °C and, on cooling to room temperature, carefully neutralised with 2 M NaHCO₃. The organic phase was extracted with CHCl₃ (3 × 30 mL) and washed with water (3 × 30 mL), brine (1 × 40 mL) and dried with magnesium sulfate. Following filtration, the solvent was removed under reduced pressure and the crude product crystallised from ethanol at –30 °C. The resulting precipitate was collected by filtration to afford 6-acetyl-2,2':6'',2'''-quaterpyridine as a white solid. Yield 1.270 g, 75%; m.p. 215–217 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.81 (s, 3 H, CH₃C=O), 7.2–7.3 (m, 1 H, Py-H), 7.82 (dd, ³J_{H,H} = 7.9, ⁴J_{H,H} = 1.7 Hz, 1 H, Py-H), 7.9–8.0 (m, 4 H, Py-H), 8.43 (dd, ³J_{H,H} = 7.9, ⁴J_{H,H} = 0.9 Hz, 1 H, Py-H), 8.54 (dd, ³J_{H,H} = 7.9, ⁴J_{H,H} = 1.7 Hz, 1 H, Py-H), 8.5–8.7 (m, 4 H, Py-H), 8.80 (dd, ³J_{H,H} = 7.6, ⁴J_{H,H} = 1.2 Hz, 1 H, Py-H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 25.9 (CH₃C=O), 121.1 (Py), 121.5 (Py), 123.9 (Py), 124.4 (Py), 136.9 (Py), 137.8 (Py), 137.9 (Py), 149.2 (Py), 154.5 (Py), 155.5 (Py), 200.4 (CH₃C=O) ppm. IR: $\tilde{\nu}$ = 1697 (C=O), 1562, 1426, 1352, 1267, 1109, 1075, 992, 804, 775, 740 cm^{–1}. ESMS: *m/z* = 353 [M + H]⁺. HRMS (FAB): calcd for C₂₂H₁₇N₄O [M + H]⁺ 353.14024; found 353.14016.

(b) Preparation of L2: 6-Acetyl-2,2':6'',2'''-quaterpyridine (1.50 g, 4.44 mmol) was suspended in an excess of 2,6-diisopropylaniline (7.86 g, 44.40 mmol, 10 equiv.) and stirred for 15 min at 160 °C on a heating mantle. A catalytic amount of formic acid was added, and the reaction mixture was stirred for an additional 20 min at temperatures between 160–200 °C. Following removal of the excess 2,6-diisopropylaniline under reduced pressure (130 °C, 0.5 Torr), the resulting brown residue was stirred in ethanol at room temperature and the resultant precipitate filtered and washed with ethanol. The residue was crystallised from a dichloromethane/hexane (1:9) mixture at room temperature and the resulting precipitate filtered, washed with hexane and dried under reduced pressure to afford L2 as a pale yellow solid. Yield 0.629 g, 60%. Recrystallisation by slow cooling of a warm nitromethane solution of L2 gave clear needles; m.p. > 260 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.10 [d, ³J_{H,H} = 6.7 Hz, 12 H, CH(Me)₂], 2.28 (s, 3 H, CH₃C=N), 2.71 [sept, 2 H, CH(Me)₂], 7.0–7.2 (m, 3 H, Ar-H), 7.2–7.3 (m, 1 H, Py-H), 7.8–7.9 (m, 1 H, Py-H), 7.91 (dd, ³J_{H,H} = 7.9, ³J_{H,H} = 7.9 Hz, 2 H, Py-H), 8.35 (d, ³J_{H,H} = 7.9 Hz, 1 H, Py-H), 8.42 (d, ³J_{H,H} = 7.9 Hz, 1 H, Py-H), 8.53 (d, ³J_{H,H} = 7.9 Hz, 1 H, Py-H), 8.59 (d, ³J_{H,H} = 7.9 Hz, 1 H, Py-H), 8.67 (m, 2 H, Py-H) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 16.3 (s, CH₃C=N), 21.9 (CH₃), 22.2 (CH₃), 27.3 (CH), 120.1 (Py), 120.2 (Py), 121.0 (Py),

122.0 (Py), 122.5 (Ar), 122.8 (Ar), 134.8 (Py), 135.9 (Py), 136.3 (Ar), 136.7 (Py), 136.9 (Py), 148.1 (Py), 154.2 (Py), 154.4 (Py), 154.6 (Py), 166.1 (C=N) ppm. IR: $\tilde{\nu}$ = 2950, 1634 (C=N), 1562, 1425, 1362, 1292, 1269, 1188, 1111, 1080, 991, 807, 759, 684 cm^{-1} . ESMS: m/z = 512 $[\text{M} + \text{H}]^+$. HRMS (FAB): Calcd. for $\text{C}_{34}\text{H}_{34}\text{N}_5$ $[\text{M} + \text{H}]^+$ 512.28142, found 512.28155.

Synthesis of [(L1)Co₂X₄] (2). (a) **X = Cl (2a):** An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous CoCl₂ (0.041 g, 0.315 mmol) in *n*BuOH (10 mL) and the contents stirred at 110 °C until the salt had completely dissolved. L1 (0.100 g, 0.157 mmol, 0.5 equiv.) was added and the reaction mixture stirred at 110 °C for a further 20 min. After cooling to room temperature, the suspension was concentrated and hexane added to induce precipitation of the product. The solid was filtered, washed with hexane and dried overnight under reduced pressure to afford [(L1)Co₂Cl₄] (2a) as a blue solid. Yield 0.099 g, 70%. Recrystallisation from warm acetonitrile gave 2a as blue blocks. IR: $\tilde{\nu}$ = 2959 (m), 2870 (w), 1594 [s, $\nu(\text{C}=\text{N})_{\text{imine}}$], 1575 (m), 1459 (s), 1430 (m), 1368 (m), 1322 (w), 1244 (m), 1194 (m), 1113 (m), 1011 (m), 936 (w), 825 (m), 795 (s), 750 (s) and 660 cm^{-1} (m); (see Table 2 for further characterisation).

(b) **X = Br, (2b):** Using an analogous procedure to that described in 2a employing CoBr₂ (0.036 g, 0.164 mmol) and L1 (0.052 g, 0.082 mmol, 0.5 equiv.) gave [(L1)Co₂Br₄] (2b) as a blue solid. Yield 0.141 g, 80%. Recrystallisation from warm acetonitrile gave 2b as a blue-green microcrystalline powder. IR: $\tilde{\nu}$ = 2960 (m), 2873 (w), 1595 [s, $\nu(\text{C}=\text{N})_{\text{imine}}$], 1574 (m), 1459 (s), 1429 (m), 1367 (m), 1323 (w), 1246 (m), 1195 (m), 1113 (m), 1011 (m), 824 (m), 796 (s), 751 (s) and 601 cm^{-1} (m); (see Table 2 for further characterisation).

Synthesis of [(L2)M₂X₄] (4–6). (a) **M = Fe, X = Cl (4):** An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous FeCl₂ (0.061 g, 0.480 mmol) in *n*BuOH (10 mL) and the contents stirred at 110 °C until the iron salt had completely dissolved. L2 (0.123 g, 0.240 mmol, 0.5 equiv.) was added and the reaction mixture stirred at 110 °C for a further 20 min. After cooling to room temperature, the suspension was concentrated and hexane added to induce precipitation of the product. The solid was filtered, washed with hexane and dried overnight under reduced pressure to afford [(L2)Fe₂Cl₄] (4) as a black-purple powder. Yield 0.112 g, 55%. Recrystallisation from warm acetonitrile gave 4 as a dark purple microcrystalline powder. IR: $\tilde{\nu}$ = 2961 (m), 2930 (w), 1598 [m, $\nu(\text{C}=\text{N})$], 1569 (m), 1460 (m), 1440 (m), 1370 (s), 1310 (w), 1263 (s), 1197 (s), 1101 (m), 1030 (m), 829 (m), 795 (s), 774 (s), 693 (m) and 655 (s); (see Table 2 for further characterisation) cm^{-1} .

(b) **M = Co, X = Cl (5a):** Using an analogous procedure to that described for 4 employing CoCl₂ (0.062 g, 0.480 mmol) and L2 (0.123 g, 0.240 mmol, 0.5 equiv.) gave [(L2)Co₂Cl₄] (5a) as a blue powder. Yield 0.126 g, 68%. Recrystallisation from warm acetonitrile solution afforded 5a(NCMe) as a blue microcrystalline powder. IR: $\tilde{\nu}$ = 2962 (m), 2928 (w), 1598 [m, $\nu(\text{C}=\text{N})$], 1588 (s), 1574 (m), 1455 (m), 1428 (m), 1383 (m), 1367 (s), 1316 (w), 1253 (s), 1200 (s), 1101 (m), 1023 (m), 820 (m), 796 (s), 775 (s), 750 (s), 693 (m) and 655 cm^{-1} (s); (see Table 2 for further characterisation).

(c) **M = Co, X = Br (5b):** Using an analogous procedure to that described for 4 employing CoBr₂ (0.105 g, 0.480 mmol) and L2 (0.123 g, 0.240 mmol, 0.5 equiv.) gave [(L2)Co₂Br₄] (5b) as a blue powder. Yield 0.090 g, 42%. Recrystallisation from hot acetonitrile solution gave 5b(NCMe) as blue blocks. IR: $\tilde{\nu}$ = 2961 (m), 2938 (w), 1595 [s, $\nu(\text{C}=\text{N})$], 1588 (s), 1574 (m), 1488 (m), 1458 (m), 1396 (w), 1316 (w), 1251 (m), 1194 (s), 1186 (s), 1010 (m), 829 (m), 786

(s), 778 (s), 769 (s) and 659 cm^{-1} (m); (see Table 2 for further characterisation).

(d) **M = Ni, X = Br (6):** Using an analogous procedure to that described for 4 employing (DME)NiBr₂ (0.148 g, 0.480 mmol) and L2 (0.123 g, 0.240 mmol, 0.5 equiv.) gave [(L2)Ni₂Br₄] (6) as a pale orange powder. Yield 0.090 g, 44%. Recrystallisation from chloroform afforded 6 as an orange microcrystalline powder. IR: $\tilde{\nu}$ = 2970 (m), 2949 (w), 1599 [m, $\nu(\text{C}=\text{N})$], 1575 (m), 1568 (s), 1464 (s), 1445 (m), 1379 (w), 1322 (w), 1254 (m), 1243 (m), 1196 (s), 1159 (s), 1013 (m), 821 (m), 802 (s), 786 (s), 749 (s), 755 (m) and 697 cm^{-1} (s); (see Table 2 for further characterisation).

Alternative Synthesis of [(L2)Ni₂Br₄] (6): A mixture of L2 (0.100 g, 0.196 mmol) and (DME)NiBr₂ (0.121 g, 0.391 mmol, 2 equiv.) were added to a Schlenk flask and dry dichloromethane (10 mL) introduced at 0 °C under nitrogen. The stirred reaction mixture was warmed to room temperature and stirring continued for a further 12 h to give a pale orange precipitate. The precipitate was filtered and washed with dichloromethane (20 mL) to yield 6 as a pale orange solid. Yield 0.176 g, 95%. See Table 2 for further characterisation.

Reaction of 6 with NCMe: A Schlenk flask was charged with 6 (0.176 g, 0.186 mmol), acetonitrile (10 mL) and the contents heated to reflux with stirring for 0.5 h. The resulting fine suspension (0.050 g of orange solid material) was filtered and the pale green filtrate concentrated to half volume and left to stand. After four days at room temperature green blocks of [(L2)Ni₂Br₂(μ -Br)(NCMe)₂]₂[NiBr₄] (7) were formed. Yield 0.020 g, 9%. IR: $\tilde{\nu}$ = 2962 (m), 2283 [w, $\nu(\text{C}\equiv\text{N})$], 1600 [m, $\nu(\text{C}=\text{N})$], 1577 (m), 1461 (s), 1443 (m), 1366 (w), 1323 (w), 1251 (m), 1196 (m), 1006 (m), 821 (m), 783 (s), 755 (m) and 697 (s) cm^{-1} . Positive FABMS: m/z = 868 $[\text{M}/2 - 1/2 \text{ NiBr}_4 - 2 \text{ MeCN}]^+$, 788 $[\text{M}/2 - 1/2 \text{ NiBr}_4 - 2 \text{ MeCN} - \text{Br}]^+$, 708 $[\text{M}/2 - 1/2 \text{ NiBr}_4 - 2 \text{ MeCN} - 2 \text{ Br}]^+$. Negative FABMS: m/z = 298 $[\text{NiBr}_3]^-$.

Synthesis of [(6-{(2,6-*i*Pr₂C₆H₃)N=CMe}-2,2'-C₁₀H₇N₂)NiBr₂] (8): An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with (DME)NiBr₂ (0.121 g, 0.391 mmol) in *n*BuOH (10 mL) and the contents stirred at 110 °C until the nickel complex had partially dissolved. 6-[(2,6-*i*Pr₂C₆H₃)N=CMe]-2,2'-C₁₀H₇N₂ (0.140 g, 0.391 mmol, 1 equiv.) was added and the reaction mixture stirred at 110 °C for a further 20 min. After cooling to room temperature, the suspension was concentrated and hexane added to induce precipitation of the product. The solid was filtered, washed with hexane and dried overnight under reduced pressure to afford [(6-{(2,6-*i*Pr₂C₆H₃)N=CMe}-2,2'-C₁₀H₇N₂)NiBr₂] (8) as a red powder. Yield 0.124 g, 55%. Recrystallisation from warm acetonitrile gave 8 as dark red blocks. FAB mass spectrum, m/z 497 $[\text{M} - \text{Br}]^+$, 417 $[\text{M} - 2\text{Br}]^+$. IR: $\tilde{\nu}$ = 1596 [$\nu(\text{C}=\text{N})_{\text{imine}}$] cm^{-1} . μ_{eff} = 2.8 BM at 293 K. C₂₄H₂₇Br₂N₃Ni: calcd. C 50.04, H 4.69, N 7.30; found C 49.95, H 4.51, N 7.66.

General Screening for Ethylene Oligomerisation: An oven-dried 200 mL Schlenk vessel equipped with magnetic stir bar was evacuated and backfilled with nitrogen. The vessel was charged with the precatalyst (0.01 mmol) and dissolved or suspended in toluene (40 mL). MAO (6.0 mmol, 300 equiv./metal centre) was introduced and the reaction mixture left to stir for 5 min. resulting in a colour change of the solution. The vessel was purged with ethylene and the contents magnetically stirred under 1 bar ethylene pressure at room temperature for the duration of the test. After 0.5 h, the test was terminated by the addition of dilute aqueous hydrogen chloride (5 mL). The organic phase was separated and dried with magnesium sulfate and filtered. Quantitative GC analysis was performed

Table 8. Crystallographic and data processing parameters for L2, **2a**, **5b**(NCMe), **7** and **8**.

Complex	L2	2a	5b (NCMe)	7	8
Formula	C ₃₄ H ₃₃ N ₅	C ₄₃ H ₄₉ Cl ₄ Co ₂ N ₅ ·MeCN	C ₃₆ H ₃₆ Br ₄ Co ₂ N ₆ ·2MeCN	C ₃₈ H ₃₉ Br ₅ Ni _{2.5} N ₇ ·10MeCN	C ₂₄ H ₂₇ Br ₂ N ₃ Ni
<i>M</i>	511.65	936.59	1072.32	1345.36	576.02
Crystal size [mm] ³	0.08 × 0.03 × 0.01	0.21 × 0.19 × 0.02	0.23 × 0.16 × 0.04	0.38 × 0.20 × 0.12	0.28 × 0.26 × 0.04
Temperature [K]	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	triclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> [Å]	6.4213(7)	17.012(4)	16.136(5)	16.852(4)	31.086(3)
<i>b</i> [Å]	11.1354(12)	18.325(4)	17.538(6)	18.486(4)	9.8651(8)
<i>c</i> [Å]	19.629(2)	15.685(4)	17.152(5)	19.344(4)	15.6922(12)
α [°]	97.3630(1)	90	90	84.739(4)	90
β [°]	92.906(2)	110.634(4)	113.153(5)	76.443(4)	111.555(2)
γ [°]	102.1910(10)	90	90	64.805(4)	90
<i>V</i> [Å ³]	1356.2(3)	4576.1(17)	4463(2)	5301(2)	4475.7(6)
<i>Z</i>	2	4	4	4	8
<i>D</i> _c [Mg m ⁻³]	1.253	1.359	1.596	1.686	1.710
<i>F</i> (000)	544	1944	2128	2684	2320
μ (Mo- <i>K</i> α) [mm ⁻¹]	0.075	0.996	4.362	4.697	4.455
Reflections collected	10471	32333	33947	41314	15823
Independent reflections	4734	8048	8436	20522	3949
<i>R</i> _{int}	0.0405	0.1889	0.1430	0.0641	0.0505
Restraints/parameters	0/357	0/525	0/495	0/960	0/276
Final <i>R</i> indices	<i>R</i> ₁ = 0.0501, <i>wR</i> ₂ = 0.1258	<i>R</i> ₁ = 0.0568, <i>wR</i> ₂ = 0.0856	<i>R</i> ₁ = 0.0759, <i>wR</i> ₂ = 0.1699	<i>R</i> ₁ = 0.0494, <i>wR</i> ₂ = 0.1017	<i>R</i> ₁ = 0.0371, <i>wR</i> ₂ = 0.0903
All data	<i>R</i> ₁ = 0.0791, <i>wR</i> ₂ = 0.1411	<i>R</i> ₁ = 0.1723, <i>wR</i> ₂ = 0.1073	<i>R</i> ₁ = 0.1607, <i>wR</i> ₂ = 0.1961	<i>R</i> ₁ = 0.1050, <i>wR</i> ₂ = 0.1096	<i>R</i> ₁ = 0.0457, <i>wR</i> ₂ = 0.0930
Goodness of fit on <i>F</i> ² (all data)	1.015	0.658	0.961	0.765	0.964

Data in common: graphite-monochromated Mo-*K* α radiation, $\lambda = 0.71073$ Å; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2]$, $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$, where *a* is a constant adjusted by the program; goodness of fit: $[\Sigma(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ where *n* is the number of reflections and *p* the number of parameters.

by taking an aliquot of the solution containing a weighed amount of a standard (*n*-heptadecene). For analysis of the oligomers by ¹H NMR spectroscopy, the solvent was removed on the rotary evaporator and the residue dissolved in CDCl₃.

Crystallographic Studies: Data for L2, **2a**, **5b**(NCMe), **7** and **8** were collected with a Bruker APEX 2000 CCD diffractometer. Details of data collection, refinement and crystal data are listed in Table 8. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections applied. Structure solution by direct methods and structure refinement on *F*² employed SHELXTL version 6.10.^[28] Hydrogen atoms were included in calculated positions (C–H = 0.96 Å) riding on the bonded atom with isotropic displacement parameters set to 1.5 *U*_{eq}(C) for methyl H atoms and 1.2 *U*_{eq}(C) for all other H atoms.

CCDC-692870 (for L2), -692871 (for **2a**), -692872 [for **5b**(NCMe)], -692873 (for **7**) and -692874 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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