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## PAPER

# Tandem ethylene oligomerisation and Friedel–Crafts alkylation of toluene catalysed by bis-(3,5-dimethylpyrazol-1-ylmethyl)benzene nickel(II) complexes and ethylaluminium dichloride†

Asheena Budhai,[a] Bernard Omondi,‡[a] Stephen O. Ojwach,§[a] Collins Obuah,[a] Emmanuel Y. Osei-Twum[b] and James Darkwa*[a]

Three ligands, 1,2-bis(3,5-dimethylpyrazol-1-ylmethyl)benzene (**L1**), 1,3-bis(3,5-dimethylpyrazol-1-ylmethyl)benzene (**L2**) and 1,4-bis(3,5-dimethylpyrazol-1-ylmethyl)benzene (**L3**), were reacted with either nickel(II) chloride or nickel(II) bromide to produce four nickel complexes, Ni(**L1**)Br$_2$ (**1**), Ni(**L1**)Cl$_2$ (**2**), Ni(**L2**)Br$_2$ (**3**), and Ni(**L1**)Br$_2$ (**4**). The complexes were either mononuclear, **1** and **2**, or polymeric, **3** and **4**, depending on the positions of the pyrazolyl units on the benzene linker in the ligand. This was established from the crystal structures of **1**, **2** and **3**. All four complexes upon activation with ethylaluminium dichloride produced a tandem catalyst system that oligomerised ethylene to mainly 1-butene and 1-hexene and subsequently used the olefins present in the reaction medium to alkylate toluene that was used as solvent in the reactions. This led to mono-, di- and tri-alkyltoluenes with ethylene, butene and hexene.

## Introduction

Late transition nitrogen-donor metal complexes continue to be investigated as ethylene transformation catalysts since Brookhart[1] demonstrated in the mid-1990s their robust nature to withstand oxo-containing monomers. In the last decade nitrogen-donor nickel catalysts in particular have received great attention; initially as ethylene polymerization catalysts,[2] but lately as ethylene oligomerization catalysts.[3] Much of the nickel oligomerization work, mainly carried out with P^N[4] and N^N[5] donor ligands, lead principally to dimerization and trimerization of ethylene; where 1-butene and 1-hexene are the dominant products. But in these dimerization and trimerization reactions, the role of aluminium co-catalysts has only recently been brought into focus following a report by Dyer and co-workers[6] in 2008. Using (P^N)nickel(II) complexes and ethylaluminium dichloride as co-catalysts, they observed ethylene oligomerization for all four nickel complexes; but only one of these nickel precursors was found to perform Friedel–Crafts alkylation of toluene, the solvent used in the oligomerization reaction.[6]

Another report by Gao and co-workers[7] appeared soon after the Dyer report; showing that ethylene oligomerization products, from another (P^N)nickel(II) complex and MAO as a co-catalyst, perform Friedel–Crafts alkylation of toluene to alkyltoluenes but only at 50 °C. It is clear from the above two reports that reaction conditions, the ligand on the nickel catalysts, and the aluminium co-catalyst may all play a role in promoting the Friedel–Crafts alkylation reaction observed in these reports, because there are several examples[4,5] where (P^N)nickel(II) complexes with MAO or ethylaluminium dichloride as co-catalysts produce only ethylene oligomers in toluene.

It is also clear that where ethylene oligomerization is followed by Friedel–Crafts alkylation the two reactions occur in tandem and promoted by a tandem catalytic system. The role ligands play in this tandem may be more important because our recent reports[8] on the use of pyrazolyl nickel complexes and ethylaluminium dichloride invariably lead to large amounts of mono-, di- and tri-butyltoluenes and other alkyltoluene products. The present report is indeed further demonstration that ethylaluminium dichloride and nickel complexes, supported on bis(pyrazol-1-yl) ligands, provide the best tandem catalyst systems that perform ethylene oligomerization and post oligomerization olefin alkylation of toluene.

[a] *Department of Chemistry, University of Johannesburg, Auckland Park Kingsway Campus, Auckland Park 2006, South Africa. E-mail: jdarkwa@uj.ac.za*

[b] *Saudi Basic Industries Corporation, P. O. Box 42503, Riyadh 11551, Saudi Arabia*

‡ Current address: School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Private Bag X54001, Durban 4000, South Africa.

§ Current address: School of Chemistry and Physics, University of KwaZulu-Natal, Pietermaritzburg Campus, Private Bag X01, Scottsville 3209, South Africa.

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# Results and discussions

## Synthesis of poly(pyrazol-1-yl) metal complexes

Three bis(3,5-dimethylpyrazol-1-ylmethyl)benzene compounds (**L1**–**L3**) were reacted with NiCl$_2$ or NiBr$_2$ to produce four-coordinate pyrazolyl nickel complexes; either as discrete mono-metallic complexes or as coordination polymers. For instance complexes **1** and **2**, formed with **L1** where the two pyrazolyl units are in 1,2-positions on the benzene linker, the ligand binds in a bidentate fashion to give four-coordinate nickel complexes that have the nickel at the centre of a tetrahedron (Scheme 1; Fig. 1 and 2). This is in contrast to the reactions of **L1** with [PdCl$_2$(NCMe)$_2$] and [PdClMe(COD)] where the square planar complexes formed require that the ligand uses one pyrazolyl unit to bind a different palladium centre; thus leading to structures in which **L1** bridges two palladium centres.[9] Ligands **L2** and **L3**, with their two pyrazolyl units in 1,3- and 1,4-positions, respectively, on the benzene linker formed complexes with NiBr$_2$ in which a pyrazolyl unit on one molecule of a ligand is bound to a different Ni atom; leading to coordination polymers (**3**–**5**) (Scheme 2). This is typified by the structure of **5** (Fig. 3).
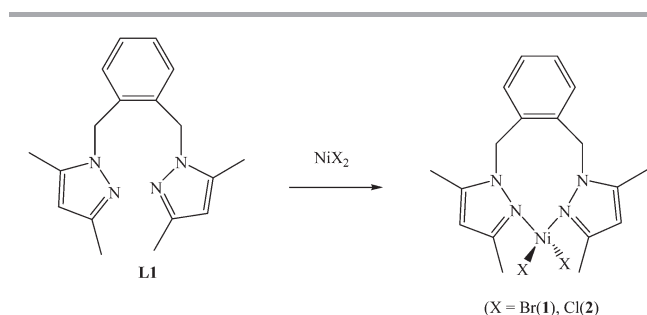


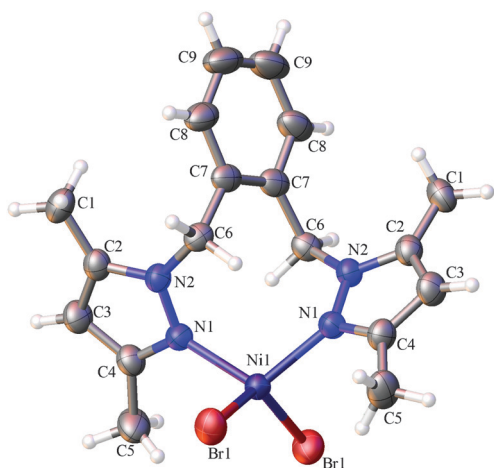**Scheme 1**   Synthesis of pyrazolyl Ni(II) complexes.



**Fig. 1**   Molecular structure of complex **1**, with the ellipsoids drawn at the 50% probability level. Solvated CH$_2$Cl$_2$ was removed for clarity. Selected bond lengths [Å] and angles [°]: N(1)–Ni(1), 2.017(3); Ni(1)–N(1)#1, 2.017(3), Ni(1)–Br(1)#1, 2.3817(5); N(1)–Ni(1)–N(1)#1, 110.14(18); N(1)–Ni(1)–Br(1)#1, 110.14(18); N(1)#1–Ni(1)–Br(1)#1, 111.69(10); N(1)#1–Ni(1)–Br(1), 97.32(10); N(1)#1–Ni(1)–Br(1)#1, 111.69(10); N(1)–Ni(1)–Br(1), 111.69(10).
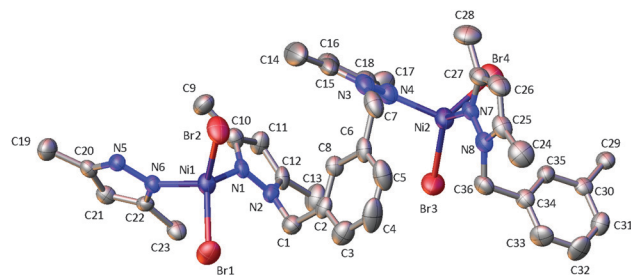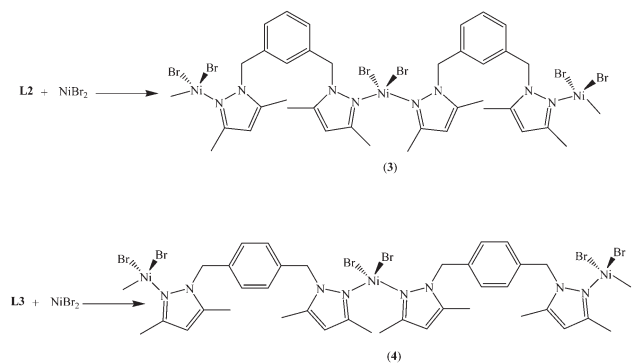


**Fig. 2**   Molecular structure of complex **3**, with the ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N(7)–Ni(2), 2.024(4); Ni(1)–Br(2), 2.3805(10); Ni(1)–Br(1), 2.3863(10); Ni(2)–Br(4); 2.4071(10); N(1)–Ni(1)–N(6), 95.74(15); N(1)–Ni(1)–Br(2), 104.73(11); N(6)–Ni(1)–Br(2), 118.39(11); N(4)–Ni(2)–Br(4), 113.93(14); N(7)–Ni(2)–Br(4), 97.52(12); Br(3)–Ni(2)–Br(4), 113.36(4).



**Scheme 2**   Synthesis of polymeric pyrazolyl Ni(II) complexes.

All the nickel complexes were isolated in moderate yields and were stable in air and moisture in solution and in the solid state without any signs of decomposition. Complexes **1**–**4** are paramagnetic with $\mu_{eff}$ (298 K) between 3.00 and 4.10 BM. These values are higher than the spin-only value of 2.83 BM expected for two unpaired electrons, but still fall within the observed range of 2.9–4.2 BM for high-spin nickel(II) complexes.[10] As a result of their paramagnetic nature they could not be characterized with NMR spectroscopy; instead they were characterized by a combination of mass spectrometry, elemental analysis and in selected cases by X-ray crystallography. Complexes **1**–**4** all showed molecular ions associated with the formulae in Scheme 1; but because **5** and **6** are not discrete molecules only fragments of a coordination polymer could be seen in the mass spectra. Fig. S1 (ESI†) is part of the mass spectrum of **5** that depicts the polymeric nature of this molecule.

## Molecular structures of complexes 1–3

Crystals of **1**, **2** (Fig. S2, ESI†) and **3**, suitable for X-ray crystallographic studies, were all grown from a mixture of dichloromethane and toluene at room temperature. Crystal and structure refinement data are compiled in Table 1. The structures of these complexes have no unusual features and would therefore not be discussed in any detail. The solid

**Table 1**  Crystal data and structure refinement for complexes **1–3**

| Parameters | 1 | 2 | 3 |
|---|---|---|---|
| Empirical formula | $C_{19}H_{24}Br_2Cl_2N_4Ni$ | $C_{18}H_{22}Cl_2N_4Ni$ | $C_{36}H_{44}Br_4N_8Ni_2$ |
| Formula weight | 597.85 | 424.01 | 1025.85 |
| Temperature | 100(2) K | 100(2) K | 100(2) K |
| Wavelength | 0.71073 Å | 0.71073 Å | 0.71073 Å |
| Crystal system | Orthorhombic | Triclinic | Triclinic |
| Space group | $C2221$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$/Å | 14.2034(7) | 9.2765(5) | 9.3446(18) |
| $b$/Å | 11.5966(7) | 10.7428(5) | 14.994(3) |
| $c$/Å | 14.6836(11) | 12.1287(6) | 15.681(3) |
| $\alpha$ | 90° | 110.976(3)° | $\alpha = 75.599(10)°$ |
| $\beta$ | 90.97° | 96.346(3)° | $\beta = 78.411(10)°$ |
| $\gamma$ | 90° | 113.712(3)° | $\gamma = 81.522(11)°$ |
| Volume | 2399.8(3) Å$^3$ | 986.47(9) Å$^3$ | 2073.7(7) Å$^3$ |
| $Z$ | 4 | 2 | 2 |
| Density (calculated) | 1.655 Mg m$^{-3}$ | 1.427 Mg m$^{-3}$ | 1.643 Mg m$^{-3}$ |
| Absorption coefficient | 4.373 mm$^{-1}$ | 1.262 mm$^{-1}$ | 4.797 mm$^{-1}$ |
| $F(000)$ | 1192 | 440 | 1024 |
| Theta range for data collection | 2.28 to 26.29° | 1.88 to 25.00° | 1.72 to 28.00° |
| Reflections collected | 8205 | 7571 | 20389 |
| Independent reflections | 2981 [$R$(int) = 0.0434] | 3468 [$R$(int) = 0.0303] | 10 006 [$R$(int) = 0.0716] |
| Completeness to theta | (=28.29°) 99.9% | (=25°) 100% | 28.00° (99.9) |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Data/restraints/parameters | 2981/0/131 | 3468/2/229 | 10 006/0/459 |
| Goodness-of-fit on $F^2$ | 1.060 | 1.047 | 0.878 |
| Final $R$ indices [$I > 2\mathrm{sigma}(I)$] | $R_1 = 0.0445$, w$R_2 = 0.1204$ | $R_1 = 0.0329$, w$R_2 = 0.0893$ | $R_1 = 0.0514$, w$R_2 = 0.0947$ |
| $R$ indices (all data) | $R_1 = 0.0473$, w$R_2 = 0.1225$ | $R_1 = 0.0398$, w$R_2 = 0.0928$ | $R_1 = 0.1453$, w$R_2 = 0.1179$ |
| Largest diff. peak and hole | 0.951 and −0.784 e Å$^{-3}$ | 0.396 and −0.480 e Å$^{-3}$ | 0.772 and −0.697 e Å$^{-3}$ |

state structures of the nickel complexes **1–3** all display distorted tetrahedral geometry. The distortion is greater in the polymeric structure (**3**) with a bond angle of 118.39(11)° for N(1)–Ni(1)–Br(2). On the other hand, the molecule in the dibromide, **1**, has a crystallographic $C_2$-symmetry axis rendering many of the atoms symmetry equivalent. For example, N(1) and N(1$^{\#}$), Br(1) and Br(1$^{\#}$) are equivalent. The mononuclear complex **2** (Fig. S2, ESI†) showed smaller deviations from the expected bond angle of 109° for a tetrahedral geometry (109.26(8)° for N(1)–Ni(1)–N(4)). All the bond distances in **1–3** are comparable and typical of four-coordinate nickel complexes that contain pyrazolyl and chloride ligands. For instance the average bond distance of 2.045(4) Å Ni(1)–N$_{pz}$ in **1–3** falls within the range of 1.992–2.048 Å calculated for seven similar compounds in the CSD.[11]

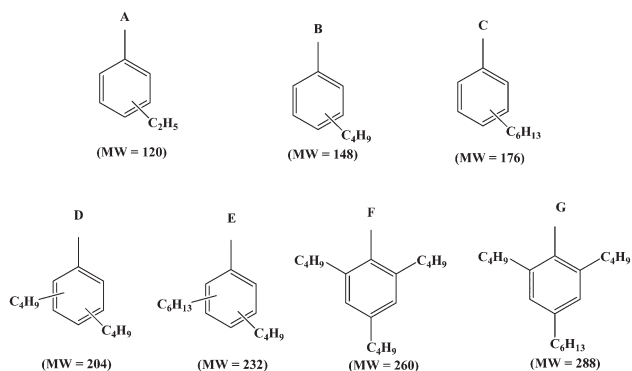## Ethylene oligomerization and Friedel–Crafts alkylation catalysis

The potential of complexes **1–4** as ethylene oligomerization catalysts was investigated, with EtAlCl$_2$ as a co-catalyst at 20 bar in hexane and toluene (80 mL). Upon activation with the co-catalysts all the complexes showed an increase in temperature within 5 min upon adding the co-catalyst; with the lowest temperature rise observed for **4** (40 °C) and the highest for **1** (72 °C) (Table 2). In hexane the catalysts produced butene as a minor product and hexene as the major product. This observation is similar to our recent report for (pyrazolyl)pyridine nickel catalysts.[8a] However, GC and GC-MS analysis of products from toluene reactions indicates that the initial oligomerization of ethylene to butene

and hexene is followed by Friedel–Crafts alkylation of toluene used as solvent to alkyltoluenes. A critical analysis of the GC-MS data of products from all four nickel catalysts investigated showed a mixture of seven alkyltoluenes (Fig. S3–S10, ESI†). This suggests that the active catalysts in these reactions are similar. Of the seven alkyltoluenes, there were: (i) the mono- (**B**), di- (**D**) and tri-butyltoluenes (**F**) as major products, (ii) mono-hexyltoluene (**C**), butyl-hexyltoluene (**E**) and di-butyl-hexyltoluenes (**G**) formed in moderate amounts and (iii) ethyltoluenes (**A**) formed as a minor product (Scheme 3). The butyltoluenes were formed from the alkylation of toluene with butene; while the ethyltoluenes (**A**) and the hexyltoluene (**C**) were formed from ethylene and hexane alkylating toluene respectively. But the formation of butyl-hexyltoluene (**E**) and di-butyl-hexyltoluenes (**G**) comes from sequential alkylation of toluene by butene and hexane. Although it is possible that ethylene and hexene can form the di- and tri-alkylated toluene products **C** and **F** respectively, we rule out **C** being di-alkylated with ethylene and **F** being tri-alkylated with hexene. This is based on the amounts of ethyltoluene and hexyltoluene formed since further alkylation products are generally much smaller than the mono-alkylated product. Indeed the GC data show that the amount of **B** is much more than the amount of **A**. The same argument holds for the formation of **F** for tri-alkylation with hexene. The formation of the alkyltoluene products, **A–G**, is adequately accounted for by the molar masses in the GC-MS data; and is clear evidence that we have tandem catalyst systems in **1–4** and EtAlCl$_2$ that first produce butene and hexene selectively, followed by Friedel–Crafts alkylation of toluene by the butene and hexene to produce alkyltoluenes.

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**Table 2** Ethylene oligomerization/Friedel–Crafts alkylation data for complexes **1–4**

| Entry | Catalyst | Al/Ni | Time (h) | Pressure (atm) | Yield$^a$ (g) | Activity (kg mol$^{-1}$ h$^{-1}$) | Product distribution% | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | C$_4$ | C$_6$ | A | B | C | D | E | F | G |
| 1 | 1 | 200 | 1 | 20 | 34.80 | 3480 | 3.94 | 16.31 | 1.02 | 36.03 | 3.14 | 16.50 | 5.80 | 15.12 | 2.14 |
| 2 | 2 | 200 | 1 | 20 | 26.77 | 2677 | — | — | 1.60 | 33.07 | 15.04 | 20.90 | 6.75 | 14.72 | 9.92 |
| 3 | 3 | 200 | 1 | 20 | 22.62 | 2262 | — | — | 0.97 | 35.66 | 12.01 | 19.00 | 4.40 | 17.40 | 10.56 |
| 4 | 4 | 200 | 1 | 20 | 27.84 | 2784 | 3.26 | 4.68 | 2.70 | 27.55 | 4.60 | 20.05 | 2.97 | 25.58 | 8.61 |
| 5 | 1 | 100 | 1 | 20 | 8.65 | 865 | 1.14 | 20.06 | 1.06 | 32.39 | 10.17 | 12.13 | 9.08 | 6.95 | 7.02 |
| 6 | 1 | 250 | 1 | 20 | 36.12 | 3612 | 2.88 | 9.05 | 2.23 | 34.31 | 8.95 | 17.00 | 8.11 | 13.24 | 5.23 |
| 7 | 1 | 300 | 1 | 20 | 38.78 | 3878 | 0.66 | 6.49 | — | 34.06 | 19.45 | 11.00 | 12.74 | 6.03 | 9.57 |
| 8 | 1 | 350 | 1 | 20 | 35.72 | 3572 | — | — | — | 30.67 | 9.93 | 27.98 | 8.53 | 19.06 | 3.83 |
| 9 | 1 | 400 | 1 | 20 | 25.90 | 2590 | 11.02 | 7.08 | — | 37.25 | 8.84 | 22.06 | 2.12 | 9.56 | 0.92 |
| 10 | 1 | 200 | 0.25 | 20 | 15.20 | 6080 | 23.97 | 18.45 | 4.02 | 29.00 | 2.11 | 10.53 | 3.80 | 9.12 | — |
| 11 | 1 | 200 | 0.50 | 20 | 22.54 | 4508 | 11.87 | 12.32 | 1.02 | 39.08 | 3.14 | 17.44 | 3.98 | 10.10 | 1.05 |
| 12 | 1 | 200 | 2 | 20 | 50.35 | 2517 | 2.44 | 12.01 | 1.32 | 38.53 | 6.44 | 13.50 | 5.50 | 13.22 | 8.04 |
| 13 | 1 | 200 | 0.50 | 10 | 9.45 | 1890 | 13.20 | 16.31 | 0.50 | 40.41 | 5.07 | 12.12 | 3.87 | 8.52 | — |
| 14 | 1 | 200 | 0.50 | 25 | 30.65 | 8130 | 15.19 | 19.95 | 1.54 | 29.15 | 4.01 | 15.13 | 4.00 | 11.03 | — |
| 15 | 1 | 200 | 0.50 | 30 | 45.46 | 9092 | 14.79 | 22.21 | 3.16 | 27.45 | 4.69 | 14.23 | 4.25 | 9.22 | — |
| 16 | 1 | 200 | 0.50 | 40 | 48.25 | 9650 | 17.57 | 24.50 | 4.14 | 25.56 | 9.26 | 10.38 | 3.70 | 4.89 | — |

*Reaction conditions*: amount of catalyst = 10.00 μmol; solvent (volume) = toluene (80 mL); temperature = 30 °C, maximum temperature attained during the reaction is 72 °C. $^a$ Determined by mass difference of 80 mL toluene (69.60 g) and mass of final solution. **A** = ethyltoluenes, **B** = mono-butyltoluenes, **D** = di-butyltoluenes, **F** = tri-butyltoluenes, **C** = mono-hexyltoluene, **E** = butyl-hexyltoluene and **G** = di-butyl-hexyltoluenes.



**Scheme 3** Friedel–Craft products.

The formation of **A** indicates the oligomerization of ethylene to butene and hexene competes with the direct alkylation of toluene by ethylene. Since **A** is a minor product, it is clear that ethylene oligomerization is much favoured over ethylene alkylation of toluene.

Three reports on similar ethylene oligomerization and post oligomerization Friedel–Crafts alkylation of toluene have recently appeared in the literature. Dyer,[6] Gao[7] and we[8] have all reported reactions that produce alkyltoluenes from ethylene oligomerization reactions. However, only selected nickel catalysts from the Dyer and Gao systems perform ethylene oligomerization and Friedel–Crafts alkylation. What is unique about our nickel catalysts is that they all catalyse ethylene oligomerization followed by the Friedel–Crafts alkylation of toluene using the ethylene oligomers formed in the reaction. This points to possible roles played by the pyrazolyl ligands in promoting the alkylation reactions; although the exact nature of the active species that performs the Friedel–Crafts alkylation remains a subject of much speculation.[6,7] The Dyer system has the Lewis acid, EtAlCl$_2$, as a co-catalyst in

an Al : Ni ratio of 14 : 1; while Gao suggests that performing the reactions at elevated temperature produces the acidic conditions required to trigger the Friedel–Crafts alkylation. It is plausible that at elevated temperature the Gao system produces alkylaluminium dihalide from MAO, used as a co-catalyst, to provide the acidic conditions required for the Friedel–Crafts reaction. However, the unique behavior of our catalysts (**1–4**) suggests that the ligand must play an active role in providing the right conditions for the Friedel–Crafts alkylation of toluene. This assertion is supported by reports by Braunstein[4a–h] and others[4i,j,5] who have used low Al : Ni ratios, typically 10–15 equivalents of EtAlCl$_2$, presumably to avoid excess co-catalysts that could catalyse the alkylation of toluene. Our system with pyrazolyl nickel complexes and EtAlCl$_2$ provides the perfect conditions for a tandem catalytic system that promotes ethylene oligomerization to butene and hexene which then alkylate toluene; emphasizing the necessity for the right ligand and the presence of an appropriate Lewis acid for the tandem reactions. We are currently working on isolating species produced when the co-catalyst reacts with nickel pre-catalysts in order to establish if indeed these are the species responsible for the Friedel–Crafts alkylation.

## Influence of catalyst structure and reaction conditions on ethylene reactions

We investigated the effect of catalyst structure on the catalytic activities of complexes **1–4** at an Al : Ni ratio of 200, 20 bar ethylene pressure and reaction time of 1 h (Table 2, entries 1–4). Under these conditions, the dichloride complex **1** showed the highest activity of 3480 kg mol$^{-1}$ Ni per h while the polymeric complex **3** had the lowest activity of 2262 kg mol$^{-1}$ Ni per h. One possible explanation for this trend is the lower solubility of **3** and **4** in comparison to **1**

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and **2**. It is also likely that the polymeric structure breaks down to discrete single molecules during the generation of the catalytically active species. The higher activity of **1** compared to **2** is consistent with our previous report[8a] and is largely attributed to electronic factors and favourable activation processes by the co-catalyst (EtAlCl$_2$). Similar trends are found in the literature.[12]

Variation of the co-catalyst to catalyst precursor ratio (Al : Ni) from 100 to 400 influenced the catalytic activities of complex **1**. The optimum Al : Ni ratio was 300 : 1; giving a TON of 3878 kg mol$^{-1}$ Ni per h. Using higher Al : Ni ratios resulted in decreased catalytic activities (Table 2, entries 5–8). The effects of ethylene pressure and reaction time on catalyst activity were also investigated using catalyst **1** (Table 1, entries 10–16). Increase in pressure from 10 to 30 bar gave a significant increase in activity from 1890 kg mol$^{-1}$ Ni per h to 9092 kg mol$^{-1}$ Ni per h; however, a further increase in pressure to 40 bar (9650 kg mol$^{-1}$ Ni per h) did not result in appreciable rise in activity, a phenomenon associated with saturation kinetics and diffusion limitations as more product forms.[13] Increasing the reaction time from 0.25 h to 2 h resulted in an increase in product yield from 15.20 g to 50.35 g but a drop in the activity from 6080 kg mol$^{-1}$ Ni per h to 2517 kg mol$^{-1}$ Ni per h consistent with catalyst degradation. We did not vary temperature due to the exothermic nature of the reactions when the pre-catalysts were activated.

## Conclusions

Four (3,5-dimethylpyrazol-1-yl)methylbenzene nickel dihalide complexes were found to be active catalysts for the dimerization and trimerization of ethylene when activated with ethylaluminium dichloride. This catalyst system subsequently catalysed the alkylation of toluene, which was used as solvent, to form several alkylated toluenes. Although, the alkylation is not selective; but it is indicative of efficacy of this catalyst systems and points to how the nickel complexes and the co-catalyst act in tandem to oligomerise ethylene and performs a subsequent alkylation of toluene to alkyltoluenes.

## Experimental section

### Materials and methods

All techniques involving air-sensitive materials were performed under a dry nitrogen atmosphere, using standard Schlenk techniques. Solvents, toluene, hexane and dichloromethane, were dried appropriately using distillation overnight in molecular sieves. All ligands (**L1**–**L3**) were prepared following literature procedures.[14] Anhydrous NiCl$_2$ and NiBr$_2$ were obtained from Sigma-Aldrich and used as received. Mass spectroscopy analyses were performed by the University of Stellenbosch, while the CHN analyses were performed by the micro analytical laboratory at University of Cape Town. Magnetic moments of nickel complexes were measured using a Magway MSB MK1 magnetic susceptibility balance. Effective magnetic moments, $\mu_{eff}$, were calculated as stated in the literature.[15]

**Synthesis of 1,2-bis(3,5-dimethylpyrazol-1-ylmethyl)benzenenickel(II) bromide (1).** A mixture of **L1** (0.27 g, 0.92 mmol) and NiBr$_2$ (0.20 g, 0.92 mmol) in methanol (20 mL) was stirred for 24 h. The resultant blue solution was evaporated and the residue recrystallized from dichloromethane–hexane solution to afford blue solid. Yield: 0.31 g, 65%. ESI-MS: $m/z$ (%) 512 (M$^+$, 35). Anal. calcd for C$_{18}$H$_{22}$Br$_2$N$_4$Ni: C, 42.15; H, 4.32; N, 10.92. Found: C, 42.50; H, 4.35; N, 11.00%. $\mu_{eff}$ = 3.00 BM.

Complexes **2**–**4** were prepared according to the procedure described for **1**.

**Synthesis of 1,2-bis(3,5-dimethylpyrazol-1-ylmethyl)benzenenickel(II) chloride (2).** Complex **2** was prepared from **L1** (0.45 g, 1.53 mmol) and NiCl$_2$ (0.20 g, 1.54 mmol) and isolated as a green solid. Yield: 0.39 g, 60%. ESI-MS: $m/z$ (%) 424 (M$^+$, 45). Anal. calcd for C$_{18}$H$_{22}$Cl$_2$N$_4$Ni: C, 50.99; H, 5.23; N, 13.21. Found: C, 51.25; H, 5.35; N, 13.00%. $\mu_{eff}$ = 4.10 BM.

**Synthesis of 1,3-bis(3,5-dimethylpyrazol-1-ylmethyl)benzenenickel(II) bromide (3).** Complex **5** was prepared from **L2** (0.27 g, 0.92 mmol) and NiBr$_2$ (0.20 g, 0.92 mmol) and isolated as blue crystals. Yield: 0.33 g, 72%. Anal. calcd for C$_{18}$H$_{22}$Br$_2$N$_4$Ni: C, 42.15; H, 4.32; N, 10.92. Found: C, 42.65; H, 4.00; N, 10.80%.

**Synthesis of 1,4-bis(3,5-dimethylpyrazol-1-ylmethyl)benzenenickel(II) bromide (4).** Complex **6** was prepared from **L3** (0.27 g, 0.92 mmol) and NiBr$_2$ (0.20 g, 0.92 mmol) and isolated as blue crystals. Yield: 0.36 g, 76%. Anal. calcd for C$_{18}$H$_{22}$Br$_2$N$_4$Ni: C, 42.15; H, 4.32; N, 10.92. Found: C, 42.00; H, 4.45; N, 11.10%.

### X-ray structure determination

Crystal evaluation and data collection for **1**–**3** were performed on a Bruker SMART 1K CCD area detector diffractometer with graphite monochromated Mo K$\alpha$ radiation (50 kV, 30 mA). Data reduction was carried out using the program SAINT+ and face indexed absorption corrections were made using the program XPREP.[16] The crystal structure was solved by direct methods using SHELX.[17] Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on $F^2$ using SHELX.[17] Hydrogen atoms were first located in the difference map then added using a function in SHELX.[17] All tables and diagrams were generated using SHELX and PLATON. Details of the data collection and refinement are found in the ESI.†

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Title: Tandem ethylene oligomerisation and Friedel–Crafts alkylation of toluene catalysed by bis-(3,5-dimethylpyrazol-1-ylmethyl)benzene nickel(II) complexes and ethylaluminium dichloride

Pyrazolylnickel dihalides and ethylaluminium dichloride provide tandem catalyst systems that oligomerise ethylene to butenes and hexenes that alkylate toluene in Friedel-Crafts type alkylation reactions. Major products are mono-, di- and tri-butyltoluenes, but remarkably the system also produces ethyltoluenes.

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