Supporting Information

Crystallographic Revelation of the role of

AlMe₃ (in MAO) in Cr-[NNN] Pyrazolyl Catalysed Ethylene Trimerisation

Jun Zhang, Aifang Li[‡] and T. S. Andy Hor*

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Kent Ridge, Singapore 117543.

[‡] *Department of Chemistry, College of Chemistry and Chemical Engineering, and the MOE Key Laboratory of Ananlytical Sciences, Xiamen University, P. R. China.*

E-mail: andyhor@nus.edu.sg; Fax: (+65) 6873 132

Experimental Section

General Information: All reactions were carried out using standard Schlenk techniques under an inert atmosphere of nitrogen or argon with an M. Braun Labmaster 130 Inert Gas System. THF, Et_2O and toluene were distilled from sodium–benzophenone. Commercial reagents, namely, NaH (60%), thionyl chloride, 3,5-dimethyl-pyrazole, Hydrazine monohydrate ($N_2H_4.H_2O$), $NaBH_4$, benzaldehyde, MAO (methylaluminoxane) (10 wt.% in toluene solution) were purchased from Aldrich and used as received. The complex $[CrCl_3(THF)_3]$ was prepared as previously reported[1]. The complex **1**[2], (pyridin-2-yl)-bis(3,5-dimethylpyrazol-1-yl)methane, (**L²**)[3], 1-methyl-1-imidazole-2-aldehyde[4], N-[2,2-bis-(3,5-methyl-pyrazol-1-yl)-ethane]-1,8-naphthal-imide[5] were prepared according to the literature methods, respectively. The NMR spectra were measured on Bruker ACF300 300 MHz FT NMR spectrometers. IR data were obtained on a Bruker IFS 48 FT-IR spectrometer with samples prepared as KBr pellets. Elemental analyses were performed by the microanalytical laboratory in house.

1. Boudjouk, P.; So, J. H. *Inorg. Synth.*, 1992, **29**, 108.
2. García-Orozco, I.; Quijada, R., Vera, K.; Valderrama, M. *J. Mol. Catal. A: Chem.*, 2006, **260**, 70.
3. Arroyo, N.; Torre, F. G.; Jalón F. A.; Manzano, B. R.; Moreno-Lara, B.; Rodríguez, A. M. *J. Organomet. Chem.*, 2000, **603**, 3641.
4. Alcalde, E.; Alemany, M.; Gisbert, M. *Tetrahedron*, 1996, **52**, 15171.
5. Reger, D. L.; Foley, E. A.; Semeniuc, R. F.; Smith, M. D. *Inorg. Chem.*, 2007, **46**, 11345.
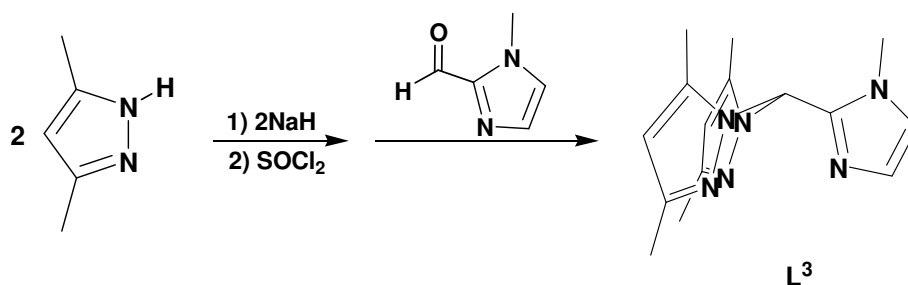
Scheme 1 Synthesis of **L³**

Synthesis of L³ (Scheme 1)**:**

(N-methylimidazol-2-yl)-bis(3,5-dimethylpyrazol-1-yl)methane (**L³**). To NaH (1.20 g, 30.0 mmol) was suspended in THF (30 mL) and cooled in an ice/water bath. 3,5-dimethyl-pyrazole (2.86 g, 30.0 mmol) was added and the resulting mixture was stirred at 0°C for 2 h. After dropwise addition of thionyl chloride (1.09 mL, 14.9 mmol) the cooling was removed, and stirred for 1h. Then 1-methyl-1-imidazole-2-aldehyde (1.64 g, 14.9 mmol), and CoCl₂ (100 mg) were added and the mixture was heated under reflux over 10 h. After cooling to room temperature, it was quenched with water and extracted three times with Et₂O (3× 20 mL). The combined organic phases were dried over anhydrous NaSO₄ and concentrated *in vacuo*. The resulting residue was purified by chromatography (ethyl acetate/hexane), and yielded **L³** (3.1 g, 73.2%) as white powder. ¹H NMR (300 MHz, CDCl₃): δ 7.55 (s, 1H, Pz₂-C*H*CH₂), 7.04 (s, 1H, Imidazolyl-*H*), 6.91 (s, 1H, Imidazolyl-*H*), 5.88 (s, 2H, Pz-*H*), 3.32 (s, 3H, Imidazolyl-C*H₃*),), 2.17 (s, 6H, Pz-C*H₃*), 2.11 (s, 6H, Pz-C*H₃*). ¹³C{¹H} NMR (75.47 MHz, CDCl₃): δ 148.59, 141.30 (s, *C*-N(Pz)), 141.68, 128.29, 122.96 (s, *C*(Imin)), 107.74 (s, *C*H(Pz)), 70.29 (s, N-*C*H), 33.13 (s, *C*H₃), 13.94, 11.41 (s, *C*H₃(Pz))
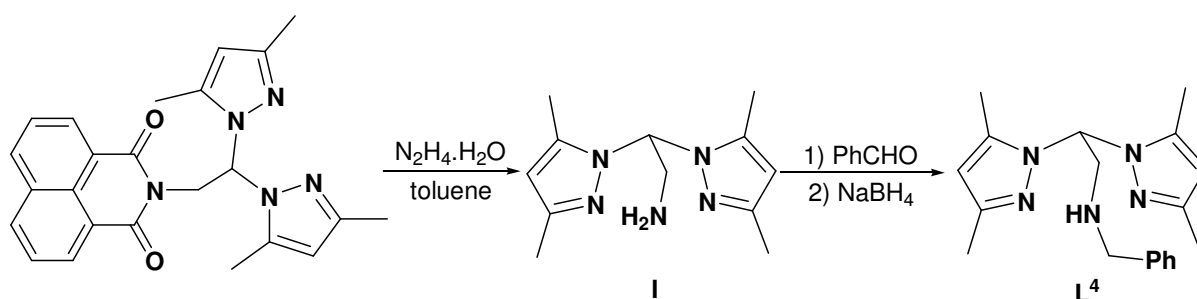
Scheme 2 Synthesis of **L⁴**

Synthesis of L⁴ (Scheme 2)**:**

2,2-Bis-(3,5-methyl-pyrazol-1-yl)-ethanamine (**I**). N-[2,2-bis-(3,5-methyl-pyrazol-1-yl)-

ethane]-1,8-naphthalimide (3.0 g, 7.3mmol) was dissolved in ethanol (15 mL). Hydrazine monohydrate (3.0 mL) was added, and the mixture was heated to reflux for 3 days. After cooling to room temperature, the solvent and excess hydrazine were removed *in vacuo*. The resulting residue was purified by chromatography (ethyl acetate/hexane), and yielded **I** 0.9g (53%) as yellow powder. ^{1}H NMR (300MHz, CDCl$_3$): δ 6.17 (t, J = 6.9 Hz, 1H, Pz$_2$C*H*CH$_2$), 5.79 (s, 2H, Pz-*H*), 3.69 (d, J = 6.9 Hz, 2H, CHC*H$_2$*NH), 2.21 (s, 6H, Pz-C*H$_3$*), 2.07 (s, 6H, Pz-C*H$_3$*). ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): δ 148.16, 140.26 (s, *C*-N(Pz)), 107.13 (s, *C*H(Pz)), 74.82 (s, N-*C*H-CH$_2$), 44.69 (s, CH-*C*H$_2$-NH$_2$), 13.83, 11.08 (s, *C*H$_3$(Pz))

N-benzyl-2,2-bis(3,5-dimethyl-pyrazol)-1-yl-ethanamine (**L^4**): Benzaldehyde (2 mL, 0.020mol) was added to a solution of **I** (4.97 g, 40 mmol) in dry methanol (20 mL), and the mixture was heated to reflux overnight. After cooling to room temperature, excess of NaBH$_4$ (1.50 g, 0.040 mol) was added in portions and the mixture stirred for 6 hours. The solvent was removed *in vacuo*, and the residue was taken in 30 mL of hexane. The organic layer was washed with water (3 x 100 mL), dried over anhydrous NaSO$_4$, and then removed the solvent via rotary evaporation to yield **L^4** (0.54g , 83%) as yellow oil. ^{1}H NMR (300MHz, CDCl$_3$): δ 7.40-7.30 (m, 5H, Ph), 6.38 (t, J = 7.2 Hz, 1H, Pz$_2$C*H*CH$_2$), 5.81 (s, 2H, Pz-*H*), 4.74 (s, 1H, N*H*), 3.88 (s, 2H, NHC*H$_2$*Ph), 3.68 (d, J = 7.2 Hz, 2H, CHC*H$_2$*NH), 2.23(s, 6H, Pz-C*H$_3$*), 2.12 (s, 6H, Pz-C*H$_3$*). ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): δ 147.89, 139.88 (s, *C*-N(pz)), 147.23, 129.72, 118.32, 113.51 (s, *C*(Ar)), 107.13 (s, *C*H(Pz)), 69.60 (s, N-*C*H-CH$_2$), 46.24 (s, CH-*C*H$_2$-NH$_2$), 13.93, 11.02 (s, *C*H$_3$(Pz)).

Synthesis of complexes 2-4

[Cr(L^2)Cl$_3$] (**2**). To a solution of (pyridin-2-yl)-bis(3,5 -dimethylpyrazol-1-yl)methane **L^2** (0.120 g, 0.43 mmol) in dry THF (10 mL) was added [CrCl$_3$(THF)$_3$] (0.160 g, 0.43 mmol), and a light green precipitate formed. The resulting mixture was stirred at room temperature for 8 h. The THF was evaporated to about one-third of its volume and 10 mL of ether was added to complete precipitation. The product was collected by filtration, washed with 10 mL of ether, and dried *in vacuo*, yielding **2** (0.175 g, 92.5%). Anal. Calcd for C$_{16}$H$_{19}$Cl$_3$CrN$_5$.H$_2$O (%): C, 41.98; H, 4.62; N, 15.30. Found: C, 42.34; H, 4.62; N, 15.05. IR (KBr, cm^{-1}): 3451, 3029, 2927, 1608, 1559, 1460,

1398, 1339, 1304, 1269, 1250, 1157, 1112, 1051, 1028, 899, 865, 813, 779, 689.

$[Cr(L^3)Cl_3]$ (**3**). This complex has been prepared analogously to **2** starting from (N-methylimidazol-2-yl)-bis(3,5-dimethylpyrazol-1-yl)methane **L³** (0.167 g, 0.587 mmol) and $[CrCl_3(THF)_3]$ (0.220 g, 0.587 mmol) (0.230 g, 88.5%). Anal. Calcd for $C_{15}H_{20}Cl_3CrN_6$ (%): C, 40.69; H, 4.55; N, 18.98. Found: C, 40.59; H, 4.78; N, 18.29. IR (KBr, cm⁻¹): 3451, 3124, 2932, 1623, 1559, 1519, 1460, 1411, 1397, 1379, 1295, 1238, 1181, 1118, 1048, 989, 974, 901, 839, 754, 710, 673, 491.

$[Cr(L^4)Cl_3]$ (**4**). This complex has been prepared analogously to **2** starting from *N*-benzyl-2,2-bis(3,5-dimethyl-pyrazol)-1-yl-ethanamine **L⁴** (0.170 g, 0.525 mmol) and $[CrCl_3(THF)_3]$ (0.196 g, 0.525 mmol) (0.140 g, 89%). Green X-ray quality crystals of **4** were grown by layer diffusion of Et₂O into MeCN solution of **4**. Anal. Calcd for $C_{19}H_{25}Cl_3CrN_5 \cdot MeCN$ (%): C, 48.24; H, 5.40; N, 16.07. Found: C, 48.21; H, 5.34; N, 16.08. IR (KBr, cm⁻¹): 3253, 3136, 2974, 2933, 2869, 1626, 1560, 1463, 1419, 1380, 1307, 1263, 1131, 1053, 985, 965, 844, 806, 761, 728, 704, 673, 599, 578.

Synthesis of Cr-Al heterometallic complexes 5-7

$[(Pz'_3CH)_2Cr_2(\mu\text{-}Cl)_2]^{2+} \cdot 2[(Me_3Al)_{0.87}(Me_2AlCl)_{0.13}(\mu\text{-}Cl)(Me_3Al)_{0.78}[(Me_2AlCl)_{0.22}]^-$ (**5**). To a suspension of complex **1** (0.100 g, 0.219 mmol) in toluene (6 mL) was added AlMe₃ (0.657 mL, 1.31 mmol), and a light green solution formed. The resulting mixture was stirred at room temperature for 5 min and filtered. Green X-ray quality crystals of **5** were grown by layer diffusion of hexane into the resulting filtrate. Yield: 0.098 g (78.8%). Anal. Calcd for $C_{43.3}H_{77.9}Al_4Cl_{4.7}Cr_2N_{12}$ (%): C, 45.40; H, 6.87; N, 14.68. Found: C, 45.00; H, 6.09; N, 14.40.

$Pz'_3CHCrMeCl(\mu\text{-}Cl)\text{-}(AlMe_3)_{0.67}(Me_2AlCl)_{0.33} \cdot MePh$ (**6**). To a suspension of complex **1** (0.100 g, 0.219 mmol) in toluene (6 mL) was added MAO (1.41 mL, 2.19 mmol), and a light green solution formed. The resulting mixture was stirred at room temperature for 5 min and filtered. Dark-green X-ray quality crystals of **5**, and **6** were grown by layer diffusion of hexane into the resulting filtrate. Yield: **5**, 76mg (61%), **6**, 10.1mg (9%). The complex **6** was air- and moisture-sensitive,

giving no satisfactory elemental analysis.

Pz'$_2$CH(μ-N)CH$_2$(μ-Ph)CrCl(μ-Cl)-AlMe$_2$ (**7**). To a suspension of complex **4** (0.130 g, 0.270 mmol) in toluene (6 mL) was added AlMe$_3$ (0.81 mL, 1.62 mmol), and a light green solution formed. The resulting mixture was stirred at room temperature for 5 min and filtered. Green X-ray quality crystals of **7** were grown by layer diffusion of hexane into the resulting filtrate. Yield: 88mg (65%). This complex was air- and moisture-sensitive, giving no satisfactory elemental analysis.

Synthesis of Cr-Al heterometallic complex 5 from 6

{Pz'$_3$CHCr(μ-Cl)}$_2$-{(Me$_3$Al)$_2$(μ-Cl)}$_2$ (**5**). To a suspension of complex **6** (0.050 g, 0.083 mmol) in toluene (6 mL) was added AlMe$_3$ (0.083 mL, 0.166 mmol), and a light green solution formed. The resulting mixture was stirred at room temperature for 5 min and filtered. The crystals of **5** were grown by layer diffusion of hexane into the resulting filtrate. Yield: 0.042 g (89%).

Trimerization of ethylene

A 200 mL stainless steel reactor was dried at 120ºC for 3 h under vacuum, and then cooled down to 80ºC. Under ethylene atmosphere, the reactor was charged with toluene (50 mL) and then the mixture of the catalyst and the proper amount of MAO cocatalyst in toluene (10mL). Then the reactor was immediately pressurized. After 30 min, the reaction was stopped by cooling the system at 0ºC, depressurizing, and quenched by addition of 5 mL of H$_2$O. A small sample of the upper-layer solution was filtered through a layer of Celite and analysed by GC. The individual oligomerization products were identified by GC-MS. The remainder of the upper-layer solution was filtered to isolate the solid polymeric products. The solid products were suspended in 10% aq. HCl and stirred for 24 h, dried under reduced pressure and weighed.

X-ray Crystallography.

The crystals were mounted on quartz fibers and X-ray data were collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50ºC, using Mo-Kα radiation (λ =

0.71073 Å). The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for absorption effects with SADABS. Structure solution and refinement were carried out with the SHELXTL suite of programs.[6] In complex **5**, each of the two $(Me_3Al)_2(\mu\text{-Cl})$ counteranions had two of the six methyl groups carbon atom not properly behaving during the refinement. By arbitrarily attributing 13% chlorine character to one carbon atom, 22% chlorine character to another carbon atom, and the remaining as carbon character, respectively, it was possible to obtain a satisfactory refinement. Complex **6** has one molecule of toluene per chromium atom in the lattice, and one of the three methyl groups (in $AlMe_3$) carbon atom not proper behaving during the refinement. By arbitrarily attributing 33% chlorine character and the remaining as carbon character, it was possible to obtain a satisfactory refinement. The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.

6.   Sheldrick, G. M.; SHELL-97, Program for crystal structure refinement, University of Göttingen: Göttingen, Germany, 1997.

Table 1 Crystal data and structure refinement for complex **5**

Identification code	8499
Empirical formula	$C_{43.3}H_{77.9}Al_4Cl_{4.7}Cr_2N_{12}$
Formula weight	1145.37
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.6770(9) A alpha = 83.008(2) deg.
	b = 10.1662(9) A beta = 89.503(2) deg.
	c = 16.9298(15) A gamma = 61.853(2) deg.
Volume	1455.4(2) A^3
Z, Calculated density	1, 1.274 Mg/m^3
Absorption coefficient	0.657 mm^-1
F(000)	588
Crystal size	0.26 x 0.20 x 0.10 mm
Theta range for data collection	1.21 to 27.50 deg.
Limiting indices	-12<=h<=12, -6<=k<=13, -21<=l<=21
Reflections collected / unique	10386 / 6659 [R(int) = 0.0258]
Completeness to theta = 27.50	99.5 %
Absorption correction	Sadabs, (Sheldrick 2001)
Max. and min. transmission	0.9372 and 0.8477
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6659 / 4 / 307
Goodness-of-fit on F^2	1.115
Final R indices [I>2sigma(I)]	R1 = 0.0691, wR2 = 0.1572
R indices (all data)	R1 = 0.0798, wR2 = 0.1632
Largest diff. peak and hole	1.070 and -0.702 e.A^-3

Table 2 Crystal data and structure refinement for complex **6**·MePh

Identification code	8498
Empirical formula	$C_{26.7}H_{41.1}AlCl_{2.3}CrN_6$
Formula weight	605.40
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 9.5897(5) A alpha = 90 deg.
	b = 18.4971(9) A beta = 100.1510(10) deg.
	c = 17.4936(9) A gamma = 90 deg.
Volume	3054.5(3) A^3
Z, Calculated density	4, 1.316 Mg/m^3
Absorption coefficient	0.627 mm^-1
F(000)	1275
Crystal size	0.40 x 0.20 x 0.14 mm
Theta range for data collection	1.62 to 27.50 deg.
Limiting indices	-12<=h<=12, -21<=k<=24, -22<=l<=19
Reflections collected / unique	21565 / 7011 [R(int) = 0.0401]
Completeness to theta = 27.50	100.0 %
Absorption correction	Sadabs, (Sheldrick 2001)
Max. and min. transmission	0.9174 and 0.7877
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7011 / 2 / 338
Goodness-of-fit on F^2	1.073
Final R indices [I>2sigma(I)]	R1 = 0.0503, wR2 = 0.1161
R indices (all data)	R1 = 0.0614, wR2 = 0.1217
Largest diff. peak and hole	0.485 and -0.530 e.A^-3

Table 3 Crystal data and structure refinement for complex **7**

Identification code	8377a
Empirical formula	$C_{21}H_{29}AlCl_2CrN_5$
Formula weight	501.37
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 18.2839(12) Å $\square$= 90°.
	b = 8.9960(6) Å $\square$= 99.425(2)°.
	c = 14.6015(10) Å $\square$ = 90°.
Volume	2369.3(3) Å^3
Z	4
Density (calculated)	1.406 Mg/m^3
Absorption coefficient	0.764 mm^{-1}
F(000)	1044
Crystal size	0.26 x 0.18 x 0.10 mm^3
Theta range for data collection	1.13 to 27.50°.
Index ranges	-23<=h<=22, -11<=k<=10, -18<=l<=18
Reflections collected	16343
Independent reflections	5444 [R(int) = 0.0437]
Completeness to theta = 27.50°	99.9 %
Absorption correction	Sadabs, (Sheldrick 2001)
Max. and min. transmission	0.9276 and 0.8262
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5444 / 0 / 277
Goodness-of-fit on F^2	1.053

Final R indices [I>2sigma(I)]   R1 = 0.0704, wR2 = 0.1841

R indices (all data)   R1 = 0.0935, wR2 = 0.1971

Largest diff. peak and hole   2.110 and -0.300 e.Å^{-3}