

Supporting Information for...

A Structurally Characterized Ni-Al Methyl-Bridged Complex with Catalytic Ethylene Oligomerization Activity

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Experimental Section

General: All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of nitrogen or argon with an M. Braun Labmaster 130 Inert Gas System. NMR spectra were measured on Bruker ACF300 300 MHz FT NMR spectrometers (¹H at 300.14 MHz, ¹³C at 75.43 MHz and ³¹P at 121.49 MHz). Mass spectra were obtained on a Finnigan Mat 95XL-T spectrometer. Elemental analyses were performed by the microanalytical laboratory in-house. Ni(COD)₂ and pentafluoroaniline was used as supplied by Fluka Chemical Co. and Lancaster, respectively. MAO (methylaluminoxane) (10 wt. % in toluene solution), EtAlCl₂ (25 wt. % in toluene solution) and AlMe₃ (2.0 M in toluene solution) were purchased from Aldrich and used as received. 1'-(Diphenylphosphino)-1-ferrocenecarboxaldehyde was synthesized by a literature procedure.¹

Synthesis of [η-C₅H₄CH=N(C₆F₅)]Fe[η-C₅H₄PPh₂] (**1**). A methanol (10 ml) solution containing 1'-(Diphenylphosphino)-1-ferrocenecarboxaldehyde (110 mg, 0.276 mmol), pentafluoroaniline (61 mg, 0.333 mmol) and acetic acid (0.5 ml) was refluxed for 24 h. The solvent was removed under reduced pressure to afford deep orange-red oil. Column chromatography on silica gel eluting with toluene gave the product compound **1** as a red solid. (52 mg, 0.092 mmol, 34 % yield). ¹H NMR (C₆D₆): δ 7.69 (s, 1 H, CH=N), 7.46-7.40 (m, 4 H, phenyls), 7.05-6.97 (m, 6 H, phenyls), 4.64 (t, 2 H, Cp), 4.22 (t, 2 H, Cp), 4.19 (t, 2 H, Cp), 4.10 (t, 2 H, Cp). ¹³C NMR (C₆D₆): δ 170.54 (CH=N), 139.98 (d, Ph), 134.73 (Ph), 134.46 (Ph), 129.50 (Ph), 129.24 (Ph), 129.15 (Ph), 80.46 (Cp), 79.66 (Cp), 79.53 (Cp), 75.53 (Cp), 75.34 (Cp), 74.29 (Cp), 73.53 (d, Cp), 71.62. ³¹P NMR (C₆D₆): δ -17.58. MS (FAB⁺): *m/z* 563 [M]⁺. Elemental analysis (%) calcd for C₂₉H₁₉F₅NPF_e: C 61.84, H 3.40, N 2.49; found: C 62.19, H 3.71, N 2.56.

(1) Wright, M. E. *Organometallics*, **1990**, *9*, 853.

Synthesis of $[\eta\text{-C}_5\text{H}_4\text{CH}=\text{N}(\text{C}_6\text{F}_5)]\text{Fe}[\eta\text{-C}_5\text{H}_4\text{PPh}_2]\text{NiAlMe}_3$ (**2**). To a red solution of **1** (34 mg, 0.06 mmol) in n-hexane (5 ml) was added $\text{Ni}(\text{COD})_2$ (17 mg, 0.06 mmol) and stirred at r.t. for 30 min to give an orange solution. AlMe_3 in toluene (60 μl , 0.12 mmol) was added by a micro volume syringe and the reaction mixture was further stirred at r.t. for 2 h. The resultant red-orange solution was filtered through a layer of celite. The solvent was removed to afford a red-orange solid of **2** (ca. 18 mg, 0.026 mmol, 43 % yield). Crystals of **2** (which co-crystallizes with $\text{Ni}(\text{COD})_2$) suitable for X-ray diffraction were grown by recrystallization from its toluene solution layered with n-hexane. ^1H NMR (C_6D_6): δ 8.33 (br), 7.88-7.85, 7.02-6.96 (phenyls), 4.75 (d), 4.58 (s), 4.23 (s), 4.17 (s), 3.82 (s), 3.77 (s), 3.65 (s), 3.38 (s), -0.31 (s), -0.53 (s). ^{31}P NMR (C_6D_6): δ 39.18. This compound was highly air- and moisture-sensitive, giving no satisfactory elemental analysis.

Oligomerization of ethylene. The catalytic activities of **2** were screened by Endeavor Parallel Pressure Reactor, following recommended procedures.

1. Prepare a stock solution of catalyst **2** (0.001 M, 5 ml).
2. Prepare 8 glass liners with 4 ml toluene as solvent.
3. Inject the catalyst solution (250 μl , 0.25 μmol) and activator solution.
4. Secure stirrer top with impellers to reactor block.
5. Program reaction temperature, pressure, volume 4 ml, run time and reaction sequence by using Endeavor Advanced Software.
6. Start Endeavor software on PC.
7. Click "Start" on Endeavor software on PC.
8. At the end of each test, the reaction mixture was cooled to 0 °C and terminated by addition of 1 ml of H_2O . The upper-layer solution was filtered through a layer of celite and analyzed by GC. The individual products of oligomerization were identified by GC-MS.

Crystal Structure Analyses. A suitable crystal of **2** was mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 °C, using $\text{MoK}\alpha$ radiation (λ 0.71073 Å). The data was corrected for Lorentz and polarisation effect with the **SMART** suite of programs² and for absorption effects with **SADABS**.³ Structure solution and refinement were carried out with the **SHELXTL** suite of programs.⁴ The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. In the asymmetric unit there is one molecule of the titled compound

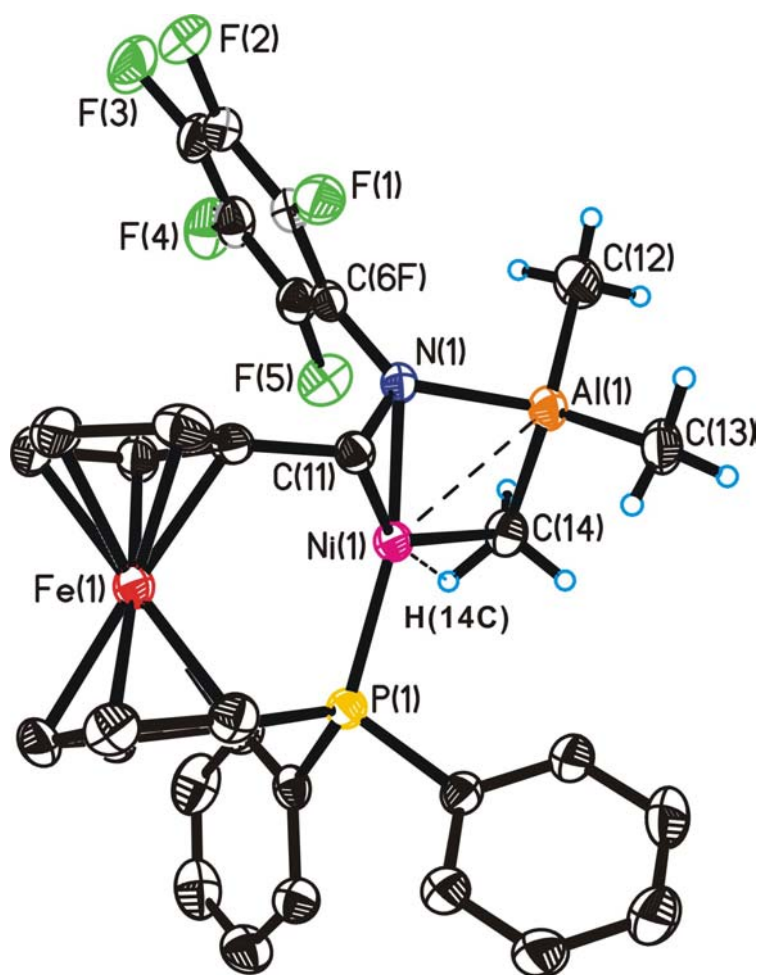
(2) SMART version 5.1, Bruker Analytical X-ray Systems, Madison, WI, 2000.

(3) Sheldrick, G. M. SADABS, a program for Empirical Absorption Correction, Göttingen, Germany, 2000.

(4) SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.

and half a molecule of Ni(COD)₂. The latter is disordered around the special position (centre of symmetry) of the unit cell. In final refinement the H atoms of the disordered C8 ring are not included. H atoms of C atoms of **2** were put at calculated positions except C11 and C14, where the H atoms were located from difference map and refined with fixed C–H distance.

ORTEP diagrams (Thermal ellipsoids are drawn at the 40% probability) and tables of crystallographic data for Complex **2**.



ORTEP diagram of complex **2**

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Table 1. Crystal data and structure refinement for 4279 (complex 2).

Identification code	4279	
Empirical formula	C ₄₀ H ₃₅ Al F ₅ Fe N Ni _{1.50} P	
Formula weight	826.55	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.2968(6) Å	∠ = 70.286(1)°.
	b = 13.399(9) Å	∠ = 82.699(1)°.
	c = 15.3641(11) Å	∠ = 80.629(1)°.
Volume	1772.3(2) Å ³	
Z	2	
Density (calculated)	1.549 Mg/m ³	
Absorption coefficient	1.325 mm ⁻¹	
F(000)	846	
Crystal size	0.40 x 0.14 x 0.10 mm ³	
Theta range for data collection	1.41 to 27.50°.	
Index ranges	-12 ≤ h ≤ 12, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19	
Reflections collected	22731	
Independent reflections	8116 [R(int) = 0.0424]	
Completeness to theta = 27.50°	99.7 %	
Absorption correction	Sadabs, (Sheldrick 2001)	
Max. and min. transmission	0.8789 and 0.6192	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8116 / 8 / 514	
Goodness-of-fit on F ²	1.059	
Final R indices [I > 2σ(I)]	R1 = 0.0592, wR2 = 0.1754	
R indices (all data)	R1 = 0.0906, wR2 = 0.1917	
Largest diff. peak and hole	0.631 and -1.913 e.Å ⁻³	