A structurally characterized Ni–Al methyl-bridged complex with catalytic ethylene oligomerization activity†

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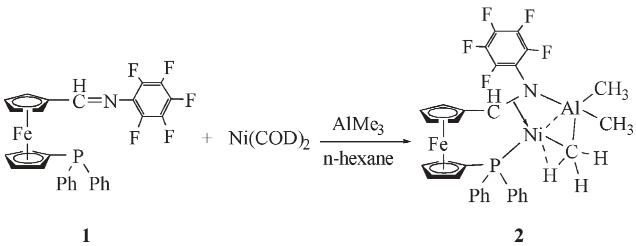
A bimetallic Ni–Al (2.5087(15) Å) complex with an agostic α-C–H, [η-$C_5H_4CH{=}N(C_6F_5)$]Fe[η-$C_5H_4PPh_2$]Ni($AlMe_3$), has been isolated and crystallographically established. The complex is active towards ethylene oligomerization/polymerization under moderate conditions.

Metallocene catalysis is a key technology in the current polyolefin industry.[1] Recently, its impact has spilled over into olefin polymerization by late metals,[2] hydrogen transfer hydroalumination[3] and intermetallic M–M′ interactions.[4] These developments originated in 1954, when Ziegler *et al.* observed an unexpected catalytic effect of Ni on the transfer of Al–H from Al(n-Bu)$_3$ to ethylene, giving butene and $AlEt_3$.[5a] This discovery laid the foundation for the Ziegler growth reaction[5b] and the production of linear high-MW polyethylene. It also triggered the rich advancement of organonickel chemistry.[6] The mechanistic origin of this "nickel effect" rapidly became a subject of immense scientific interest. Its inhibition on the polymerization process also carries a technological significance. Wilke *et al.* suggested that the key intermediates are Ni(0), with multi-centred Ni(μ-C)Al moieties rather than Ni(II).[7] Pörschke *et al.* followed-up with a series of elegant experiments that demonstrated the Lewis acidity of Ni(0) towards s/p block organometals.[8] Eisch *et al.* proposed an intermediate with a direct Ni–Al bond.[9] With this background and our interest in heterometallic syntheses[10] and catalysis,[11,12] we decided to trap, isolate and structurally identify the elusive intermediate Ni(0)–AlR_3 in order to understand better the intermetallic interaction in this key step. Similar experiments with $AlMe_2H$ or $LiAlH_2R_2$ (R = H, Bu) established an Al–H–Ni bridge[13] but there was no report on the use of the actual co-catalyst AlR_3 or other related non-hydrides as substrates. Our strategy was to design a suitable ligand that could support and stabilize not just a notoriously unstable Ni(0)–Al(III) bimetallic complex, but also facilitate the cross-metallic hydride or alkyl migration and obtain structural evidence of such a process. These targets are met by the use of a new hemilabile and heterodifunctional[14] fluoro ligand [η-$C_5H_4CH{=}N(C_6F_5)$]Fe[η-$C_5H_4PPh_2$] (**1**) which promotes an active intermetallic interaction that could model the process behind the "Ziegler Nickel Effect". The importance of hemilability and ethylene oligomerization has been elegantly reviewed by Braunstein *et al.*[15]

Reaction of Ni(COD)$_2$ with **1** and $AlMe_3$ in n-hexane gave a Ni–Al bimetallic complex [η-$C_5H_4CH{=}N(C_6F_5)$]Fe[η-$C_5H_4PPh_2$]-Ni($AlMe_3$) (**2**), which was isolated as a red, air- and moisture-sensitive solid (Scheme 1). In solution under the protection of argon, **2** remains unchanged for several hours at rt or two days at −30 °C. Crystals of **2** (co-crystallizes with adventitious Ni(COD)$_2$) suitable for X-ray diffraction were grown by recrystallization from its toluene solution layered with n-hexane. Its structure (Fig. 1) reveals a bimetallic complex with two new features: a π-imine bridging the metals and a bridging methyl group with an agostic C–H–Ni interaction.‡ These unique bridging functionalities help to lock the two metals into proximity (Ni···Al 2.5087(15) Å), even closer than an intermediate in the methyl transfer Ni–Al binuclear complex (Ni···Al 2.691(1) Å)[16] and the hydride-bridged ($C_7H_{13}N$)(Me_2AlH)Ni(CDT) (Ni···Al 2.731(1) Å) (CDT = *trans*, *trans*, *trans*-1,5,9-cyclododecatriene).[13b] Complex **2** provides a structural motif for the multi-centred Ni–C–Al bonding between Ni(0) and AlR_3 presumed in the "nickel effect".[7b] Similar Lewis acidic Ni(0) behavior, albeit without the agostic H, was observed towards other metals, *viz.* Li, Na and Mg,[8] and more recently Zn-alkyls.[17]

There are three major features that distinguish our system from the reported [(C_2H_4)Ni–H–M],[18] namely: (1) we did not observe any active terminal or bridging hydride, (2) a functional imine is used to model the original ethylene in the Ziegler system and (3) the bimetallic interaction is assisted by the multi-functional iminophosphine.

Unexpectedly, **2** shows an α-agostic hydrogen at Ni in a bridging methyl group that originated from $AlMe_3$. Similar α-C–H agostic interactions have been found in a few other unrelated dimeric systems such as $Mn_2(CH_2Ph)_4(PMe_3)_2$.[19] The bridging Al–C (Al–C(14) 2.079(5) Å) is notably longer and presumably weaker than the terminal Al–C (average 1.957(5) Å). Complex **2** thus models an active intermediate that uses methyl to carry an active hydrogen across the metals before it is released to the attached



Scheme 1

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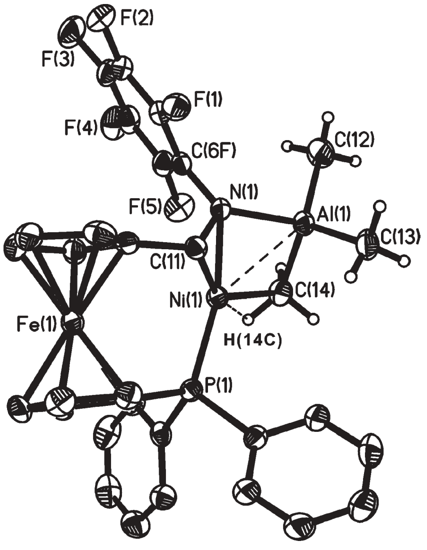

Fig. 1 ORTEP representation (40% ellipsoids) of the X-ray structure of **2**·0.5Ni(COD)$_2$ (Ni(COD)$_2$ and H atoms (excepted those of AlMe$_3$) are omitted for clarity). Selected bond lengths (Å) and angles (°): Ni(1)···Al(1) 2.5087(15), Ni(1)–C(11) 1.903(4), Ni(1)–N(1) 1.958(4), Ni(1)–P(1) 2.1510(13), Ni(1)–C(14) 2.174(5), Al(1)–N(1) 2.000(4), Al(1)–C(12) 1.956(5), Al(1)–C(13) 1.959(5), Al(1)–C(14) 2.079(5), N(1)–C(11) 1.441(5), N(1)–C(6F) 1.407(5), Ni(1)···H(14C) 1.97(6), C(14)–H(14C) 0.97(3); C(14)–H(14C)–Ni(1) 89(3), C(11)–Ni(1)–N(1) 43.81(16), C(11)–Ni(1)–P(1) 102.12(13), N(1)–Ni(1)–P(1) 145.92(11), N(1)–Ni(1)–Al(1) 51.42(11), P(1)–Ni(1)–Al(1) 145.52(5), N(1)–Al(1)–Ni(1) 49.93(11), Al(1)–C(14)–Ni(1) 72.25(16), Ni(1)–N(1)–Al(1) 78.65(14).

olefin (modelled by the imine). It also demonstrates the active step of hydroalumination, whereby Al–R is oxidatively added to Ni(0).[17,20] The Ni···H(14C) (1.97(6) Å)[21] contact is significantly weaker than those of "typical" β-H agostic Ni(II)-alkyls [Me$_2$NN]NiR (R = Et, Pr) (1.66 and 1.61 Å).[22] ^{1}H NMR spectra of **2** from rt to −80 °C in toluene-d_8 could not substantiate such an interaction in solution, which was observed in other Ni(II)-alkyls with agostic β-Hs.[22] The VT ^{1}H NMR spectrum (toluene-d_8) gives only one Al-methyl resonance (δ −0.62), suggesting rapid exchange. This resonance resolves to three signals (δ 0.05, −0.41 and −0.51) at −80 °C, consistent with the molecular structure in the solid state.

Some preliminary data on the catalytic activities of **2** in ethylene oligomerization/polymerization are given in Table 1. Without an activator, **2** shows a short activity life (6 min) for the oligomerization of ethylene with a TOF {21 200 mol of C_2H_4 per mol of Ni h^{-1}}, producing 1-butene (entry 1). Surprisingly, using AlMe$_3$ as activator, **2** catalyses ethylene to produce an insoluble polymer (entry 2), whilst butene is obtained as the sole product when MAO is used (entry 3). The molecular weight of the polyolefin product is controlled by "chain transfer processes", which involve a co-catalyst such as aluminum alkyls.[23] Co-catalyst can significantly affect the oligomerization result.[24] MAO has been shown to be an effective co-catalyst for methylation and/or ionization of the Ni centre; AlMe$_3$ is only very effective for methylating the Ni centre, not for ionization. However, with EtAlCl$_2$, the ethylene oligomerization activity is enhanced (entries 4–8), which is possibly attributed to facile *in situ* formation of a Ni–alkyl, leading to an active Ni–hydride *via* β-elimination. The result is consistent with the observations of Braunstein *et al.*[14a]

Elevated temperature (60 °C) results in a higher productivity (entry 5), suggesting that **2** is thermally stable (under the experimental conditions) with a reasonable lifetime. At 80 °C, it remains active for 1 h with a lower productivity, which may be due to the lower ethylene solubility at higher temperatures.[25] The TOF rises from 84 000 (entry 5) to 200 000 (entry 7) upon addition of 730 equivalents of EtAlCl$_2$, during which the selectivity for C$_6$ rises from 37 to 76 mol% of ΣC. We also witnessed a ~2-fold increase in TOF when the pressure was increased from 300 (entry 4) to 450 (entry 8) psi. Under similar conditions, the activity of **2** (entry 5, TOF 84 000) is comparable to that of a related monometallic Ni(0)-isocyanide complex [C$_5$H$_4$CH=N(C$_6$F$_5$)]Fe[η-C$_5$H$_4$PPh$_2$]-Ni^0(CN*t*-Bu)$_3$, which has a TOF of 96 000.[26] This result may indicate that the bimetallic intermediate is common in these systems.

Isolation and crystallographic elucidation of **2** suggested that we can harness the "Ziegler Nickel Effect" by designing suitable ligands, such as **1**, that can play a dual-role, *viz.* protecting the activated Ni from coordinative unsaturation and bringing Al into close proximity. It thus promotes olefin attachment, hydrogen transfer and the overall hydroalumination or carboalumination process. It was unexpected that the electron-poor imine can function as a four electron donor, with π-coordination at the low-valent d-metal and σ donation at the normal-valent p-metal. This bridge lends stability to **2** and distinguishes it from all other similar bimetallics reported. The rich organometallic chemistry uncovered within a single compound has opened-up another direction in this research. Since solid state materials such as NiAl or Ni$_3$Al can be

Table 1 Oligomerization/polymerization of ethylene with **2**[a]

							Oligomer/mol%[c]			
Entry	Activator	T/°C	Pressure/psi	Al/Ni	Time/h	TOF[b]	C$_4$/ΣC	C$_6$/ΣC	C$_{\geqslant 8}$/ΣC	α-olefin
1	—	30	300	—	0.1	21 200	100	0	0	—
2[c]	AlMe$_3$	30	300	1000	1	1 900	0	0	0	—
3	MAO	30	300	1000	3	8 800	100	0	0	53 (C$_4$)
4	EtAlCl$_2$	30	300	146	3	53 333	62	38	0	12 (C$_6$)
5	EtAlCl$_2$	60	300	146	1	84 000	60	37	3	8 (C$_6$)
6	EtAlCl$_2$	80	300	146	1	16 000	72	26	3	7 (C$_6$)
7	EtAlCl$_2$	60	300	730	2	200 000	20	76	4	7 (C$_6$)
8	EtAlCl$_2$	30	450	730	2	92 000	61	39	0	12 (C$_6$)

[a] Optimized by the Endeavor Catalyst Screening System. Conditions: 0.25 μmol of catalyst, 4 ml of toluene. [b] TOF = mol of ethylene consumed per mol of Ni h^{-1}. [c] Isolated insoluble polymer 54 mg.

formed from an amorphous intermediate with an Ni–H–Al entity,[27] we are in active pursuit of new molecular precursors to intermetallic alloys.[28]

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Notes and references

‡ **2**·0.5Ni(COD)$_2$: $C_{40}H_{35}AlF_5FeNNi_{1.5}P$, M_r = 826.55, triclinic, space group *P*-1, a = 9.2968(6), b = 13.3990(9), c = 15.3641(11) Å, α = 70.286(1), β = 82.699(1), γ = 80.629(1)°, V = 1772.3(2) Å^3, Z = 2, ρ = 1.549 Mg m^{-3}, F(000) = 846, l(Mo-K$_\alpha$) = 0.71073 Å, μ = 1.325 mm^{-1}, T = 223(2) K, crystal dimensions: 0.40 × 0.14 × 0.10 mm. Siemens SMART diffractometer equipped with a CCD detector. Of 22731 reflections measured, 8116 unique reflections (R_{int} = 0.0424) were used in refinement. The whole Ni(COD)$_2$ can be generated by the crystal symmetry and is disordered around the special position (centre of symmetry) of the unit cell. In the final refinement, the H atoms of the disordered C_8 rings are not included. Final R = 0.0592 (R_w = 0.1754). CCDC 283379. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517824j.

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