

# Bis(imino)pyridine Complexes of the First-Row Transition Metals: Alternative Methods of Activation

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The use of  $\text{AlEt}_3$  (TEA) in combination with  $[\text{Ph}_3\text{C}][\text{Al}(\text{O}^t\text{Bu}^{\text{F}})_4]$  (TA) for the activation of a range of bis(imino)pyridine complexes of vanadium, chromium, iron, and cobalt is reported. It is shown that this activator combination successfully replaces MMAO, in some cases showing improvements in terms of activity and productivity. Furthermore, when activities and productivities are considered in terms of the aluminum center (MMAO vs TEA), the true cost driver in the commercialization of most catalyst systems, then in nearly all cases a significant improvement is seen.

## Introduction

The use of bis(imino)pyridine complexes of the first-row transition metals for the oligomerization and polymerization of olefins,<sup>1</sup> most especially ethylene, has seen considerable interest over the past decade,<sup>2</sup> the unique ability of this class of ligand to allow the use of iron and cobalt centers having drawn particular attention.<sup>2c</sup> There is now strong evidence to suggest that the electron-donating and -accepting ability of this ligand scaffold, combined with its manifold reactivity pathways toward alkylation, is responsible for this behavior.<sup>2c,3</sup>

The high activity of bis(imino)pyridine complexes for ethylene oligomerization to give highly linear oligomers that are largely terminal olefins (often >90%  $\alpha$ -olefin in each carbon number fraction) has won them many plaudits.<sup>2</sup> However, barriers still remain to the commercial development of these systems, primarily the use of large excesses of methylalumoxane (MAO)- or modified methylalumoxane (MMAO)-based activator (in most cases >500 equiv relative to the transition metal), which then represents the majority of the cost of the overall catalyst package.<sup>4,5</sup> Thus the true cost driver when considering the optimization of such catalyst packages is not the transition metal complex, but the aluminum activator.<sup>4,5</sup>

Notably, trialkyl aluminum reagents,  $\text{AlR}_3$ , where R is ethyl or heavier, are significantly lower in cost than methylalumoxane-based reagents which are derived from trimethylaluminum. The replacement of methylalumoxane-based activators, with trialkylaluminums in combination with alkyl-abstracting reagents and weakly coordinating anions, has long been known in the area of olefin polymerization, the most notable example being the use of fluorinated boranes or borate salts.<sup>6</sup> While the use of, for example,  $\text{AlEt}_3$  (TEA) in combination with  $[\text{Ph}_3\text{C}][\text{B}(\text{Ph}^{\text{F}})_4]$

(TB) has been one of the most successful examples of this methodology, it has nonetheless suffered from several problems relating to catalyst deactivation. The first of these is exchange of groups between the trialkylaluminum and the borate, thus destroying the weakly coordinating nature of the borate anion,<sup>6a,7</sup> and second is transfer of fluorinated aryl groups from the borate to the transition metal center.<sup>8</sup> Recent developments in this area have seen the use of fluorinated aluminates as weakly coordinating anions, which offer the advantages of being less coordinating than borates, while displaying increased stability.<sup>9</sup> The use of TEA in combination with  $[\text{Ph}_3\text{C}][\text{Al}(\text{O}^t\text{Bu}^{\text{F}})_4]$  (TA) has been successfully used to replace MMAO in the Cr-PNP ethylene tetramerization catalyst system to greatly reduce the amount of aluminum used overall.<sup>10</sup>

Several groups have studied the alkylation of bis(imino)pyridine iron complexes,<sup>3,11–13</sup> and notably Chirik has used alkyl-abstracting reagents to generate iron-alkyl cations coupled with fluorinated borate-based anions.<sup>13a</sup> While extremely elegant, the

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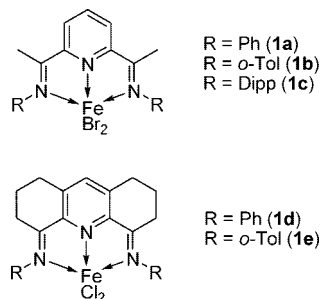
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**Figure 1.** Iron complexes prepared for use in catalysis.

catalysis described using these isolated iron-alkyl salts was notably inferior to the standard system of iron-halide precursor and MAO. However, examples of fluorinated borate-based anions in combination with triisobutylaluminum to activate bis(imino)pyridine complexes of iron(II) chloride *in situ* have also been demonstrated by the groups of Herrmann<sup>14</sup> and Small<sup>15</sup> with some success.

Herein, we describe the use of the TEA/TA combination to successfully replace MMAO or TEA/TB in the activation of bis(imino)pyridine complexes of a range of first-row transition metal halide salts. We demonstrate that when the activity and productivity for a given catalyst system is considered in terms of the aluminum activator instead of the transition metal (TM), then in nearly all cases an improvement is observed over the MMAO-based systems, and surprisingly, even when conventional activities and productivities are calculated based on the transition metal, many of the examples still show improved activity over MMAO-based variants.

## Results and Discussion

Known to be the most active metal in combination with this ligand class, a series of iron complexes of bis(imino)pyridine ligands were prepared (Figure 1). Three different imine substituent variants of the ligand were chosen, as it is well understood that for systems of this type increasing bulk on the imino substituent leads to a greater preference for chain propagation over chain termination, and hence higher molecular weight products. Thus the phenyl-, *o*-tolyl (*o*-Tol)-, and 2,6-diisopropylphenyl (Dipp)-substituted variants of the ligand were examined to give a broad spread of product profiles, from purely oligomers to polymer. A cyclic version of the bis(imino)pyridyl ligand has also been reported; thus the iron complexes of the phenyl and *o*-tolyl variants of this ligand were also prepared.<sup>16</sup>

Each of the iron complexes was screened for ethylene oligomerization/polymerization with MMAO to provide a benchmark and then with TEA/TA to see if an improvement could be realized with this activator combination (see Table 1). In order to provide a comparison between aluminate- and borate-based weakly coordinating anions, **1a** was also screened with TEA/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and TEA/TB. The general conditions used for the catalysis were 8 bar of ethylene pressure and to start

**Table 1. Results of Ethylene Oligomerization Using Bis(imino)pyridine Iron Complexes<sup>a</sup>**

entry	cat. ( $\mu\text{mol}$ )	cocat <sup>b</sup> (equiv)	<i>t</i> (min)	based on Al		based on transition metal		% PE	% liq	g total	<i>K</i> <sup>c</sup>	C <sub>4</sub> (1 - C <sub>4</sub> )	C <sub>6</sub> (1 - C <sub>6</sub> )	C <sub>8</sub> (1 - C <sub>8</sub> )	C <sub>10</sub> (1 - C <sub>10</sub> )	C <sub>12+</sub>
				prod <sup>d</sup>	act <sup>d</sup>	prod <sup>e</sup>	act <sup>e</sup>									
1	<b>1a</b> (10)	TEA/TA (100/1.5)	9	400	2700	40 400	269 600	0	100	11.35	0.24	76.7 (96.5)	18.3 (72.3)	3.9 (73.3)	0.8 (63.1)	0.2
2	<b>1a</b> (5)	TEA/TA (100/1.5)	20	2,320	6970	232 400	697 300	0	100	32.61	0.29	70.9 (99.2)	20.6 (80.8)	6.2 (88.2)	1.6 (99.1)	0.6
3	<b>1a</b> (5)	TEA/TA (100/1.5)	33	5,740	10 440	574 200	1 043 900	0	100	80.53	0.28	75.0 (99.2)	16.9 (79.6)	5.9 (86.8)	1.6 (90.2)	0.6
4	<b>1a</b> (10)	MMAO (500)	117	180	90	88 800	45 500	0	100	24.90	0.3	71.0 (98.9)	21.1 (72.1)	5.6 (78.2)	1.6 (77.9)	0.7
5	<b>1a</b> (5)	MMAO (500)	120	330	160	162 300	81 100	0	100	22.76	0.31	69.6 (95.1)	21.3 (37.4)	6.7 (59.5)	1.7 (45.6)	0.6
6	<b>1a</b> (20)	TEA/B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (100/2.5)	9	80	520	7800	52 100	0	100	4.38	0.30	70.7 (96.0)	20.9 (90.8)	6.1 (92.8)	1.7 (92.6)	0.6
7	<b>1a</b> (20)	TEA/TB (100/1.5)	10	160	960	16 000	96 000	0	100	8.98	0.24	76.6 (97.7)	18.4 (86.4)	3.9 (85.7)	0.9 (81.0)	0.3
8	<b>1a</b> (10)	TEA/TB (100/1.5)	52	720	830	72 000	83 100	0	100	20.21	0.25	75.6 (99.3)	18.7 (90.1)	4.3 (92.6)	1.0 (95.7)	0.4
9	<b>1b</b> (5)	TEA/TA (100/1.5)	6.8	6,670	58 560	667 000	5 856 400	0.5	99.5	93.00	0.65	35.2 (99.6)	23.0 (98.8)	13.9 (97.9)	8.7 (96.8)	19.1
10	<b>1b</b> (5)	MMAO (500)	9.8	1,340	8200	671 600	4 097 900	3.9	96.1	94.20	0.65	34.2 (99.7)	22.2 (99.2)	13.6 (98.4)	8.6 (98.2)	21.3
11	<b>1c</b> (10)	TEA/TA (100/1.5)	8	160	1280	16 400	127 800	98.8	1.2	4.60	-	96.3 (97.6)	3.7 (100)	0	0	0
12	<b>1c</b> (10)	MMAO (500)	12	40	220	22 000	110 000	100	0	6.17	-	0	0	0	0	0
13	<b>1d</b> (20)	TEA/TA (100/1.5)	9	170	1030	16 900	102 600	0	100	9.50	0.45	77.3 (96.0)	15.3 (91.8)	4.2 (88.2)	1.5 (84.1)	1.7
14	<b>1d</b> (20)	MMAO (500)	22	60	150	28 100	75 400	0	100	15.76	0.37	77.8 (97.6)	16.7 (86.9)	3.7 (82.3)	1.1 (74.6)	0.7
15	<b>1e</b> (20)	TEA/TA (100/1.5)	111	1580	850	157 500	85 100	4.7	95.3	88.37	0.64	35.3 (98.6)	23.8 (97.3)	14.4 (97.7)	9.3 (92.1)	17.2
16	<b>1e</b> (20)	MMAO (500)	62	260	250	130 300	125 200	5.9	94.1	73.08	0.61	35.6 (98.6)	25.9 (98.1)	14.8 (98.3)	9.0 (91.8)	14.7
17	<b>1e</b> PhCl (10)	TEA/TA (100/1.5)	21	2570	7130	256 800	713 400	2.2	97.8	72.05	0.70	41.4 (98.9)	23.7 (98.1)	13.0 (98.3)	7.9 (93.0)	14.0
18	<b>1e</b> PhCl (10)	MMAO (500)	50	400	480	200 700	237 500	2.9	97.1	56.30	0.62	36.4 (97.8)	25.3 (98.8)	14.3 (99.1)	8.8 (94.7)	15.2

<sup>a</sup> General conditions: Toluene (100 mL), *p*(ethylene) = 8 bar, *T* = 30 °C. <sup>b</sup> MMAO = MMAO-3A; TEA/TB = Et<sub>3</sub>Al/Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]; TEA/TA = Et<sub>3</sub>Al/Ph<sub>3</sub>C][Al(O<sup>*t*</sup>Bu)<sub>2</sub>]<sub>4</sub>. <sup>c</sup> (mol ethene) (mol Al)<sup>-1</sup> h<sup>-1</sup>. <sup>d</sup> (mol ethene) (mol Al)<sup>-1</sup> h<sup>-1</sup>. <sup>e</sup> (mol ethene) (mol Fe)<sup>-1</sup> h<sup>-1</sup>. <sup>f</sup> (mol ethene) (mol Fe)<sup>-1</sup> h<sup>-1</sup>. <sup>g</sup> Average *K* value over the carbon ranges C<sub>6</sub>-C<sub>18</sub>; it should be noted that a nonconstant *K* value was observed, the value increasing slightly with carbon number, as has been previously reported.

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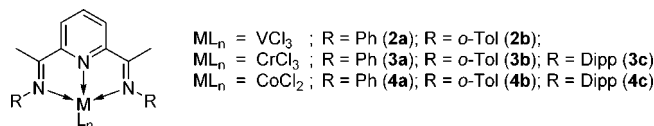
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runs at 20 °C and, after control of the initial exotherm,<sup>17</sup> to maintain the vessel temperature at 30 °C for the duration of the run. Initial screening runs of **1a** with both MMAO and TEA/TA were performed using 20 μmol of precatalyst; however in both cases, this resulted in such a dramatic exotherm (in excess of 100 °C) that the runs were terminated. Even dropping the precatalyst loading to 10 μmol still gave significant exotherms that led to catalyst deactivation, as observed by the rate of ethylene uptake, while a further reduction to 5 μmol allowed sufficient control of the initial exotherm that more stable running could be achieved (Table 1, entries 1 and 4 as compared to entries 2, 3, and 5).<sup>18</sup> It can be seen that TEA/TA successfully replaced MMAO as activator, surprisingly giving a 12-fold increase in TM activity<sup>19</sup> to 1 043 900 (mol ethene) (mol Fe)<sup>-1</sup> h<sup>-1</sup>. When the performance is considered in terms of the aluminum usage however, it can be seen that an improvement by as much as a 64-fold increase in activity and 17-fold in productivity is observed. Interestingly, there was no significant change in selectivity, both catalysts giving only liquid products and only a very slight drop in Schulz–Flory constant upon changing to TEA/TA. It should be noted that the TEA/TA system did appear to be more sensitive toward temperature than the MMAO-activated system, the former showing noticeable catalyst deactivation when the temperature reached 50 °C, in contrast to the latter, which could reach ~70 °C during the exotherm stage without being significantly effected. Thus the difference in performance between entries 2 and 3 is assigned to better control of the exotherm with entry 3; this run showed no appreciable catalyst deactivation during the course of the run and was terminated only because the autoclave had filled.

When TEA/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was used for the activation of **1a** (Table 1, entry 6), a relatively poor TM activity of 52 000 (mol ethene) (mol Fe)<sup>-1</sup> h<sup>-1</sup> was observed. Even though conducted with 20 μmol of precatalyst, the temperature of the reaction medium never exceeded 35 °C, yet the catalyst showed a lifetime of only 9 min, giving a poor productivity. In contrast, the use of TEA/TB gave a catalyst with a similar TM activity to that activated with MMAO, and again a drop in catalyst loading was required to achieve optimal performance (Table 1, entries 7 + 8). Notably, although the catalyst still produced only liquid product, there was a drop in Schulz–Flory constant to 0.25 with this activator. For formally cationic oligomerization initiators the coordinating strength of the anion has been shown to effect the selectivity observed, and thus this drop in Schulz–Flory constant is rationalized in a similar fashion.<sup>10b</sup> The improvement in performance upon switching from TEA/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to TEA/TB is to be expected, given that the anion formed *in situ* with the former, MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>-</sup>, is inherently more coordinating than B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> and is also known to undergo ready substituent exchange.<sup>6a,7,10b</sup>

The activation of precatalyst **1b** showed an improvement when switching from MMAO to TEA/TA (Table 1, entries 9



**Figure 2.** Vanadium, chromium, and cobalt complexes prepared for use in catalysis.

and 10), although less dramatic than with **1a**. Again there was no significant change in any of the selectivities, except a slight decrease in polymer formation from 3.9% to 0.5%. It is noteworthy that the *o*-tolyl variant **1b** shows a significantly greater tolerance to elevated temperatures than **1a**; hence, despite brief exotherms to ~80 °C before the run temperature was restored to 30 °C, no deactivation of the catalyst was observed during the course of the run. For precatalysts **1a** and **1b**, it is noted that a nonconstant *K* value was calculated, showing a slight increase in value with increasing carbon number, as has been previously reported.<sup>20</sup> The polymerization variant of the precatalyst, **1c**, showed no significant change in selectivity upon changing from MMAO to the TEA/TA activator combination, producing almost exclusively polymer (Table 1, entries 11 and 12). It can be seen that again MMAO was successfully replaced, although only a slight increase in TM activity was observed upon switching to TEA/TA, and in fact the TM productivity was lower. However, when viewed in terms of aluminum usage, the TEA/TA activator combination is significantly better in terms of both activity and productivity. It should be noted that the low productivity of both runs is most likely due to entrapment of the still active catalyst within the polymer product.

In order to further explore this system, the complexes **1d** and **1e** with the cyclic backbone variants of the bis(imino)pyridine ligands were screened; **1d** with TEA/TA gave a TM activity improvement while showing decreased TM productivity as compared to MMAO, while **1e** gave the inverse situation (Table 1, entries 13–16). It was noted that complexes **1d** and **1e** showed particularly low solubility in toluene, and so despite being a less desirable choice of solvent, **1e** was re-examined in chlorobenzene. As expected a significant leap in both activity and productivity was observed for both activators; however TEA/TA gave significantly better results (Table 1, entries 17 and 18).

An overall consideration of the difference between activation of **1a–e** with TEA/TA and MMAO reveals the former always gives better TM activity, with the exception of **1e** in toluene. However, the situation is more mixed for TM productivity, with a distinct preference for a given activator for certain catalysts. Significantly though, when considered from the perspective of aluminum usage, an increase in activity and productivity is achieved in all cases.

Given the successful application of this activator combination to the iron complexes, a further exploration of the first-row transition metals was undertaken. Figure 2 depicts the vanadium, chromium, and cobalt complexes of bis(imino)pyridine ligands prepared. Again, each complex was screened with both MMAO and TEA/TA so that a direct comparison could be made, the results obtained being shown in Table 2.

Considering the vanadium-based precatalysts **2a** and **2b**, it can be seen that TEA/TA gives a distinctly more active catalyst based on transition metal, but at the expense of TM productivity,

(17) It is well known that catalysts of this type are thermally sensitive, so control of the initial exotherm is crucial to obtain meaningful results. The autoclaves used for catalysis were Buchi Miniclave (250 mL) vessels, equipped with an integral flow jacket and internal cooling coil; thus significant cooling power could be achieved via the external thermal fluid circulated by a Haake bath and cold tap water feeding the cooling coil.

(18) Further details of this comparison between entries 1 and 4 versus entries 2, 3, and 5 can be found in the Supporting Information, including gas uptake profiles.

(19) In order to provide clarity during discussion, the terms TM activity and TM productivity are used to refer to those calculated on the transition metal, while the terms Al activity and Al productivity are used to refer to those figures based on the amount of trialkylaluminum used (and do not include the Al in the aluminate anion; hence 100 TEA + 1.5 TA, would use 100 equiv for the aluminum usage, not 101.5).

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which is lower than with MMAO; even the aluminum productivity is still lower for **2a**. For the chromium precatalysts, **3a** and **3b**, both show clear improvements in TM activity, but only **3b** shows increased TM productivity, while **3c** showed significant reductions on both counts. Once again though, when calculated on aluminum, **3a–c** were all more active and productive, although only just so in the case of **3c**. The cobalt examples **4a–c** show a clear preference for MMAO, with none showing improved TM activity or productivity, although the aluminum-based figures are preferable for **4b** and **4c**, while **4a** showed poorer performance with TEA/TA even based on aluminum. Interestingly, with **4b** a disproportionate amount of C<sub>4</sub> is formed (Table 2: entry 13,  $K_{C_4/C_6} = 0.06$ ; entry 14,  $K_{C_4/C_6} = 0.03$ ) as compared to the remainder of the carbon fractions, for which a nonconstant, slightly increasing  $K$  value is observed.<sup>20</sup>

Considering all of the precatalysts **1–4(a–e)** tested, it is useful to establish an overall picture. Clearly, the cobalt-based precursors benefit least from a switch of activator away from MMAO and represent outliers in this regard. Meanwhile, those based on iron show the most improvement, while vanadium- and chromium-based initiators lie in between, showing some significant TM activity enhancements, but generally at the expense of TM productivity. From the industrial perspective however the TEA/TA combination would provide the most economical activator package for the majority of the precatalysts, even those including cobalt.

In terms of explaining the general trends observed, it is noted that in the majority of cases significant TM activity enhancements are observed with the fluorinated aluminate anion, but most often at the cost of overall TM productivity. Given the belief that this anion is the least coordinating reported to date,<sup>9</sup> we rationalize a lesser degree of association between the transition metal center of the active catalyst and the anion than when the anion is “MMAO-Me<sup>-</sup>”. Assuming that binding of ethylene is the rate-limiting step and that this is inhibited by the degree of interaction between the transition metal center and “MMAO-Me<sup>-</sup>”, this binding is favored by the more weakly associated fluorinated aluminate anion. However, this weaker association clearly impacts the stability of the active species, which appears to be decreased, leading to lower overall TM productivity in most cases. However, it is clear from the results that there remains a degree of specificity between precatalyst and activator for optimal performance.

## Conclusions

In conclusion, we have shown that the TEA/TA activator combination can successfully replace MMAO in ethylene oligomerization catalyst systems based on a range of transition metals and bis(imino)pyridine ligand variants. In most cases an increase in activity based on the transition metal is achieved, but sometimes at the expense of overall productivity, although crucially for the iron variants an increase in productivity is normally observed. Significantly however, when considered from the perspective of the aluminum usage, the cost driver in these catalyst packages, the economics of a process based on these catalysts could be beneficially affected by a switch of activator package to TEA/TA in nearly all cases.

## Experimental Section

The ligands {2,6-[RN=C(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N (R = 2,6-<sup>i</sup>Pr<sub>2</sub>Ph, 2-Me-Ph) and transition metal halide salts were purchased from Strem, tris(pentafluorophenyl)borane and triethylaluminum from Aldrich,

Table 2. Results of Ethylene Oligomerization Using Vanadium, Chromium, and Cobalt Complexes<sup>a</sup>

entry	cat. (μmol)	cocat. <sup>b</sup> (equiv)	t (min)	based on Al		based on transition metal		g total	K <sup>f</sup>	C <sub>4</sub> (1 - C <sub>4</sub> )	C <sub>6</sub> (1 - C <sub>6</sub> )	C <sub>8</sub> (1 - C <sub>8</sub> )	C <sub>10</sub> (1 - C <sub>10</sub> )	C <sub>12+</sub>
				prod <sup>b</sup>	act <sup>c</sup>	prod <sup>d</sup>	act <sup>e</sup>							
1	<b>2a</b> (10)	TEA/TA (100/1.5)	5	110	1360	11 400	136 400	3.19	0.28	72.9 (98.8)	20.7 (57.5)	4.2 (41.3)	1.3 (37.8)	0.8
2	<b>2a</b> (10)	MMAO (500)	64	200	190	98 900	92 400	27.74	0.17	82.7 (99.5)	14.3 (94.4)	2.5 (87.6)	0.5 (77.3)	0.1
3	<b>2b</b> (10)	TEA/TA (100/1.5)	10	110	680	11 300	67 900	3.17	0.58	41.0 (100)	25.2 (100)	15.4 (100)	7.1 (100)	11.2
4	<b>2b</b> (10)	MMAO (500)	72	80	70	41 500	34 600	11.64	0.47	55.4 (99.5)	26.1 (75.4)	11.7 (99.3)	2.9 (98.6)	4.0
5	<b>3a</b> (10)	TEA/TA (100/1.5)	6	310	3130	31 300	313 100	8.78	0.6	96.3 (95.0)	3.4 (11.9)	0.3 (42.2)	0.1 (100)	0
6	<b>3a</b> (10)	MMAO (500)	42	70	100	33 500	47 800	9.39	0.78	56.0 (83.0)	43.3 (1.0)	0.7 (100)	0	0
7	<b>3b</b> (10)	TEA/TA (100/1.5)	19	2,340	7470	233 500	746 700	65.52	0.1	91.9 (99.7)	7.6 (61.3)	0.5 (50.6)	>0.1 (100)	0
8	<b>3b</b> (10)	MMAO (500)	20	350	1060	175 400	529 300	49.2	0.2	92.8 (99.9)	7.0 (52.8)	0.2 (59.6)	0	0
9	<b>3c</b> (10)	TEA/TA (100/1.5)	3	10	100	500	9600	0.14	0.14	100 (100)	0	0	0	0
10	<b>3c</b> (10)	MMAO (500)	3	4	90	2200	44 000	0.62	0.62	91.8 (95.8)	3.2 (100)	0	0	0
11	<b>4a</b> (5)	TEA/TA (100/1.5)	2.5	1	30	100	3100	0.02	0	100 (86.2)	0	0	0	0
12	<b>4a</b> (10)	MMAO (500)	2	10	210	3500	106 000	0.99	0	99.5 (72.0)	0	0	0	0
13	<b>4b</b> (5)	TEA/TA (100/1.5)	8.0	90	670	8900	66 600	1.25	0.53	87.8 (99.4)	5.2 (100)	2.1 (100)	1.3 (100)	3.6
14	<b>4b</b> (10)	MMAO (500)	2	20	620	10 300	308 200	2.88	0.65	96.1 (97.9)	3.3 (79.1)	0.3 (100)	0.1 (100)	0.1
15	<b>4c</b> (10)	TEA/TA (100/1.5)	13	120	570	12 200	56 500	3.43	0.7	100 (100)	0	0	0	0
16	<b>4c</b> (10)	MMAO (500)	10	70	410	34 500	207 000	9.68	0	100 (100)	0	0	0	0

<sup>a</sup> General conditions: Toluene (100 mL), *p*(ethylene) = 8 bar,  $T = 30\text{ }^{\circ}\text{C}$ . <sup>b</sup> MMAO = MMAO-3A; TEA/TA = Et<sub>3</sub>Al/Ph<sub>3</sub>C][C<sub>6</sub>F<sub>5</sub>]<sub>4</sub>]; TEA/TB = Et<sub>3</sub>Al/Ph<sub>3</sub>C][Al(O<sup>*t*</sup>Bu)<sup>F</sup>]<sub>4</sub>]. <sup>c</sup> (mol ethene) (mol Al)<sup>-1</sup>. <sup>d</sup> (mol ethene) (mol Al)<sup>-1</sup> h<sup>-1</sup>. <sup>e</sup> (mol ethene) (mol TM)<sup>-1</sup>. <sup>f</sup> Averaged  $K$  value over the carbon ranges C<sub>6</sub>–C<sub>18</sub>; if fractions up to C<sub>18</sub> were not present, no  $K$  value is quoted.

trityl tetrakis(pentafluorophenyl)borate from Albemarle, and MMAO-3A<sup>21</sup> and TEA from Akzo Nobel; all materials were used as received. The ligands {2,6-[PhN=C(CH<sub>3</sub>)<sub>2</sub>]C<sub>5</sub>H<sub>3</sub>N<sup>15,22</sup> and 4,5-bis(arylimino)-1,2,3,4,5,6,7,8-octahydroacridine (aryl = Ph, *o*-Tol),<sup>16</sup> trityl tetrakis(perfluorophenyl)aluminate,<sup>23</sup> and the metal complexes **1a-e**,<sup>16,24</sup> **2a-c**,<sup>25</sup> **3a-c**,<sup>26</sup> and **4a-c**<sup>22a,26</sup> were all prepared by literature procedures or slight modifications thereof. Solvents were procured from Aldrich, purified using an Innovative Technologies solvent purification system, and deoxygenated prior to use. All operations were conducted under inert atmosphere using an argon-filled glovebox and standard Schlenk techniques. Elemental analyses were performed by the Science Technical Support Unit of London Metropolitan University.

Catalysis was performed in 250 mL volume Buchi Miniclaves equipped with stainless steel vessels with integral thermal-fluid jackets. Ethylene (grade 4.5) was supplied by Linde and passed through oxygen- and moisture-scrubbing columns prior to use; ethylene flow was measured using a Siemens Sitrans F C Massflo system (Mass 6000–Mass 2100), and the data were logged. GC analysis was performed using an Agilent Technologies 6850 Network GC system equipped with a PONA column (50 m × 0.20 mm × 0.50 μm) using hydrogen as carrier gas. All catalytic tests were allowed to run until ethylene uptake had ceased, either due to catalyst deactivation or because the autoclave had filled.

**Typical Catalytic Run with MMAO.** A 250 mL stainless steel reactor equipped with mechanical stirring, cooling loop, and external heating/cooling jacket was heated to 80 °C under Ar purge for 10 min. After cooling to room temperature, the reactor was charged

with the solid precatalyst and replaced under an Ar atmosphere. Toluene (50 or 100 mL) was added to the reactor, the vessel was vigorously stirred, and the temperature was maintained at 20 °C. MMAO-3A was then added to the reactor, the vessel immediately charged with 8 bar of ethylene, and the pressure kept constant throughout the reaction by the continuous addition of ethylene, which was monitored via a flow-meter. Once ethylene uptake had ceased, the gas supply was closed and the reactor cooled in an ice/water bath. Excess ethylene was bled and the reactor contents were treated sequentially with 1000 μL of nonane (GC internal standard), MeOH, and 10% HCl. A sample of the organic phase was taken for GC-FID analysis. Any solid formed was collected, washed repeatedly with 10% HCl and EtOH, dried overnight, and weighed.

**Typical Catalytic Run with TEA and TA, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, or TB Cocatalyst.** A 250 mL stainless steel reactor equipped with mechanical stirring, cooling loop, and external heating/cooling jacket was heated to 80 °C under Ar purge for 10 min. After cooling to room temperature, the reactor was charged with the solid precatalyst and replaced under an Ar atmosphere. A solution of TA, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, or TB was added to the reactor as a solution in toluene (50 or 100 mL) and the reactor maintained at 20 °C. AlEt<sub>3</sub> was then added to the reactor, the vessel immediately charged with 8 bar of ethylene, and the pressure kept constant throughout the reaction by the continuous addition of ethylene, which was monitored via a flow-meter. Once ethylene uptake had ceased, the gas supply was closed and the reactor cooled in an ice/water bath. Excess ethylene was bled and the reactor contents were treated sequentially with 1000 μL of nonane (GC internal standard), MeOH, and 10% HCl. A sample of the organic phase was taken for GC-FID analysis. Any solid formed was collected, washed repeatedly with 10% HCl and EtOH, dried overnight, and weighed.

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**Supporting Information Available:** Analytical data (CHN) for all ligands and complexes prepared. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(21) MMAO-3A is a modified alumoxane cocatalyst sourced from Akzo Nobel with the general formula [–Al(R)–O–]<sub>n</sub>, where R = Me (75%), <sup>i</sup>Bu (25%).

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