Selective Dimerization/Oligomerization of α-Olefins by Cobalt Bis(imino)pyridine Catalysts Stabilized by Trifluoromethyl Substituents: Group 9 Metal Catalysts with Productivities Matching Those of Iron Systems

Kilian P. Tellmann, Vernon C. Gibson,* Andrew J. P. White, and
David J. Williams

Department of Chemistry, Imperial College London, Exhibition Road, London SW7 2AZ, U.K.

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A series of bis(imino)pyridine ligands containing aryl substituents with *o*-trifluoromethyl units, along with their cobalt and iron complexes, has been prepared and characterized. The crystal structures of several complexes are reported. Both the cobalt and iron complexes, when activated by methylaluminoxane cocatalysts, afford much higher olefin oligomerization/polymerization activities than their nonfluorinated relatives. Enhanced performance is seen not only in higher peak activities but also in longer catalyst lifetimes, suggesting that the trifluoromethyl group significantly improves catalyst stability. The most impressive activity increase is observed for a cobalt catalyst combining an *o*-CF_3 and an *o*-F unit. This system is more active than its iron counterpart in ethylene polymerization, reaching >100 000 g $mmol^{-1}$ h^{-1} bar^{-1}. Propene, 1-butene, and 1-hexene are oligomerized by this catalyst at rates much higher than for nonfluorinated relatives. Highly linear dimers predominate in each case, the remainder being trimeric and tetrameric products. The principal product of propene dimerization is 1-hexene (60−73% of total), whereas for 1-butene and 1-hexene internal olefins are obtained (*E* isomers predominate). No isomerization of 1-hexene is seen under the reaction conditions. The catalysts operate by a mechanism involving (1,2)- followed by (2,1)-insertion steps. Combinations of chain growth and step growth account for the formation of linear trimers and tetramers of propene.

Introduction

The discovery of highly active iron- and cobalt-based olefin polymerization catalysts in the late 1990s has led to much interest in the chemistry of transition-metal complexes bearing terdentate bis(imino)pyridine ligands.[1−4] Many studies have reported the effects of ligand substitution patterns on activity and selectivity.[5] However, in all cases it has generally been found that the iron-based catalysts are typically at least an order of magnitude more active than their cobalt relatives. The difference in activity is even more pronounced for oligomerization systems, which bear sterically less demanding substituents on the bis(imino)pyridine ligands. Here, we show not only that judicious fluorination of the imino aryl substituents results in unprecedented activities for cobalt catalysts, activities that in some cases surpass those observed for the most active iron catalysts, but also that these catalysts dimerize propene, 1-butene, and 1-hexene with remarkably high selectivities. These findings represent significant improvements in terms of activity and selectivity over previous reports for nonfluorinated as well as other fluorinated cobalt bis(imino)pyridine complexes.[6−8] Indeed, some examples of the latter have been reported as being inactive for ethylene polymerization.[8]

Complex Synthesis and Characterization

The series of bis(imino)pyridine ligands **1a**−**c** containing an *o*-trifluoromethyl substituent were prepared by simple Schiff-base condensation procedures (Scheme 1).[9] **1a**−**c** are readily complexed to cobaltous and ferrous bromides to afford complexes **2a**−**c** and **4a**−**c** in high purity;[10,11] the known compounds **3** and **5** were prepared in an analogous fashion as benchmarks for the catalytic studies.[2]

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* To whom correspondence should be addressed. E-mail: v.gibson@imperial.ac.uk.

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[7] Small, B. L. *Organometallics* **2003**, *22*, 3178.

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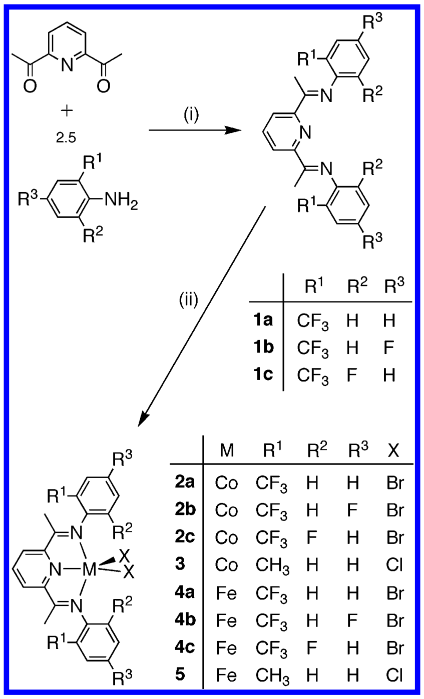
[9] Ligand **1c** was independently prepared and recently published by Esteruelas et al.[4]

10.1021/om049297q CCC: $30.25

Scheme 1[a]



	R^1	R^2	R^3
1a	CF_3	H	H
1b	CF_3	H	F
1c	CF_3	F	H

	M	R^1	R^2	R^3	X
2a	Co	CF_3	H	H	Br
2b	Co	CF_3	H	F	Br
2c	Co	CF_3	F	H	Br
3	Co	CH_3	H	H	Cl
4a	Fe	CF_3	H	H	Br
4b	Fe	CF_3	H	F	Br
4c	Fe	CF_3	F	H	Br
5	Fe	CH_3	H	H	Cl

[a] Reagents and conditions: (i) Dean–Stark, benzene, cat. H_2SO_4; (ii) $CoCl_2$, $CoBr_2{\cdot}6H_2O$, $FeCl_2$ or $FeBr_2$ in THF.

The magnetic moments of the resulting paramagnetic complexes were determined using an Evans balance to be 3.9–4.2 μ_B for cobalt complexes **2a**–**c** and 4.8–5.2 μ_B for iron complexes **4a**–**c**. These values are in good agreement with the spin-only values expected for high-spin d^7 (Co^{2+}) and d^6 (Fe^{2+}) centers. Crystals of **2a**–**c** and **4a**,**b** suitable for X-ray analysis were obtained by recrystallization from saturated dichloromethane or acetone solutions layered with hydrocarbon solvent. In the case of **2c**, crystals solvated with both dichloromethane (**2c**$\cdot 0.5CH_2Cl_2$) and acetone (**2c**$\cdot 0.5Me_2CO$) were obtained. The structures of the corresponding cobalt and iron complexes (**2a** and **4a**, **2b** and **4b**) are isomorphous, and the two solvates of **2c** have unit cells very similar to each other. The molecular structures of **2c**$\cdot 0.5CH_2Cl_2$ and **4b** are shown in Figure 1, whereas those of **2a**,**b**, **2c**$\cdot 0.5Me_2CO$, and **4a** are provided in the Supporting Information.

The complexes **2a**–**c** and **4a**,**b** all have very similar structures with distorted-square-based-pyramidal geometries at the metal centers and approximate C_s symmetry overall. It is notable that the aryl ring substituents within each complex adopt a mutually syn orientation with the CF_3 groups pointing away from the apical ligand. This arrangement is also seen in other bis(imino)pyridine complexes with mono-ortho-substituted N-aryl rings.[1b,2b,12,13] Furthermore, as is typical in complexes of this kind, the aryl rings are oriented approximately orthogonal with respect to the ligand backbone to minimize intra- and interligand repulsions.

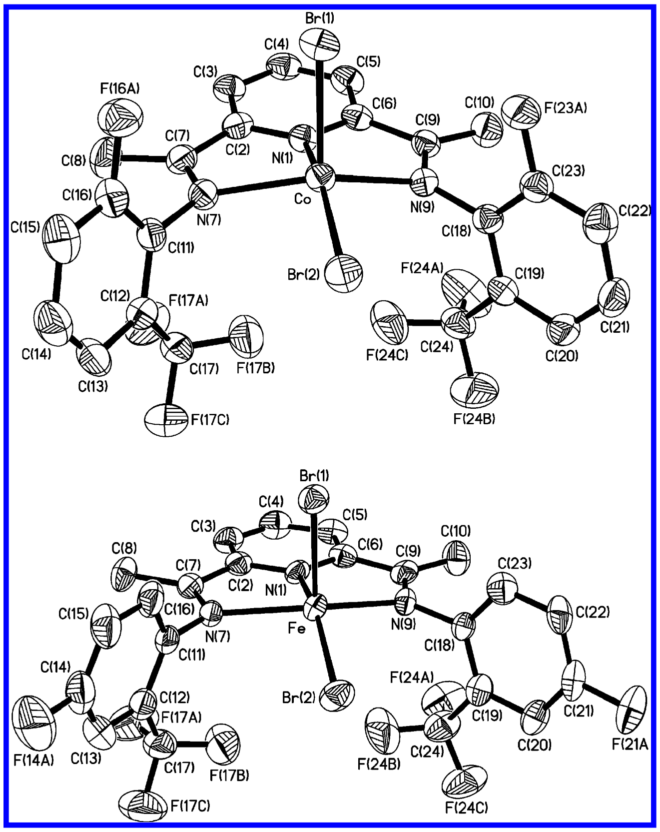


Figure 1. Thermal ellipsoid plots of **2c** (top, 30% probability ellipsoids) and **4b** (bottom, 50% probability ellipsoids). Hydrogen atoms and cocrystallized solvent molecules are omitted for clarity.

For the two complexes shown in Figure 1, the coordinating atoms of the basal plane (the nitrogen atoms and the basal bromine) are coplanar to within 0.10 Å (**2c**) and 0.04 Å (**4b**), with the metal centers residing 0.49 Å (**2c**, M = Co) and 0.44 Å (**4b**, M = Fe) above this plane. As expected, the M–N(py) distances (2.052(4)–2.122(5) Å) are noticeably shorter than those to the imino nitrogen atoms (2.142(5)–2.212(4) Å), and with the Fe–N bonds being generally longer than their Co–N counterparts. The double-bond character of the imino linkages has been retained in each case (C=N in the range 1.255(9)–1.293(8) Å), and the py–imino bonds C2–C7 and C6–C9 (between 1.469(10) and 1.498(9) Å) show no evidence of delocalization between these π systems. Further structural data for these and the other structures are included in the Supporting Information.

Polymerization and Oligomerization of Ethylene

Upon activation by a methylaluminoxane cocatalyst (MAO or coMAO[14]), all of the fluorinated precatalysts gave highly active ethylene polymerization catalysts (Table 1), with activities typically in the range 6000–17 000 g $mmol^{-1}$ h^{-1} bar^{-1} over 60 min runs. For the fluorinated cobalt catalysts **2a**–**c** (8000–15 000 g $mmol^{-1}$ h^{-1} bar^{-1}) this represents a marked contrast to the benchmark system **3**, which typically shows activites of 13–26 g $mmol^{-1}$ h^{-1} bar^{-1} (cf. entry 1, Table 1 and ref 3b) if activated in the absence of ethylene and up to about 100 g $mmol^{-1}$ h^{-1} bar^{-1} if activated in the

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[10] The complexes were at times already of analytical purity at this point. Satisfactory elemental analyses have been obtained for all complexes by recrystallization from dichloromethane/hexane.

[11] Complex **2c** has recently been claimed, but no characterization data were reported. Pelascini, F.; Peruch, F.; Lutz, P.; Wesolek, M.; Kress, J. *Macromol. Rapid. Commun.* **2003**, *24*, 768.

[12] Drew, M. G. B.; Hollis, S. *Acta Crystallogr.* **1978**, *B34*, 2853.

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[14] MAO is made by partial, extremely careful hydrolysis of $AlMe_3$. For coMAO, a 90:10 mixture of $AlMe_3$ and Al^iBu_3 is hydrolyzed.

Table 1. Ethylene Polymerization Results[a]

					product yield[b]				
run no.	precat. (amt (μmol))	cocat. (Al:M)	C_2H_4 press (bar)	run time (min)	total mass (g)	solid share (%)	α^c/M_n^d	chain end ratio[e]	activity[f] (g $mmol^{-1}$ h^{-1} bar^{-1})
1[g]	**3** (20.0)	MAO (400)	4.0	60	1.05	0	0.66/–	1.0:1	13
2	**3** (20.0)	MAO (400)	4.0	60	8.62	0	0.57/–	1.0:1	108
3	**3** (20.0)	coMAO (400)	4.0	60	7.94	0	0.55/–	1.0:1	99
4	**2a** (0.50)	MAO (2000)	1.0	60	4.18	13	0.73/1600	1.0:1	8 360
5	**2a** (0.50)	coMAO (2000)	1.0	60	4.48	12	0.73/1900	1.0:1	8 960
6	**2b** (0.50)	MAO (2000)	1.0	60	5.24	7	0.74/1200	1.0:1	10 500
7	**2b** (0.50)	coMAO (2000)	1.0	60	4.42	7	0.74/940	1.0:1	8 840
8	**2c** (0.50)	MAO (2000)	1.0	60	6.22	95	–/2600	1.0:1	12 400
9	**2c** (0.50)	coMAO (2000)	1.0	60	7.66	95	–/2400	1.0:1	15 300
10	**2c** (0.50)	coMAO (2000)	1.0	10	4.50	95	–/2200	1.0:1	54 000
11	**2c** (0.50)	coMAO (2000)	1.0	2	2.15	96	–/2400	1.0:1	129 000
12	**5** (10.0)	MAO (100)	1.0	60	22.72	64	0.77/520	3.1:1	2 270
13	**5** (10.0)	coMAO (100)	1.0	60	27.38	15	0.70/470	2.1:1	2 740
14	**4a** (0.50)	MAO (2000)	1.0	60	3.16	94	–/2700	2.3:1	6 320
15	**4a** (0.50)	coMAO (2000)	1.0	60	7.70	97	–/2800	1.8:1	15 400
16	**4b** (0.50)	MAO (2000)	1.0	60	5.98	96	–/2700	1.7:1	12 000
17	**4b** (0.50)	coMAO (2000)	1.0	60	8.66	96	–/2100	1.9:1	17 300
18	**4c** (0.50)	MAO (2000)	1.0	60	3.43	>99	–/4300	5.1:1	6 860
19	**4c** (0.50)	coMAO (2000)	1.0	60	3.61	>99	–/3900	8.3:1	7 220

[a] General conditions: a 0.5 L glass autoclave filled with a suspension of precatalyst in toluene (200 cm^3) at ambient temperature is saturated with ethylene and subsequently activated with either MAO or coMAO. [b] Oligomers were characterized and quantified by GC, using 2,2,4,4,6,8,8-heptamethylnonane as internal standard; the solid share is expressed in mass percent. [c] α value calculated from the molar ratio of C_{16} to C_{14}. [d] Determined by ^1H NMR for solid product in d_{10}-*p*-xylene at 110 °C. [e] Ratio of saturated (methyl) to unsaturated (vinyl) chain ends. [f] Quoted per hour for all entries, including shorter runs (#10 and #11), and rounded to three significant figures for larger numbers. [g] Precatalyst activated with MAO in toluene *prior* to ethylene exposure under an inert atmosphere.

presence of ethylene (entry 2). This latter, improved method of activation was employed in subsequent runs for all precatalysts[15] (the effect of in situ activation is negligible for the iron-based catalysts). It is therefore clear that introduction of an *o*-trifluoromethyl group boosts the activities of cobalt catalysts by 2 orders of magnitude, whereas the activities of iron catalysts are increased by up to a factor of 6.

In the cobalt series, catalyst activity increases in the series **2a** < **2b** < **2c**, with values of 9600, 10 500, and 15 300 g $mmol^{-1}$ h^{-1} bar^{-1}, respectively. The overall trend in activity implies that the addition of extra fluorine atoms to the ligand framework further enhances monomer turnover rates in addition to the already beneficial impact of the trifluoromethyl group. In this respect, an *o*-F appears to have a more potent influence than a *p*-F group, although this effect may be more than purely electronic in nature. In terms of the cocatalyst, which also serves as a poison scavenger, there are no major differences between MAO and coMAO: the latter is somewhat better than the former for precatalysts **2a**,**c** (entry 5 vs 4, 9 vs 8), whereas the opposite appears to be the case for precatalyst **2b** (entry 6 vs 7).

For the iron catalysts, the productivity order is **4c** < **4a** < **4b**, with activities of 7220, 15 400, and 17 300 g $mmol^{-1}$ h^{-1} bar^{-1}, respectively. For this metal, the effects of ligand and cocatalyst are quite different from those of the cobalt catalysts. Placement of a fluorine atom in the second ortho position of the phenyl ring actually reduces catalyst activity, whereas a *p*-F increases it. Also, precatalysts activated with coMAO achieve higher turnover numbers than those activated with MAO, an effect that appears more pronounced for the more open systems **4a**,**b**.

Significantly higher activity figures may be obtained for shorter runs, given the greater catalyst activity in the early stages of the run (see below), and particularly if the activity figures are extrapolated to 60 min. Relative to a 60 min ethylene polymerization run with catalyst **2c**/coMAO (entry 9), activity figures are boosted to 54 000 and 129 000 g $mmol^{-1}$ h^{-1} bar^{-1} (entries 10 and 11) when reducing the run time to 10 and 2 min. The latter figure corresponds to an activity of 2.2×10^6 g (g of Co)$^{-1}$ h^{-1}, the equivalent of a turnover frequency in excess of 76 000 min^{-1} at 1.0 bar of ethylene pressure. To the best of our knowledge, this currently represents the most active group 9 olefin polymerization catalyst. Indeed, ligand system **c** is the first example where a cobalt bis(imino)pyridine catalyst is more active for C–C bond formation than its iron counterpart.

Examination of the kinetic profiles (see Supporting Information) for ethylene oligomerization/polymerization catalysts derived from **2b**, **3** and **4b**, **5** clearly illustrate how the fluorinated catalysts **2b**/MAO and **4b**/MAO outperform their respective benchmarks **3** and **5** in terms of both stability and peak activity. The lifetimes of the fluorinated derivatives exceed those of the benchmark systems by a factor of approximately 4, whereas, in terms of peak activity, **2b**/MAO and **4b**/MAO may be estimated to consume about 50% more ethylene than either **3**/MAO or **5**/MAO. The kinetic profiles also shed light on the higher activity of the *o*-CF_3-containing catalysts at shorter reaction times, as described for **2c** above, since ethylene uptake peaks around 5 min into the run, with catalyst death ensuing after about 30 min under the conditions employed. In view of the fact that catalyst activity diminishes over time and that M_n does not vary over time (entries 9–11),

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[15] Activation of the cobalt complex bearing 2,6-difluorophenyl groups attached to the imine moiety ($R^1 = R^2 = F$, $R^3 = H$ in Scheme 1)—independently prepared and recently reported by Qian and coworkers[8]—according to this protocol showed it to be active for ethylene oligomerization. After treatment with MAO, its activity was determined as 4 g $mmol^{-1}$ h^{-1} bar^{-1} in a 60 min run at 1.0 bar of ethylene pressure ($\alpha = 0.71$).

it is clear that **2c**/coMAO does not represent a highly controlled system for ethylene polymerization, unlike the effect of fluorinated ligands on some early-transition-metal systems reported recently.[16,17]

As has been shown for other ethylene oligo- and polymerization catalysts, the steric influence exerted by the groups placed in the ortho positions of the N-aryl groups has, among other contributing factors, a profound influence on the rate of chain termination relative to chain propagation and, hence, molecular weight of the generated poly(ethylene)s. This is also the case for the complexes reported here. For cobalt complexes **2a**–**c** relative to **3**, replacement of the *o*-CH_3 group with an *o*-CF_3 group leads to products with increased molecular weights. For precatalysts **2a** and **2b**, oligomers following a Schulz–Flory distribution of higher α-value than benchmark **3** represent the main product in combination with some solid PE of low molecular weight. In accordance with expectations, the introduction of an additional ortho substituent in precatalyst **2c** further raises the product molecular weight, the principal product now being solid poly(ethylene) with an M_n value of 2400 Da. The polymers produced from all these catalysts are linear PEs containing both saturated and unsaturated end groups in a 1:1 ratio and, therefore, simply represent α-olefins of elevated molecular weight. The equimolar amounts of methyl and vinyl end groups in the polymer are consistent with chain termination arising by β-H transfer exclusively.

Similarly, for the iron complexes **4a**–**c**, introduction of the trifluoromethyl substituent increases product moleceular weights to the extent that the vast majority of the product is a solid—as opposed to the liquid oligomers made by **5**—and consist of linear poly(ethylene)s with M_n values ranging from 2100 to 4300 Da. The greater quantity of saturated chain ends to unsaturated chain ends is readily accounted for by chain transfer to aluminum as a second termination chain mechanism (in addition to β-H transfer). This catalyst behavior is also observed in nonfluorinated systems, where it has been studied in some detail.[1c]

Oligomerization of Propene, 1-Butene, and 1-Hexene

In an initial screen, precatalysts **2a**,**c** (Co), as well as precatalysts **4a**,**c** (Fe), were tested for their activity in propene oligomerization at 0 °C and 1.0 bar, following activation with MAO (Al:M = 1000). After 30 min, the runs were terminated by addition of aqueous hydrochloric acid and worked up. Surprisingly, no product was formed from either of the iron catalysts. This result stands in contrast to the observed capability of nonfluorinated iron catalysts to either polymerize or oligomerize propene, when more or approximately equally bulky, but electron-releasing, aryl substituents are employed.[18] The cobalt derivatives **2a**,**c**, however, formed oligomers. The superior activity of the catalyst derived from **2c**/MAO led us to investigate this system in more detail.

Table 2. Oligomerization of α-Olefins by Precatalyst 2c[a]

run no.	α-olefin feed	θ (°C)	product mass (g)[b]	dimer share (%)[c]	activity	
					g mmol^{-1} h^{-1}	g (g of Co)$^{-1}$ h^{-1}
20[d]	C_3H_6 (1.0 bar)	−20	0.077	88	15	261
21	C_3H_6 (1.0 bar)	0	0.369	81	148	2 510
22	C_3H_6 (1.0 bar)	−20	2.796	72	1140	19 300
23	C_4H_8 (10 g)	0	0.131	92	52	887
24	C_4H_8 (10 g)	−20	0.371	90	148	2 510
25	C_6H_{12} (10 g)	0	0.160	92	64	1 090
26	C_6H_{12} (10 g)	−20	0.544	90	217	3 690
27	C_6H_{12} (neat)	0	0.894	86	358	6 070
28	C_6H_{12} (neat)	−20	1.225	83	490	8 310

[a] General conditions: a Schlenk tube containing a suspension of precatalyst **2c** (0.0050 mmol) in either 100 cm^3 of toluene (runs 1–7) or 50.0 cm^3 of 1-hexene (runs 8 and 9) was cooled to the desired temperature, exposed to the monomer (runs 1–7), and subsequently activated with MAO (Al:Co = 1000:1). Runs were terminated after 30 min by addition of an excess of 1 M HCl (aq). [b] Products quantified by GC, using 2,2,4,4,6,8,8-heptamethylnonane as internal standard. [c] Dimer share of total product mass. [d] Performance of precatalyst **3** at 0.020 mmol loading under otherwise identical conditions.

The results of propene, 1-butene, and 1-hexene oligomerization runs are collected in Table 2. These substrates are oligomerized by **2c**/MAO with high activities: up to 19 000, 2510, and 8310 g (g of Co)$^{-1}$ h^{-1}, respectively,[19] over 30 min runs at −20 °C, despite the reduced temperatures employed to dissolve/condense adequate amounts of the gaseous monomers. The performance of **2c** relative to **3** under identical conditions mirrors earlier observations, in that the fluorinated catalyst is about 2 orders of magnitude more active than its nonfluorinated analogue. Regardless of α-olefin feedstock, linear dimers are the principal products in every case (72–92%), whereas the trimers are always branched in the case of products derived from 1-butene and 1-hexene, and partly so for products derived from propene.

For propene, the outstanding activity increases relative to the benchmark system **3**/MAO (entries 20 vs 22) are accompanied by significantly higher product selectivities, with 91% of the C6 fraction being 1-hexene for **2c**/MAO (benchmark **3**, 65%). At 0 °C, the 1-hexene selectivity within the C6 fraction is slightly lower (87%) for the fluorinated catalyst, but given the lower concentration of tri- and tetramers, a larger proportion of the overall product fraction is 1-hexene (72%) relative to the run at −20 °C (66%) as detailed in Table 3. The only other products within the C6 fraction are 2-hexenes, where the *E* isomer prevails over the *Z* isomer by about 2:1 (Figure 2, Table 3). None of the thermodynamically most stable dimer (3-hexene) is observed by either GC or NMR, consistent with 1- and 2-hexenes arising by a (1,2)- followed by a (2,1)-propene insertion. The absence of 3-hexene confirms that 1-hexene is not isomerized by the catalyst. Indeed, examination of the residual feedstock from 1-hexene oligomerization runs 25 and 26 revealed it to be 99.6–99.7% 1-hexene, with ≤0.4% representing the thermodynamically more stable *E*

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[17] Reinartz, S.; Mason, A. F.; Lobkovsky, E. B.; Coates, G. W. *Organometallics* **2003**, *22*, 2542.

[18] Small, B. L.; Brookhart, M. *Macromolecules* **1999**, *32*, 2120.

[19] The activities for α-olefin dimerization/oligomerization are expressed in g (g of Co)$^{-1}$ h^{-1} to aid comparison with other systems in the literature, where this is a commonly encountered unit. For ease of reference with the ethylene polymerization data, catalyst activities are also quoted in units of g mmol^{-1} h^{-1} bar^{-1} in Table 2.

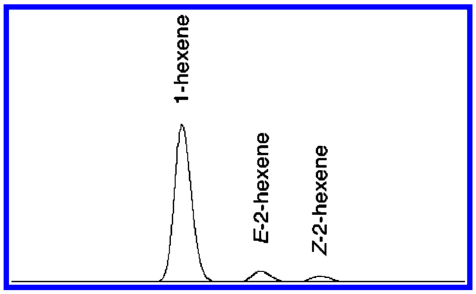

Figure 2. GC trace of propylene dimers made by the MAO-activated cobalt complex **2c** (91% 1-hexene, run #22, Table 3).

isomers of 2- and 3-hexene. This implies that the oligomerization products, as well as the monomer feedstock, are not prone to isomerization by the fluorinated cobalt catalyst. This aspect of the system is particularly noteworthy, since many dimerization catalysts also isomerize substantial amounts of the kinetic product to the thermodynamic product. This frequently represents an undesired side reaction, given the higher economic and environmental value of terminal (and/or linear) olefins with respect to internal (and/or branched) olefins as precursors to important chemical derivatives.[20]

Higher propene oligomers ($n > 2$) are only observed up to $n = 3$ for the benchmark system (run 20, Table 3), whereas with the catalyst **2c**/MAO, tetramers are always detected, albeit in small quantities. Both the C9 and C12 fractions consist entirely of internal olefins. In the case of **2c**/MAO, both fractions contain some linear products, which become increasingly significant at lower reaction temperatures and constitute the majority (56%) of the trimer fraction at −20 °C (run 22, Table 3). The benchmark system, in contrast, produces a far smaller proportion (8 mol %) of trimeric product under these conditions, 94% of which are branched (run 20, Table 3). By variation of the standard run time from 10 to 60 min (runs 22 and 29−31), we were able to establish that the higher propene oligomers ($n > 2$) are formed in larger proportion in the later stages of a run and that the linearity of the higher oligomers (cf. C9 and C12 fractions) increases with longer run times. This issue, as well as the occurrence of linear trimers and tetramers of propene, will be revisited in the mechanistic discussion.

For 1-butene, analysis of the products by GC and NMR indicated the dimers to be highly linear olefins, consisting of almost equimolar amounts of 2- and 3-octenes, in a 47:53 ratio for the experiment carried out at 0 °C and a 46:54 ratio for the experiment performed at −20 °C. In each case, the *E* isomer predominates, as determined quantitatively by GC for the 2-octenes (supported by $^{13}C\{^1H\}$ NMR), or qualitatively for the 3-octenes (by $^{13}C\{^1H\}$ NMR). Relative to the results obtained for propene oligomerization, the catalyst activities are lower and trimers are also less easily formed. Both of these factors may be rationalized in terms of the additional steric requirements for insertion of a butene molecule relative to propene. Furthermore, catalyst regioselectivity is also diminished.

The catalyst generated from **2c**/MAO oligomerizes 1-hexene with activities ranging from 1090 g (g of Co)$^{-1}$ h^{-1} at 0 °C and relatively modest monomer concentration to 8310 g (g of Co)$^{-1}$ h^{-1} at −20 °C. The product analysis by GC and NMR revealed the dimers to be almost exclusively linear (98%-99%), internal olefins. The 1-hexene trimers, however, are branched without exception, as in the case of 1-butene. All linear 1-hexene dimers are internal olefins with the double bond not located in any of the 1-, 2-, and 6-positions of the chain, as determined by NMR, leaving the isomers of 3-, 4-, and 5-dodecene as possible reaction products. From a mechanistic perspective (see Discussion) the 3-alkene may be ruled out, to leave 4- and 5-dodecene as the predicted 1-hexene dimers to be formed by action of the catalyst **2c**/MAO. In terms of double-bond geometries, a significant bias exists toward *E* isomers ($E/Z > 3$), based on the relative peak heights in the $^{13}C\{^1H\}$ NMR.

Discussion

The presence of an *o*-trifluoromethyl group in the aryl substituents of cobalt and iron bis(imino)pyridine catalysts clearly gives rise to greater olefin oligomerization/polymerization activities than for their nonfluorinated relatives. Enhanced performance is seen not only in higher peak activities, presumably a consequence of the enhanced electrophilicity of the metal centers in the fluorinated derivatives, but also in longer catalyst lifetimes, suggesting that the trifluoromethyl group significantly improves catalyst stability. The most impressive activity increases are observed for the cobalt catalyst **2c**, which contains one *o*-CF_3 and an *o*-F unit. This system is even more active than its iron counterpart in ethylene polymerization, reaching >100 000 g mmol^{-1} h^{-1} bar^{-1}.

Propene, 1-butene, and 1-hexene are oligomerized by **2c**/MAO with activities much higher than for their nonfluorinated relatives. Highly linear dimers are mostly obtained in each case, the remainder being trimeric and tetrameric products. The principal product of propene dimerization is 1-hexene (60−73% of total), whereas for 1-butene and 1-hexene internal olefins are obtained (*E* isomers predominate). Furthermore, the cobalt catalyst **2c**/MAO effectively does not isomerize 1-hexene under the reaction conditions. These findings compare favorably, in terms of monomer isomerization, with a recent report[7] by Small on cobalt bis(imino)pyridine catalysts stabilized by electron-rich ligands. In addition, the benchmark system **3**/MAO is outperformed in terms of turnover rates and dimer selectivity. Under the conditions employed by Small,[7] however, the linearity of the propene tri- and tetramers generated by **3**/MAO is much greater (>94%) than is found by us (C9 fraction: 6.3%) in toluene at −20 °C (Table 3). The higher oligomers ($n > 2$) also account for a larger share of the total product weight than observed by us, presumably due to much higher monomer concentrations (liquid monomer versus gaseous/partially dissolved monomer).

Mechanism of α-Olefin Oligomerization

The mechanism governing the formation of the oligomeric products must satisfy the following observations: (a) all α-olefin dimers are linear; (b) 3-hexenes are not observed in the propene dimer fraction; (c)

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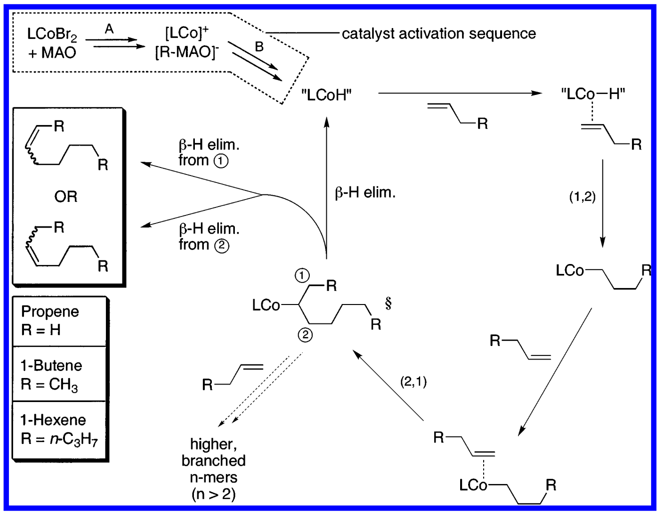
[20] Cornils, B., Herrmann, W. A., Eds. *Applied Homogeneous Catalysis with Organometallic Compounds*; Wiley-VCH: Weinheim, Germany, 2002.

Table 3. Analysis of Propene Oligomers Formed by Precatalyst 2c: Effect of Temperature and Run Time[a]

				product distribn (C_6 fraction)[b]			molar ratio[c]			
run no.	θ (°C)	run time (min)	activity (g (g of Co)$^{-1}$ h^{-1}	1-hexene (%)	(*E*)-2-hexene (%)	(*Z*)-2-hexene (%)	C6/C9	C9/C12	C9 linearity (%)	C12 linearity (%)
20[d]	−20	30	261	65	22	13	11.2:1	n/a	6.3	n/a
21	0	30	2 510	87	9	4	7.34:1	10.7:1	33	12
29	−20	10	27 200	91	6	3	6.73:1	12.3:1	35	12
30	−20	20	27 300	90	6	3	5.57:1	9.42:1	45	19
22	−20	30	19 300	91	6	3	4.63:1	7.38:1	56	28
31	−20	60	10 900	90	6	3	3.98:1	6.33:1	63	34

[a] Products analyzed by GC (checked against references where possible) and NMR. [b] Percentages expressed relative to total weight of C_6 fraction; sum may be less than unity because of rounding errors. [c] Molar ratios of fraction totals. [d] Performance of precatalyst **3** at 0.020 mmol loading under otherwise identical conditions.

Scheme 2. Proposed Mechanism for the Dimerization of α-Olefins



1-butene and 1-hexene dimers formed by **2c**/MAO are invariably internal olefins; (d) a mixture of branched and linear *n*-mers ($n > 2$) is observed during propene oligomerization; (e) no 1- or 2-nonenes occur among the propene trimers; (f) linearity in the higher propene *n*-mers ($n > 2$) increases with time; (g) the *n*-mers ($n > 2$) of 1-butene and 1-hexene are always branched; (h) product distributions do not follow a standard mathematical distribution (e.g. Schulz−Flory, Poisson); (i) the degree of product isomerization is very low (cf. propene dimers; 1-hexene feedstock).

Since no branched dimeric products are observed, dimer formation must occur first by a (1,2)-insertion, followed by (2,1)-insertion. Furthermore, the absence of a distribution of oligomers indicates that product formation for higher oligomers ($n > 2$) does not necessarily occur via consecutive insertions alone. This conclusion is supported by the fact that the molar quantities of higher oligomers diminish more quickly than in a geometric series, as illustrated for the C6/C9 and C9/C12 mole ratios of the propene oligomers. From these two observations it is plausible to conclude that, following insertion of a second monomer unit in a (2,1)-fashion, an α-branched cobalt alkyl is formed which preferentially undergoes β-H elimination, as opposed to further insertion of another α-olefin.

Consideration of these points leads us to propose the mechanism for α-olefin dimerization shown in Scheme 2. Following initial treatment of the cobalt(II) dihalide precursor with MAO, an active catalyst is obtained according to a pathway recently outlined.[21,22] This catalyst then passes through one product-generating cycle and terminates the chain by β-H elimination, to give a cobalt hydride-like species, formulated here as "LCoH". However, it should be noted that this cobalt hydride complex "LCoH" must differ from the reported neutral, diamagnetic Co(I) hydride complex,[23] because of the inability of the latter to form C−C bonds. Whether this is due to the charge, the spin state, the oxidation state, or the participation of a secondary agent, or even a combination thereof, is uncertain.

The putative cobalt hydride species "LCoH" then undergoes two consecutive insertions, followed preferentially by chain termination via β-H elimination. The (1,2)−(2,1) order of monomer additions adequately accounts for the observation of the linear olefin dimers 1- and 2-hexene for propene and 2- and 3-octene for 1-butene, as determined by GC and NMR. Assuming that the same mechanism is adopted for 1-hexene, the dimerization products ought to be a mixture of 4- and 5-dodecene. This is consistent with the experimental observations. Similar conclusions about the underlying mechanism have been proposed for the nonfluorinated oligomerization catalysts.[7]

Despite the catalyst's pronounced preference for α-olefin dimerization, insertion of a third monomer unit into an α-branched cobalt alkyl must occur, albeit slowly, to generate the branched trimers (or tetramers) detectable by GC. The ratio of the molar sum of all the *branched* higher *n*-mers ($n > 2$) to the sum of dimers would therefore represent the underlying relative rates of further monomer insertions into an α-branched cobalt alkyl (chain propagation) and β-H elimination/transfer from this species (chain termination).[24] From the GC data, values of the ratio $k_{\text{prop}}/k_{\text{term}}$ are estimated to be ca. 1/9 for propene, 1/9 for 1-butene, and 1/11 for 1-hexene in toluene solution. The similarity of the values for each medium supports the assumption of a single fundamental mechanism for formation of branched *n*-mers ($n > 2$).

Clearly, it is impossible to form linear propene trimers and tetramers by *successive* insertions, since monomer insertion into the cobalt−hexyl species § (Scheme 2),

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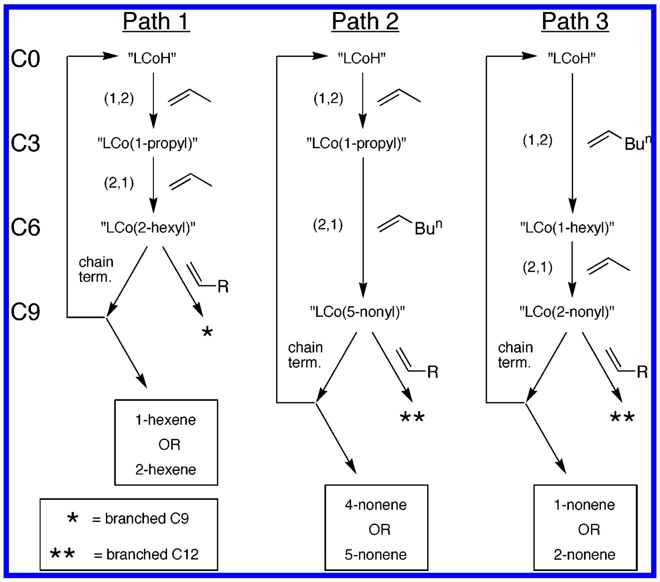
(21) Gibson, V. C.; Humphries, M. J.; Tellmann, K. P.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2001**, 2252.

(22) Kooistra, T. M.; Knijnenburg, Q.; Smits, J. M. M.; Horton, A. D.; Budzelaar, P. H. M.; Gal, A. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 4719.

(23) (a) Gibson, V. C.; Tellmann, K. P.; Humphries, M. J.; Wass, D. F. *Chem. Commun.* **2002**, 2316. (b) Tellmann, K. P.; Humphries, M. J.; Rzepa, H.S Gibson, V. C. *Organometallics* **2004**, *23*, 5503.

(24) Chain termination normally occurs exclusively by β-H elimination/transfer in cobalt bis(imino)pyridine catalysts, regardless of ligand size.

Scheme 3. Plausible Mechanistic Pathways for Generation of Propene Trimers



whether in (1,2)- or (2,1)-fashion, must lead to a branched product (Scheme 3, path 1).[25] By logical consequence, these olefins have to be produced by another mechanism that has to operate, by necessity, in stepwise fashion. This view is also supported by the increasing degree of linearity in the propene trimer and tetramer fractions, the longer the run time.

Two reaction sequences that afford linear propene trimers involve the codimerization of propene and 1-hexene, following the same regioselectivity as established for homodimerization, and differ only by the order of addition (cf. Scheme 3). In path 2, propene is inserted first in a (1,2)-fashion, to give a cobalt 5-nonyl species, whereas by path 3, propene is inserted (2,1) after 1-hexene, to afford a cobalt 2-nonyl species. Following chain termination by β-H elimination, these organocobalt complexes yield 4-/5-nonene (path 2) or 1-/2-nonene (path 3). Of the two possible products, only the former is observed by GC and NMR, and hence the mechanistic pathway 3 may be ruled out. This preferred order of addition is consistent with the higher relative concentration of propene at any stage during the reaction (being present in excess); furthermore, the ease of insertion into a putative cobalt hydride like species is probably greater for propene than for 1-hexene on steric grounds (cf. relative oligomerization activities of C_3H_6 vs C_6H_{12}).

By direct analogy, the linear propene tetramers must be formed by dimerization of the 1-hexene, formed by initial dimerization of the monomer. Indeed, the fact that 1-hexene always constitutes the principal reaction product in the oligomerization of propene with **2c**/MAO implies that it is consumed significantly more slowly (for formation of linear tri- and tetramers) than it is produced (by simple dimerization). It is therefore possible to conclude that propene inserts far more readily into a cobalt 1-propyl species than 1-hexene.

Summary and Conclusion

Exceptionally high productivities have been achieved in ethylene oligomerization/polymerization reactions using bis(imino)pyridine complexes of iron and cobalt containing trifluoromethyl groups. These judiciously fluorinated catalysts show greater activities than their nonfluorinated relatives as a consequence of both higher peak activities and longer catalyst lifetimes, suggesting that the trifluoromethyl group not only increases the electrophilicity of the metal centers but also significantly improves catalyst stability. The most impressive activity increases are observed for the cobalt catalyst **2c**, which contains one *o*-CF_3 and an *o*-F unit. This system is even more active than its iron counterpart in ethylene polymerization, reaching $>100\,000$ g mmol^{-1} h^{-1} bar^{-1}. The fluorinated catalysts are also shown to dimerize propene, 1-butene, and 1-hexene with high selectivities via a mechanism dominated by (1,2)- followed by (2,1)-insertion steps. Combinations of chain growth and step growth account for the formation of linear trimers and tetramers of propene. Significantly, no isomerization of terminal olefins to internal olefins is seen.

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Supporting Information Available: Kinetic profiles showing monomer uptake for ethylene oligomerization/polymerizations, experimental procedures for the preparation of ligands and complexes, as well as the methods employed for olefin oligomerization/polymerization, and solid-state structures and crystallographic details for complexes **2a**–**c** and **4a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049297Q

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[25] At least in the absence of chain walking, a phenomenon only observed in certain group 10 complexes, but for which no evidence is seen in **2c**/MAO or closely related group 9 catalysts. For leading references concerning chain walking in group 10 metal complexes, see: Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169 and references therein.