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Neutral Bimetallic Nickel(II) Phenoxyiminato Catalysts for Highly Branched Polyethylenes and Ethylene−Norbornene Copolymerizations

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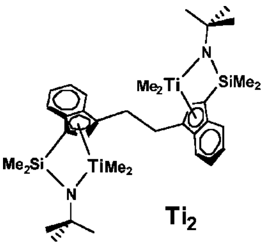
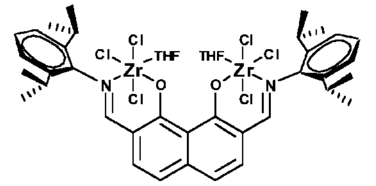
Summary: The synthesis and characterization of novel bimetallic, neutrally charged dinickel 2,7-diimino-1,8-dioxynaphthalene polymerization catalysts is reported. Ethylene polymerizations as well as ethylene-co-norbornene copolymerizations display increased catalytic activity, methyl branch formation, and comonomer enchainment selectivity versus the monometallic analogues. Furthermore, these systems turn over in the absence of cocatalyst under mild conditions.

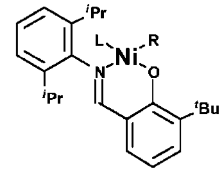
The remarkable enchainment cooperativity effects displayed by single-site group 4 bimetallic olefin polymerization catalysts include significantly enhanced activity, chain branching, and comonomer enchainment selectivity.[1] Moreover, these effects roughly scale inversely with the intermetallic distance and are evident in both constrained geometry[1] and aryloxyiminato[2] group 4 catalysts (e.g., **Ti$_2$**, **FI^2-Zr$_2$**, respectively). Since studies to date have focused exclusively on group 4 metals, the question arises as to whether such cooperativity effects are limited to early transition metals or might be more pervasive. To explore this issue, we focused on Ni(II) complexes, which are active olefin polymerization catalysts,[3] as exemplified by the Ni phenoxyiminates of Grubbs, which afford LDPEs having moderate molecular weights and 10−55 branches/1000 C atoms.[4] This general ligand architecture confers distinctive electronic, steric, and catalytic characteristics on the metal center, and we report here the synthesis of binuclear 2,7-diimino-1,8-dioxynaphthalene Ni(II) catalysts **FI^2-Ni$_2$-A** and **FI^2-Ni$_2$-B**, in which rigid ligation enforces Ni···Ni distances as small as ~3.1 Å,[5] and initial observations on ethylene polymerization and copolymerization characteristics. It will be seen that these catalysts exhibit non-negligible cooperativity effects—the first reported for a group 10 metal—manifested in enhanced polymerization activity, enhanced methyl chain branching, and enhanced comonomer incorporation under mild reaction conditions and not requiring a cocatalyst.[6]



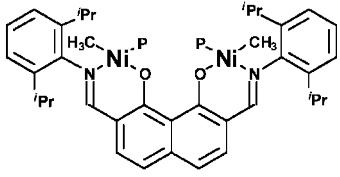
Ti$_2$



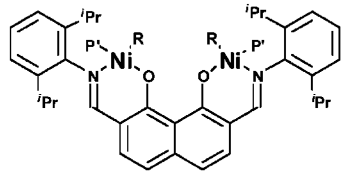
FI^2-Zr$_2$



FI-Ni-A, L = PMe$_3$
FI-Ni-B, L = PPh$_3$



FI^2-Ni$_2$-A, P = PMe$_3$



FI^2-Ni$_2$-B, P' = PPh$_3$
R = Me, 1-Naphthyl

The sodium salt of ligand **FI^2-H$_2$**[2] was obtained by treating 2,7-di(2,6-diisopropylphenyl)imino-1,8-dihydroxynaphthalene[2] with NaH in THF. The bimetallic catalysts **FI^2-Ni$_2$-A** and **FI^2-Ni$_2$-B** were prepared as shown in Scheme 1 (for details, see Supporting Information). The imine protons in the **Ni$_2$FI^2-A** ^{1}H NMR spectrum exhibit a characteristic $^4J_{PH} \approx 9$ Hz, corresponding to PMe$_3$ coordination *trans* to the ketimine

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(5) Ni−Ni = 3.09 Å in the crystal structure of a Ni$_2$L$_2$(OPMe$_3$)$_2$ thermolysis product (Rodriguez, B. A.; Delferro, M.; Marks, T. J., unpublished results).

(6) For binuclear Ni(II) catalysts having less rigid ligation, longer intermetallic distances, and minimal cooperative polymerization effects, see: (a) Chen, Q.; Yu, J.; Huang, J. *Organometallics* **2007**, *26*, 617–625. (b) Hu, T.; Tang, L.; Li, X.; Li, Y.; Hu, N. *Organometallics* **2005**, *24*, 2628–2632. (c) Zhang, D.; Jin, G. *Organometallics* **2003**, *22*, 2851–2854. (d) U.S. Patent 0270811, 2006.

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Scheme 1. Synthesis of Binuclear Catalysts FI^2-Ni$_2$-A and FI^2-Ni$_2$-B and Mononuclear Catalyst FI^{2}TMS-Ni

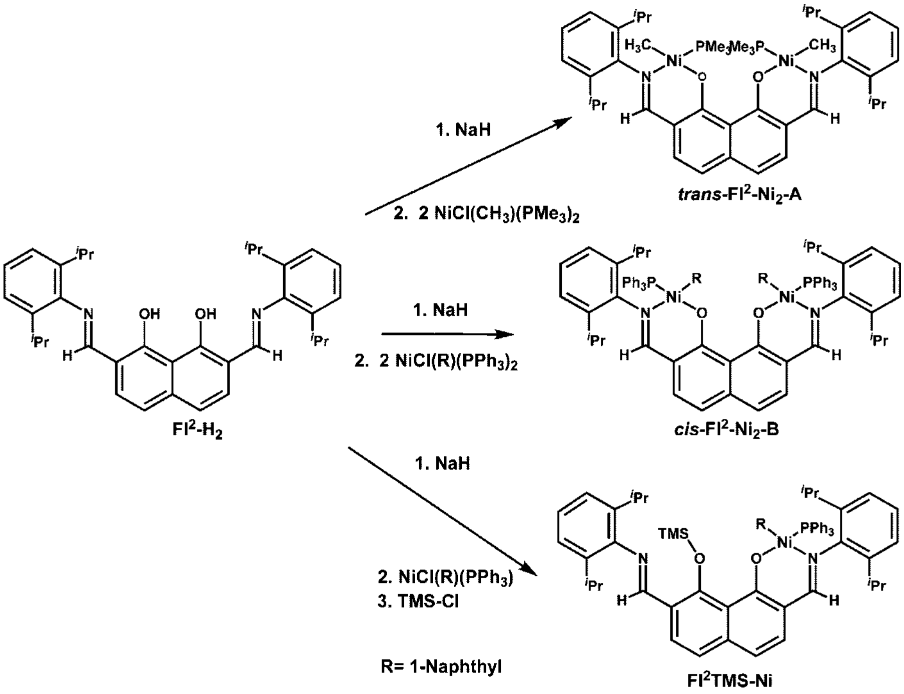

Table 1. Ethylene and Ethylene-*co*-Norbornene Polymerization Data for Nickel FI^2-Ni$_2$, FI^2-Ni, and FI Catalysts

entry	catalyst	cocatalyst	comonomer	polymer yield (g)	M_w[d]	M_w/M_n	total Me/1000 C[e]	mp, °C[f]	activ[g]	comon incorp[h]
1	**FI^2-Ni$_2$-A**[a]	Ni(cod)$_2$		0.663	10 300	2.6	80	68	7.1	
2	**FI^2-Ni$_2$-B**[a]	Ni(cod)$_2$		0.684	10 100	2.6	93	66	7.4	
3	**FI^2-Ni$_2$B**[j]	Ni(cod)$_2$		0.631	10 700	2.6	92	68	6.8	
4	**FI^2-Ni$_2$-B**[k]	Ni(cod)$_2$		0.566	10 900	2.6	86	68	6.2	
5	**FI-Ni-A**[a]	Ni(cod)$_2$		0.167	11 700	2.5	52	93	3.6	
6	**FI-Ni-B**[a]	Ni(cod)$_2$		0.175	10 500	2.5	54	97	3.7	
7	**FI^{2}TMS-Ni**[a]	Ni(cod)$_2$		0.141	11 200	2.6	40	98	3.3	
8	**FI^2-Ni$_2$-A**[b]			0.103	6000	2.7	102	60	0.2	
9	**FI^2-Ni$_2$-B**[b]			0.196	7000	2.7	105	61	0.4	
10	**FI-Ni-A**[b]			[i]						
11	**FI-Ni-B**[b]			[i]						
12	**FI^2-Ni$_2$-A**[c]	Ni(cod)$_2$	norbornene	0.558	66 400	5.2	34	107	1.3	9
13	**FI^2-Ni$_2$-B**[c]	Ni(cod)$_2$	norbornene	0.504	65 800	4.5	38	106	1.2	11
14	**FI-Ni-A**[c]	Ni(cod)$_2$	norbornene	0.072	63 200	2.3	9	124	0.3	3
15	**FI-Ni-B**[c]	Ni(cod)$_2$	norbornene	0.066	64 000	2.1	11	124	0.3	3

[a] Polymerizations carried out with 10 μmol of catalyst and 2 equiv of cocatalyst/Ni at 25 °C for 40 min in 25 mL of toluene at 7.0 atm of ethylene. [b] Polymerizations carried out with 20 μmol of catalyst at 25 °C for 2 h in 25 mL of toluene at 7.0 atm of ethylene. [c] Polymerizations carried out with 20 μmol of catalyst and 2 equiv of cocatalyst/Ni at 25 °C for 90 min in 25 mL of toluene and 225 equiv of norbornene at 7.0 atm of ethylene. [d] GPC vs polyethylene standard; uncorrected. [e] By ^{1}H NMR. [f] Determined by DSC. [g] kg polyethylene/mol of Ni·h atm. [h] Molar percentage by ^{13}C NMR. [i] No polymer obtained. [j] Polymerizations carried out with 10 μmol of catalyst and 2 equiv of cocatalyst/Ni at 25 °C for 60 min in 25 mL of toluene at 7.0 atm of ethylene. [k] Polymerizations carried out with 10 μmol of catalyst and 2 equiv of cocatalyst/Ni at 25 °C for 90 min in 25 mL of toluene at 7.0 atm ethylene.

(confirmed by 2D ^{1}H – ^{1}H NOESY).[7] Close proximity of the Ni-CH$_3$ group and the methyls of one ^{i}Pr group is also detected. In contrast, $^4J_{PH} \approx 6$ Hz and the 1D ^{1}H NOESY indicate *cis* PPh$_3$ binding in **FI^2-Ni$_2$-B**.[7] The ^{31}P singlets in both complexes are consistent with the proposed **FI^2-Ni$_2$-A** and **FI^2-Ni$_2$-B** symmetries. For control experiments, mononuclear **FI-Ni-A** and **FI-Ni-B** were synthesized by reaction of the corresponding monosalicylaldiminate sodium salt[4] with the aforementioned Ni(II) precursors. In both monometallic complexes, the PR$_3$ (R = Me, Ph) ligand is bound *trans* to the ketimine group ($^4J_{PH} \approx$ 9 Hz; see Supporting Information for data). A second monometallic control complex was prepared by reaction of 1.0 equiv of the Ni(II) precursor with the disodium salt of **FI^2-H$_2$**, followed by addition of TMS-Cl in situ to yield **FI^2(TMS)-Ni** (Scheme 1). Stepwise Ni incorporation can be monitored by integration of the now inequivalent isopropyl and imine ^{1}H NMR resonances. These monometallic complexes are designed to probe the nature and extent of Ni−Ni cooperativity effects on polymerization.

Room-temperature ethylene homopolymerizations using the present catalysts were carried out in the presence of the phosphine scavenger/cocatalyst Ni(cod)$_2$ under conditions minimizing mass transport and exotherm effects (see Supporting Information for details).[1,2] Bimetallic **FI^2-Ni$_2$-A** and **FI^2-Ni$_2$-B** afford polyethylenes with molecular weights comparable to those produced by the mononuclear analogues and with polydispersities consistent with single-site processes (Table 1). However, the bimetallic catalysts exhibit a 2-fold greater polymerization activity along with increased methyl (and only methyl; see

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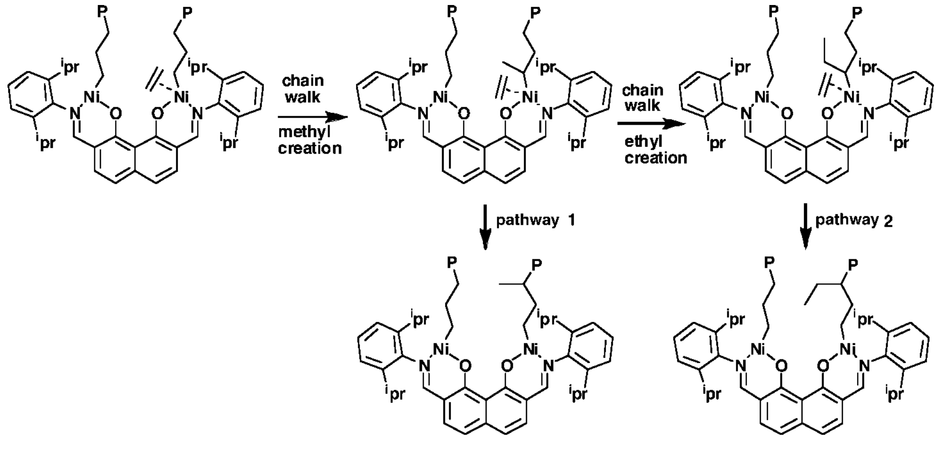
(7) Zhang, L.; Brookhart, M.; White, P. S. *Organometallics* **2006**, *25* (8), 1868–1874.

Scheme 2. Branch Formation Pathways in FI^2-Ni$_2$ Mediated Ethylene Homopolymerization



below) branching. The branch density by ^{1}H NMR[8] is ~2× that achieved by the mononuclear catalysts under identical reaction conditions and is confirmed by depressed DSC-determined melting points (Table 1). In the absence of a cocatalyst, the mononuclear systems do not produce polyethylene.[10] In contrast, the present bimetallic catalysts produce polyethylenes with increased branching densities and concurrently depressed melting points, albeit at somewhat reduced polymerization rates versus the cocatalyzed polymerizations (Table 1).[11] This particular productivity difference between **FI^2-Ni$_2$-A**, **FI^2-Ni$_2$-B**, and the mononuclear analogues may reflect phosphine dissociation-related steric and electronic factors. Typically, equilibria between such phosphine-coordinated and uncoordinated species heavily favor the former;[3d] however the proximate bulky phosphine ligands in **FI^2-Ni$_2$-A** and **FI^2-Ni$_2$-B** may favor phosphine dissociation.

Control homopolymerization experiments were also carried out with catalyst **FI^{2}TMS-Ni**, having a single Ni center bound to the **FI^2** ligand. The results (Table 1) indicate comparable polymerization activities and branch densities to that of the mononuclear catalysts **FI-Ni-A** and **FI-Ni-B** under identical conditions and argue that neither the **FI^2** ligand nor steric bulk alone ensures enhanced homopolymerization activity or branching. While most data in Table 1 are the result of 40 min polymerization trials, ethylene polymerizations were also carried out for 60 and 90 min, with four of the catalysts, and the results verify continuing polymerization activity beyond 40 min. Homopolymerizations at higher temperatures (≥40 °C), with or without cocatalyst, yield minimal polymer. Rather, bis-chelating **Ni$_2$(FI^2)$_2$L$_2$** complexes are identified, reminiscent of the analogous mononuclear phenoxyiminato catalysts.[4]

In regard to homopolymer microstructure, the ^{13}C NMR spectra of the polyethylenes produced by all of the monometallic catalysts exhibit five prominent non-polyethylene backbone resonances assignable[12] to methyl branches, ethyl branches, and carbons α, β, and γ to the branches at δ 21.0, 35.0, 39.1, 28.2, and 31.5 ppm, respectively. In contrast, note that the polyethylenes derived from the bimetallic catalysts contain almost exclusively methyl branches. Thus, the ^{13}C NMR spectra of the **FI^2-Ni$_2$-A/FI^2-Ni$_2$-B**-derived products exhibit, in addition to backbone resonances, only four prominent signals, assignable[12] to methyl branches and carbons α, β, and γ to the branch at δ 21.0, 39.1, 28.2, and 31.5 ppm, respectively. The extent of ethyl branching amounts to ≤1% of the total branching (see Supporting Information). While further mechanistic experiments will be required to define additional aspects of the branch-forming pathways, at this stage it appears likely that the presence of the second Ni center suppresses insertion pathway 2 versus pathway 1 (Scheme 2) via an interplay of Ni$_2$-associated steric and electronic/coordination factors.

Ethylene + norbornene copolymerizations were also investigated, and modest comonomer enchainment levels are achieved with the present mononuclear catalysts, in accord with results for comparable mononuclear systems[11] (Table 1). In marked contrast, ethylene + norbornene copolymerizations mediated by binuclear **FI^2-Ni$_2$-A** and **FI^2-Ni$_2$-B** proceed with 3−4 times greater activity and achieve 3−4 times greater selectivity for comonomer enchainment, while product molecular weights are comparable (as in the homopolymerization cases).

These results show that, for single-site d^8 Ni(II) aryloxyiminato ethylene polymerization catalysts, a proximate catalytically active Ni site substantially increases activity, degree of and selectivity for methyl group branching, and comonomer incorporation selectivity versus the mononuclear analogues. Furthermore, these binuclear catalysts produce highly branched polyethylenes in the absence of a cocatalyst. Further studies are underway to better define the scope and mechanisms of these and related processes, including low-temperature NMR to identify any intermetallic agostic effects.

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Supporting Information Available: Details of catalyst synthesis, polymerization experiments, and polymer characterization; NMR spectra of representative polymer samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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