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Role of Electron-Withdrawing Remote Substituents in Neutral Nickel(II) Polymerization Catalysts

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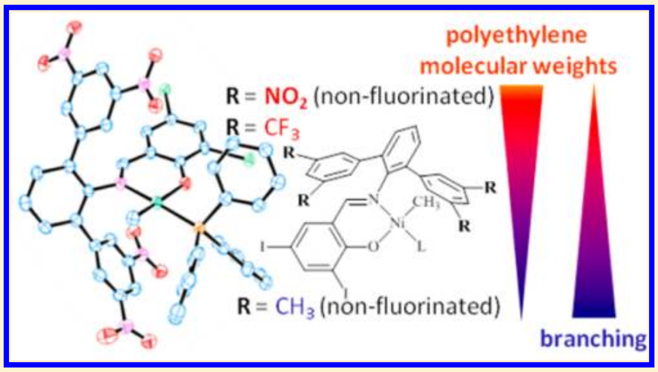
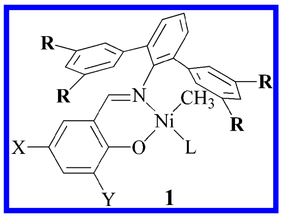
S *Supporting Information*



ABSTRACT: The novel neutral κ^2-*N,O*-salicylaldiminato Ni(II) complex, [κ^2-*N,O*-{2,6-(3′,5′-$R_2C_6H_3)_2C_6H_3$-N═C(H)-(3,5-I_2-2-O-C_6H_2)}$NiCH_3$(pyridine)] (**1a-pyr**, R = NO_2), with four nitro substituents on the N-terphenyl motif is a catalyst precursor for ethylene polymerization to yield linear higher molecular weight polyethylene (e.g., M_n 2.1 × 10^5 g mol^{-1} and only 2 methyl branches per 1000 carbon atoms). A comparison with other known catalyst precursors at various polymerization conditions shows that the catalytic properties in terms of linearity and molecular weight are similar to the fluorinated catalyst precursor with R = CF_3, showing that the latter is not singular, but rather suppression of chain transfer and branch formation by β-hydride elimination can also be brought about by nonfluorinated electron-withdrawing remote substituents.

Catalytic polymerization of olefins by complexes of d^8 metals has been studied intensely due to several unique features by comparison to the more established catalysts based on early transition metals.[1] Due to their lower oxophilicity, they are more tolerant toward functional groups.[2] Also, ethylene[3] and 1-olefins[3,4] can be converted to unique branching patterns. On the other hand, some late transition metal catalysts display a very high selectivity for linear ethylene chain growth even in the presence of 1-olefins, which is of practical relevance in oligomerization[5] and polymerization[6] catalysis.

Of the different major cationic and neutral catalyst systems studied,[1,7] neutral salicylaldiminato Ni(II) catalysts[8] stand out in their tolerance toward aqueous reaction media, enabling catalytic emulsion polymerizations.[9] We have previously reported that in N-terphenyl-substituted catalysts (**1**) substituents (R) on the peripheral aromatic rings have a remarkable effect on the catalytic properties, despite their remoteness from the active sites.[10] Depending on the substituents, high molecular weight linear polyethylene or low molecular weight, highly branched oligomers are formed. Studies of a range of patterns of different substituents in the 3′,5′- and/or 4′-position (e.g., CF_3, Me, *t*Bu, OMe) showed that the catalytic properties correlate with their electronic character.[10−12] More electron-donating substituents favor branch formation and chain transfer, which both occur through β-hydride elimination as the underlying step. The observed effect of substituents can be related to very similar barriers of β-hydride elimination ($\Delta G^{\ddagger}_{\beta\text{-elim}}$) and ethylene insertion chain growth ($\Delta G^{\ddagger}_{\text{ins}}$).[13] Small relative changes in $\Delta G^{\ddagger}_{\beta\text{-elim}}$ and $\Delta G^{\ddagger}_{\text{ins}}$ exerted by the electronics of R can then alter the ratio $\Delta G^{\ddagger}_{\text{ins}}/\Delta G^{\ddagger}_{\beta\text{-elim}}$ to a noticeable extent, resulting in entirely different materials obtained.[12b] However, these considerations are based essentially on only one type of electron-withdrawing substituent that can yield linear high molecular weight polymer, namely, the trifluoromethyl group. Consequently, CF_3 groups have been suggested to be unique in that the formation of linear high molecular weight polyethylenes with these catalysts is due to an F···H interaction with the growing chain.[14] Note that a similar interaction has been considered to occur in living ethylene polymerization by fluorinated salicylaldiminato Ti catalysts with nonremote F-substituents.[15] In structurally related enolatoimine Ti catalysts a Ti···F interaction with the very electrophilic metal center directly observed in solution provides a plausible alternative explanation for the living character of polymerization with these Ti catalysts.[16]



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In order to further probe this issue, we sought to study a representative of **1** with nonfluorinated electron-withdrawing remote 3′,5′-substituents.

Bromination of 1,3-dinitrobenzene in sulfuric acid at 80−85 °C by addition of *N*-bromosuccinimide in small portions

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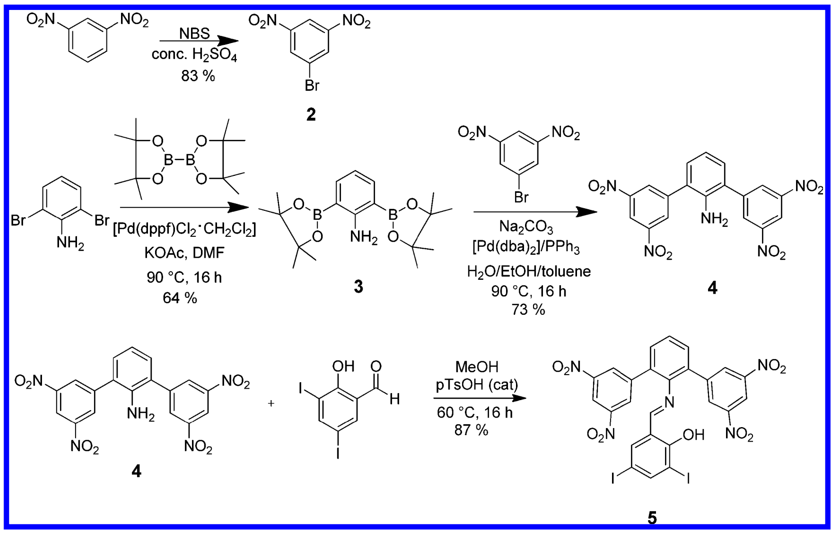
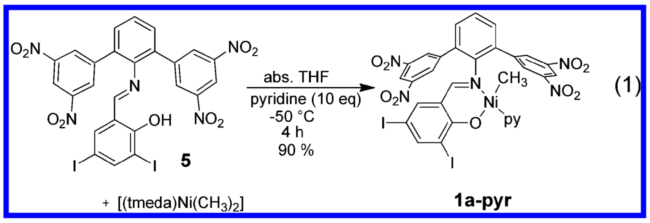
Scheme 1. Synthesis of the Nitro-Substituted Salicylaldimine 5



yielded 1-bromo-3,5-dinitrobenzene **2**.[17] Borylation of 2,6-dibromoaniline with bis(pinacolato)diboron in the presence of [Pd(dppf)$_2$Cl$_2$·CH$_2$Cl$_2$] in DMF at 90 °C afforded 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline **3** (Scheme 1).[18] 2,6-Bis(3′,5′-dinitrophenyl)aniline (**4**) was prepared by Suzuki coupling of **3** with 2.1 equiv of **2**.[12a] Acid-catalyzed condensation of this nitro-substituted terphenylamine **4** and 3,5-diiodosalicylaldehyde afforded the desired salicylaldimine **5** (for characterization data of all compounds see the Supporting Information, SI).

The targeted NO$_2$-substituted nickel(II) pyridine complex was generated by reaction of salicylaldimine **5** with 1.05 equiv of [(tmeda)Ni(CH$_3$)$_2$] and 10 equiv of pyridine in THF solution at −50 °C under strict exclusion of oxygen (eq 1), to yield crystalline, deep red **1a-pyr** in 90% yield. The observation of a single resonance for the Ni-CH$_3$ group at −0.56 ppm (^{1}H NMR) and −6.5 ppm (^{13}C), respectively, shows that only a single isomer of **1a-pyr** is present. The observation of only a single well-resolved ($^4J_{HH}$ = 1.6 Hz) resonance for the four protons in the 2′,6′-positions evidences an unhindered rotation of the aryl groups. Since the crystals of **1a-pyr** obtained were not suitable for X-ray diffraction analyses, crystals of the corresponding triphenylphosphine complex **1a-PPh$_3$** (generated by replacing pyridine for PPh$_3$) were grown. Single-crystal X-ray crystallography (Figure 1) shows all four NO$_2$ groups to be in the plane of the phenyl rings in the solid-state structure of the square planar complex. The coordination geometry with the methyl group *trans* to the oxygen donor agrees with other salicylaldiminato complexes.[8b,10,14] While the quality of the data does not allow for a detailed discussion of bond lengths and angles, overall there are no indications of unusual strong devations of the structure vs known terphenyl analogues.



(1)

1a-pyr and the known analogs **1b-pyr** (R = CF$_3$) and **1c-pyr** (R = CH$_3$) were studied as single-component catalyst precursors for ethylene polymerization in toluene solution at various temperatures and ethylene pressures (Table 1). Moderate activities up to 2.0 × 10^4 TO h^{-1} were observed with **1a-pyr** (entries 1 to 3). **1a-pyr** requires higher polymerization temperatures to enhance pyridine dissociation, compared to the CF$_3$-substituted analogue **1b-pyr**. Possibly, a stronger electron-withdrawing character of the nitro groups increases the electron deficiency of the Ni(II) center and enhances pyridine binding. However, when **1a-pyr** was combined with B(C$_6$F$_5$)$_3$ as a pyridine scavenger, polymerization activity increased significantly (4.2 × 10^4 TO h^{-1}, entry 4) under otherwise identical conditions. The activity of the catalyst **1a-pyr**/B(C$_6$F$_5$)$_3$ decreased only slightly over time, as concluded from mass-flow traces reflecting ethylene consumption at 50 °C (40 bar ethylene pressure), and the catalyst is active for at least ca. 2 h. By comparison, a previously studied 3-NO$_2$ monosubstituted Ni(II) catalyst was deactivated completely within 20 min (and yielded slightly branched PE, entry 13).[10]

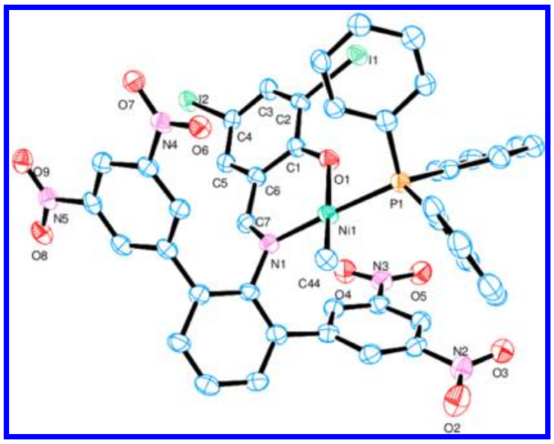


Figure 1. X-ray crystal structure of complex **1a-PPh$_3$** drawn with 50% probability ellipsoids. All hydrogen atoms and pentane molecules are omitted for clarity.

Both **1a-pyr** and **1b-pyr** produce high molecular weight linear polyethylene with very few branches (Table 1). As expected, degrees of branching increase with temperature, while molecular weights decrease, due to an increased β-hydride elimination at higher temperature. In detail, **1a-pyr** produced

Table 1. Ethylene Polymerization Results with Complexes 1a-pyr, 1b-pyr, and 1c-pyr as Precatalysts[a]

entry	precatalyst	T [°C]	yield [g]	TOF[b]	M_n [10^3 g/mol][c]	M_w/M_n[c]	T_m [°C][d]	crystallinity [%][d]	branches/1000 C[e]
1	**1a-pyr**	30	0.90	4.8	214.9	1.5	132	65	2
2	**1a-pyr**	50	1.61	8.6	47.7	3.2	121	55	11
3	**1a-pyr**	70	3.69	19.8	9.6	2.2	108	55	15
4[f]	**1a-pyr**	50	7.76	41.6	17.6	2.6	113	53	14
5[g]	**1a-pyr**	50	5.94	31.8	24.6	4.1	110	53	15
6	**1b-pyr**	30	5.24	28.1	174.6	1.8	131	60	3
7	**1b-pyr**	50	14.11	75.6	31.6	4.0	123	64	8
8	**1b-pyr**	70	26.21	140.4	9.6	2.1	115	64	11
9[g]	**1b-pyr**	50	4.24	22.7	16.7	2.6	120	63	8
10	**1c-pyr**	30	2.19	11.7	2.0[h]	n.d.	n.d.	n.d.	80[h]
11	**1c-pyr**	50	6.04	32.4	1.4[h]	n.d.	n.d.	n.d.	80[h]
12	**1c-pyr**	70	3.34	17.9	1.0[h]	n.d.	n.d.	n.d.	85[h]
13[10]	R = NO_2/H[i]	50	3.0	5.4	11.0	2.6	106	n.d.	26

[a] Polymerization conditions: 10 μmol of precatalyst, 100 mL of toluene, 40 bar of C_2H_4, 40 min. [b] 10^3 × mol [C_2H_4] × mol^{-1} [Ni] × h^{-1}. [c] Determined by GPC at 160 °C. [d] Determined by DSC. [e] Determined by ^{13}C NMR spectroscopy. [f] 1 equiv of $B(C_6F_5)_3$ added. [g] 1 equiv of $B(C_6F_5)_3$ added; 8 bar of C_2H_4 pressure. [h] Determined by ^1H NMR spectroscopy. [i] 40 μmol of precatalyst.

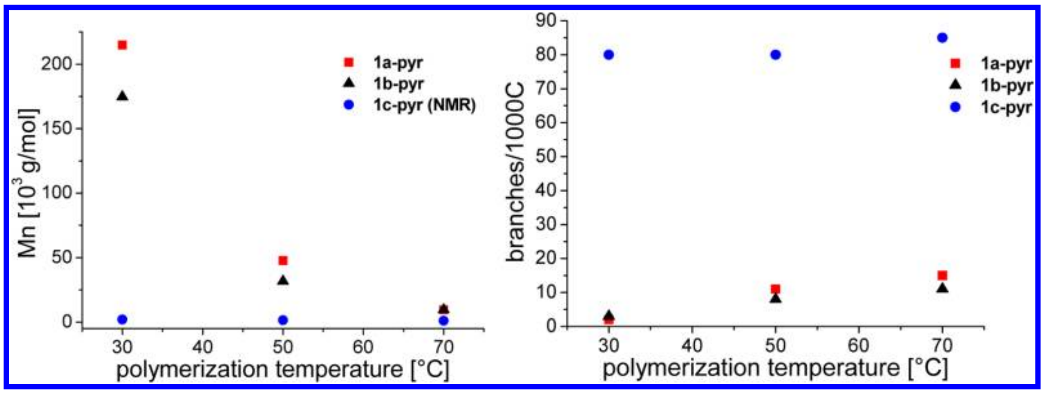


Figure 2. Polymer molecular weights (M_n, left) and methyl branches per 1000 carbon atoms (right, from ^{13}C NMR spectroscopy) for complexes **1a-pyr**, **1b-pyr**, and **1c-pyr** at various polymerization temperatures (40 bar of ethylene pressure).

polyethylenes with slightly higher molecular weights (215 × 10^3 g mol^{-1} at 30 °C and 48 × 10^3 g mol^{-1} at 50 °C) vs **1b-pyr** (174 × 10^3 g mol^{-1} at 30 °C and 32 × 10^3 g mol^{-1} at 50 °C). At 70 °C molecular weights are essentially identical (9.6 × 10^3 g mol^{-1}). Also, branching is virtually identical with both catalysts (2 vs 3, 11 vs 8, and 15 vs 11 methyl branches/1000C, entry 1 vs 6, entry 2 vs 7, and entry 3 vs 8, Figure 2). At a polymerization temperature of 70 °C, in addition to methyl branches also small amounts of higher branches are observed for both catalysts (Figures S3 and S6).

Overall, with both types of electron-withdrawing substituents (Hammett substituent constant $\sigma_m(NO_2) = 0.71$ and $\sigma_m(CF_3) = 0.43$)[19] a similar higher molecular weight linear polymer microstructure is obtained. This is also most clearly underlined by comparison to catalysis with the electron-donating substituted analogue (**1c-pyr**,[10] R = Me; $\sigma_m(CH_3) = -0.07$).[19] Under otherwise identical conditions of polymerization temperature and ethylene concentration, in all cases highly branched (80–85 branches/1000 carbon atoms) low molecular weight polyethylene ((1–2) × 10^3 g mol^{-1}, entries 10–12) is formed (Figure 2).

In conclusion, these findings show that the prototypical 3′,5′-trifluoromethyl-substituted terphenyl motif[10,11,12a,14] is not singular in suppressing chain transfer and branching in this type of catalysts. The nonfluorinated 3′,5′-nitro-substituted analogue reported here likewise affords higher molecular weight linear polyethylene. This is consistent with the observation that the electronic character of the remote substituents is decisive for the control of the polymer microstructure. Given that this class of catalysts is, for example, advantageously compatible with polar reaction media including water, and here the control of microstructure is decisive, for example, for potentially resolving general issues of polymer processing, this is a relevant guideline for further development of such polymerization catalysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text giving experimental details, NMR data, CIF files, and analytical data for the compounds prepared in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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