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Substituent Effects in (κ^2-*N*,*O*)-Salicylaldiminato Nickel(II)−Methyl Pyridine Polymerization Catalysts: Terphenyls Controlling Polyethylene Microstructures

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A series of (κ^2-*N*,*O*)-salicylaldiminato Ni(II)−methyl pyridine complexes **7-pyr** and **8-pyr** derived from 3,5-diiodosalicyaldehyde (**3a**) and 3-(9-anthryl)salicylaldehyde (**3b**), and terphenylamines 2,6-(3,5-R-4-R′-C_6H_2)$_2C_6H_3$−NH_2 (**4a**, R = CF_3, R′ = H; **4b**, R = ^{t}Bu, R′ = H; **4c**, R = ^{t}Bu, R′ = OH; **4d**, R = Me, R′ = H; **4e**, R = Me, R′ = MeO; **4f**, R = MeO, R′ = H; **4g**, R = MeO, R′ = MeO), was prepared by reaction of the respective salicylaldimine (**5a**−**f**, **6a**−**g**) with [(tmeda)Ni(CH_3)$_2$] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) or [(pyridine)$_2$Ni(CH_3)$_2$]. Complexes **7-pyr** and **8-pyr** are highly active single component catalysts for the polymerization of ethylene, producing a wide range of different polyethylene microstructures. While comparable complexes derived from **3a**, **3b**, 5-nitrosalicylaldehyde, 3-*tert*-butylsalicylaldehyde, 3,5-[3,5-(CF_3)$_2C_6H_3$]$_2$-salicylaldehyde, and 2,6-[3,5-(CF_3)$_2C_6H_3$]$_2C_6H_3$−NH_2 afford polyethylenes with similar degrees of branching, variation of the terphenyl moieties in complexes **7-pyr** and **8-pyr** allows access to a wide range of polyethylene microstructures under identical reaction conditions. The X-ray diffraction analyses of complexes **7b-pyr** and **8f-pyr** are reported.

Introduction

The discovery of highly active nickel and palladium diimine catalysts for the polymerization of ethylene and α-olefins[1] has triggered an outburst of research activity in the field of late transition metal-catalyzed olefin polymerization. Issues of academic and industrial interest, such as, for example, the copolymerization of ethylene and 1-olefins with polar acrylate monomers incompatible with early transition metal polymerization catalysts,[2] or the incorporation of substantial branching in ethylene homopolymers by catalytic polymerization,[1,3] have been met early on, providing access to new polymer microstructures and material properties. Further, single component precatalysts have been proven synthetically accessible,[1] thereby enabling detailed mechanistic studies and a deeper understanding of the processes involved in late transition metal-catalyzed insertion polymerization not only by these catalysts.[4]

Following these findings, new families of highly active late transition metal olefin polymerization precatalysts have been developed.[5,6] These include a minor number of single component catalysts promoting ethylene polymerization in the absence of any activator.[7] Even a small number of complexes where displacement of phosphines by ethylene is prerequisite for ethylene insertion behave as single component catalysts producing high molecular weight polyethylene,[7d,e,8,9] instead of the most commonly observed oligomers.[10] Particularly, neutral κ^2-(*N*,*O*)-salicylaldiminato nickel methyl or phenyl complexes of type **1** were reported to be highly active and stable precatalysts tolerant to polar media, and to produce high crystallinity high molecular weight polyethylene, even when L = PPh_3 and no phosphine scavenger was present (Chart 1).[7d] The steric bulk of the anthryl

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(1) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414−6415.

(2) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888−899.

(3) For an earlier example of a nickel(II) complex producing branched, low molecular weight ethylene homopolymer, see: (a) Keim, W.; Appel, R.; Storeck, A.; Krüger, C.; Goddard, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 116−117. (b) Keim, W. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 191−200.

(4) (a) Svejda, S. A.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1999**, *121*, 10634−10635. (b) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686−6700.

(5) For reviews, see: (a) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169−1203. (b) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283−316. (c) Mecking, S. *Coord. Chem. Rev.* **2000**, *203*, 325−351. (d) Mecking, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 534−540.

(6) For earlier work reporting nickel-based polymerization catalysts, see: (a) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466−467. (b) Reference 3a,b. (c) Ostoja Starzewski, K. A.; Witte, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 599−601. (d) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123−134.

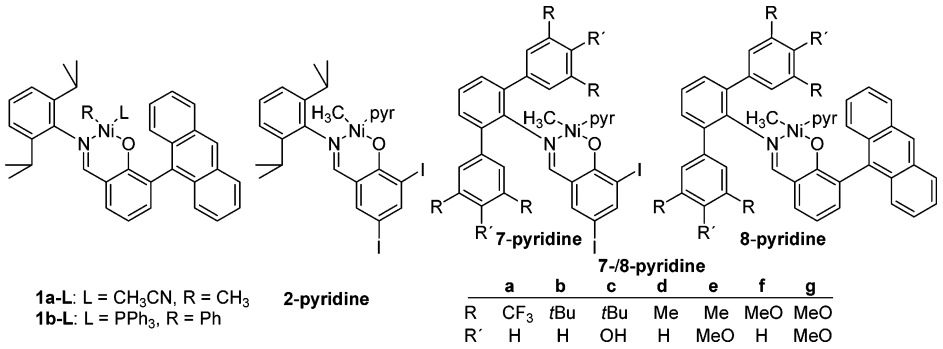
(7) Neutral nickel *P*,*O*-chelates (SHOP-type): (a) Reference 6a−d. (b) Kuhn, P.; Sémeril, D.; Jeunesse, C.; Matt, D.; Neuburger, M ; Mota, A. *Chem.-Eur. J.* **2006**, *12*, 5210−5219. (c) Nickel/palladium diimine complexes: ref 1. (d) Nickel salicylaldiminato complexes: Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460−462. (e) Nickel anilinotropone complexes: Hicks, F. A.; Brookhart, M. *Organometallics* **2001**, *20*, 3217−3219. (f) Cationic nickel *P*,*O*-chelates: Liu, W.; Malinoski, J. M.; Brookhart, M. *Organometallics* **2002**, *21*, 2836−2838. (g) Cyclopentadienyl cobalt complexes: Daugulis, O.; Brookhart, M.; White, P. S. *Organometallics* **2003**, *22*, 4699−4704. (h) Neutral iminopropanamide complexes: Diamanti, S. J.; Ghosh, P ; Shimizu, F ; Bazan, G. C. *Macromolecules* **2003**, *36*, 9731−9735.

(8) (a) Jenkins, J. C.; Brookhart, M. *Organometallics* **2003**, *22*, 250−256. (b) Hicks, F. A.; Jenkins, J. C.; Brookhart, M. *Organometallics* **2003**, *24*, 3533−3545. (c) Jenkins, J. C.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 5827−5842.

(9) Göttker-Schnetmann, I.; Korthals, B.; Mecking, S. *J. Am. Chem. Soc.* **2006**, *128*, 7708−7709.

(10) Representative oligomerization catalysts: (a) Reference 6a. (b) Desjardins, S. Y.; Cavell, K. J.; Jin, H.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, *515*, 233−243. (c) Pietsch, J.; Braunstein, P.; Chauvin, Y. *New J. Chem.* **1998**, 467−472. (d) Chen, Y.; Wu, G.; Bazan, G. C. *Angew. Chem., Int. Ed.* **2005**, *44*, 1108−1112.

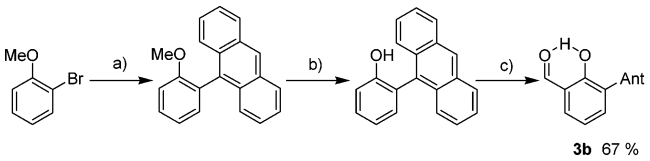
Chart 1. κ^2-(*N*,*O*)-Salicylaldiminato Nickel Methyl Complexes of Type 1, 2, 7, and 8



substituent in **1b-PPh$_3$** is believed to promote phosphine dissociation from **1b**, and to protect the catalytically active nickel center toward deactivation routes, which ultimately afford bis-chelate complexes [(κ^2-*N*,*O*)$_2$Ni], thus facilitating long-lasting high activity ethylene polymerization.[7d,11,12,16d]

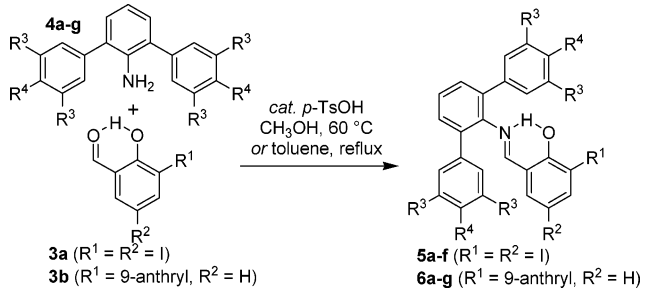
Driven by our interest to conduct ethylene polymerization in highly polar aqueous media,[13] we have shown that a similar and easily accessible κ^2-(*N*,*O*)-salicylaldiminato nickel−methyl pyridine complex **2-pyr** derived from commercially available 3,5-diiodosalicylaldehyde produces high molecular weight polyethylene dispersions in aqueous miniemulsion, although its activity is an order of magnitude smaller in aqueous systems as compared to homogeneous toluene solution.[14] Interestingly, replacement of the 2,6-diisopropylphenyl moiety by different terphenyls led to much more active precatalysts **7a**,**d**,**f-pyr** that, in addition, produced materials ranging from high molecular weight semicrystalline polyethylene with a low degree of branching to low molecular weight amorphous material with a high degree of branching depending on the 3′,5′-substitution of the terphenyl under otherwise identical reaction conditions.[15] These findings and the reported high activity of complexes **1-L** (vide supra) have prompted us to combine the (expected) high activity supported by the anthryl substitution and the possibility to influence the microstructure of the produced polymers by introducing different terphenyl substituents in complexes of type **8-pyr** (Chart 1). Here, we report the synthesis and the catalytic activity of new κ^2-(*N*,*O*)-salicylaldiminato nickel methyl complexes of type **7-pyr** and **8-pyr** as well as the microstructures of the polyethylenes obtained.

Scheme 1. Synthesis of 3-(9-Anthryl)salicylaldehyde (3b)



a): 1. Mg/THF, 65 °C, 2. -20 °C, anthrone/THF/toluene, 1h, 20 °C, 3. 3N HCl
b): 1. -78 to 20 °C, CH_2Cl_2, 1.4 equiv. BBr_3, 14 h, 20 °C, 2. MeOH
c): 1. $MgBr_2{\cdot}(Et_2O)_n/Et_3N$/toluene, 2. $(H_2C{=}O)_n$, 2h, 80 °C Ant = 9-anthryl

Scheme 2. Synthesis of Salicylaldimines 5a−f, 6a−g



Results and Discussion

Improved Synthesis of 3-(9-Anthryl)salicylaldehyde (3b). In contrast to commercially available 3,5-diiodosalicylaldehyde (**3a**), 3-(9-anthryl)salicylaldehyde (**3b**) is only accessible via multistep syntheses in moderate to good yield.[16] In analogy to a procedure developed by Grubbs et al.,[12,16b] we have improved and simplified the synthesis of **3b** (67% overall yield) starting from 2-bromoanisole and anthrone by (a) conducting the final formylation/oxidation sequence of 2-(9-anthryl)phenol in the presence of freshly prepared $MgBr_2{\cdot}(Et_2O)_n$ under strict TLC control (Scheme 1),[17] and (b) cocrystallization of the product as **3b**·$^1/_2$**CH$_2$Cl$_2$** from the crude reaction mixture in CH_3OH/CH_2Cl_2, thus avoiding chromatographic workup (see experimental section for details).

Synthesis of Salicylaldimines 5a−f, 6a−g. Condensation of aldehydes **3a**,**b** with *m*-terphenylamines **4a−g** that are readily accessible from 2,6-dibromoaniline and the respective 3,5-substituted aryl boronic acids (for details, see experimental part) yields the desired salicylaldimines in high yields (78−94%) in analogy to known procedures (Scheme 2 and Table 1). In most cases, the low solubility of the salicylaldimines in CH_3OH enables their straightforward isolation from the crude reaction

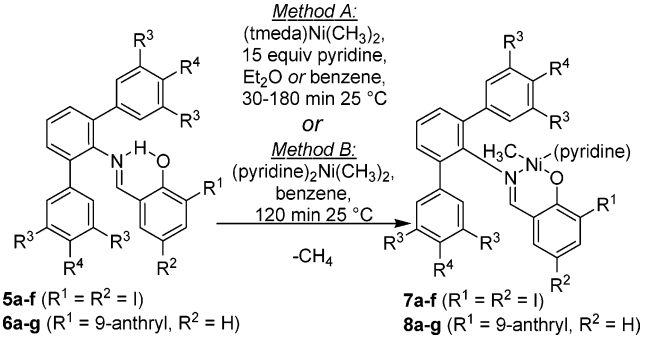
(11) Chan, M. S. W.; Deng, L. Q.; Ziegler, T. *Organometallics* **2000**, *19*, 2741−2750.
(12) Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Waltman, A. W.; Grubbs, R. H. *Chem. Commun.* **2003**, 2272−2273.
(13) (a) Mecking, S.; Held, A.; Bauers, F. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 544−561. (b) Mecking, S.; Claverie, J. In *Late Transition Metal Polymerization Catalysis*; Rieger, B., Baugh, L. S., Kacker, S., Striegler, S., Eds.; Wiley−VCH: Weinheim, 2003; pp 231−278. (c) Claverie, J. P.; Soula, R. *Prog. Polym. Sci.* **2003**, *28*, 619−662. (d) Mecking, S. *Colloid Polym. Sci.* **2007**, *285*, 605−619.
(14) (a) Bauers, F. M.; Mecking, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3020−3022. (b) Bauers, F. M.; Mecking, S. *Macromolecules* **2001**, *34*, 1165−1167.
(15) Zuideveld, M.; Wehrmann, P.; Röhr, C.; Mecking, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 869−873.
(16) Viable synthetic routes are reported by, for example: (a) Bansleben, D. A.; Friedrich, S. K.; Younkin, T. R.; Grubbs, R. H.; Wang, C.; Li, R. T. WO Patent Application 9842664 to W. R. Grace & Co. (b) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149−3151. (c) Bansleben, D. A.; Friedrich, S.; Younkin, T. R.; Grubbs, R. H.; Wang, C.; Li, R. T. U.S. Patent Application 6410664 to Cryovac Inc. (d) Bansleben, D. A.; Connor, E. F.; Grubbs, R. H.; Henderson, J. I.; Younkin, T. R.; Nadjydi, A. R., Jr. WO Patent Application 2000056787 to Cryovac Inc. (e) Gibson, V. C.; Goh, C.; Yong, P. K. WO Patent Application 2002090365 to BP Chemicals Limited. (f) Reference 12. (g) Jones, D. J.; Gibson, V. C.; Green, S. M.; Maddox, P. J.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 11037−11046.
(17) Commercially available Lewis acids, for example, $SnCl_4$, $MgCl_2$, and $MgBr_2$, did not perform as good as freshly prepared $MgBr_2$ diethyl ether complex.

Table 1. Synthesis of Salicylaldimines 5a−f, 6a−g

	product salicylaldimines		salicylaldehyde			terphenylamine			
				3			**4**		yield
entry	**5**	**6**		R^1	R^2		R^3	R^4	**5**,**6** [%][e]
1[a]	a[c]		a	I	I	a	CF_3	H	87[f]
2	b[c]		a	I	I	b	^{t}Bu	H	83
3[b]	c[d]		a	I	I	c	^{t}Bu	OH	83[b]
4[a]	d[c]		a	I	I	d	Me	H	90[f]
5	e[c]		a	I	I	e	Me	MeO	94
6[a]	f[c]		a	I	I	f	MeO	H	91[f]
7[b]		a[c]	b	Ant	H	a	CF_3	H	92[b]
8		b[c]	b	Ant	H	b	^{t}Bu	H	93
9[b]		c[c]	b	Ant	H	c	^{t}Bu	OH	92[b]
10		d[c]	b	Ant	H	d	Me	H	86
11		e[c]	b	Ant	H	e	Me	MeO	89
12		f[d]	b	Ant	H	f	MeO	H	78
13		g[c]	b	Ant	H	g	MeO	MeO	94

[a] See ref 15. [b] See ref 9. [c] Obtained from methanol/cat. *p*-TsOH. [d] Obtained from refluxing toluene/cat. *p*-TsOH. [e] Isolated yield. [f] The general procedure described here (cf. experimental section) gave higher yields than the procedure reported in ref 15.

Scheme 3. Synthesis of κ^2-(*N*,*O*)-Salicylaldiminato Nickel(II) Methyl Pyridine Complexes 7-pyr and 8-pyr



suspensions by filtration. Efficient condensation of **3b** with **4f** could not be achieved in methanol due to incomplete conversion. However, azeotropic water removal in toluene gave the desired salicylaldimine **6f** in good yield.

Synthesis of κ^2-(*N*,*O*)-Salicylaldiminato Nickel(II) Methyl Pyridine Complexes (7a−f-pyr, 8a−g-pyr). Preparation of complexes **7a−f-pyr** and **8a−g-pyr** was accomplished by reaction of the respective salicylaldimine **5a−f**, **6a−g** either with 1 equiv of [(tmeda)Ni(CH_3)$_2$][18] and 15 equiv of pyridine (method A) or with 1.05 equiv of the recently reported [(pyridine)$_2$Ni(CH_3)$_2$][19] (method B) in diethyl ether suspension or benzene solution at 25 °C under strict exclusion of oxygen (Scheme 3). In our view, the use of [(pyridine)$_2$Ni(CH_3)$_2$] simplifies the synthesis of complexes **7-pyr** and **8-pyr** as it is more readily accessible than [(tmeda)Ni(CH_3)$_2$] (although not more stable).[20]

Consumption of the starting salicylaldimines **5a−f**, **6a−g** and either nickel−dimethyl source is particularly fast in benzene solution as evidenced by the observable ceasing of methane evolution within 5−10 min at 25 °C. ^{1}H NMR monitoring of a 1:1 reaction mixture of **5a** and [(pyridine)$_2$Ni(CH_3)$_2$] in benzene-d_6 (J. Young tube) reveals a clean conversion to one nickel−methyl-containing species and methane within less than 15 min at 25 °C. At this point, excess pyridine present in the reaction mixture results in dynamical broadening of all signals observed. However, after removal of the (frozen) solvent and excess pyridine, and redissolution in benzene-d_6, exclusively one (sharp) set of signals is observed by ^{1}H NMR spectroscopy originating from compound **7a-pyr**. Reaction of salicylaldimines **5a−f**, **6a−g** with both [(tmeda)Ni(CH_3)$_2$] and [(pyridine)$_2$Ni(CH_3)$_2$] gave similarly high yields. Table 2 gives the method performing better overall including preparative workup.

Additional phenolic (i.e., acidic) protons present in the terphenyl moieties of salicylaldimines **5c** and **6c** or complexes **7c-pyr** and **8c-pyr** (R^3 = ^{t}Bu, R^4 = OH) do not interfere with either nickel−methyl source, that is, [(tmeda)Ni(CH_3)$_2$], [(pyridine)$_2$Ni(CH_3)$_2$], or the formed products **7c-pyr**, **8c-pyr** to a noticeable extent on the basis of (a) the integration of an observable ^{1}H NMR resonances of these phenolic protons for **7c-pyr** and **8c-pyr**, (b) similarly high stabilities of benzene-d_6 solutions of all complexes **7** and **8** over weeks without detectable decomposition or formation of methane in the absence of oxygen, and (c) similarly high yields as compared to the synthesis of all other complexes **7-pyr** and **8-pyr**. The high selectivity of either nickel−methyl source for the salicyl OH-group as well as the stability of complexes **7c**, **8c** is likely related to a higher acidity when compared to the terphenyl OH-groups. In addition, the terphenyl OH-groups are more sterically protected by the adjacent ^{t}Bu-groups when compared to the salicyl OH-group.

All complexes **7-pyr** and **8-pyr** are diamagnetic in solution as evidenced by sharp resonances except for the (somewhat dynamically broadened) signals of the pyridine ligand in the ^{1}H and ^{13}C NMR spectra. Therefore, a square planar coordination geometry of the nickel center is proposed for all new complexes **7-pyr** and **8-pyr**. Most characteristic, the nickel-bound methyl groups resonate between −0.5 and −1.1 ppm in the ^{1}H NMR and between −7.6 and −9.1 in the ^{13}C NMR spectra, respectively, for all complexes **7-pyr** and **8-pyr**. The 2′- and 6′-positions as well as substituents in the 3′- and 5′-positions of the *m*-terphenyl moieties give rise to one set of ^{13}C and ^{1}H NMR resonances for all complexes **7-pyr** and **8-pyr**, respectively, at 25 °C, indicating free rotation of the 3′,5′-disubstituted arene rings (for the numbering, refer to Chart 2).[21]

(18) Kaschube, W.; Pörschke, K. R.; Wilke, G. *J. Organomet. Chem.* **1988**, *355*, 525−532.

(19) Cámpora, J.; Conejo, M. d. M.; Mereiter, K.; Palma, P.; Pérez, C.; Reyes, M. L.; Ruiz, C. *J. Organomet. Chem.* **2003**, *683*, 220−239.

(20) We note that the versatility of [(pyridine)$_2$Ni(CH_3)$_2$] is somewhat restricted when compared to [(tmeda)Ni(CH_3)$_2$]: While stronger coordinating and less volatile donor ligands such as phosphines displace pyridine in, for example, complex **7a-pyr**, preparation of similar acetonitrile complexes requires the use of [(tmeda)Ni(CH_3)$_2$], because displacement of pyridine by acetonitrile is not complete even when a huge excess of acetonitrile is used: Göttker-Schnetmann, I.; Berkefeld, A.; Mecking, S., unpublished results.

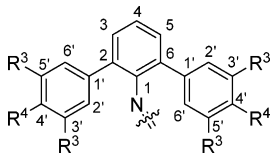
(21) For a detailed investigation on the rotation in related *ortho*-monoalkyl-biaryls, see: (a) Lunazzi, L.; Mazzanti, A.; Minzoni, M.; Anderson, J. E. *Org. Lett.* **2005**, *7*, 1291−1294. (b) Mazzanti, A.; Lunazzi, L.; Minzoni, M.; Andreson, J. E. *J. Org. Chem.* **2006**, *71*, 5474−5481.

Table 2. Synthesis of κ^2-(*N*,*O*)-Salicylaldiminato Nickel(II) Methyl Pyridine Complexes 7-pyr and 8-pyr

	7a-pyr	7b-pyr	7c-pyr	7d-pyr	7e-pyr	7f-pyr	8a-pyr	8b-pyr	8c-pyr	8d-pyr	8e-pyr	8f-pyr	8g-pyr
R^1	I	I	I	I	I	I	Ant	Ant	Ant	Ant	Ant	Ant	Ant
R^2	I	I	I	I	I	I	H	H	H	H	H	H	H
R^3	CF_3	^{t}Bu	^{t}Bu	Me	Me	MeO	CF_3	^{t}Bu	^{t}Bu	Me	Me	MeO	MeO
R^4	H	H	OH	H	MeO	H	H	H	OH	H	MeO	H	MeO
yield [%][a]	>90[b]	93	91	>90[b]	91	>90[b]	92	91	91	89	96	92	92
method	A	A	B	A	B	A	B	B	A	A	B	B	B

[a] Isolated yield. [b] Yield taken from ref 15. (A) Starting from [(tmeda)Ni(CH_3)$_2$]. (B) Starting from [(pyridine)$_2$Ni(CH_3)$_2$].

Chart 2. Numbering of the *m*-Terphenyl Moieties in Complexes 7-pyr and 8-pyr



Additional features comprise the observation of $^4J_{HH}$ couplings (1.8−2.2 Hz) for the 4- and 6-protons of the 3,5-diiodosalicylaldimine moieties of complexes **7-pyr**. Further, characteristic high field shifts of the averaged *ortho*- (δ = 7.40−7.32), *meta*- (5.82−5.54 ppm), and the *para*-protons (6.27−6.14 ppm) of the nickel-bound pyridine ligand in complexes **8-pyr** are observed (likely arising from anisotropic shielding by the anthryl substituent) when compared to complexes **7-pyr** (*o*-H, 8.34−8.18; *m*-H, 6.40−6.31; *p*-H, 6.70−6.62 ppm) and free pyridine (for details, see experimental section).

While complexes **7a**−**f-pyr** and **8a**−**e-pyr** are isomerically pure by ^{1}H NMR spectroscopy and exhibit a *trans*-arrangement of the phenolic oxygen and the methyl group bound to the nickel center as evidenced by NOESY experiments of **7b**-,**7c-pyr** and **8a**−**c-pyr**, minor amounts of a second isomer with a supposed *cis*-arrangement of nickel bound oxygen and the methyl group are detectable for the anthryl-substituted complexes **8f-pyr** (*trans*:*cis*: ca. 12:1) and **8g-pyr** (trans:cis: ca. 20:1).[22] Such a mixture of *trans*- and *cis*-isomers (in a 3:1 ratio) was also observed for the anthryl-substituted complex **1a-CH$_3$CN** (Chart 1) in solution, with the *trans*- and *cis*-isomers exchanging on the NMR time scale, while complex **1b-PPh$_3$** (Chart 1) exhibits exclusively *trans*-geometry in solution.[12,16b] For comparison of catalytic activity, we have prepared the novel pyridine complex **1a-pyr** and note here that in benzene-d_6 solution **1a-pyr** exists exclusively as the *trans*-isomer. We therefore conclude that while fine-tuning (cf., the *trans*:*cis* ratios in **8f-pyr** and **8g-pyr**) is already influenced by pure electronics of the ligand backbone (i.e., the salicylaldimine **6f** or **6g** in complexes **8f-pyr** and **8g-pyr**), a more coarse influence is exerted by the stereoelectronic nature of the respective donor-ligand (i.e., pyridine vs acetonitrile in **1a-pyr** vs **1a-CH$_3$CN**).

X-ray diffraction analyses of complexes **7b-pyr** and **8f-pyr** exhibit a slightly (tetrahedral) distorted square planar coordination geometry of the nickel center and confirm a *trans*-arrangement of the oxygen atom (O1) and the nickel-bound methyl group (C1) also in the solid state (Figures 1 and 2).

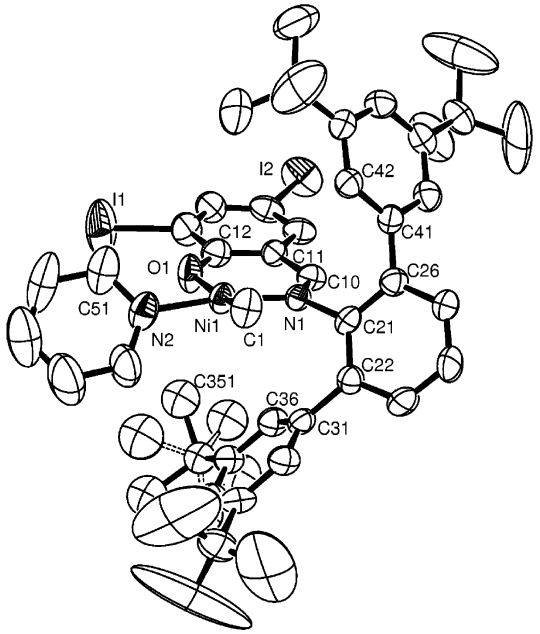


Figure 1. X-ray diffraction analysis of complex **7b-pyr** with 50% probability ellipsoids. The solid-state structure is disordered with the *tert*-butyl group C351−C357 occupying two split positions. Hydrogen atoms and cocrystallized solvent molecules are omitted for clarity. Selected bond distances and angles are given in Table 3.

Bond distances and angles for the nickel center are in the expected range and show only minor deviations when compared to **7a-pyr**[15] and **1a-CH$_3$CN**[12] (Table 3).

The positioning of the terphenyl moiety closely resembles that in the already known structure of **7a-pyr**,[15] given, for example, by similar dihedral angles C10−N1−C21−C26 (**7a-pyr**, 72°; **7b-pyr**, 62°; **8f-pyr**, 65°), C21−C26−C41−C42 (**7a-pyr**, 40°; **7b-pyr**, 62°; **8f-pyr**, 46°), and C21−C22−C31−C36 (**7a-pyr**, 63°; **7b-pyr**, 48°; **8f-pyr**, 46°) (for the numbering scheme, refer to Figure 1). A marked difference found in the coordination sphere of the nickel center of these complexes is the positioning of the pyridine ring, given, for example, by the dihedral angle O1−Ni−N2−C51 −51° (**7b-pyr**), −47° (**8f-pyr**), when compared to −107° (**7a-pyr**).

In view of the influence of the 3′,5′-substituents of the terphenyl moieties on the polymer microstructure obtained (vide infra), we note here that the closest distance between the nickel center and a *tert*-butyl methyl-carbon in **7b-pyr** (i.e., Ni1−C351, Figure 1) amounts to 4.190 as compared to 4.355 Å for the shortest Ni−CF_3-distance in the solid-state structure of complex **7a-pyr**.[15] With respect to complex **8f-pyr**, the closest distance of the nickel center to a 3′,5′-methoxy-carbon atom on the terphenyl substituent (i.e., Ni1−C431) amounts to 4.232 Å (Figure 2). Further, we find the anthryl substituent of complex **8f-pyr** similarly twisted against the salicylaldimine plane, given by, for example, C12−C13−C61−C62 77° (**8f-pyr**) when compared to 65° (**1a-CH$_3$CN**)[12] and 80° (**1b-PPh$_3$**).[16b]

(22) One reviewer pointed to the possibility that the minor complex present could be the pyridine-free dimeric species [(κ^2-*N*,*O*)NiMe)$_2$]. We cannot totally exclude the reversible formation of the proposed pyridine-free dimers (as irreversibly observed for (κ^2-*P*,*O*)-nickel complexes). However, NMR spectra of single crystals of complex **8f-pyr·1.5C$_6$H$_6$** obtained by recrystallization exhibit the same isomeric ratio as amorphous material obtained after solvent-sublimation from synthetic method B, thus excluding an irreversible formation of such dimer and free pyridine. In addition, the elemental analysis of complexes **8f-pyr** (and somewhat less convincing **8g-pyr**) is in accordance with a higher nitrogen content than expected for the pyridine-free dimeric structure.

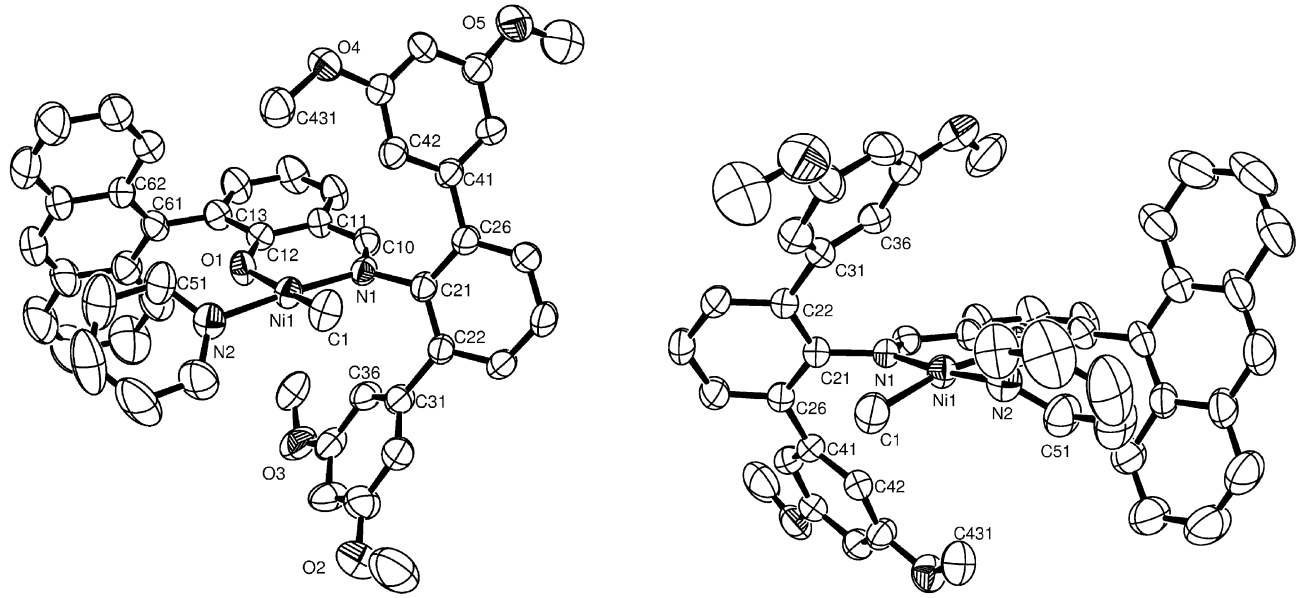


Figure 2. X-ray diffraction analysis of complex **8f-pyr** with 50% probability ellipsoids in two orientations showing the coordination geometry at nickel (left) and the twisting of terphenyl and anthryl moieties (right). Hydrogen atoms and cocrystallized solvent molecules are omitted for clarity. Selected bond distances and angles are given in Table 3.

Table 3. Selected Bond Distances and Angles at the Nickel Center in Complexes 7a-pyr, 7b-pyr, 8f-pyr, and 1a-CH_3CN[a]

	Ni−N1 [Å]	Ni−O1 [Å]	Ni−C1 [Å]	Ni−N2 [Å]	O1−Ni−N1 [deg]	N1−Ni−C1 [deg]	C1−Ni−N2 [deg]	N2−Ni−O1 [deg]
7b-pyr	1.900(7)	1.949(7)	1.991(9)	1.890(7)	92.7(3)	95.3(3)	88.9(3)	85.1(3)
8f-pyr	1.897(2)	1.9051(15)	1.936(2)	1.912(2)	93.21(7)	94.37(10)	88.89(10)	84.25(8)
7a-pyr[b]	1.896(3)	1.908(3)	1.931(4)	1.897(4)	92.64(12)	96.25(17)	87.47(17)	83.69(13)
1a-CH_3CN[c]	1.8872(16)	1.9107(13)	1.931(2)	1.8588(19)	94.12(6)	92.88(9)	89.07(9)	83.87(6)

[a] For the numbering scheme, refer to Figure 1. [b] Taken from ref 15. [c] Taken from ref 12.

Table 4. Polymerization Results with Complexes 1a-pyr, 7-pyr, and 8-pyr as Precatalysts[a]

entry	precatalyst	yield [g PE]	TON 10^{-4} × mol [C_2H_4] × mol^{-1} [Ni]	TOF 10^{-4} × mol [C_2H_4] × mol^{-1} [Ni] × h^{-1}	T_m [°C]	branches /1000C	crystallinity[e] [%]	M_n[f]	M_w/M_n
1	**1a-pyr**	8.55	3.1	4.6	131	6[c]	47	200	2.0
2	**7a-pyr**[b]	7.48	2.7	4.0	124	10[c]	50	16	3.0
3	**8a-pyr**	7.97	2.8	4.3	117	13[c]	44	43	3.0
4	**7b-pyr**	9.41	3.6	5.4	90	38[c]	31	11	2.7
5	**8b-pyr**	12.40	4.7	7.1	96	31[c]	32	11	2.8
6	**7c-pyr**	9.85	3.5	5.3	92	32[c]	28	14	2.0
7	**8c-pyr**	8.28	3.0	4.5	96	30[c]	35	16	2.8
8	**7d-pyr**[b]	6.10	2.1	3 3		76[d]		1.1	2.1
9	**8d-pyr**	9.16	3.3	4.9		92		3.2	3.9
10	**7e-pyr**	4.47	1.7	2.6		81[d]		0.8	2.1
11	**8e-pyr**	4.71	1.8	2.7		88[d]		0.9	2.7
12	**7f-pyr**[b]	4.50	1.6	2.4		79[d]		1.9	2.5
13	**8f-pyr**	3.59	1.3	1.9		80[d]		4.0	4.3
14	**8g-pyr**	4.27	1.5	2.3		78[d]		10[g]	5.3

[a] Reaction conditions: 10 μmol of precatalyst, 50 °C, 40 min, 40 bar of ethylene in 100 mL of toluene. [b] Catalytic activity was reported in ref 15; values given here differ slightly due to a different polymerization protocol applied here. [c] Exclusively methyl branches detected by ^{13}C NMR spectroscopy. [d] >80% methyl branches by ^{13}C NMR spectroscopy. [e] Obtained from DSC data on the basis of $\Delta H_m = 293$ J g^{-1} for 100% crystallinity. [f] In 10^3 g mol^{-1}; obtained by GPC versus linear polyethylene standards at 160 °C. [g] Bimodal distribution.

Catalytic Ethylene Polymerization with κ^2-(*N*,*O*)-Salicylaldiminato Nickel(II) Methyl Pyridine Complexes 7a−f-pyr and 8a−g-pyr. Complexes **7a−f-pyr** and **8a−g-pyr** as well as **1a-pyr** behave as single component ethylene polymerization catalysts at temperatures above 15 °C, reaching their highest productivities in the range between 40 and 75 °C. Probably due to impurities in the ethylene used (3.5 grade, 99.95% purity), productivities did not increase linearly with increasing precatalyst concentrations at very low precatalyst concentrations. That is, smaller amounts than 2 μmol of precatalysts, for example, **8a−c-pyr** (applied as a freshly prepared stock solution in each case), did not yield substantial amounts of polyethylenes. Such effects might be induced by solvent impurities at very low catalyst loadings. However, polymerization runs using, for example, 10 μmol of precatalyst **8a-pyr**, 50 °C, 40 bar of ethylene in 200 mL of toluene instead of 100 mL of toluene result in similar turnover frequencies (4.82×10^4 TO h^{-1}, as compared to 4.3×10^4 TO h^{-1}, Table 5, entry 2 as compared to Table 4, entry 3), which underlines the notion that solvent impurities are not responsible for these activity effects. To obtain reliable polymerization data without substantial reactor clogging (e.g., with precatalysts **1a-pyr**, **7a-pyr**, and **8a-pyr**, vide infra), we have conducted standardized polymerization reactions for 40 min under 40 bar of ethylene at 50 °C using 10 μmol of catalyst and monitored the ethylene uptake by means of mass-flow meters. By assuming catalyst-independent saturation kinet-

Table 5. Polymerization Results for Catalysts Derived from Terphenylamine 4a[a]

entry	precatalyst	*n*[cat] [μmol]	yield [g PE]	TOF $10^4 \times$ mol [C_2H_4] $\times$ mol^{-1} [Ni] $\times$ h^{-1}	T_m [°C]	branches /1000C[b]	crystallinity[c] [%]	M_n[d]	M_w/M_n
1	**7a-pyr**	16	22.6	4.98	124	10	50	16	3.0
2	**8a-pyr**	10	13.5	4.82	117	13	44	43	3.0
3	**9a-pyr**	40	11	0.98	111	15	45	20	2.3
4	**10a-pyr**	20	15	2.68	114	15	49	8.5	2.4
5	**11a-pyr**	15	1.50	0.35	114	14	49	9.6	2.2

[a] Reaction conditions: 50 °C, 60 min, 40 bar of ethylene in 200 mL of toluene. [b] Exclusively methyl branches detected by ^{13}C NMR spectroscopy. [c] Obtained from DSC data on the basis of $\Delta H_m = 293$ J g^{-1} for 100% crystallinity. [d] In 10^3 g mol^{-1}; obtained by GPC at 160 °C versus linear polyethylene standards.

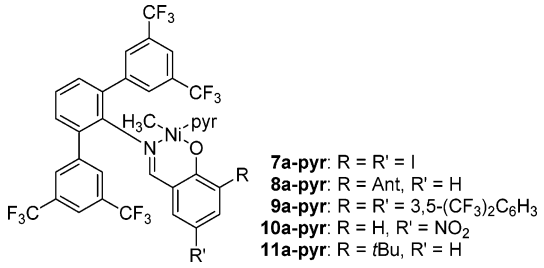
ics of the polymerization reaction with respect to [ethylene],[23] this procedure enabled (a) comparison of the activity and stability of anthryl-substituted (**1a-pyr** and **8a−g-pyr**) versus diiodo-substituted catalysts **7a−f-pyr**, and (b) comparison of the microstructures of the obtained polyethylenes as a function of the precatalyst (Table 4).

Notably, while anthryl-substituted complex **8b-pyr** is the most active precatalyst under these polymerization conditions (TOF ca. 71.000 TO h^{-1}, entry 5), all diiodo-substituted complexes **7-pyr** perform similarly well when compared to the respective anthryl-substituted complexes **8-pyr**, and to **1a-pyr**. Further, the anthryl versus diiodo substitution does not exert a major influence on the degree of branching of the obtained polyethylenes.

In contrast, and as already found for complexes **7a-**,**7d-**,**7f-pyr**, the degree of branching of obtained polyethylenes is highly sensitive to the 3′,5′-substitution pattern of the terminal arene rings of the terphenyl moieties in both complexes **7-pyr** and **8-pyr**. As these 3′,5′-substituents appear to be far away from the catalytically active nickel center (vide supra, Figures 1 and 2 and ref 15), we had suggested earlier for complexes **7a-**,**d-**,**f-pyr** that the microstructure control exerted by these substituents is more electronic than steric in nature.[15] That is, more electron-deficient *N*-aryl substituents result in higher molecular weights and lower degrees of branching supposedly by suppressing chain walking and chain transfer relative to ethylene insertion. To further probe this hypothesis, complexes **7b-**,**7c-pyr**, **8b-**,**8c-pyr**, containing *tert*-butyl substituents (even bulkier than the CF_3-groups in **7a-pyr** and **8a-pyr**) with properties electronically similar to those of the methyl-substituted complexes **7d-pyr** and **8d-pyr**, have been prepared for this study. These complexes, however, produce polyethylenes with (a) significantly higher molecular weight (e.g., **7b-pyr**: $M_n = 11 \times 10^3$ g mol^{-1}) and less branching (e.g., **7b-pyr**: 38 methyl branches per 1000 carbon atoms) than that obtained with **7d-pyr** ($M_n = 1.1 \times 10^3$ g mol^{-1}, 66 methyl-, 4 ethyl-, 6 C_{4+}-branches per 1000 carbon atoms) or **8d-pyr** ($M_n = 3.2 \times 10^3$ g mol^{-1}, 72 methyl-, 6 ethyl- 14 C_{4+}-branches), and (b) significantly higher degree of branching than that obtained with complexes **7a-pyr** (10 methyl branches per 1000 carbon atoms) or **8a-pyr** (13 methyl branches per 1000 carbon atoms). Therefore, it seems that, in addition to an increased electron-withdrawing character of the 3′,5′-substituents, sterically more demanding 3′,5′-substituents also favor the formation of higher molecular weight polyethylenes with low branching content,

(23) The kinetic order of the catalysts under investigation with respect to ethylene is likely 0th order in ethylene at 40 bar. We have not conducted systematic studies with respect to the order in ethylene, but we have observed that for exemplified catalysts (**7a-pyr**, **8a-pyr**, and **8f-pyr**) low ethylene pressures (20, 10, and 5 bar of ethylene) result in increasingly lower activities, while ethylene pressures >30 bar result in saturation behavior. Polymerization conditions studied here were intended to compare activities and polymer microstructures under identical reaction conditions, that is, including saturation behavior.

Chart 3. κ^2-(*N*,*O*)-Salicylaldiminato Nickel(II) Methyl Pyridine Complexes Derived from Terphenylamine 4a



even though the distance of these groups to the nickel center is quite high (vide supra).

As already stated, the degree of branching of the polyethylenes obtained with complexes **7-pyr** and **8-pyr** is mainly insensitive to the substitution of the salicyl-ring and highly sensitive to the respective terphenyl substituent (vide supra). If this observation holds true in general, complexes **9a−11a-pyr** (for details, see experimental part) derived from terphenylamine **4a** should produce polyethylenes with a microstructure similar to that of **7a-pyr**, **8a-pyr**, despite the variety of stereoelectronic modifications exerted, for example, by the *o*-H and *p*-NO_2 versus *o*-^{t}Bu and *p*-H substituents in **10a-pyr** and **11a-pyr** (Chart 3). Polymerization results with these complexes are summarized in Table 5 and confirm the more general notion that it is the terphenyl substituent in these catalysts that exclusively controls the degree of branching.

Under the conditions studied here (50 °C; reaction times of 40−120 min), all catalysts are quite stable. In more detail, complexes **1a-pyr** and **7a−11a-pyr** derived from 2,6-diisopropylaniline or terphenylamine **4a** appear to exhibit constant polymerization activities over time as evidenced by the respective mass-flow traces (for details, see Supporting Information) and polymer yields in 40- and 60-min (and for **7a-pyr**: 120 min) polymerization runs. Further, complexes **7b**,**c-pyr**, **8b**,**c-pyr** show a slight decrease in polymerization activity over time reaching one-half of the initial activity after ca. 1.5−2.0 h, while one-half of the initial activities after ca. 1 h were observed with complexes **7d−f-pyr**, **8d−g-pyr**. At 70 °C, the decrease in polymerization activities over time is more pronounced as evidenced by the mass-flow traces of, for example, polymerizations with precatalyst **8b**,**c-pyr** (Supporting Information).

While, in principle, mass transfer limitations due to coprecipitation of the catalyst with the formed polyethylene may result in decreasing ethylene consumption, we note here that only in case of catalysts derived from 2,6-diisopropylaniline or terphenylamine **4a** (i.e., **1a-pyr**, **7a−11a-pyr**) were substantial amounts of precipitated polyethylene present in the crude reaction mixture, while reaction mixtures obtained with complexes **7d−f-pyr** and **8d−g-pyr** remained homogeneous throughout the polymerization. We therefore conclude that the positive effect of the anthryl substituent in complexes **1a-L** on the long-

term stability does not hold in general when the anthryl substituent is combined with terphenyl substituents as in complexes **8-pyr**. Following the rational given by Grubbs et al.,[12] that the anthryl substituent of complexes **1a-L** suppresses the formation of catalytically inactive bis[(κ^2-*N*,*O*)-salicylaldiminato]nickel complexes due to its bulkiness, and considering similarly sterically congested situations for the bis-chelation of salicylaldimines **6a**−**g** (i.e., bearing anthryl and terphenyl substituents) by nickel(II), we believe that a different decomposition mechanism might be operative for complexes **8-pyr** when compared to complexes **1a-L**.

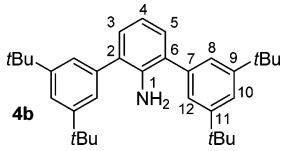
Summary and Conclusion

A new high yield synthesis of (κ^2-*N*,*O*)salicylaldiminato nickel methyl complexes **1a-pyr**, **7-pyr**, and **8-pyr** from salicylaldimines **5a**−**f**, **6a**−**g** and [(pyridine)$_2$Ni(CH$_3$)$_2$] has been presented. Complexes **7-pyr** and **8-pyr** were studied in the polymerization of ethylene and proved to be highly active with turnover frequencies as high as ca. 71.000 mol ethylene mol^{-1} [Ni] h^{-1} at 50 °C, 40 bar of ethylene. Anthryl-substituted complexes **1a-pyr** and **8-pyr** exhibit polymerization activities similar to those of complexes **7-pyr** derived from 3,5-diiodosalicylaldehyde. Independent of the stereoelectronic modification of the salicyl-ring, the 3′,5′-substitution of the terphenyl group has a major impact on the polyethylene microstructure. Electron-withdrawing as well as sterically demanding 3′,5′-substituents decrease the degree of branching (and increase molecular weight) in the obtained polyethylenes as compared to electron-donating and small substituents. Complexes **1a-pyr** and **7a**−**11a-pyr** derived from terphenylamine **4a** are highly stable polymerization catalysts, while all other complexes **7-pyr** and **8-pyr** slowly deactivate under the reaction conditions studied.

Experimental Section

General Considerations and Materials. All manipulations of air- and moisture-sensitive substances were carried out using standard Schlenk, vacuum, and glovebox techniques under argon or nitrogen. Pentane and dichloromethane were distilled from calcium hydride, benzene and toluene from sodium, and diethyl ether and THF from blue sodium benzophenone ketyl under argon prior to use. Pyridine and triethylamine were deoxygenated, distilled from potassium hydroxide, and stored in Rotaflo-flasks prior to use. Petrol ether (bp 55−85 °C) for column chromatography was distilled once by rotavap to remove high boiling impurities. All other solvents were commercial grade. 2-Bromoanisole, anthrone, BBr_3, 1,2-dibromoethane, 2,6-dibromoaniline, 3,5-diiodosalicylaldehyde, 3-(*tert*-butyl)salicylaldehyde, and 5-nitrosalicyladehyde were used as received from Aldrich. Paraformaldehyde was dried over P_2O_5 prior to use. 3,5-Bis[3,5-bis(trifluoromethyl)-phenyl]-salicylaldehyde and complex **9a-pyr** were prepared according to known procedures.[24] [(tmeda)Ni(CH$_3$)$_2$][18] was purchased from MCat and stored at −30 °C in a glovebox prior to use. [(pyridine)$_2$Ni-(CH$_3$)$_2$][19] was synthesized by a modified literature procedure and stored at −30 °C in a glovebox prior to use. Terphenylamines **4a**,**d**,**f** were synthesized in analogy to ref 15. Salicylaldimines **5a**,**d**,**f** described in ref 15 were obtained in improved yield using the general procedure described here. Terphenylamine **4c** and salicylaldimines **5c**,**6c** were synthesized according to ref 9. Boronic acids were synthesized in analogy to known standard procedures except for 3,5-di(*tert*-butyl)-4-hydroxyphenyl boronic acid, which was prepared in analogy to a known procedure.[25] Column chromatography: Merck silica gel 60. TLC: Merck silica gel 60F$_{254}$ plates. R_f-values refer to TLC tests. NMR spectra were recorded on a Varian Inova 400 or a Bruker Avance DRX 600 instrument. ^{1}H chemical shifts were referenced to residual protiated solvent. ^{13}C chemical shifts were referenced to deuterated solvents. The assignment of chemical shifts for new salicylaldimines and complexes is based on ^{1}H, ^{1}H,^{1}H-gCOSY, ^{13}C{^{1}H}, DEPT135, ^{1}H,^{13}C-gHMQC, and ^{1}H,^{13}C-gHMBC NMR experiments. Elemental analyses were carried out at the Department of Chemistry at the University of Konstanz. Polymerization reactions were conducted in a 300 mL Büchi miniclave equipped with a heating/cooling jacket supplied by a thermostat controlled by a thermocouple dipping into the polymerization mixture. Ethylene uptake of the autoclave was monitored via Bronkhorst mass-flow meters. Ethylene of 3.5 grade supplied by Gerling Holz + Co. was used without further purification. Molecular weights of obtained polyethylenes were determined by NMR analyses or GPC versus linear polyethylene standards on a PL220 instrument equipped with mixed B columns using trichlorobenzene/0.0125% BHT at 160 °C. ^{1}H and ^{13}C NMR analyses of obtained polyethylenes were conducted in 1,1,2,2-tetrachloroethane-d_2 at 130 °C. Integration of ^{13}C NMR spectra is based on inverse gated decoupled experiments with an acquisition time of ca. 1.2 s and a relaxation delay of 1 s in the presence of 0.5 wt % Cr(acac)$_3$ as relaxation aid. Differential scanning calorimetry (DSC) of obtained polymers was measured on a Netzsch DSC 204 F1 with a heating/cooling rate of 10 °C min^{-1}. DSC data reported are from second heating cycles.

General Procedure for the Preparation of Terphenylamines (4a−**g).** To a mixture of 2,6-dibromoaniline, 2.3 equiv of the respective aryl boronic acid, 1 mol % Pd(dba)$_2$, and 2.1 mol % PPh$_3$ in an argon-filled Schlenk flask was added toluene (1.5 mL per mmol boronic acid). The suspension was stirred at 25 °C until the initially purple suspension turned orange (ca. 10 min), ethanol/water (1:1) (0.5 mL per mmol boronic acid) and 4 equiv of Na$_2$CO$_3$ were added, and the suspension was heated to 95 °C with vigorous stirring for 10−48 h. The resulting biphasic mixture was stirred for 30−60 min under air (resulting in formation of palladium black) and poured into a separatory funnel, and water and diethyl ether were added until all salts and organic material dissolved. The organic layer was separated (and filtrated through a plug of celite to remove Pd black), the aqueous phase was extracted with additional 2 × 25 mL of diethyl ether, and the combined organic phases were concentrated under reduced pressure (35 °C, 650 mbar, then 20 mbar). Analytically pure terphenylamines **4a**−**g** were obtained after column chromatography of the residues on silica. Analytical data of terphenylamines **4a**,**d**,**f** are given in ref 15.

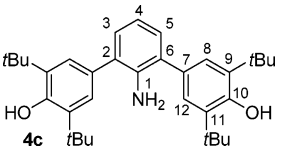


2,6-Bis[3,5-di(*tert*-butyl)phenyl]aniline (4b). Following the general procedure, 1.64 g (3.49 mmol, 87%) of 2,6-bis[3,5-di(*tert*-butyl)phenyl]aniline (**4b**) was obtained from 2,6-dibromoaniline (1.004 g, 4 mmol), 3,5-di(*tert*-butyl)phenylboronic acid (2.155 g, 9.2 mmol), Pd(dba)$_2$ (23 mg, 41 μmol), PPh$_3$ (22.6 mg, 86 μmol), and Na$_2$CO$_3$ (1.70 g, 16 mmol) as a white solid after 16 h at 95 °C and column chromatography using petrol ether/toluene (30:1, R_f = 0.2) as eluent. ^{1}H NMR (399.8 MHz, C$_6$D$_6$, 25 °C): δ 7.55 (s, 6H, 2 × 8-, 10-, and 12-H), 7.31 (d, $^3J_{HH}$ = 7.6 Hz, 2H, 3- and 5-H), 6.91 (t, $^3J_{HH}$ = 7.6 Hz, 1H, 4-H), 3.79 (s, 2H, NH$_2$), 1.30 (s, 36H,

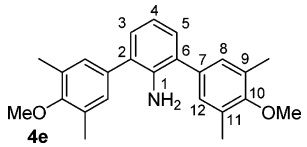
(24) Wehrmann, P.; Zuideveld, M.; Thomann, R.; Mecking, S. *Macromolecules* **2006**, *39*, 5995−6002.

(25) Irlapati, N. R.; Baldwin, J. E.; Adlington, R. M.; Pritchard, G. J. *Org. Lett.* **2003**, *5*, 2351−2354.

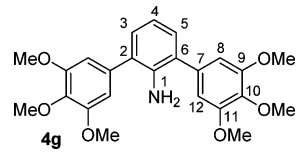
4 × ^{t}Bu). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ 151.5 (C_q, 2 × C9 and C11), 141.7 (C_q, C1), 140.2 (C_q, 2 × C7), 130.1 (CH, C3 and C5), 129.2 (C_q, C2 and C6), 124.1 (CH, 2 × C8 and C12), 121.1 (CH, 2 × C10), 118.5 (CH, C4), 35.0 (C_q, 4 × ^{t}Bu), 31.6 (CH3, 4 × ^{t}Bu). Anal. Calcd for $C_{34}H_{47}N$ (469.74 g mol^{-1}): C, 86.93; H, 10.08; N, 2.98. Found: C, 86.77; H, 9.82; N, 3.18.



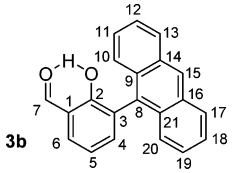
2,6-Bis[3,5-di(*tert*-butyl)-4-hydroxyphenyl]aniline (4c). Following the general procedure, 1.631 g (3.25 mmol, 81%) of 2,6-bis[3,5-di(*tert*-butyl)-4-hydroxyphenyl]aniline (**4c**) was obtained from 2,6-dibromoaniline (1.004 g, 4 mmol), 3,5-di(*tert*-butyl)-4-hydroxyphenylboronic acid (2.300 g, 9.2 mmol), $Pd(dba)_2$ (23 mg, 41 μmol), PPh_3 (22.6 mg, 86 μmol), and Na_2CO_3 (1.70 g, 16 mmol) as an off-white solid after 20 h at 95 °C and column chromatography using petrol ether/toluene (10:1) as eluent [R_f = 0.2 (PE/E = 4:1)]. ^1H NMR (399.8 MHz, C_6D_6, 25 °C): δ 7.52 (s, 4H, 2 × 8- and 12-H), 7.30 (d, $^3J_{HH}$ = 7.6 Hz, 2H, 3- and 5-H), 6.91 (t, $^3J_{HH}$ = 7.6 Hz, 1H, 4-H), 4.99 (s, 2H, 2 × OH), 3.82 (s, 2H, NH_2), 1.36 (s, 36H, 4 × ^{t}Bu). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ 153.4 (C_q, 2 × C10), 142.1 (C_q, C1), 136.5 C_q, 2 × C9 and C11), 132.1 (C_q, 2 × C7), 129.9 (CH, C3 and C5), 129.2 (C_q, C2 and C6), 126.5 (CH, 2 × C8 and C12), 118.5 (CH, C4), 34.5 (C_q, 4 × ^{t}Bu), 30.4 (CH_3, 4 × ^{t}Bu). Anal. Calcd for $C_{34}H_{47}NO_2$ (501.74 g mol^{-1}): C, 81.39; H, 9.44; N, 2.79. Found: C, 80.99; H, 9.62; N, 2.90.



2,6-(4-Methoxy-3,5-dimethylphenyl)aniline (4e). Following the general procedure, 526 mg (1,46 mmol, 73%) of 2,6-bis(4-methoxy-3,5-dimethyphenyl)aniline (**4e**) was obtained from 2,6-dibromoaniline (500.2 mg, 2 mmol), 4-methoxy-3,5-dimethylphenylboronic acid (830 mg, 4.6 mmol), $Pd(dba)_2$ (12 mg, 21 μmol), PPh_3 (12 mg, 46 μmol), and Na_2CO_3 (848 mg, 8 mmol) as an off-white solid after 34 h at 95 °C and column chromatography using petrol ether (PE)/diethyl ether (E) (3:1) as eluent [R_f = 0.5 (PE/E = 3:1)]. Substantial amounts of homocoupling product were also isolated. ^1H NMR (399.8 MHz, $CDCl_3$, 25 °C): δ 7.17 (s, 4H, 2 × 8- and 12-H), 7.09 (d, $^3J_{HH}$ = 7.9 Hz, 2H, 3- and 5-H), 6.85 (t, $^3J_{HH}$ = 7.9 Hz, 1H, 4-H), 3.90 (s br, 2 H, NH_2), 3.80 (s, 6H, 2 × OCH_3), 2.36 (s, 12H, 2 × 9- and 11-CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 25 °C): δ 156.2 (C_q, 2 × C10), 140.7 (C_q, C1), 135.2 and 127.8 (C_q each, C2, C6, and 2 × C7), 131.2 (C_q, C9 and C11), 129.6 (CH, 2 × C8 and C12), 129.3 (CH, C3 and C5), 118.0 (CH, C4), 59.7 (CH_3, 2 × 10-OCH_3), 16.1 (CH_3, 2 × 9- and 11-CH_3). Anal. Calcd for $C_{24}H_{27}NO_2$ (361.48 g mol^{-1}): C, 75.79; H, 7.53; N, 3.87. Found: C, 76.00; H, 7.80; N, 3.54.



2,6-Bis(3,4,5-trimethoxyphenyl)aniline (4g). Following the general procedure, 1.203 g (2.83 mmol, 71%) of 2,6-bis(3,4,5-trimethoxyphenyl)aniline (**4g**) was obtained from 2,6-dibromoaniline (1.004 g, 4 mmol), 3,4,5-trimethoxyphenylboronic acid (1.951 g, 9.2 mmol), $Pd(dba)_2$ (23 mg, 41 μmol), PPh_3 (22.6 mg, 86 μmol), and Na_2CO_3 (1.70 g, 16 mmol) as a white solid after 34 h at 95 °C and column chromatography using petrol ether (PE)/diethyl ether (E) (3:1) as eluent [R_f = 0.3 (PE/E = 3:1)]. Substantial amounts of homocoupling product were also isolated. **4g**, ^1H NMR (399.8 MHz, $CDCl_3$, 25 °C): δ 7.15 (d, $^3J_{HH}$ = 7.6 Hz, 2H, 3- and 5-H), 6.88 (t, $^3J_{HH}$ = 7.6 Hz, 1H, 4-H), 6.72 (s, 4H, 2 × 8- and 12-H), 3.91 (s, 6H, 2 × 10-OCH_3), 3.89 (s, 12H, 2 × 9- and 11-OCH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 25 °C): δ 153.4 (C_q, 2 × C9 and C11), 140.6 (C_q, C1), 137.1 (C_q, 2 × C10), 135.1 (C_q, 2 × C7), 129.5 (CH, C3 and C5), 127.9 (C_q, C2 and C6), 117.9 (CH, C4), 106.2 (CH, 2 × C8 and C12), 60.9 (CH_3, 2 × 10-OCH_3), 56.1 (CH_3, 2 × 9- and 11-OCH_3). Anal. Calcd for $C_{24}H_{27}NO_6$ (425.47 g mol^{-1}): C, 67.75; H, 6.40; N, 3.29. Found: C, 68.00; H, 6.76; N, 3.08.



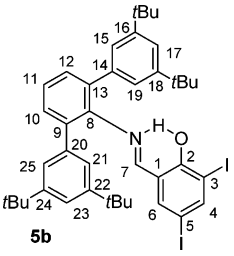
2-(9-Anthryl)anisol. A 500 mL three-neck flask equipped with a reflux condenser and a 250 mL dropping funnel was charged with magnesium turnings (1.340 g, 55.1 mmol) under argon. THF (3 mL) and 1,2-dibromoethane (100 mg) were added by syringe, and the mixture was allowed to stand for ca. 5 min without stirring until evolution of ethylene was observed. A solution of 2-bromoanisole (9.352 g, 50 mmol) in THF (120 mL) was carefully added over 45 min under gentle reflux with no heating. The mixture was stirred for an additional 30 min and cooled to −20 °C (isopropanol/dry ice). A solution of anthrone (9.715 g, 50 mmol) in 200 mL of THF/toluene (1:1) was added over 30 min under vigorous stirring. The resulting mixture was allowed to warm to 20 °C, stirred for an additional 30 min, and poured into 100 mL of ice-cold 3 N HCl. The mixture was stirred for 60 min. After phase separation, the aqueous phase was extracted with 2 × 30 mL of toluene, and the combined organic (and acidic) phases were concentrated to dryness. The resulting residue was recrystallized from boiling methanol to give 13.30 g (46.8 mmol, 93.5%) of 2-(9-anthryl)anisol as a pale yellowish solid.

2-(9-Anthryl)phenol. To a solution of 2-(9-anthryl)anisol (5.707 g, 20 mmol), tetrabutylammonium iodide (12.91 g, 33 mmol), and 60 mL of dry dichloromethane in a 250 mL Schlenk tube was added a solution of BBr_3 (6.263 g, 25 mmol) in 5 mL of dichloromethane within 5 min at −78 °C (isopropanol/dry ice). The cooling bath was removed, and the solution was stirred for 40 h at 20 °C. After careful addition of 5 mL of methanol (30 min), the resulting mixture was extracted with 4 × 50 mL of water. The organic phase was concentrated to dryness, and the resulting solid was dispersed in 5 mL of ethanol under sonication, filtrated, and washed with 2 × 2 mL of cold methanol to leave 4.925 g (18.2 mmol, 91.1%) of 2-(9-anthryl)phenol as a pale yellow solid after removal of residual solvent under high vacuum (10^{-3} mbar).

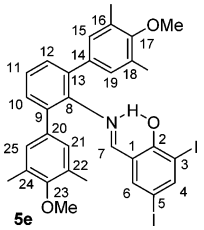
2-Hydroxy-3-(9-anthryl)benzaldehyde·$^1/_2CH_2Cl_2$ (3b). To a mixture of magnesium turnings (1.10 g, 45 mmol) and 5 mL of diethyl ether in a 500 mL Schlenk tube connected to a 100 mL dropping funnel with pressure release was added a solution of 1,2-dibromoethane (9.400 g, 50 mmol) in 80 mL of diethyl ether over 90 min and gentle reflux (*Caution*: ethylene evolution). The mixture was stirred until all magnesium dissolved, the dropping funnel was replaced by a septum, and the solvent and remaining 1,2-dibromoethane were removed under vacuum (20 °C, 10^{-3} mbar, then 60 min, 100 °C, 10^{-3} mbar). To the freshly prepared $MgBr_2$·$(Et_2O)_n$ were added solid 2-(9-anthryl)phenol (4.900 g, 18.1 mmol), paraformaldehyde (1.522 g, 50.7 mmol), and finally 150 mL of toluene. The resulting mixture was stirred with a high mass stirring

bar (alternatively a mechanical stirrer may be used) for 10 min at 20 °C, triethylamine (3.542 g, 35 mmol) was added by syringe while color change from pale yellow to orange was observed, and slowly heated to 80 °C under vigorous stirring, while the dispersed solids became sticky. After 120 min at 80 °C, a TLC test indicated consumption of the starting phenol. The organic phase was decanted and evaporated to ca. 25 mL (55 °C, 20 mbar), and the resulting mixture was cooled to 20 °C, poured into 200 mL of 1 N HCl, stirred for 20 min, and finally extracted with diethyl ether (4 × 50 mL). The combined organic phases were dried over Na_2SO_4 and concentrated to dryness (20−80 °C, 650−20 mbar). The crude product thus obtained (5.31 g) was dissolved in the minimum amount of boiling dichloromethane (ca. 7−8 mL) and allowed to slowly cool to 20 °C. The resulting solution was carefully layered with 10 mL of methanol and allowed to stand for 1 d at +5 °C after which 4.465 g (13.10 mmol, 72.4%) analytically pure crystals of 2-hydroxy-3-(9-anthryl)-benzaldehyde·$^1/_2CH_2Cl_2$ (**3b**) had deposited. Repeated crystallization from the mother liquor yielded another crop of 0.42 g (1.23 mmol, 6.8%) of compound **3b** (combined yield: 79.2%). ^{1}H NMR (399.8 MHz, C_6D_6, 25 °C): δ 11.57 (s, 1H, OH), 9.28 (s, 1H, 7-H), 8.24 (s, 1H, 15-H), 7.83 and 7.73 (m each, 2H each, 10-, 13-, 17-, and 20-H), 7.24 and 7.16 (m each, 2H and 3H, 11-, 12-, 18-, 19-, and 4-H), 6.88 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.9 Hz, 1H, 6-H), 6.63 (vt, J_{HH} = 7.8 Hz, 1H, 5-H). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25 °C): δ 196.6 (CH, C7), 160.4 (C_q, C2), 140.1 (CH, C4), 133.7 (CH, C6), 132.0 and 131.0 (C_q each, C9, C14, C16, and C21), 131.6 (C_q, C8), 129.0 and 126.6 (CH each, C10, C13, C17, and C20), 127.9 (C_q, C3) 127.8 (CH, C15), 125.9 and 125.3 (CH each, C11, C12, C18, and C19), 121.1 (C_q, C1), 119.6 (CH, C5).

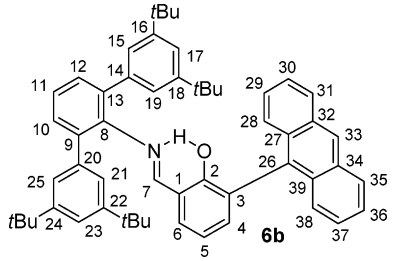
General Procedure for the Preparation of Salicylaldimines 5a−f, 6a−g. Unless otherwise noted, the following general procedure gave satisfactory results: To a mixture of 1.2 mmol of the respective salicylaldehyde **3a**,**b**, 1.2 mmol of the respective terphenylamine **4a**−**g**, and 5 mg of *p*-toluene sulfonic acid hydrate in a 50 mL flask was added 15 mL of methanol. The suspension was heated to 60 °C for 30−120 min while all starting materials dissolved, then sonicated at 25 °C for 5 min to facilitate precipitation of the product, and stirred for 12−18 h at 25 °C. The resulting suspension was cooled to 0 °C and filtrated, and the residue was washed with 3 × 3 mL of cold methanol (0 °C) and dried in vacuum (10^{-3} mbar) to yield analytically pure samples.



Salicylaldimine 5b. Following the general procedure, 824 mg (1.00 mmol, 83%) of compound **5b** was obtained after 14 h, concentration of the reaction mixture to ca. 5 mL (70 °C, 1 bar), and crystallization as a pale orange powder. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 13.85 (s br, 1H, OH), 7.93 (d, $^4J_{HH}$ = 1.9 Hz, 1H, 4-H), 7.70 (s, 1H, 7-H), 7.48 (d, $^3J_{HH}$ = 7.8 Hz, 2H, 10- and 12-H), 7.40 (t, $^3J_{HH}$ = 7.8 Hz, 1H, 11-H), 7.33 (s, 2H, 17- and 23-H), 7.18 (s, 4H, 15-, 19-, 21-, and 25-H), 6.92 (d, $^4J_{HH}$ = 1.9 Hz, 1H, 6-H), 1.25 (s, 36H, 4 × ^{t}Bu). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 °C): δ 166.3 (C_q, C7), 159.9 (C_q, C2), 150.8 (C_q, C16, C18, C22, and C24), 148.6 (CH, C4), 143.9 (C_q, C8), 139.8 (CH, C6), 138.1 and 135.9 (C_q each, C9, C13, C14, and C20), 129.9 (CH, C10 and C12), 126.3 (CH, C11), 124.3 (CH, C15, C19, C21, and C25), 121.1 (CH, C17 and C23), 120.4 (C_q, C1), 86.7 (C_q, C5), 79.1 (C_q, C3), 34.8 (C_q, 4 × ^{t}Bu), 31.4 (CH_3, 4 × ^{t}Bu). Anal. Calcd for $C_{41}H_{49}NOI_2$ (825.64 g mol^{-1}): C, 59.64; H, 5.98; N, 1.70. Found: C, 60.00; H, 6.31; N, 1.40.

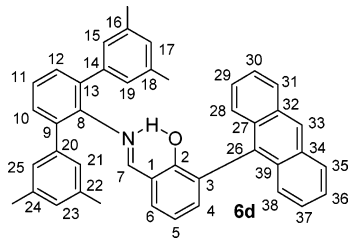


Salicylaldimine 5e. Following the general procedure, 811 mg (1.13 mmol, 94%) of compound **5e** was obtained after 12 h as an orange powder. ^{1}H NMR (399.8 MHz, C_6D_6, 25 °C): δ 13.98 (s br, 1H, OH), 7.71 (d, $^4J_{HH}$ = 1.9 Hz, 1H, 4-H), 7.32 (d, $^3J_{HH}$ = 7.7 Hz, 2H, 10- and 12-H), 7.30 (s, 1H, 7-H), 7.12 (t, $^3J_{HH}$ = 7.7 Hz, 1H, 11-H), 7.04 (s, 4H, 15-, 19-, 21-, and 25-H), 6.57 (d, $^4J_{HH}$ = 1.9 Hz, 1H, 6-H), 3.36 (s, 6H, 2 × OCH_3), 2.17 (s, 12H, 4 × CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25 °C): δ 166.3 (CH, C7), 160.3 (C_q, C2), 156.9 (C_q, C17 and C23), 149.0 (CH, C4), 144.6 (C_q, C8), 140.1 (CH, C6), 135.4 and 135.0 (C_q each, C9, C13, C14, and C20), 131.2 (C_q, C16, C18, C22, and C24), 130.6 (CH, C15, C19, C21, and C25), 130.1 (CH, C10 and C12), 126.5 (CH, C11), 120.5 (C_q, C1), 87.4 (C_q, C5), 79.8 (C_q, C3), 59.3 (CH_3, 2 × OCH_3), 16.2 (CH_3, 16-, 18-, 22-, and 24-CH_3). Anal. Calcd for $C_{31}H_{29}NO_3I_2$ (717.38 g mol^{-1}): C, 51.90; H, 4.07; N, 1.95. Found: C, 52.11; H, 4.48; N, 1.75.

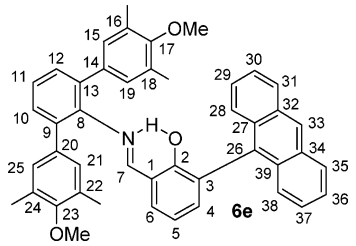


Salicylaldimine 6b. Following the general procedure, 834 mg (1.11 mmol, 93%) of compound **6b** was obtained after 14 h as a pale yellow powder. ^{1}H NMR (399.8 MHz, C_6D_6, 25 °C): δ 12.96 (s br, 1H, OH), 8.20 (s, 1H, 33-H), 7.85 (s, 1H, 7-H), 7.84 and 7.78 (m each, 2H each, 28-, 31-, 35- and 38-H), 7.46 (d, $^3J_{HH}$ = 7.6 Hz, 2H, 10- and 12-H), 7.39 (s, 6H, 15-, 17-, 19-, 21-, 23- and 25-H), 7.29 (m, 4H, 29-, 30-, 36- and 37-H), 7.15 (t, $^3J_{HH}$ = 7.6 Hz, 1H, 11-H), 7.02 (dd, $^3J_{HH}$ = 8.0 Hz and $^4J_{HH}$ = 2.0 Hz, 1H, 4-H), 6.60 (dd, $^3J_{HH}$ = 8.0 Hz and $^4J_{HH}$ = 2.0 Hz, 1H, 6-H), 6.52 (t, (dd, J_{HH} = 8.0, 1H, 5-H), 1.19 (s, 36H, 4 × ^{t}Bu). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25 °C): δ 169.3 (CH, C7), 160.0 (C_q, C2), 150.9 (C_q, C16, C18, C22, and C24), 145.9 (C_q, C8), 139.5 and 136.5 (C_q each, C9, C13, C14, and C20), 136.4 (CH, C4), 133.3 (C_q, C26), 132.0 and 131.0 (C_q each, C27, C32, C34, and C39), 132.0 (CH, C6), 130.4 (CH, C10 and C12), 128.8 and 127.5 (CH each, C28, C31, C35, and C38), 127.3 (C_q, C33), 127.1 (C_q, C3), 126.1 (CH, C11), 125.3 and 125 (CH each, C29, C30, C36, and C37), 124.8 (CH, C15, C19, C21, and C25), 121.0 (CH, C17 and C23), 119.5 (C_q, C1), 118.4 (CH, C5), 34.9 (C_q, 4 × ^{t}Bu), 31.5 (CH_3, 4 × ^{t}Bu). Anal. Calcd for $C_{55}H_{59}NO$ (750.06 g mol^{-1}): C, 88.07; H, 7.93; N, 1.87. Found: C, 87.61; H, 8.28; N, 1.70.

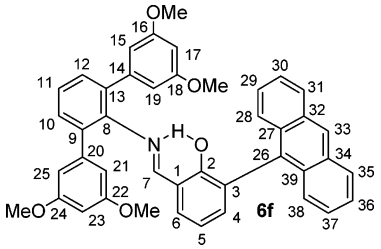
Salicylaldimine 6d. Following the general procedure, 602 mg (1.03 mmol, 86%) of compound **6d** was obtained after 12 h as a pale yellow powder. ^{1}H NMR (399.8 MHz, C_6D_6, 25 °C): δ 13.17 (s, 1H, OH), 8.23 (s, 1H, 33-H), 7.87 and 7.81 (m each, 2H each, 28-, 31-, 35-, and 38-H), 7.85 (s, 1H, 7-H), 7.35 (d, $^3J_{HH}$ = 7.9 Hz, 2H, 10- and 12-H), 7.26 (m 4H, 29-, 30-, 36-, and 37-H), 7.12 (t, $^3J_{HH}$ = 7.9 Hz, 1H, 11-H), 7.05 (s, 4H, 15-, 19-, 21-, and 25-



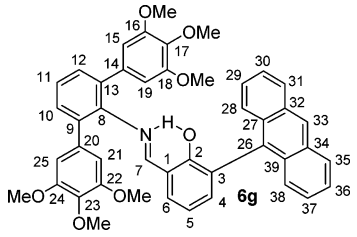
H), 7.04 (dd, $^3J_{HH}$ = 7.9 and $^4J_{HH}$ = 1.9 Hz, 1H, 4-H), 6.64 (s, 2H, 17- and 23-H), 6.60 (dd, $^3J_{HH}$ = 7.9 and $^4J_{HH}$ = 1.9 Hz, 1H, 6-H), 6.52 (vt, $^3J_{HH}$ = 7.9, 1H, 5-H), 2.16 (s, 12 H, 4 × CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ 168.5 (CH, C7), 160.1 (C_q, C2), 145.9 (C_q, C8), 139.7 and 135.4 (C_q each, C9, C13, C14, and C20), 137.7 (C_q, C16, C18, C22, and C24), 136.3 (CH, C15, C19, C21, and C25), 133.5 (C_q, C26), 132.2 (CH, C6), 132.1 and 131.1 (C_q each, C27, C32, C34, and C39), 130.1 (CH, C10 and C12), 128.9 (CH, C17 and C23), 128.8 and 127.2 (CH, C28, C31, C35, and C39), 128.2 (CH, C15, C19, C21, and C25), 127.3 (CH, C33), 127.1 (C_q, C3), 126.0 (CH, C11), 125.4 and 125.1 (CH each, C29, C30, C36, and C37), 119.2 (C_q, C1), 118.6 (CH, C5), 21.2 (CH_3, 16-, 18-, 22-, and 24-CH_3). Anal. Calcd for $C_{43}H_{35}NO$ (581.74 g mol^{-1}): C, 88.78; H, 6.06; N, 2.41. Found: C, 88.31; H, 5.78; N, 2.10.



Salicylaldimine 6e. Following the general procedure, 688 mg (1.07 mmol, 89%) of compound **6e** was obtained after 18 h as a pale yellow powder. ^1H NMR (399.8 MHz, C_6D_6, 25 °C): δ 13.14 (s, 1H, OH), 8.24 (s, 1H, 33-H), 7.89 (s, 1H, 7-H), 7.85 and 7.79 (m each, 2H each, 28-, 31-, 35-, and 38-H), 7.35 (d, $^3J_{HH}$ = 7.8 Hz, 2H, 10- and 12-H), 7.25 (m, 4H, 29-, 30-, 36-, and 37-H), 7.13 (t, $^3J_{HH}$ = 7.8 Hz, 1H, 11-H), 7.05 (dd, $^3J_{HH}$ = 7.6 and $^4J_{HH}$ = 2.0 Hz, 1H, 4-H), 6.60 (dd, $^3J_{HH}$ = 7.6 and $^4J_{HH}$ = 2.0 Hz, 1H, 6-H), 6.53 (vt, J_{HH} = 7.6 Hz, 1H, 5-H), 3.26 (s, 6H, 2 × OCH_3), 2.13 (s, 12H, 4 × CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ 168.3 (CH, C7), 160.1 (C_q, C2), 156.6 (C_q, C17 and C23), 145.8 (C_q, C8), 136.3 (CH, C4), 135.2 and 135.1 (C_q each, C9, C13, C14, and C20), 133.5 (C_q, C26), 132.2 (CH, C6), 132.0 and 131.1 (C_q each, C27, C32, C34, and C39), 130.8 (CH, C15, C19, C21, and C25), 130.7 (C_q, C16, C18, C22, and C24), 129.9 (CH, C10 and C12), 128.8 and 127.1 (CH each, C28, C31, C35, and C35), 127.2 (CH, C33), 127.1 (C_q, C3), 126.0 (CH, C11), 125.5 and 125.2 (CH each, C29, C30, C36, and C37), 119.2 (C_q, C1), 118.5 (CH, C5), 59.1 (CH_3, 2 × OCH_3), 16.1 (CH_3, 16-, 18-, 22-, and 24-CH_3). Anal. Calcd for $C_{45}H_{39}NO_3$ (641.80 g mol^{-1}): C, 84.21; H, 6.12; N, 2.18. Found: C, 84.20; H, 6.30; N, 2.10.



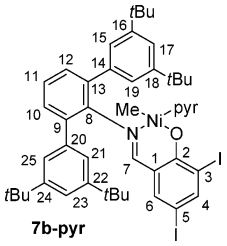
Salicylaldimine 6f. The preparation of compound **6f** failed following the general procedure due to incomplete conversion (<60% by NMR) even after prolongated reaction times. However, **6f** was obtained by the following procedure: A solution of 2-hydroxy-3-(9-anthryl)benzaldehyde·$^1/_2CH_2Cl_2$ (**3b**) (409 mg, 1.2 mmol) and 2,6-bis(3,5-dimethoxyphenyl)aniline (364 mg, 1.2 mmol) in 60 mL of toluene was refluxed for 6 h with a Dean-Starck apparatus (150 °C bath temperature). The solvent was removed under reduced pressure (50 °C, 300 to 20 mbar), 10 mL of methanol was added, and the resulting mixture was sonicated for 30 min. The resulting pale yellow solid was collected by filtration, washed with small portions of cold methanol (0 °C), and dried in a vacuum to yield 601 mg (0.93 mmol, 78%). ^1H NMR (95:5 mixture of two isomers, main isomer reported) (399.8 MHz, C_6D_6, 25 °C): δ 13.41 (s, 1H, OH), 8.23 (s, 1H, 33-H), 7.84 (vd, J = 8.0 Hz, 2H, 28- and 38-H), 7.81 (s, 1H, 7-H), 7.75 (vd, J = 8.0 Hz, 31- and 35-H), 7.37 (d, $^3J_{HH}$ = 7.8 Hz, 2H, 10- and 12-H), 7.26 (m, 4H, 29-, 30-, 36-, and 37-H), 7.05 (m, 2H, 11-H and 4-H), 6.71 (s, 4H, 15-, 19-, 21-, and 25-H), 6.63 (m, 1H, 6-H), 6.53 (m, 1H, 5-H), 6.46 (s, 2H, 17- and 23-H), 3.26 (s, 12H, 4 × OCH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ 168.4 (CH, C7), 161.3 (C_q, C16, C18, C22, and C24), 160.0 (C_q, C2), 145.8 (C_q, C8), 141.7 (C_q each, C9 and C13), 136.6 (CH, C4), 135.2 (C_q, C14 and C20), 133.2 and 127.1 (C_q each, C3 and C26), 132.4 (CH, C6), 132.0 and 131.1 (C_q each, C27, C32, C34, and C39), 130.2 (CH, C31 and C35), 128.8 (CH, C28 and C38), 127.3 (CH, C33), 127.1 (CH, C10 and C12), 126.2 (CH, C11), 125.6 and 125.2 (CH each, C29, C30, C36, and C37), 119.3 (C_q, C1), 118.9 (CH, C5), 108.1 (CH, C15, C19, C21, and C25), 100.5 (CH, C17 and C23), 55.0 (CH3, 4 × OCH_3). Anal. Calcd for $C_{43}H_{35}NO_5$ (645.74 g mol^{-1}): C, 79.98; H, 5.46; N, 2.17. Found: C, 79.13; H, 5.66; N, 1.87.



Salicylaldimine 6g. Following the general procedure, 797 mg (1.13 mmol, 94%) of compound **6g** was obtained after 12 h as an off-white powder. ^1H NMR (399.8 MHz, C_6D_6, 25 °C): δ 13.43 (s, 1H, OH), 8.22 (s, 1H, 33-H), 7.87 (s, 1H, 7-H), 7.82 and 7.68 (m each, 2H each, 28-, 30-, 35-, and 38-H), 7.45 (d, $^3J_{HH}$ = 7.9 Hz, 2H, 10- and 12-H), 7.24 (m, 4H, 29-, 30-, 36-, and 37-H), 7.20 (t, $^3J_{HH}$ = 7.9 Hz, 1H, 11-H), 7.03 (d, $^3J_{HH}$ = 7.4 Hz, 1H, 4-H), 6.69 (s, 4H, 15-, 19-, 21-, and 25-H), 6.59 (m, 1H, 6-H), 6.54 (m, 1H, 5-H), 3.80 (s, 6H, 17- and 23-OCH_3), 3.37 (s, 12H, 16-, 18-, 22-, and 24-OCH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ 168.3 (CH, C7), 159.9 (C_q, C2), 154.1 (C_q, C16, C18, C22, and C24), 145.9 (C_q, C8), 138.8 (C_q, C17 and C23), 136.6 (CH, C4), 135.4 (C_q, C9 and C13), 134.8 (C_q, C14 and C20), 132.9 and 127.2 (C_q each, C26 and C3), 132.3 (CH, C6), 132.0 and 131.0 (C_q each, C27, C32, C34, and C39), 130.3 (CH, C10 and C12), 128.8 and 126.9 (CH each, C28, C31, C35, and C38), 127.3 (CH, C33), 126.2 (CH, C11), 125.8 and 125.3 (CH each, C29, C30, C36, and C37), 119.2 (C_q, C1), 119.0 (CH, C5), 108.0 (CH, C15, C19, C21, and C25), 60.5 (CH_3, 17- and 23-OCH_3), 56.0 (CH_3, 16-, 18-, 22-, and 24-OCH_3). Anal. Calcd for $C_{45}H_{39}NO_7$ (705.79 g mol^{-1}): C, 76.58; H, 5.57; N, 1.98. Found: C, 77.00; H, 5.11; N, 1.67.

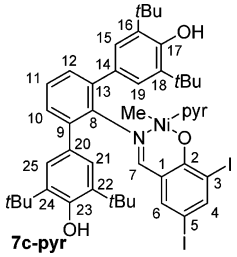
General Procedure for the Synthesis of (κ^2-*N,O*)-Salicylaldiminato Nickel Methyl Pyridine Complexes (7a−f-pyr and 8a−g-pyr). Method A. To [(tmeda)$NiMe_2$] (20.4 mg, 100 μmol) and the respective salicylaldimine **5a**−**f**, **6a**−**f** (100 μmol) in a 10 mL septum capped Schlenk tube was added a solution of pyridine (120 mg, 1.52 mmol) in 5 mL of benzene at 25 °C. Immediate methane evolution was observed, which ceased within 5−10 min. The

resulting orange to red solution was stirred for an additional 30 min at 25 °C, and all volatiles were then removed by sublimation at −10 °C (crushed ice/sodium chloride) under high vacuum (10^{-3} mbar). Alternatively, the reaction was conducted in 8 mL of diethyl ether containing pyridine (120 mg, 1.52 mmol) where salicylaldimines did not completely dissolve, methane evolution was much slower, and the reaction time was prolonged to 3 h at 25 °C, after which time all volatiles were removed in vacuo (10^{-3} mbar). Independent of the solvent used, the resulting solid was transferred to a Schlenk frit, washed with 4 × 2 mL of pentane, and dried under high vacuum (10^{-3} mbar) to yield an analytically pure sample of pyridine complexes **7a**−**f-pyr** and **8a**−**g-pyr**. **Method B.** To [(pyridine)$_2$NiMe$_2$] (26.0 mg, 105 μmol) and the respective salicylaldimine **5a**−**f**, **6a**−**f** (100 μmol) in a 10 mL septum capped Schlenk tube was added benzene (5 mL) at 25 °C. Immediate methane evolution was observed, which ceased within 5−10 min. The resulting orange to red solution was stirred for an additional 120 min at 25 °C, during which time excess [(pyridine)$_2$NiMe$_2$] decomposed to nickel black. The resulting mixture was filtrated to remove nickel black, the residue was extracted with benzene (4 × 0.5 mL), and all volatiles were removed by sublimation at −10 °C (crushed ice/sodium chloride) under high vacuum (10^{-3} mbar) to yield analytically pure samples of pyridine complexes **7a**−**f-pyr** and **8a**−**g-pyr**.

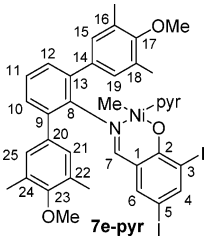


Complex 7b-pyr. Following the general procedure of method A, 90.9 mg (93.0 μmol, 93.0%) of compound **7b-pyr** was obtained from [(tmeda)NiMe$_2$] (20.4 mg, 100 μmol), salicylaldimine **5b** (82.6 mg, 100 μmol), and pyridine (120 mg, 1.52 mmol) in diethyl ether as a red powder. Method B gave 89.8 mg (91.9 μmol, 91.9%) of compound **7b-pyr** from [(pyridine)$_2$NiMe$_2$] (26.0 mg, 105 μmol) and salicylaldimine **5b** (82.6 mg, 100 μmol). Crystals suitable for X-ray analysis were obtained within 4 d at 25 °C after layering a solution of complex **7b-pyr** (26 mg) in 0.4 mL of benzene with 3 mL of pentane.

Crystallographic Data for 7b-pyr·1.5C$_6$H$_6$. $C_{56}H_{65}N_2OI_2Ni$, M_r = 1093.63, monoclinic, space group $P2_1/c$ (no. 14), a = 17.81(7), b = 18.24(7), c = 19.05(7) Å, α = 90.00(7)°, β = 114.45(7)°, γ = 90.00(7), V = 5643(38) Å^3, Z = 4, ρ_{calcd} = 1.280, μ = 14.76 cm^{-1}, no. of rflns measd = 32 147, no. of unique rflns = 9923, no. of rflns $I > 2\sigma(I)$ = 5173, R1($I > 2\sigma(I)$) = 0.0548, R1 (all data) = 0.1066, wR_2 = 0.1450, T = 293(2) K, GOF = 0.889. The intensity data were collected on a Bruker AXS CCD diffractometer with graphite-monochromated Mo Kα radiation (0.71070 Å). The structure was solved by direct methods with SHELLXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97. Hydrogen atoms were treated in a riding model. One *tert*-butyl group is disordered and was refined isotropically over two split positions. **7b-pyr.** ^{1}H NMR (399.8 MHz, C$_6$D$_6$, 25 °C): δ 8.29 (m, 2H, *o*-H pyridine), 7.95 (d, $^4J_{HH}$ = 1.9 Hz, 1H, 4-H), 7.70 (s, 4H, 15-, 19-, 21-, and 25-H), 7.60 (s, 2H, 17- and 23-H), 7.49 (d, $^3J_{HH}$ = 7.8 Hz, 2H, 10- and 12-H), 7.18 (d, $^3J_{HH}$ = 7.8 Hz, 1H, 11-H), 6.89 (s, 1H, 7-H), 6.69 (d, $^4J_{HH}$ = 1.9 Hz, 1H, 6-H), 6.67 (m, 1H, *p*-H pyridine), 6.40 (m, 2H, *m*-H pyridine), 1.40 (s, 36H, 4 × ^{t}Bu), −0.55 (s, 3H, Ni−CH$_3$). ^{13}C{^{1}H} NMR (100.5 MHz, C$_6$D$_6$, 25 °C): δ 168.2 (CH, C7), 163.3 (C$_q$, C2), 151.8 (CH, *o*-C pyridine), 151.0 (C$_q$, C16, C18, C22, and C24), 150.5 (C$_q$, C8), 148.7 (CH, C4), 142.0 (CH, C6), 139.6 and 137.2 (C$_q$ each, C9, C13, C14, and C20), 135.8 (CH, *p*-C pyridine), 129.8 (CH, C10 and C12), 126.5 (CH, C11), 125.6 (CH, C15, C19, C21, and C25), 122.7 (CH, *m*-C pyridine), 121.4 (C$_q$, C1), 121.2 (CH, C17 and C23), 96.8 (C$_q$, C5), 71.4 (C$_q$, C3), 35.2 (C$_q$, 4 × ^{t}Bu), 31.7 (CH$_3$, 4 × ^{t}Bu), −7.6 (CH$_3$, Ni−CH$_3$). Anal. Calcd for $C_{47}H_{56}N_2OI_2Ni$ (977.46 g mol^{-1}): C, 57.75; H, 5.77; N, 2.87. Found: C, 58.00; H, 5.95; N, 3.06.

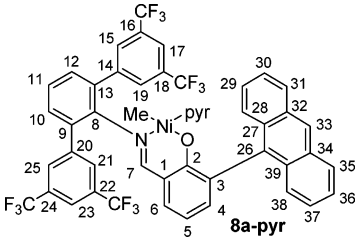


Complex 7c-pyr. Following the general procedure of method A, 90.1 mg (89.3 μmol, 89.3%) of compound **7c-pyr** was obtained from [(tmeda)NiMe$_2$] (20.4 mg, 100 μmol), salicylaldimine **5c** (85.8 mg, 100 μmol), and pyridine (120 mg, 1.52 mmol) in benzene solution as a red powder. Method B gave 92.2 mg (91.3 μmol, 91.3%) of compound **7c-pyr** from [(pyridine)$_2$NiMe$_2$] (26.0 mg, 105 μmol) and salicylaldimine **5c** (85.8 mg, 100 μmol). ^{1}H NMR (399.8 MHz, C$_6$D$_6$, 25 °C): δ 8.34 (m, 2H, *o*-H pyridine), 7.99 (d, $^4J_{HH}$ = 2.1 Hz, 1H, 4-H), 7.68 (s, 4H, 15-, 19-, 21-, and 25-H), 7.50 (d, $^3J_{HH}$ = 7.8 Hz, 2H, 10- and 12-H), 7.13 (t, $^3J_{HH}$ = 7.8 Hz, 1H, 11-H), 6.78 (s, 1H, 7-H), 6.70 (m, 1H, *p*-H pyridine), 6.63 (d, $^4J_{HH}$ = 2.1 Hz, 1H, 6-H), 6.49 (m, 2H, *m*-H pyridine), 5.07 (s, 2H, 2 × OH), 1.48 (s, 36H, 4 × ^{t}Bu), −0.62 (s, 3H, Ni−CH$_3$). ^{13}C{^{1}H} NMR (100.5 MHz, C$_6$D$_6$, 25 °C): δ 168.3 (CH, C7), 163.4 (C$_q$, C2), 153.5 (C$_q$, C17 and C23), 151.8 (CH, *o*-C pyridine), 150.0 (C$_q$, C8), 148.7 (CH, C4), 141.9 (CH, C6), 137.0 (C$_q$, C9 and C13), 136.1 (C$_q$, C16, C18, C22, and C24), 135.9 (CH, *p*-C pyridine), 131.4 (C$_q$, C14 and C20), 129.2 (CH, C10 and C12), 128.3 (CH, C15, C19, C21, and C25), 126.7 (CH, C11), 122.9 (CH, *m*-C pyridine), 122.0 (C$_q$, C1), 96.7 (C$_q$, C5), 71.4 (C$_q$, C3), 34.7 (C$_q$, 4 × ^{t}Bu), 30.5 (CH$_3$, 4 × ^{t}Bu), −8.0 (CH$_3$, Ni−CH$_3$). Anal. Calcd for $C_{47}H_{56}N_2O_3I_2Ni$ (1008.46): C, 55.98; H, 5.50; N, 2.78. Found: C, 56.41; H, 5.89; N, 2.45.

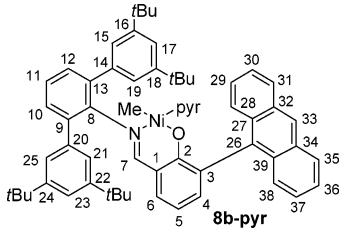


Complex 7e-pyr. Following the general procedure of method A, 74.2 mg (85.4 μmol, 85.4%) of compound **7e-pyr** was obtained from [(tmeda)NiMe$_2$] (20.4 mg, 100 μmol), salicylaldimine **5e** (71.8 mg, 100 μmol), and pyridine (120 mg, 1.52 mmol) in benzene solution as a red powder. Method B gave 78.9 mg (90.8 μmol, 90.8%) of compound **7e-pyr** from [(pyridine)$_2$NiMe$_2$] (26.0 mg, 105 μmol) and salicylaldimine **5e** (85.8 mg, 100 μmol). ^{1}H NMR (399.8 MHz, C$_6$D$_6$, 25 °C): δ 8.18 (m, 2H, *o*-H pyridine), 7.97 (d, $^4J_{HH}$ = 2.0 Hz, 1H, 4-H), 7.43 (d, $^3J_{HH}$ = 7.8 Hz, 2H, 10- and 12-H), 7.39 (s, 4H, 15-, 19-, 21-, and 25-H), 7.15 (1H occluded by C$_6$D$_5$H, 11-H), 7.13 (s, 1H, 7-H), 6.88 (d, $^4J_{HH}$ = 2.0 Hz, 1H, 6-H), 6.62 (m, 1H, *p*-H pyridine), 6.31 (m, 2H, *m*-H pyridine), 3.38 (s, 6H, 17- and 23-OCH$_3$), 2.28 (s, 12H, 16-, 18-, 22-, and 24-CH$_3$), −0.60 (s, 3H, Ni−CH$_3$). ^{13}C{^{1}H} NMR (100.5 MHz, C$_6$D$_6$, 25 °C): δ 167.6 (CH, C7), 163.4 (C$_q$, C2), 157.1 (C$_q$, C17 and C23), 151.8 (CH, *o*-C pyridine), 149.9 (C$_q$, C8), 148.9 (CH, C4), 141.9 (CH, C6), 136.0 and 135.7 (C$_q$ each, C9, C13, C14, and C20), 135.8

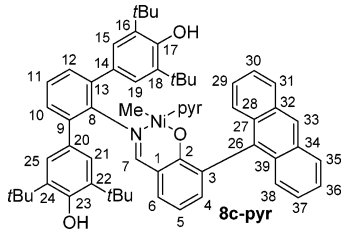
(CH, *p*-C pyridine), 131.5 (CH, C15, C19, C21, and C25), 130.9 (C_q, C16, C18, C22, and C24), 129.9 (CH, C10 and C12), 126.3 (CH, C11), 122.7 (CH, *m*-C pyridine), 121.3 (C_q, C1), 97.3 (C_q, C5), 71.7 (C_q, C3), 59.4 (CH_3, 17- and 23-OCH_3), 16.4 (CH_3, 16-, 18-, 22-, and 24-CH_3), −7.9 (CH_3, Ni−CH_3). Anal. Calcd for $C_{37}H_{36}N_2O_3I_2Ni$ (869.19 g mol^{-1}): C, 51.13; H, 4.17; N, 3.22. Found: C, 51.54; H, 4.29; N, 3.29.



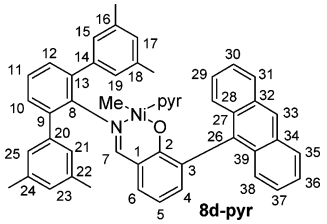
Complex 8a-pyr. Following the general procedure of method A, 82.7 mg (87.1 μmol, 87.1%) of compound **8a-pyr** was obtained from [(tmeda)$NiMe_2$] (20.4 mg, 100 μmol), salicylaldimine **6a** (79.8 mg, 100 μmol), and (pyridine 120 mg, 1.52 mmol) in diethyl ether as an orange-red powder. Method B gave 88.0 mg (92.3 μmol, 92.3%) of compound **8a-pyr** from [(pyridine)$_2$$NiMe_2$] (26.0 mg, 105 μmol) and salicylaldimine **6a** (79.8 mg, 100 μmol). ^{1}H NMR (399.8 MHz, C_6D_6, 25 °C): δ 8.27 (s, 4H, 15-, 19-, 21-, and 25-H), 8.07 (s, 1H, 33-H), 7.89 and 7.73 (m each, 2H each, 28-, 31-, 35-, and 38-H), 7.71 (s, 2H, 17- and 23-H), 7.33 (m br, 2H, *o*-H pyridine), 7.31 and 7.18 (m each, 2H each, 29-, 30-, 36-, and 37-H), 7.12 (dd, $^3J_{HH}$ = 7.8 and $^4J_{HH}$ = 1.8 Hz, 1H, 4-H), 6.92 (m, 4H, 10−12-H and 7-H), 6.67 (dd, $^3J_{HH}$ = 7.8 and $^4J_{HH}$ = 1.8 Hz, 1H, 6-H), 6.38 (vt, J_{HH} = 7.8 Hz, 1H, 5-H), 6.14 (m, 1H, *p*-H pyridine), 5.54 (m, 2H, *m*-H pyridine), −1.08 (s, 3H, Ni−CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25 °C): δ 168.1 (CH, C7), 166.2 (C_q, C2), 150.9 (C_q,C8), 150.3 (CH, *o*-C pyridine), 141.8 (C_q, C9 and C13), 137.8 (CH, C4), 136.4 (C_q, C26), 135.2 (CH, *p*-C pyridine), 133.4 (C_q, C10 and C14), 133.3 (CH, C6), 131.9 and 130.0 (C_q each, C27, C32, C34, and C39), 131.8 (C_q, q, $^2J_{CF}$ = 33 Hz, C16, C18, C22, and C24), 131.2 (C_q, C3), 130.9 (CH, C15, C19, C21, and C25), 130.7 (CH, C10 and C12), 128.1 and 128.0 (CH each, C28, C31, C35, and C38), 126.6 (CH, C11), 125.5 (CH, C33), 125.2 and 124.9 (CH each, C29, C30, C36, and C37), 124.1 (C_q, q, $^1J_{CF}$ = 272 Hz, 4 × CF_3), 122.1 (CH, *m*-C pyridine), 121.1 (CH, m, C17 and C23), 119.2 (C_q, C1), 114.1 (CH, C5), −8.3 (CH_3, Ni−CH_3). Anal. Calcd for $C_{49}H_{30}N_2OF_{12}Ni$ (949.56 g mol^{-1}): C, 61.99; H, 3.18; N, 2.95. Found: C, 61.36; H, 3.40; N, 3.21.



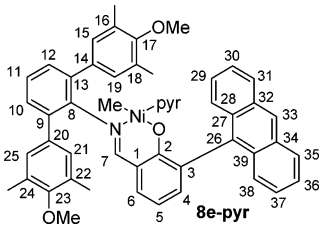
Complex 8b-pyr. Following the general procedure of method A, 78.4 mg (86.8 μmol, 86.8%) of compound **8b-pyr** was obtained from [(tmeda)$NiMe_2$] (20.4 mg, 100 μmol), salicylaldimine **6b** (75.1 mg, 100 μmol), and pyridine (120 mg, 1.52 mmol) in benzene as an orange-red powder. Method B gave 82.1 mg (90.9 μmol, 90.9%) of compound **8b-pyr** from [(pyridine)$_2$$NiMe_2$] (26.0 mg, 105 μmol) and salicylaldimine **5b** (75.1 mg, 100 μmol). ^{1}H NMR (399.8 MHz, C_6D_6, 25 °C): δ 8.12 (s, 1H, 33-H), 8.07 and 7.79 (m each, 2H each, 28-, 31-, 35-, and 38-H), 7.85 (s, 4H, 15-, 19-, 21-, and 25-H), 7.55 (s, 2H, 17- and 23-H), 7.54 (d, $^3J_{HH}$ = 7.8 Hz, 2H, 10- and 12-H), 7.35 (m, 2H, *o*-H pyridine), 7.34 (s, 1H, 7-H), 7.29 and 7.25 (m each, 2H each, 29-, 30-, 36-, and 37-H), 7.20 (t, $^3J_{HH}$ = 7.8 Hz, 1H, 11-H), 7.19 (dd, $^3J_{HH}$ = 7.9 and $^4J_{HH}$ = 1.9 Hz, 1H, 4-H), 6.67 (dd, $^3J_{HH}$ = 7.9 and $^4J_{HH}$ = 1.9 Hz, 1H, 6-H), 6.39 (vt, $^3J_{HH}$ = 7.9 Hz, 1H, 5-H), 6.23 (m, 1H, *p*-H pyridine), 5.71 (m, 2H, *m*-H pyridine), 1.40 (s, 36H, 4 × ^{t}Bu), −0.71 (s, 3H, Ni−CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25 °C): δ 169.2 (CH, C7), 165.5 (C_q, C2), 151.0 (C_q, C8), 151.0 (CH, *o*-C pyridine), 150.8 (C_q, C16, C18, C22, and C24), 140.0 and 137.5 (C_q each, C9, C13, C14, and C20), 137.6 (C_q, C26), 136.6 (CH, C4), 134.7 (CH, *p*-C pyridine), 133.6 (CH, C6), 132.0 and 131.2 (C_q each, C27, C32, C34, and C39), 130.4 (C_q, C3), 130.0 (CH, C10 and C12), 128.9 and 128.2 (CH each, C28, C31, C35, and C38), 126.3 (CH, C11), 125.6 (CH, C15, C19, C21, and C25), 125.3 (CH, C33), 125.0 and 124.6 (CH each, C29, C30, C36, and C37), 121.7 (CH, *m*-C pyridine), 121.3 (C_q, C1), 121.0 (CH, C17 and C23), 112.9 (CH, C5), 35.2 (C_q, 4 × ^{t}Bu), 31.8 (CH_3, 4 × ^{t}Bu), −8.7 (CH_3, Ni−CH_3). Anal. Calcd for $C_{61}H_{67}N_2ONi$ (902.91 g mol^{-1}): C, 81.15; H, 7.48; N, 3.10. Found: C, 80.88; H, 7.10; N, 3.00.



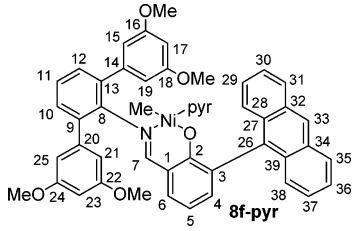
Complex 8c-pyr. Following the general procedure of method A, 85.3 mg (91.2 μmol, 91.2%) of compound **8c-pyr** was obtained from [(tmeda)$NiMe_2$] (20.4 mg, 100 μmol), salicylaldimine **6c** (78.2 mg, 100 μmol), and pyridine (120 mg, 1.52 mmol) in diethyl ether as an orange-red powder. Method B gave 84.8 mg (90.7 μmol, 90.7%) of compound **8c-pyr** from [(pyridine)$_2$$NiMe_2$] (26.0 mg, 105 μmol) and salicylaldimine **6c** (78.2 mg, 100 μmol). ^{1}H NMR (399.8 MHz, C_6D_6, 25 °C): δ 8.14 (s, 1H, 33-H), 8.13 and 7.82 (m each, 2H each, 29-, 30-, 36-, and 36-H), 7.83 (s, 4H, 15-, 19-, 21-, and 25-H), 7.55 (d, $^3J_{HH}$ = 7.8 Hz, 2H, 10- and 12-H), 7.36 (m, 2H, *o*-H pyridine), 7.33 and 7.28 (m each, 2H each, 28-, 31-, 35-, and 38-H), 7.25 (s, 1H, 7-H), 7.20 (t, $^3J_{HH}$ = 7.8 Hz, 1H, 11-H), 7.18 (dd, $^3J_{HH}$ = 8.0 Hz and $^4J_{HH}$ = 2.0 Hz, 1H, 4-H), 6.62 (dd, $^3J_{HH}$ = 8.0 Hz and $^4J_{HH}$ = 2.0 Hz, 1H, 6-H), 6.40 (vt, J_{HH} = 8.0 Hz, 1H, 5-H), 6.27 (m, 1H, *p*-H pyridine), 5.82 (m, 2H, *m*-H pyridine), 4.99 (s, 2H, 2 × OH), 1.46 (s, 36H, 4 × ^{t}Bu), −0.78 (s, 3H, Ni−CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25 °C): δ 169.3 (CH, C7), 165.5 (C_q, C2), 153.2 (C_q, C17 and C23), 151.0 (CH, *o*-C pyridine), 150.5 (C_q, C8), 137.8 (C_q, C26), 137.1 (C_q, C9 and C13), 136.3 (CH, C4), 135.9 (C_q, C16, C18, C22, and C24), 134.7 (CH, *p*-C pyridine), 133.5 (CH, C6), 132.0, 131.9, and 131.2 (C_q each, C14, C20, C27, C39, C32, and C34), 130.4 (C_q, C3), 129.3 (CH, C10 and C12), 129.0, 128.4, and 128.3 (CH each, C15, C19, C21, C25, C28, C31, C35, and C38), 126.5 (CH, C11), 125.3 (CH, C33), 125.0 and 124.7 (CH each, C29, C30, C36, and C37), 122.8 (C_q, C1), 121.9 (CH, *m*-C pyridine), 112.9 (CH, C5), 34.8 (C_q, 4 × *t*Bu), 30.5(CH_3, 4 × ^{t}Bu), −9.1 (CH_3, Ni−CH_3). Anal. Calcd for $C_{61}H_{66}N_2O_3Ni$ (934.90 g mol^{-1}): C, 78.37; H, 7.22; N, 3.00. Found: C, 78.00; H, 7.53; N, 2.84.



Complex 8d-pyr. Following the general procedure of method A, 65.4 mg (89.2 μmol, 89.2%) of compound **8d-pyr** was obtained from [(tmeda)NiMe$_2$] (20.4 mg, 100 μmol), salicylaldimine **6d** (58.2 mg, 100 μmol), and pyridine (120 mg, 1.52 mmol) in benzene solution as an orange-red powder. ^{1}H NMR (399.8 MHz, C_6D_6, 25 °C): δ 8.11 (s, 1H, 33-H), 7.93 and 7.77 (m each, 2H each, 28-, 31-, 35-, and 38-H), 7.71 (s, 1H, 7-H), 7.53 (s, 4H, 15-, 19-, 21-, and 25-H), 7.43 (d, $^3J_{HH}$ = 7.6 Hz, 2H, 10- and 12-H), 7.37 (s, 2H, *o*-H pyridine), 7.14 (m, 6H, 4-, 11-, 29-, 30-, 36-, and 37-H), 6.94 (dd, $^3J_{HH}$ = 7.6 and $^4J_{HH}$ = 1.8 Hz, 1H, 6-H), 6.85 (s, 2H, 17- and 23-H), 6.48 (t, J_{HH} = 7.6 Hz, 1H, 5-H), 6.19 (m, 1H, *p*-H pyridine), 5.58 (m, 2H, *m*-H pyridine), 2.22 (s, 12H, 4 × CH_3), −0.72 (s, 3H, Ni−CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25 °C): δ 168.5 (CH, C7), 165.7 (C_q, C2), 151.0 (CH, *o*-C pyridine), 150.7 (C_q, C8), 140.6 and 137.5 (C_q each, C9, C13, 14 and C20), 137.6 (C_q, C16, C18, C22, and C24), 136.7 (C_q, C26), 136.7 (CH, C4), 134.6 (CH, *p*-C pyridine), 133.9 (CH, C6), 132.0 and 131.2 (C_q each, C27, C32, C34, and C39), 130.6 (C_q, C3), 130.1 (CH, C10 and C12), 129.0 (CH, C15, C19, C21, and C25), 128.9 (CH, C17 and C23), 128.5 and 128.2 (CH each, C28, C31, C35, and C38), 125.9 (CH, C11), 125.4 (CH, C33), 125.0 and 124.7 (CH each, C29, C30, C36, and C37), 121.7 (CH, *m*-C pyridine), 120.7 (C_q, C1), 113.1 (CH, C5), 21.5 (CH_3, 16-, 18-, 22-, and 24-CH_3), −8.3 (CH_3, Ni−CH_3). Anal. Calcd for $C_{49}H_{42}N_2ONi$ (733.58 g mol^{-1}): C, 80.23; H, 5.77; N, 3.82. Found: C, 80.00; H, 5.86; N, 3.43.

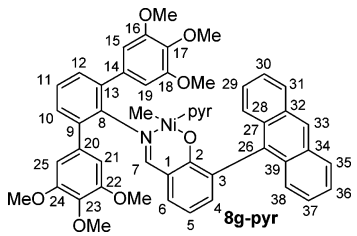


Complex 8e-pyr. Following the general procedure of method A, 66.2 mg (83.4 μmol, 83.4%) of compound **8e-pyr** was obtained from [(tmeda)NiMe$_2$] (20.4 mg, 100 μmol), salicylaldimine **6e** (64.2 mg, 100 μmol), and pyridine (120 mg, 1.52 mmol) in a diethyl ether suspension as an orange powder. Method B gave 75.2 mg (95.7 μmol, 95.7%) of compound **8e-pyr** from [(pyridine)$_2$NiMe$_2$] (26.0 mg, 105 μmol) and salicylaldimine **6e** (64.2 mg, 100 μmol). ^{1}H NMR (399.8 MHz, C_6D_6, 25 °C): δ 8.10 (s, 1H, 33-H), 7.89 and 7.75 (m each, 2H each, 28-, 31-, 35-, and 38-H), 7.71 (s, 1H, 7-H), 7.56 (s, 4H, 15-, 19-, 21-, and 25-H), 7.42 (d, $^3J_{HH}$ = 7.6 Hz, 2H, 10- and 12-H), 7.37 (m, 2H, *o*-H pyridine), 7.21 (dd, $^3J_{HH}$ = 7.6 and $^4J_{HH}$ = 2.0 Hz, 1H, 4-H), 7.19 and 7.10 (m each, 2H each, 29-, 30-, 36-, and 37-H), 7.17 (t, $^3J_{HH}$ = 7.6 Hz, 1H, 11-H), 6.95 (dd, $^3J_{HH}$ = 7.6 and $^4J_{HH}$ = 2.0 Hz, 1H, 6-H), 6.50 (vt, J_{HH} = 7.6 Hz, 1H, 5-H), 6.21 (m, 1H, *p*-H pyridine), 5.60 (m, 2H, *m*-H pyridine), 3.29 (s, 6H, 17- and 23-OCH_3), 2.27 (s, 12H, 16-, 18-, 22-, and 24-CH_3), −0.73 (s, 3H, Ni−CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25 °C): δ 168.4 (CH, C7), 165.7 (C_q, C2), 156.8 (C_q, C17 and C23), 150.9 (CH, *o*-C pyridine), 150.7 (C_q, C8), 137.4 (C_q, C26), 136.7 (CH, C4), 136.4 and 136.1 (C_q each, C9, C13, C14, and C20), 134.6 (CH, *p*-C pyridine), 133.8 (CH, C6), 131.9 and 131.1 (C_q each, C27, C32, C34, and C39), 131.6 (CH, C15, C19, C21, and C25), 130.7 (C_q, C3), 130.6 (C_q, C16, C18, C22, and C24), 130.0 (CH, C10 and C12), 128.4 and 128.2 (CH each, C28, C31, C35, and C38), 125.9 (CH, C11), 125.4 (CH, C33), 125.0 and 124.7 (CH each, C29, C30, C36, and C37), 121.7 (CH, *m*-C pyridine), 120.7 (C_q, C1), 113.1 (CH, C5), 59.2 (CH_3, 17- and 23-OCH_3), 16.4 (CH_3, 16-, 18-, 22-, and 24-CH_3), −8.6 (CH_3, Ni−CH_3). Anal. Calcd for $C_{51}H_{46}N_2O_3Ni$ (793.63 g mol^{-1}): C, 77.18; H, 5.84; N, 3.53. Found: C, 76.43; H, 6.12; N, 3.01.



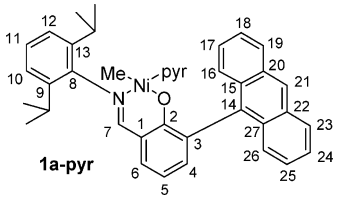
Complex 8f-pyr. Following the general procedure of method A, 70.7 mg (88.6 μmol, 88.6%) of compound **8f-pyr** was obtained from [(tmeda)NiMe$_2$] (20.4 mg, 100 μmol), salicylaldimine **6f** (64.6 mg, 100 μmol), and pyridine (120 mg, 1.52 mmol) in a diethyl ether suspension as an orange-red powder. Method B gave 72 mg (92.1 μmol, 92.1%) of compound **8f-pyr** from [(pyridine)$_2$NiMe$_2$] (26.0 mg, 105 μmol) and salicylaldimine **6f** (70.6 mg, 100 μmol). Crystals suitable for X-ray analysis were obtained within 3 d at 25 °C after layering a solution of complex **8f-pyr** (20 mg) in 0.4 mL of benzene with 1 mL of pentane/diethyl ether (3:1).

Crystallographic Data for 8f-pyr·1.5C$_6$H$_6$. $C_{58}H_{51}N_2O_5Ni$, M_r = 914.72, triclinic, space group *P*-1 (no. 2), a = 10.116(3), b = 15.276(4), c = 16.317(5) Å, α = 85.398(5), β = 80.664(5), γ = 81.100(6)°, V = 2454.2(12) Å^3, Z = 2, ρ_{calcd} = 1.238, μ = 4.46 cm^{-1}, no. of rflns measd = 17 777, no. of unique rflns = 11 188, no. of rflns $I > 2\sigma(I)$ = 4353, R1($I > 2\sigma(I)$) = 0.0406, R1, all data = 0.1403, wR_2 = 0.0850, T = 293(2) K, GOF = 0.682. The intensity data were collected on a Bruker AXS CCD diffractometer with graphite-monochromated Mo Kα anode radiation (0.71070 Å). The structure was solved by direct methods with SHELLXS-97. Hydrogen atoms were treated in a riding model. **8f-pyr.** ^{1}H NMR (399.8 MHz, C_6D_6, 25 °C): δ 8.11 (s, 1H, 33-H), 7.88 and 7.76 (m each, 2H each, 29-, 30-, 36-, and 37-H), 7.58 (s, 1H, 7-H), 7.44 (d, $^3J_{HH}$ = 8.0 Hz, 2H, 10- and 12-H), 7.40 (m, 2H, *o*-H pyridine), 7.23 (d, $^4J_{HH}$ = 2.0 Hz, 4H, 15-, 19-, 21-, and 25-H), 7.16 (m, 5H, 4-, 28-, 31-, 35-, and 38-H), 7.09 (t, $^3J_{HH}$ = 8.0 Hz, 1H, 11-H), 6.82 (dd, $^3J_{HH}$ = 8.0 Hz and $^4J_{HH}$ = 2.0 Hz, 1H, 6-H), 6.68 (t, dd, $^3J_{HH}$ = 2.0 Hz, 2H, 17- and 23-H), 6.40 (vt, J_{HH} = 8.0 Hz, 1H, 5-H), 6.18 (m, 1H, *p*-H pyridine), 5.56 (m, 2H, *m*-H pyridine), 3.55 (s, 12H, 4 × OCH_3), −0.72 (s, 3H, Ni−CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25 °C): δ 168.3 (CH, C7), 165.6 (C_q, C2), 161.3 (C_q, C16, C18, C22, and C24), 150.8 (CH, C8 and *o*-C pyridine), 142.4 and 136.3 (C_q each, C9, C13, C14, and C20), 137.1 (C_q, C26), 136.9 (CH, C4), 134.7 (CH, *p*-C pyridine), 133.9 (CH, C6), 132.0 and 131.0 (C_q each, C27, C32, C34, and C39), 130.6 (C_q, C3), 130.1 (CH, C10 and C12), 128.2 and 127.9 (CH each, C28, C31, C35, and C38), 126.3 (CH, C11), 125.4 (C_q, C33), 125.1 and 124.8 (CH each, C29, C30, C36, and C37), 121.9 (CH, *m*-C pyridine), 120.7 (C_q, C1), 113.3 (CH, C5), 109.1 (CH, C15, C19, C21, and C25), 100.8 (CH, C17 and C23), 55.3 (CH_3, 4 × OCH_3), −8.2 (CH_3, Ni−CH_3). Anal. Calcd for $C_{49}H_{42}N_2O_5Ni$ (797.57 g mol^{-1}): C, 73.79; H, 5.31; N, 3.51. Found: C, 74.00; H, 5.40; N, 3.40.

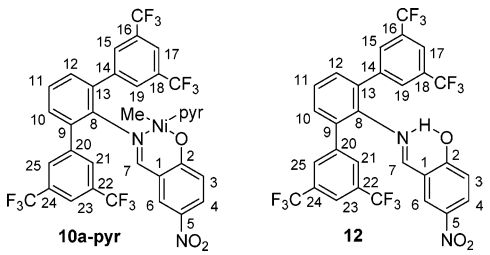


Complex 8g-pyr. Following the general procedure method A, 77.4 mg (90.3 μmol, 90.3%) of compound **8g-pyr** was obtained from [(tmeda)NiMe$_2$] (20.4 mg, 100 μmol), salicylaldimine **6g** (70.6 mg, 100 μmol), and pyridine (120 mg, 1.52 mmol) in diethyl ether as an orange-red powder. Method B gave 72 mg (92.1 μmol, 92.1%) of compound **8g-pyr** from [(pyridine)$_2$NiMe$_2$] (26.0 mg, 105 μmol) and salicylaldimine **6g** (70.6 mg, 100 μmol). ^{1}H NMR (399.8 MHz,

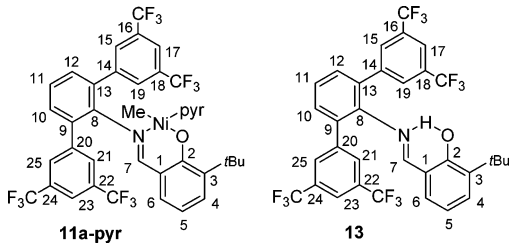
C_6D_6, 25 °C): δ 8.11 (s, 1H, 33-H), 7.83 and 7.75 (m each, 2H each, 29-, 30-, 36-, and 37-H), 7.54 (s, 1H, 7-H), 7.52 (d, $^3J_{HH}$ = 8.0 Hz, 2H, 10- and 12-H), 7.35 (m, 2H, *o*-H pyridine), 7.25 (s, 4H, 15-, 19-, 21-, and 25-H), 7.23 (t, $^3J_{HH}$ = 8.0 Hz, 1H, 11-H), 7.16 (m, 5H, 4-, 28-, 31-, 35-, and 38-H), 6.77 (dd, $^3J_{HH}$ = 8.0 Hz and $^4J_{HH}$ = 2.0 Hz, 1H, 6-H), 6.39 (vt, J_{HH} = 8.0 Hz, 1H, 5-H), 6.16 (m, 1H, *p*-H pyridine), 5.59 (m, 2H, *m*-H pyridine), 3.86 (s, 6H, 17- and 23-OCH_3), 3.70 (s, 12H, 16-, 18-, 22-, and 24-OCH_3), −0.76 (s, 3H, Ni−CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ168.3 (CH, C7), 165.5 (C_q, C2), 154.0 (Cq, C16, C18, C22, and C24), 150.8 (C_q, C17 and C23), 150.5 (CH, *o*-C pyridine), 139.0 and 136.4 (Cq each, C9, C13, C14, C20), 136.9 (CH, C4), 136.8 (C_q, C26), 134.9 (CH, *p*-C pyridine), 133.7 (CH, C6), 131.9 and 131.0 (C_q each, C27, C32, C34, and C39), 130.7 (C_q, C3), 129.8 (CH, C10 and C12), 128.7 and 128.5 (CH each, C28, C31, C35, and C38), 126.3 (CH, C11), 125.5 (C_q, C33), 125.2 and 124.9 (CH each, C29, C30, C36, C37), 122.1 (CH, *m*-C pyridine), 120.7 (C_q, C1), 113.4 (CH, C5), 109.4 (CH, C15, C19, C21, and C25), 60.7 (CH_3, 17- and 23-OCH_3), 56.4 (CH_3, 16-, 18-, 22-, and 24-OCH_3), −8.7 (CH_3, Ni−CH_3), C8 not detected. Anal. Calcd for $C_{45}H_{38}N_2O_7Ni$ (857.62 g mol^{-1}): C, 71.43; H, 5.41; N, 3.27. Found: C, 71.00; H, 5.72; N, 2.84.



Complex 1a-pyr. Following the general procedure method A, 113 mg (186 μmol, 93%) of compound **1-pyr** was obtained from [(tmeda)$NiMe_2$] (40.8 mg, 200 μmol), 2-anthracen-9-yl-6-[(2,6-di-isopropylphenylimino)-methyl]-phenol (91.4 mg, 200 μmol), and pyridine (240 mg, 3.04 mmol) in benzene as an orange-red powder. ^{1}H NMR (399.8 MHz, C_6D_6, 25 °C): δ 8.16 (s, 1H, 21-H), 8.06 and 7.75 (d each, J_{HH} = 8.8 Hz, 2H each, 16-, 19-, 23- and 26-H), 7.79 (s, 1H, 7-H), 7.75 (m, 2H, *o*-H pyridine), 7.36 and 7.18 (d each, $^3J_{HH}$ = 7.2 Hz, each, 1H each, 4- and 6-H), 7.11 and 6.94 (m:t, J_{HH} = 7.4 Hz, 5:2H, 10−12-, 17-, 18-, 24-, and 25-H), 6.67 (vt, $^3J_{HH}$ = 7.2 Hz, 1H, 5-H), 6.27 (vt br, J_{HH} = 7.2 Hz, 1H, *p*-H pyridine), 5.61 (vt br, J_{HH} = 6.2 Hz, 2H, *m*-H pyridine), 4.26 (m, 2H, 2 × ^{i}Pr), 1.44 and 1.12 (d each, $^3J_{HH}$ = 7.2 Hz each, 6:6H, 2 × ^{i}Pr), −0.80 (s, 3H, Ni−CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ 166.5 (CH, C7), 166.2 (C_q, C2), 151.5 (CH, *o*-C pyridine), 150.2 (C_q, C8), 141.2 (C_q, C9 and C13), 137.1 (CH each, C4), 135.0 (*p*-C pyridine), 134.1 (CH, C6), 132.0 and 131.3 (C_q each, C15, C20, C22, and C27), 131.0 (C_q, C3 and C14), 128.5 and 128.1 (CH each, C16, C19, C23, and C26), 126.5 (CH, C10 and C12), 125.6 (CH, C21), 123.6 (CH, C11), 122.2 (CH, *m*-C pyridine), 120.5 (C_q, C1), 113.7 (CH, C5), 28.5 (CH, 2 × ^{i}Pr), 28.5 and 25.0 (CH_3 each, 2 × ^{i}Pr), −7.3 (CH_3, Ni−CH_3). Anal. Calcd for $C_{39}H_{38}N_2ONi$ (609.43 g mol^{-1}): C, 76.86; H, 6.28; N, 4.60. Found: C, 76.40; H, 6.71; N, 4.08.



Synthesis of Complex 10a-pyr. (a) Preparation of Salicylaldehyde 12. Following the general procedure for the synthesis of salicylaldimines, condensation of terphenylamine **4a** (518 mg, 1 mmol) with 5-nitrosalicylaldehyde (167 mg, 1 mmol) in 15 mL of methanol gave salicylaldimine **12** (500 mg, 0.75 mmol, 75%). ^{1}H NMR (399.8 MHz, $CDCl_3$, 25 °C): δ 12.79 (s, 1H, OH), 8.12 (dd, $^3J_{HH}$ = 9.2 Hz, $^4J_{HH}$ = 2.8 Hz, 1H, 4-H), 8.06 (s, 1H, 7-H), 7.89 (d, $^4J_{HH}$ = 2.8 1H, 6-H), 7.87 (s, 4H, 15-, 19-, 21-, and 25-H), 1.83 (s, 2H, 17- and 23-H), 7.58 (m, 3H, 10−12-H), 7.02 (d, $^3J_{HH}$ = 9.2 Hz, 1H, 5-H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 25 °C): δ 168.4 (CH, C7), 166.0 (Cq, C2), 144.5 (Cq, C8), 140.4 and 132.1 (C_q each, C9, C13, C14, and C20), 140.1 (C_q, C5), 132.1 (q, $^2J_{CF}$ = 34 Hz, C16, C18, C22, and C24), 131.5 (CH, C10 and C12), 129.8 (CH, C15, C19, C21, and C25), 129.3 (CH, C4), 128.3 (CH, C6), 127.5 (CH, C11), 123.0 (q, $^1J_{CF}$ = 272 Hz, 4 × CF_3), 121.4 (m, CH, C17 and C23), 118.4 (CH, C3), 116.7 (C_q, C1). (**b) Preparation of Complex 10a-pyr.** To a mixture of [(tmeda)Ni-$(CH_3)_2$] (100 mg, 0.49 mmol) and salicalyldimine **12** (326 mg, 0.49 mmol) in a 25 mL Schlenk flask was added a solution of 0.5 mL of pyridine in diethyl ether (10 mL) at −30 °C under stirring. The temperature was slowly raised to 0 °C, while the color changed to orange-red. After 2 h at 0 °C, the solvent was removed under vacuum (10^{-3} mbar), and the residue was washed with small amounts of cold pentane to leave complex **10a-pyr** as an orange powder (213 mg, 0.26 mmol, 53%). ^{1}H NMR (399.8 MHz, CD_2Cl_2, 25 °C): δ 8.33 (m br, 2H, *o*-H pyr), 8.28 (s, 4H, 15-, 19-, 21-, and 25-H), 8.02 (s, 2H, 17- and 23-H), 7.93 (dd, $^3J_{HH}$ = 9.2 Hz, $^4J_{HH}$ = 2.8 Hz, 1H, 4-H), 7.88 (d, $^4J_{HH}$ = 2.8 Hz, 1H, 6-H), 7.68 (s br, 2H, 7-H and *p*-H pyr), 7.55 (m, 3H, 10−12-H), 7.20 (m br, 2H *m*-H pyr), 6.33 (d, $^3J_{HH}$ = 9.2 Hz, 3-H), −0.98 (s, 3H, Ni−CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2, 25 °C): δ 171.2 (C_q, C2), 168.2 (CH, C7), 150.9 (CH br, *o*-C pyr), 149.6 (C_q, C8), 141.0 and 133.0 (C_q each, C9, C13, C14, and C20), 137.1 (CH br, *p*-C pyr), 135.5 (C_q, C5), 131.8 (CH, C6), 131.7 (q, $^2J_{CF}$ = 33 Hz, C16, C18, C22, and C24), 131.1 (CH, C10 and C12), 130.6 (CH br, C15, C19, C21, and C25), 128.8 (CH, C4) 127.5 (CH, C11), 123.5 (q, $^1J_{CF}$ = 272 Hz, 4 × CF_3), 123.2 (CH br, *m*-C pyr), 122.6 (CH, C3), 121.5 (m, CH, C17 and C23), 117.7 (C_q, C1), −7.3 (CH_3, Ni−CH_3).



Synthesis of Complex 11a-pyr. (a) Preparation of Salicylaldehyde 13. Following the general procedure for the synthesis of salicylaldimines, condensation of terphenylamine **4a** (518 mg, 1 mmol) with 3-(*tert*-butyl)alicylaldehyde (178 mg, 1 mmol) in 15 mL of methanol gave salicylaldimine **13** (589 mg, 0.87 mmol, 87%). ^{1}H NMR (399.8 MHz, C_6D_6, 25 °C): δ 12.61 (s, 1H, OH), 7.68 (s, 4H, 15-, 19-, 21-, and 25-H), 7.56 (s, 2H, 17- and 23-H), 7.12 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, 4-H), 6.93 (m, 4H, 7-H and 10−12-H), 6.38 (vt, J_{HH} = 7.6 Hz, 5-H), 6.22 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, 6-H), 1.49 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ 170.9 (CH, C7), 160.9 (C_q, C2), 146.1 (C_q, C8), 141.2 and 132.1 (C_q each, C9, C13, C14, and C20), 138.2 (C_q, C3), 132.0 (q, $^2J_{CF}$ = 33 Hz, C16, C18, C22, and C24), 131.9 (CH, C4), 131.0 (CH, C10 and C12), 130.6 (CH, C6), 130.2 (m br, CH, C15, C19, C21, and C25), 126.4 (CH, C11), 123.8 (q, $^1J_{CF}$ = 271 Hz, 4 × CF_3), 121.0 (m, CH, C17 and C23), 118.9 (CH, C5), 117.9 (C_q, C1), 35.0 (C_q, ^{t}Bu), 29.3 (CH_3, ^{t}Bu). (**b) Preparation of Complex 11a-pyr.** To a mixture of [(tmeda)Ni-$(CH_3)_2$] (100 mg, 0.49 mmol) and salicylaldimine **13** (332 mg, 0.49 mmol) in a 25 mL Schlenk flask was added a solution of 0.5 mL

of pyridine in diethyl ether (10 mL) at −30 °C under stirring. The temperature was slowly raised to 0 °C under stirring, while the color changed to orange-red. After 2 h at 0 °C, the solvent was removed under vacuum (10^{-3} mbar), and the residue was washed with small amounts of cold pentane to leave complex **11a-pyr** as an orange powder (343.8 mg, 0.295 mmol, 60%). ^{1}H NMR (399.8 MHz, C_6D_6, 25 °C): δ 8.45 (m br, 2H, *o*-H pyr), 8.28 (s, 4H, 15-, 19-, 21-, and 25-H), 7.79 (s, 2H, 17- and 23-H), 7.10 (d, $^3J_{HH}$ = 7.2 Hz, 1H, 4-H), 6.90 (m, 4H, 7-H and 10−12-H), 6.54 (m br, 1H, *p*-H pyr), 6.46 (d, $^3J_{HH}$ = 7.2 Hz, 1H, 6-H), 6.27 (m br, 3H, 5-H and *m*-H pyr), 0.97 (s, 9H, ^{t}Bu), −0.88 (s, 3H, Ni−CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25 °C): δ 168.0 (CH, C7), 166.9 (C_q, C2), 151.2 (C_q, C8), 150.7 (CH, *o*-C pyr), 142.0 and 133.8 (C_q each, C9, C13, C14, and C20), 140.8 (C_q, C3), 136.1 (CH, *p*-C pyr), 131.9 (CH, C6), 131.8 (q, $^2J_{CF}$ = 33 Hz, C16, C18, C22, and C24), 131.5 (CH, C4), 131.0 (CH, C15, C19, C21, and C25), 130.7 (CH, C10 and C12), 126.4 (CH, C11), 124.1 (q, $^1J_{CF}$ = 271 Hz, 4 × CF_3), 123.4 (CH, *m*-C pyr), 121.0 (CH, C17 and C23), 118.9 (C_q, C1), 113.9 (CH, C5), 34.5 (C_q, ^{t}Bu), 28.9 (CH_3, ^{t}Bu), −8.1 (CH_3, Ni−CH_3).

General Procedure for the Polymerization of Ethylene in Toluene. 95 mL of toluene was cannula-transferred to a 3× evacuated and argon-filled reactor thermostated to 44 °C. The solvent was saturated 3× with 5 bar of ethylene under stirring (500 rpm) over a total of 15 min. The reactor was vented with a slow ethylene flow remaining (1.1 bar), and 5 mL of a toluene solution containing 10 μmol of the respective catalysts **1a-pyr**, **7-pyr**, or **8-pyr** was injected by syringe/Teflon-cannula. The injection-valve was closed, and the reactor was pressurized with 40 bar of ethylene, while the temperature rose to 49−51 °C within 2 min. The temperature of the thermostate was adjusted to 48.5 °C, resulting in a polymerization temperature in the reactor between 49.5 and 51 °C. After a total of 40 min stirring at 500 rpm, 40 bar of ethylene, the reaction was quenched by terminating the ethylene flow, carefully venting the reactor, and pouring the reaction mixture into 200 mL of technical grade methanol. The resulting mixtures containing precipitated polyethylenes in case of complexes **1a-pyr**, **7a-c-pyr**, and **8a-c-pyr** were stirred for 1 h at 20 °C, the polymer collected by filtration, washed with 2 × 50 mL of methanol and 50 mL of acetone, and dried to constant weight under vacuum (50 °C, 20 mbar). In case of polyethylenes obtained with complexes **7d−f-pyr**, **8d−g-pyr**, workup was as follows: The homogeneous solution was evaporated to dryness under reduced pressure (60−80 °C, 500−20 mbar). To the resulting highly viscous orange-yellowish oil was added methanol (10 mL), the resulting mixture was vigorously stirred for 30 min at 55 °C, the mixture was cooled to 0 °C, and the yellowish methanol phase was decanted. Finally, residual solvent was removed at 50 °C, 20 mbar for 2 d. Characterization data and yields are given in Table 4.

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Supporting Information Available: Examples of ^{1}H and ^{13}C{^{1}H} NMR spectra of new compounds and obtained polyethylenes, GPC traces, mass-flow traces, and CIF files containing the X-ray diffraction analyses of complexes **7b-pyr** (CCDC-629991) and **8f-pyr** (CCDC-629992). This material is available free of charge via the Internet at http://pubs.acs.org.