Manganese(II) Complexes in Ethene Polymerization

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A series of manganese(II) dichloro complexes made *in situ* and bearing mainly various nitrogen ligands was studied with a parallel screening method in order to identify catalytically active complexes for ethene polymerization using methylaluminoxane (MAO) as a cocatalyst. From the series two of the most active octahedral manganese(II) complexes, those bearing tetradentate nitrogen ligands with chiral bridges, [*N*,*N*′-bis(quinoline-2-methylene)diiminocyclohexane]$MnCl_2$ (**1**) and {*N*,*N*′-(6,6′-dimethylbiphenyl-2,2′-diyl)-bis[(2-pyridyl)methyl]diimine}$MnCl_2$ (**2**), were selected for more detailed studies. According to their solid-state structures, it is common for these C_2-symmetric manganese complexes to have a distorted-octahedral coordination geometry where chlorides occupy cis positions with wide Cl−Mn−Cl angles (132−135°). The highest activity in ethene polymerization (67 kg of PE/((mol of Mn) h)) was obtained with **1**/MAO at 80 °C. Furthermore, the alkylation of **1** and **2** with MeMgBr and (benzyl)MgBr was investigated, but only their monobenzyl derivatives were isolable.

Introduction

Late transition metal catalyzed olefin polymerization has attracted a great deal of interest during the past decade, and new catalyst systems, now covering nearly all late transition metals, have been reported.[1] While manganese compounds are frequently used as catalyst precursors in many other reactions, e.g., epoxidation of alkenes,[2] oxidation of sulfides[3] and hydrocarbons,[4] and various asymmetric reactions,[5] thus far only a few manganese catalysts have been reported for olefin polymerization.[6]

The capability of the homogeneous manganese complexes tris(acetylacetonato)manganese ([$Mn(acac)_3$]),[6a] bis(cyclopentadienyl)manganese ([Cp_2Mn]),[6a] and Mn(salen)Cl[6a] to polymerize ethene after methylalumoxane (MAO) activation has been demonstrated, although very low activities have been reported. In this respect, Mn complexes bearing scorpionate ligands are conspicuous, as they provide moderate activity in ethene polymerization when activated with $Al(i\text{-}Bu)_3/[Ph_3C][B(C_6F_5)_4]$.[6c] It is worth noting that manganese complexes bearing bis(imino)-pyridine and related ligands, commonly known as the most efficient ligand framework for Fe(II)- and Co(II)-based polymerization catalysts, are unable to polymerize ethene.[7] Apparently, the choice of ligand has a significant role in the manganese-catalyzed polymerization reactions.

In this study, a parallel screening method was used to access a large number of Mn/ligand combinations with sufficient steric and electronic diversity for a rapid evaluation of various catalyst candidates for ethene polymerization. After identification of the suitable ligand candidates, the corresponding Mn(II) complexes were studied in more detail. In this respect, the synthesis and structures of novel manganese complexes bearing tetradentate nitrogen ligands, their conversion into alkyl complexes, and their reactivity in ethene polymerization were investigated.

Results and Discussion

Parallel Screening. For an identification of possible Mn(II)-based ethene polymerization catalysts, a parallel screening procedure was utilized, as this method provides a reliable and straightforward access to a relatively large amount of catalyst candidates on a reasonable time scale. The ligand library consisted of 16 different ligands, including a series of diimines and 2,6-bis(imino)pyridyl ligands as prototypes for ligand precursors generally used in olefin polymerization with late transition metal complexes. In addition, various bulky protonated diamine, tetradentate imine, and mono- and bidentate phosphine ligands were included in the library (Chart 1). Furthermore, with bidentate imines, the metal to ligand ratio was varied from 1:1 to 1:2.

Late transition metal complexes are often formed with high yields simply by stirring the metal salt and a ligand in a proper solvent.[8] Hence, Mn(II) complexes for the parallel screening

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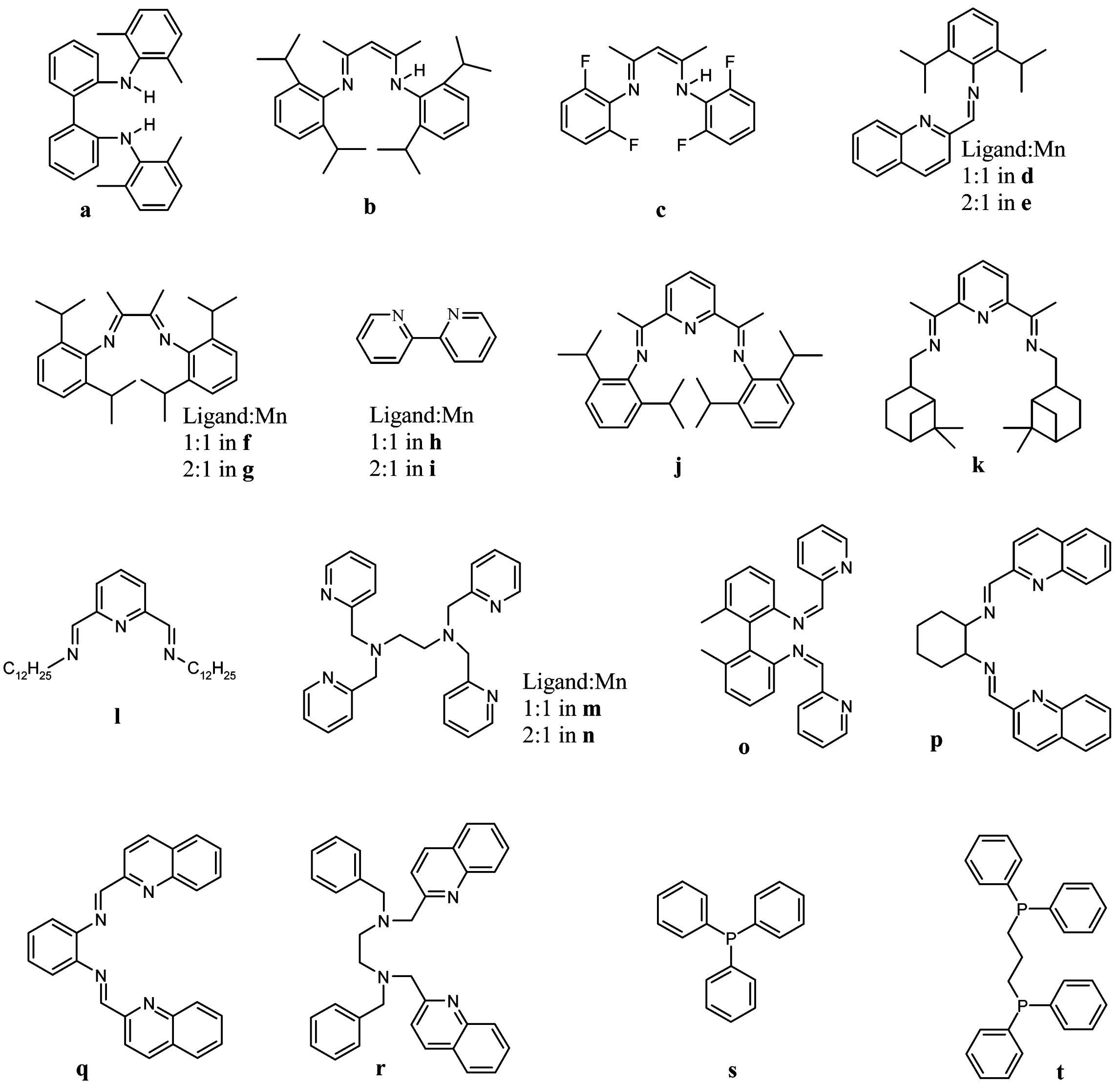
Chart 1. Selected Examples of the Ligands Used in the Primary Screening[a]



[a] Ligands **h**/**i**, **m**/**n**, **s**, and **t** were purchased from commercial sources and used as such. Ligands **a**, **b**, **f**/**g**, and **j**−**r** were synthesized according to literature procedures,[11] and the preparation of ligands **c** and **d**/**e** is described in the Experimental Section.

were synthesized *in situ* in a glove box under an argon atmosphere using small glass reactors sealed with septa. Dry THF appeared to be the most suitable solvent for the complex preparation. To ensure the complex formation, a long reaction time, 48 h, was applied and during this period solid $MnCl_2$ disappeared completely.

The primary screening of ethene polymerizations was done in a 1 L steel autoclave[9] containing 10 small glass reactors. Complexes made *in situ*, toluene, and MAO were loaded into the separate glass reactors in a glovebox, and the autoclave was sealed. After ethene pressure was introduced (5 bar), the autoclave was kept 1 h at room temperature, followed by heating to 60 °C. In these experiments complexes based on ligands **e**, **g**, **i**, **o**, and **p** were able to produce polyethene (PE) (Chart 1).[10] Apparently, a tetradentate imine ligand or two bis(imine) ligands are able to create a suitable coordination sphere for Mn(II) to be active in ethene polymerization.

As was observed for the series of tetradentate ligands **o**−**r**, even minor modifications in the ligand structure can be detrimental for catalytic properties. While the manganese complexes bearing chiral ligands **o** and **p** are active in ethene polymerization, **q**, with a phenyl bridge, is not (Chart 1). As shown previously, phenyl-bridged tetradentate ligands such as **q** prefer a planar coordination with late transition metals and

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[9] For a more detailed description of the autoclave setup, see: Lahtinen, P.; Korpi, H.; Haavisto, E.; Leskelä, M.; Repo, T. *J. Comb. Chem.* **2004**, *6*, 967−973.

[10] Results of the parallel screening: ligands **a**−**d**, **f**, **h**, **j**−**n**, and **q**−**t**, no polymer; ligands **g** and **i**, 1−2 mg of polymer; ligands **e**, **o**, and **p**, 3−6 mg of polymer. Melting points of the polymers were 130−135 °C (determined with a melting point apparatus).

[11] References to ligand synthesis are as follows; the letters correspond to the ligands presented in Chart 1: (**a**) Kettunen, M.; Vedder, C.; Brintzinger, H.-H.; Mutikainen, I.; Leskelä, M.; Repo, T. *J. Eur. Chem.* **2005**, 1081−1089. (**b**) Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514−1516. (**f**/**g**) tom Dieck, H.; Munz, C.; Mueller, C. *Z. Naturforsch.* **1981**, *36B*, 823−832. (**j**) Small, B. L.; Brookhart, M.; Bennet, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049−4050. (**k**) Abu-Surrah, A. S.; Lappalainen, K.; Piironen, U.; Lehmus, P.; Repo, T.; Leskelä, M. *J. Organomet. Chem.* **2002**, *648*, 55−61. (**l**) Valkama, S.; Lehtonen, O.; Lappalainen, K.; Kosonen, H.; Castro, P.; Repo, T.; Torkkeli, M.; Serimaa, R.; ten Brinke, G.; Leskelä, M.; Ikkala, O. *Macromol. Rapid Commun.* **2003**, *24*, 556−560. (**o**) Ettunen, M.; Vedder, C.; Schaper, F.; Leskelä, M.; Mutikainen, I.; Brintzinger, H. H. *Organometallics* **2004**, *23*, 3800−3807. (**p**) Abu-Surrah, A.; Laine, T.; Repo, T.; Fawzi, R.; Steinmann, M.; Rieger, B. *Acta Crystallogr.* **1997**, *C53*, 1458−1459. (**q**) Yliheikkilä, K.; Lappalainen, K.; Castro, P. M.; Ibrahim, K.; Löfgren, B.; Leskelä, M.; Repo, T. *Eur. Polym. J.* **2006**, *42*, 92−100. (**r**) Ibrahim, K.; Yliheikkilä, K.; Löfgren, B.; Abu-Surrah, A.; Lappalainen, K.; Leskelä, M.; Repo, T.; Seppälä, J. *J. Eur. Polym.* **2004**, *40*, 1095−1104.

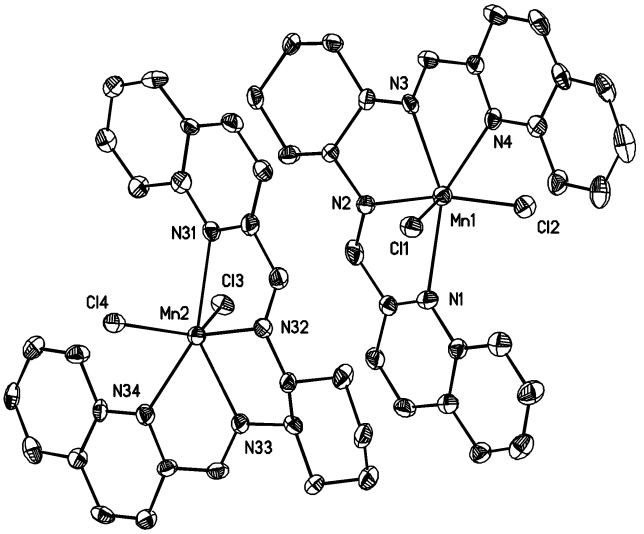

Figure 1. ORTEP drawing of [(1*R*,2*R*)-(−)-*N*,*N′*-bis(quinoline-2-methylene)diiminocyclohexane]manganese(II) chloride (complex **1**). Two independent molecules are displayed. H atoms and one CH_2Cl_2 solvent molecule are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

thus occupy equatorial sites in the octahedral coordination sphere, leaving chlorides in the trans orientation.[12] Altogether, the observations made above indicate that a ligand backbone that distorts the equatorial N_4Mn plane is beneficial for the catalytic activity. In addition, the Mn complex based on the ethylene-bridged ligand **r** proved to be inactive in ethene polymerization. Whether this is due to either structural freedom[2a,13] of the ethylene bridge or replacement of the diimine functionality with diamine still remains indistinguishable. In accordance with previous reports[7] and despite the major modifications of the imino substituents, the series of Mn(II) complexes with bis(imino)pyridine ligands **j**−**l** turned out to be inactive. It has been proposed that the inability of bis(imino)pyridineMn(II) complexes to catalyze olefin polymerization is due to the high-spin d^5 electronic configuration of manganese, which destabilizes Mn−alkyl bonding.[7a]

On the basis of these results from the primary screening, three major requirements for a manganese-based olefin polymerization catalyst bearing imine ligands can be determined: (1) common for the active Mn catalysts is the presence of two imine pyridine/quinoline functionalities separated by two carbon atoms, (2) active Mn(II) complexes are six-coordinated, and (3) chiral ligand backbones that distort the planar coordination of the tetradentate ligands in the octahedral coordination sphere of Mn are beneficial.

Synthesis and Solid-State Structures. On the basis of the results of the primary screening, the three most active Mn(II) catalysts were chosen for a more detailed study. Manganese(II) complexes **1**−**3** were prepared in practically quantitative yield by the reaction of $MnCl_2$ and ligands **p**,[14] **o**,[15] and **e**, respectively. Since the complexes were insoluble in THF and Et_2O, the excess ligand was removed easily by washing raw products with these solvents. Single crystals of **1** and **2** were obtained from CH_2Cl_2 by slow evaporation of the solvent, whereas all our attempts to crystallize **3** gave only a microcrystalline powder.

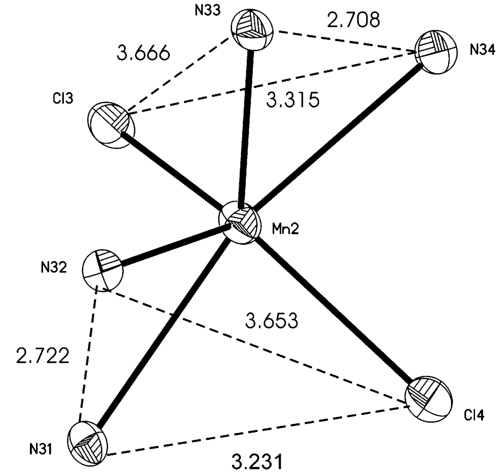

Figure 2. ORTEP drawing of the coordination sphere of complex **1** (Mn2), illustrating the extensive rhombic distortion of the octahedral geometry. The distortion of Mn1 is similar.

Table 1. Crystallographic Data for Complexes 1 and 2

	1	**2**
formula	$C_{26}H_{24}N_4MnCl_2\cdot$ CH_2Cl_2	$C_{26}H_{22}N_4MnCl_2\cdot$ $3CH_2Cl_2$
fw	603.26	771.09
space group	$P2_1$	$P\bar{1}$ (No. 2)
a, Å	9.249(2)	9.767(1)
b, Å	27.100(4)	12.913(1)
c, Å	11.653(2)	13.741(1)
α, deg	90.0	84.13
β, deg	107.78(3)	77.98(1)
γ, deg	90.0	85.77
V, $Å^3$	2781.3(9)	1683.7(2)
d_{calcd}, g cm^{-3}	1.441	1.521
Z	4	2
μ, cm^{-1}	0.883	1.054
λ, Å	0.710 73	0.710 73
T, K	173(2)	173(2)
R^b	0.0555	0.0948
$R_w{}^c$	0.0989	0.2289
Flack param	0.03(2)	

[a] In complex **2** three methylene dichloride solvent molecules were found in a disordered state, which is reflected in the final *R* value. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$ for observed reflections ($I > 2\sigma(I)$). [b] $R_w = \{\sum[w(F_o{}^2 - F_c{}^2)^2]\}^{1/2}$ for all data.

X-ray diffraction measurements of the tetradentate complexes confirmed the assumption made above that a chiral bridging unit can have a significant role in turning inactive Mn(II) complexes into catalytically active ones. As shown for **1** in Figure 1, the chiral cyclohexyl group twists the N_4−Mn basal plane and thus causes a substantial rhombic distortion in the octahedral geometry of Mn(II) (Figure 2). As a consequence, chlorine atoms are bent away from their apical positions toward the cis conformation. For the two independent molecules in the unit cell, the Cl−Mn−Cl angles were 132 and 135° and the distorted N_4−Mn basal planes were practically perpendicular to the plane of $MnCl_2$ (Table 2).

In comparison to **1**, the biphenyl-bridged **2** has an even more distorted coordination sphere. The pyridine nitrogen atoms are shifted away from the N_4−Mn basal plane, and planes defined by N1−Mn−N2 and N3−Mn−N4 bisect each others with a 49.0(2)° angle (Figures 3 and 4). As in the case of **1**, due to the twisted-octahedral geometry the chlorine atoms are shifted away from their apical positions toward the cis orientation with a

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1 and 2

	1[a]		**1**[a]	**2**
Mn2−N32(imine)	2.288(5)	Mn1−N2(imine)	2.289(5)	2.317(5)
Mn2−N33(imine)	2.292(5)	Mn1−N3(imine)	2.299(5)	2.345(5)
Mn2−N31(pyridine)	2.510(4)	Mn1−N1(pyridine)	2.508(4)	2.336(5)
Mn2−N34(pyridine)	2.495(5)	Mn1−N4(pyridine)	2.485(5)	2.323(5)
Mn2−Cl4	2.401(2)	Mn1−Cl2	2.407(2)	2.4844(19)
Mn2−Cl3	2.398(2)	Mn1−Cl1	2.403(2)	2.4763(19)
Cl3−Mn2−Cl4	132.46(7)	Cl1−Mn1−Cl2	135.60(7)	133.17(7)
N31−Mn2−N34	152.64(18)	N1−Mn1−N4	151.99(18)	154.72(19)
N32−Mn2−N33	70.91(17)	N2−Mn1−N3	71.29(18)	81.71(17)
N31−Mn2−Cl3	85.33(13)	N1−Mn1−Cl1	85.34(13)	83.80(13)
N32−Mn2−Cl3	115.42(14)	N2−Mn1−Cl1	103.42(15)	131.60(14)
N33−Mn2−Cl3	102.79(14)	N3−Mn1−Cl1	111.41(13)	87.14(13)
N34−Mn2−Cl3	85.24(13)	N4−Mn1−Cl1	85.49(13)	85.27(13)
N31−Mn2−Cl4	82.24(13)	N1−Mn1−Cl2	82.83(13)	86.11(13)
N32−Mn2−Cl4	102.33(14)	N2−Mn1−Cl2	111.63(15)	86.00(13)
N33−Mn2−Cl4	116.65(14)	N3−Mn1−Cl2	105.18(14)	131.14(13)
N34−Mn2−Cl4	85.36(13)	N4−Mn1−Cl2	85.38(13)	84.88(14)

[a] Data for two independent molecules of complex **1**.

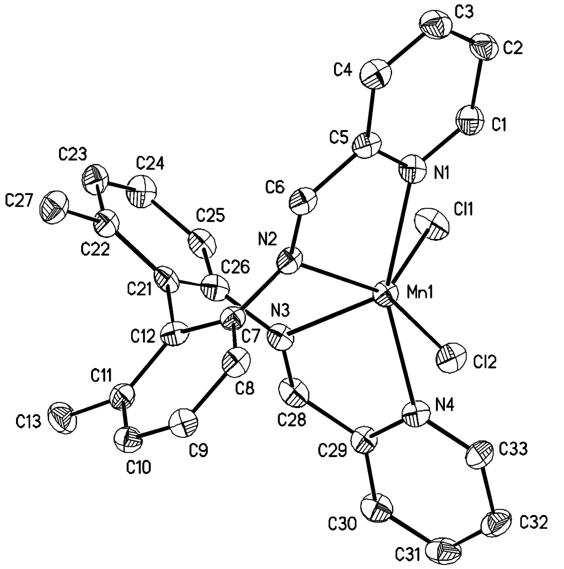

Figure 3. ORTEP drawing of the coordination sphere of complex **2**. H atoms and three CH_2Cl_2 solvent molecules are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

rather wide angle, 133°, and the N2−Mn−N3 plane is perpendicular to the plane of $MnCl_2$. Despite the distorted-octahedral coordination in **1** and **2**, both complexes have a molecular C_2 symmetry.

Solid-state structures for iron(II) and cobalt(II) dichloro complexes bearing the same ligand as **2** have been reported earlier.[16] Due to the rigid biphenyl-bridged ligand, both Fe(II) and Co(II) complexes have slightly distorted octahedral coordination spheres where the pyridyl moieties occupy the apical positions and the imine nitrogens together with the chlorides are, in practice, coplanar and form the basal plane. This orientation of the ligand framework brings the chlorides clearly cis to each other, and the Cl−M−Cl angle is substantially smaller for the iron(II) (111°) and cobalt(II) complexes (109°) than for **2** (133°). Within these complexes the M−Cl bond lengths are practically same for Fe and Co (2.40 Å), while the Mn−Cl bonds are noticeably longer (statistically 2.48 Å for **2**). Quite surprisingly, the ability of the Fe complex to catalyze ethene polymerization after MAO activation is negligible.[16]

Bis(imino)pyridine Mn(II) complexes have been extensively studied because of their relevance to highly active Fe(II) analogues.[7] In fact, within this ligand framework the coordination geometry of manganese(II) dichloride is isostructural with iron(II) dichloride and can be described as a distorted-square-pyramidal arrangement.[7b] In comparison, the bis(imino)pyridine Mn(II) complex has a narrower Cl−Mn−Cl angle (120°) than **1** (132° and 135°) and **2** (133°) and shorter Mn−Cl bond distances (2.31−2.35 Å) than in **1** (2.40−2.41 Å) and in **2** (2.48 Å). Thus, despite the appropriate coordination parameters, MAO-activated bis(imino)pyridine Mn(II) complexes are inactive in ethene polymerization. However, another structural parameter that separates catalyst precursors **1** and **2** from inactive species can be detected.

While imine N−Mn bond lengths are rather constant for all of the Mn complexes described above (2.29−2.35 Å), pyridine N_{Py}−Mn distances deviate noticeably. The N_{Py}−Mn bonding with the bis(imino)pyridine ligand is rather short (2.20 Å), while in **1** the quinoline N−Mn distances are remarkably elongated (2.49−2.51 Å), even when compared to those in **2** (2.32−2.34 Å). This noticeable difference in the coordination strength of the pyridyl lone pairs, together with the elongated Mn−Cl bonds, might be significant with regard to the catalytic properties of these Mn complexes. Interestingly, a distortion of the N−Mn bond lengths similar to that in **1** and **2** can be also be visualized, although to a lesser extent, from the previously published solid-state structures of [bis(pyridine-2-methylene)diiminocyclohexane]-$MnCl_2$[3b] and bis(bipyridine)$MnCl_2$,[17] which, according to a preliminary screening, possess some catalytic activity after MAO activation.

The diimine ligands **o** and **p** or bipyridine, while coordinating to $MnCl_2$, cause distortion in the octahedral coordination sphere, whose amplitude depends on the structure of the ligand. In addition, being strong field ligands, they can cause further splitting of the d orbitals. This is seen as an elongation of Mn−N_{Py} bonds. Qualitatively, the elongated N_{Py}−Mn bonds leads to reduced electron donation from the ligand and an increased Lewis acidity of Mn, which might explain the observed ethene polymerization activity of **1** and **2** after MAO activation.[18] For

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(18) The ligand **r** from the primary screening (inactive) has similarities with *N,N′*-dimethyl-*N,N′*-bis(pyridylmethyl)ethane-1,2-diamine, for which a solid-state structure with $Mn^{II}Cl_2$ has been reported.[12] This ligand provides a distorted-octahedral coordination sphere for Mn(II), leaving the chloride anions in mutual cis positions. Despite the replacement of the diimine functionality with diamine, the Mn−N bond length (2.366(2) Å) is in the range of the Mn−N(imine) distances considered here. However, the pyridine N−Mn distance is significantly shorter than in **1** and **2** (see also ref 3b).

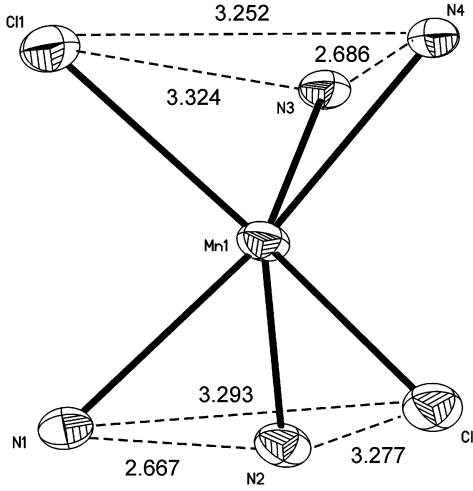


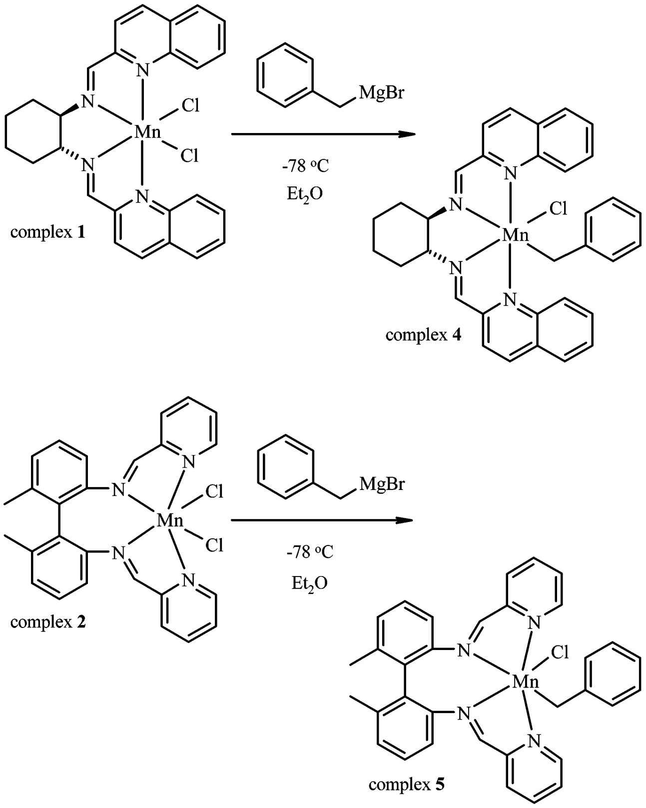
Figure 4. ORTEP drawing of the coordination sphere of **2**, illustrating the distortion of the octahedral geometry toward the antiprismatic organization.

Fe(II) and Co(II) complexes bearing the ligand **e**, the pyridine N−M distances are short and (2.21 and 2.18 Å, respectively) indicate tight coordination. Thus, one possible explanation for the negligible polymerization activity of Fe and Co complexes is their reduced Lewis acidity due to extensive electron donation from the pyridine lone pairs.

Synthesis of Manganese Alkyl Derivatives. It is generally accepted that in the activation of transition metal complexes for olefin polymerization, complexes are converted to corresponding alkyl derivatives by the treatment with aluminum alkyls, most commonly *in situ* with MAO. Such alkyl complexes are prerequisites for the formation of metal alkyl cations, generally considered as catalytically active centers for olefin polymerization. Consequently, transition metal alkyl complexes,[19] including manganese alkyl complexes,[7a,20] are of significant interest.

To avoid decomposition and the formation of hydrolysis and oxidation products, the entire preparation of alkyl complexes was carried out in a glovebox. The treatment of dichloro manganese(II) derivatives **1** and **2** with (benzyl)MgBr provided the monobenzyl manganese complexes **4** and **5** with high yields, while attempts to synthesize dibenzyl derivatives failed (Scheme 1). It seems that the bulky twisted tetradentate ligands in **1** and **2** are shielding the metal center from further substitution with a relatively large benzyl group. Though complexes **4** and **5** were treated afterward with an excess of (benzyl)MgBr, only the monoalkylated species were isolated. These octahedral mono(benzyl)Mn complexes were adequately stable for EI-MS, micro TOF-MS, and IR characterization.

Scheme 1. Synthesis of Manganese Alkyl Derivatives from Manganese(II) Dichloro Complexes 1 and 2



Although Mn(II) dialkyl species are, in general, well-known,[21] dialkyl derivatives of these octahedral complexes turn out to be highly reactive. Treatment of **1** and **2** with (methyl)MgBr gave highly air- and moisture-sensitive products, which contained, according to HR ESI-MS measurements, dimethyl complexes. In particular, these air-sensitive compounds undergo rapid decomposition during IR and EI-MS measurements, yielding inaccurate results in analyses. It has been shown previously that alkylated bis(imino)pyridine manganese complexes undergo reductive decomposition, and as a result, mono- and zerovalent species are formed.[7a] In addition, the imine ligand can be subject to alkylation.[19b,22] Accordingly, it has been concluded that these reactions might be reasons for their negligible catalytic activity.[7a,19b,22]

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(23) Alkyl complexes were also studied in ethene polymerization. In general, MAO-activated dichloro complexes were more active than the corresponding TIBA/B$(C_6F_5)_3$-activated alkyl complexes. Furthermore, complex **1**/MAO produced polyethene, while the corresponding TIBA/B$(C_6F_5)_3$-activated alkyl complexes resulted in oligomers. The activated alkyl complexes were extremely unstable, and their transfer into the 1 L polymerization reactor without minor air contact was very complicated. This might induce the poor polymerization behavior and production of oligomeric products.

Table 3. Selected Ethene Polymerization Results Catalyzed by MAO-Activated Complexes 1−3[a,23]

cat.	n_{cat} (μmol)	cocat.	[Al]: [Mn]	T_p[b] (°C)	activity[c]	$10^{-3}M_w$[d]	M_w/ M_n[d]	T_m[e] (°C)
1	10	MAO	1000	60	23	1796	6.92	135
1	10	MAO	500	60	10	1184	5.25	135
1	10	MAO	500	80	67	527	28.23[f]	136
2	20	MAO	2000	60	13	729	14.75[f]	136
3	20	MAO	2000	60	17	712	11.08[f]	137

[a] Polymerization conditions: toluene 220 mL, ethene 5 bar, polymerization time 90 min. [b] Polymerization temperature. [c] Activity in kg of PE/((mol of cat) h). [d] Determined by GPC against polystyrene standards. [e] Onset melting temperatures of the polyethenes after heating the samples to 230 °C and cooling down again to 30 °C (cooling and heating rate 10 °C/min). [f] Bimodal molar mass distribution.

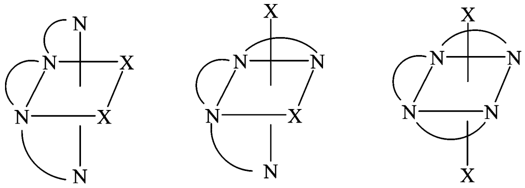
Polymerization. Ethene polymerizations with the Mn complexes **1**−**3** were carried out in toluene solution using 30% MAO as a cocatalyst. The activation process of these manganese complexes turned out to be rather sensitive to the applied temperature. When the complexes were first treated at room temperature with MAO and then heated to the desired polymerization temperatures, reproducible activity levels were achieved. In contrast, catalysts exhibited no or very poor ethene polymerization activities when MAO treatment was done at elevated temperatures.

From the series of catalysts the highest polymerization activity, 67 kg of PE/((mol of cat) h), was observed for the MAO-activated complex **1** at 80 °C and under 5 bar of ethene pressure (Table 3). Although the average activity level is not competitive with that of Fe(II) bis(imino)pyridine complexes,[1] it can be considered high among the homogeneous manganese catalyst systems described in the literature.[6] At 60 °C, the MAO-activated complex **1** produced very high molar mass polyethene (1200−1700 kg/mol) with relative narrow molar mass distribution, though slight tailing toward the low molar mass region was observed. A rise in the polymerization temperature to 80 °C led to PE with clear bimodal molar mass distribution and a decrease in the molar mass of the produced polymer.

Despite variations in the polymerization conditions, the activity of the biphenyl-bridged **2** remained low, below 15 kg of PE/((mol of cat) h). Moreover, the unbridged complex **3**, bearing the ligand **e**, gave activities practically equal with those of **2**. Both **2** and **3** produced high molar mass polyethene with bimodal molar mass distribution.

Although the alkylation experiments underline the high reactivity of the dialkyl−Mn species, and thus formation of radical species via complex degradation is possible, the bimodality of the polymer strongly suggests the presence of two different, structurally defined catalytically active centers. Probably, the high polymerization temperature causes intramolecular fluctuation of the coordination sphere of the activated manganese complexes. Intuitively, unbridged **3** has the needed structural freedom for the isomerization, while for the manganese complexes **1** and **2** bearing the rigid chiral ligands the structural fluctuation is more restricted. However, the existence of structural isomerization of similar manganese complexes has been verified by crystal structure determination,[13,24] and the three possible conformational isomers for tetradentate ligands in an octahedral coordination sphere are illustrated in Chart 2. In addition, a similar fluctuation of the complex geometry during the activation has been reported for Fe(II) derivatives of **2** by Brintzinger et al.[16]

Chart 2. Possible Conformational Isomers of a Tetradentate Ligand in Octahedral Coordination Geometry[a,25]



[a] X can be a chlorine atom or an alkyl or polymer group.

Conclusions

Parallel screening is an efficient method to identify new catalytically active complexes for various reactions, in this case for Mn(II)-based polymerization catalysts. In this way, a relatively large amount of catalyst precursors made *in situ* were studied on a short time scale. From the screening experiments, three manganese(II) dichloro complexes, two bearing a chiral tetradentate ligand and one having two bidentate nitrogen ligands, were identified to be active in ethene polymerization and were chosen for further studies. Consequently, on the basis of these results, three essential requirements for the active manganese(II) catalyst precursors can summarized: (1) they are six-coordinated, 17-electron species, (2) ligands with imine pyridine/quinoline moieties separated by two carbon atoms must be present, and (3) there must be distortion of the octahedral configuration of the manganese by the coordination of the ligand framework. Hence, conjugated nitrogen ligands, particularly a combination of imino and pyridine or quinoline donors, have unique properties in the area of manganese-based polymerization catalysis. After MAO activation their Mn(II) complexes were proved to be active in ethene polymerization and the activity level of these polymerizations was high among the known homogeneous manganese systems. Probably, the high polymerization temperature causes intramolecular fluctuation of the coordination sphere of the activated manganese complexes. The results above offer an interesting route for the further development of Mn-based olefin polymerization catalysts.

Experimental Section

General Considerations. Complex syntheses and polymerization experiments were performed under an argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (HPLC grade) were dried over sodium flakes and distilled before use. Anhydrous manganese(II) chloride ($MnCl_2$) was purchased from Aldrich and stored under an argon atmosphere. Other reagents of high purity grade were purchased from commercial sources and used as received. MAO (30% in toluene) was obtained from Borealis Polymers Ltd.

The mass spectrum of complex **1** was recorded with a Mariner electrospray ionization MS (ESI-MS), and the mass spectra of complexes **2**−**7** were measured with a Bruker MicrOTOF Esquire 3000Plus instrument. The mass spectra of complexes **4** and **6** were measured with a JEOL JMS-SX102 EI^+ instrument (70 eV), using a direct inlet method. Infrared spectra were measured on a Perkin-Elmer SpectrumOne spectrometer using an ATR sampling accessory. NMR spectra were recorded in $CDCl_3$ at 25 °C on a Varian Gemini 200 spectrometer operating at 200 MHz (^1H NMR) and 50.286 MHz (^{13}C NMR). Elemental analyses were performed with an EA 1110 CHNS-O CE instrument.

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Molar masses and molar mass distributions of polyethene samples were determined with a Waters Alliance GPCV 2000 high-temperature gel chromatographic device. HMW7, 2*HMWGE, and HMW2 Waters Styrogel columns were used for GPC. Measurements were performed in 1,2,4-trichlorobentzene (TCB) at 160 °C relative to polyethene standards, and 2,6-di-*tert*-butyl-4-methylphenol was used as a stabilizer. Chromatograms were calibrated using linear polystyrene standards. DSC measurements were performed on a Mettler Toledo Star system. Melting temperatures of PE were measured from 30 to 230 °C using a heating rate of 10 °C/min. The melting temperature was determined from the second heating curve.

Parallel Screening. Small glass reactors (Radleys Discovery Technologies, carousel reaction station) were loaded with different ligands and manganese(II) chloride and sealed with septa. Solvent (THF, 4 mL) was added to each reactor through a septum, and stirring was continued at room temperature for 48 h to ensure the complex formation. After this, the solvent (THF) was evaporated. A mixture of MAO (30%) and toluene was added to each reactor, and the reactors were then placed in a custom-made steel autoclave.[9] After addition of ethene (5 bar), the autoclave was kept at room temperature for 1 h. Subsequently, the autoclave was placed in the oil bath (60 °C) for 18 h. The batch polymerizations were stopped by depressurizing the reactor and by adding acidified methanol (1% HCl). Precipitated polymer was stirred in methanol overnight and dried in an oven (60 °C) to constant weight.[10] Control reactions with combinations of THF, $MnCl_2$, and MAO without a ligand were inactive in polymerization.

Preparation of Ligands. Ligands **h/i, m/n**, **s**, and **t** were purchased from commercial sources and used as such. Ligands **a, b, f/g**, and **j**−**r** were prepared according to earlier published procedures.[10]

Ligand c, Bis(2,6-difluorophenyl)-NAcNAc. This ligand was synthesized from 2,6-difluoroaniline (55 mmol, 7.1 g, 5.92 mL) and 2,4-pentanedione (25.8 mmol, 2.58 g, 2.70 mL). The starting materials were dissolved in toluene, and a catalytic amount of *p*-toluenesulfonic acid was added. The reaction mixture was refluxed for 12 h with a Dean−Stark apparatus. Toluene was evaporated, and subsequently 100 mL of Et_2O, 80 mL of H_2O, and 10 g of Na_2CO_3 were added. After the dissolution of solids, the Et_2O phase was separated and washed with saturated Na_2CO_3 solution (2 × 10 mL) and brine (10 mL) and dried over $MgSO_4$. The evaporation of Et_2O gave an off-white crystalline solid as a product. The pure product (5.1 g, 62%) was obtained by recrystallization from absolute EtOH. ^{1}H NMR ($CDCl_3$): δ 1.95 (s, 6H, $-CH_3$), 5.11 (s, 1H, $-CH{=}$), 6.88−7.04 (m, 6H, H_{arom}), 12.2 (s, 1H, N*H*). ^{13}C NMR ($CDCl_3$): δ 20.75 (s, CH_3), 97.71 (s, $=CH-$), 111.73−158.92 (C_{arom}, multiplets due to the ^{19}F couplings), 163.23 (s, $C{=}N$). EI-MS: *m/z* 322 ([$C_{17}H_{14}N_2F_4$] (M^+), 80%), 195 ($M^+ - C_6H_3F_2$, 100%), 154, ($M^+ - C_6H_3F_2NC_2H_4$, 90%).

Ligand d/e, 2-[(2,6-Diisopropylphenylimino)methyl]quinoline. This ligand was synthesized by a modified literature procedure, reported earlier for 2-{[(2,6-diisopropylphenyl)imino]methyl}-pyridine.[26] Ethanol (40 mL), 2,6-diisopropylaniline (1.6 g, 9.1 mmol), and 2-quinolinecarboxaldehyde (1.3 g, 7.8 mmol) were combined and refluxed for 20 min. The solvent was removed, and the raw product was purified by column chromatography on basic alumina using pentane/ethyl acetate (3:1) as an eluent. Recrystallization from *n*-pentane yielded yellow crystals (2.2 g, 89%, 7.0 mmol). ^{1}H NMR ($CDCl_3$): δ 1.21 (d, 12 H, H_{Me}), 3.02 (m, 2H, $CHMe_2$), 7.0−8.5 (10 H, H_{arom}, H_{imine}). ^{13}C NMR ($CDCl_3$): δ 23.62 ($-CH_3$), 28.19 ($-CH-$, isopropyl), 118.47, 122.95, 123.24, 124.71, 127.98, 129.26, 130.13, 136.90, 137.28, 148.19, 148.60, 154.72 (C_{arom}), 163.57 ($-HC{=}N$). EI-MS: *m/z* 316 ([$C_{22}H_{24}N_2$] (M^+), 40%), 301 ($M^+ - CH_3$, 50%), 273 ($M^+ - C_3H_7$, 45%).

Preparation of Complexes. [*N,N′*-Bis(quinoline-2-methylene)-diiminocyclohexane]manganese(II) Dichloride (1). Manganese(II) chloride (0.18 g, 1.4 mmol) was added to a stirred solution of (1*R*,2*R*)-(−)-*N,N′*-bis(quinoline-2-methylene)diiminocyclohexane (DQDEC; 0.73 g, 1.9 mmol)[27] in THF (30 mL). The solution slowly turned yellow, and stirring was continued for 48 h at room temperature. The yellow product was filtered and washed with THF (2 × 10 mL) and Et_2O (2 × 10 mL) and dried under vacuum (0.73 g, 99%). Crystals suitable for single-crystal diffraction studies were obtained by slow evaporation of solvent (CH_2Cl_2). Anal. Found: C, 59.97; H, 5.16; N, 10.93. Calcd: C, 60.25; H, 4.67; N, 10.81. ESI-MS: *m/z* 540.6 ([M + Na] 10%). IR: ν 1641 m (C═N, ligand), 1655 m cm^{-1} (C═N, complex).

{*N,N′*-(6,6′-Dimethylbiphenyl-2,2′-diyl)bis[(2-pyridyl)methyl]-diimine}manganese(II) Dichloride (2). This complex was synthesized as described above for **1**. Manganese(II) chloride (0.20 g, 1.6 mmol) and *N,N′*-(6,6′-dimethylbiphenyl-2,2′-diyl)bis(2-pyridylmethyl)diimine[15] (0.74 g, 1.9 mmol) were used. Yellow crystals (0.79 g, 97%) grew, similarly to the path described for complex **1**. Anal. Found: C, 60.07; H, 4.38; N, 11.13. Calcd: C, 60.48; H, 4.29; N, 10.88. HR-MS (ESI): *m/z* calcd for [$C_{26}H_{22}N_4MnCl_2$], 515.059 65; *m/z* obsd, 515.059 74; error, 0.18 ppm. IR: ν 1632 m, 1585 m, 1567 s (C═N, ligand), 1632 s, 1592 s, 1568 m cm^{-1} (C═N, complex).

Bis{2-[((2,6-diisopropylphenyl)imino)methyl]quinoline}-manganese(II) Dichloride (3). Manganese(II) chloride (0.13 g, 1.1 mmol) and 2,6-bis(1-methylethyl)-*N*-(2-quinoline-2-methylene)-phenylamine (**e**; 0.70 g, 2.2 mmol) were mixed in toluene (20 mL). The isolation and purification of complex **3** was analogous to the methods described above for complex **1**. Yield: 0.73 g, 91%. HR-MS (ESI): *m/z* calcd for [$C_{44}H_{48}N_4$], 758.2709; *m/z* observed, 758.2686; error, 3.01 ppm. IR: ν 1634 s (in ligand C═N), 1630 s cm^{-1} (in complex C═N).

Preparation of Manganese Alkyl Complexes. [*N,N′*-Bis-(quinoline-2-methylene)diiminocyclohexane]benzylmanganese-(II) Chloride (4). A solution of (benzyl)MgBr in Et_2O (1 M, 0.8 mL, 0.8 mmol) was added via a syringe to a solution of complex **1** (0.2 g, 0.4 mmol) in Et_2O (10 mL) at −78 °C. Stirring was continued for 5 h, and the resulting mixture was kept in a freezer (−20 °C) overnight. All volatiles were then removed under vacuum, and the brown residue was extracted with THF, followed by filtration through a PTFE syringe filter in a glovebox. The resulting solution was evaporated off under vacuum. The brown product (0.19 g, 83%) was crystallized by layering THF and hexane. Despite our efforts, only the monoalkylated species could be prepared. The alkylated complex **4** was treated afterward with an excess of (benzyl)Mg, but no further alkylation occurred. HR-MS (ESI): *m/z* calcd for [$C_{33}H_{31}N_4MnCl$ + H]$^+$, 574.1695; obsd, *m/z* 574.1691; error, 0.25 ppm. EI-MS: *m/z* 574 ([$C_{33}H_{31}N_4MnCl$] (M^+), 3%), 483 ($M^+ - C_7H_7$, 6%). IR: ν 700.75 s (monosubstituted benzene ring), 749.90 s (monosubstituted benzene ring), 1565.16 w, 1600.55 w, 1618.25 w cm^{-1} (aromatic, not present in the corresponding dichloro complex).

{*N,N′*-(6,6′-Dimethylbiphenyl-2,2′-diyl)bis[(2-pyridyl)methyl]-diimine}benzylmanganese(II) Chloride (5). A solution of (benzyl)MgBr in Et_2O (1 M, 0.8 mL, 0.8 mmol) was added via a syringe to a solution of complex **2** (0.2 g, 0.4 mmol) in Et_2O (10 mL) at −78 °C. Stirring was continued for 5 h, and the resulting mixture was kept in a freezer (−20 °C) overnight. After 2 h of stirring at −20 °C the brown solution and yellow residue turned dark green. All volatiles were then removed under vacuum, and the solid residue was extracted with toluene and THF. The reddish brown extracts were filtrated through a PTFE syringe filter, and solvents were

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evaporated off under vacuum. The brown product was crystallized by layering THF and hexane. As above, only the monoalkylated species were observed. Yield: 0.21 g, 92%. HR-MS (ESI): m/z calcd for $[C_{33}H_{29}N_4MnCl + H]^+$, 572.1534; m/z obsd, 572.1522; error, 2.08 ppm. EI-MS: m/z 572 ($[C_{33}H_{29}N_4MnCl]$ (M^+), 5%), 487 ($M^+ - C_7H_7$, 52%), 491 ($M^+ - C_7H_7MnCl$, 50%). IR: ν 699 and 732 s (monosubstituted benzene ring, not present in the corresponding dichloro complex), 2845 and 2921 m cm^{-1} ($-CH_2-$).

Methylation of Manganese Dichloro Complexes. Reaction of 1 with MeMgBr. Complex **1** (0.1 g, 0.2 mmol) and MeMgBr in Et_2O (3.0 M, 0.2 mL, 0.6 mmol) were mixed in Et_2O at −78 °C. The isolation and purification of the resulting product was analogous to that described above for alkyl complex **4**. Yield of the brown product: 0.09 g. HR-MS (ESI): m/z calcd for the dimethyl Mn derivative ($C_{28}H_{31}N_4Mn$), 478.1923; m/z obsd, 478.1925; error, 0.41 ppm. Due to the rapid decomposition of the compound in the air, EI-MS measurements and IR measurements were not feasible.

Reaction of 2 with MeMgBr. Complex **2** (0.1 g, 0.2 mmol) and MeMgBr in Et_2O (3.0 M, 0.2 mL, 0.6 mmol) were mixed in Et_2O at −78 °C. A procedure identical with that described for alkyl complex **4** was then carried out. Yield of the brown product: 0.07 g. HR-MS (ESI): m/z calcd for the dimethyl Mn derivative ($C_{28}H_{28}N_4Mn + Na$), 498.1586; m/z obsd, 498.1569; error, 3.59 ppm. Due to the rapid decomposition of the compound in the air, EI-MS measurements and IR measurements were not feasible.

Single-Crystal X-ray Diffraction Studies. Crystal data for complexes **1** and **2** were collected with a Nonius KappaCCD area-detector diffractometer at 173(2) K using Mo Kα radiation (graphite monochromator); $\lambda = 0.710\,73$ Å. Software used: data reduction, COLLECT;[28] absorption correction, SADABS;[29] solution and refinement, SHELX97;[30] graphics, SHELXTL/PC.[31] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined on calculated positions. The displacement factors of the H atoms were 1.2× (1.5×) those of the host atom. Crystallographic data for complexes **1** and **2** are given in Table 1.

Ethene Polymerization. Polymerizations were carried out in a Büchi 1.0 L stainless steel autoclave equipped with a temperature-controlling unit. Mechanical stirring (800 rpm) was applied, and the partial pressure of ethene and the reaction temperature were kept constant during the polymerization. Ethene consumption was measured with a calibrated mass flow meter and monitored online together with the temperature and pressure.

Toluene (200 mL), the cocatalyst (MAO, 30%) and the catalyst precursor (20 μmol) were introduced into the argon-purged reactor. Once the polymerization temperature was reached, the reactor was charged with ethene to the appropriate pressure. The polymerization was stopped by pouring the contents of the vessel into methanol that was acidified with concentrated hydrochloric acid (1%). The solid polyethene was filtered, washed with methanol, and dried overnight at 60 °C to a constant weight.

When alkylated manganese complexes were used, the catalyst solutions were prepared in a glovebox. TIBA (2.0 mmol) was dissolved in toluene (20 mL), and the mixture was stirred for 20 min. An alkyl complex (20 μmol) was added, and after 10 min of stirring it was activated with $B(C_6F_5)_3$ (21 μmol). The solution was transferred immediately from the glovebox into the thermostated reactor charged with toluene (200 mL) and the appropriate ethene pressure. The polymerization was stopped as described above.

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Supporting Information Available: CIF files giving crystal data for **1** and **2** and GPC chromatograms of PE prepared with **1**/MAO at different reaction temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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