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Neutral and Cationic Alkylmanganese(II) Complexes Containing 2,6-Bisiminopyridine Ligands

Carmen M. Pérez,[a] Antonio Rodríguez-Delgado,[a] Pilar Palma,[a] Eleuterio Álvarez,[a] Enrique Gutiérrez-Puebla,[b] and Juan Cámpora*[a]

Abstract: Manganese alkyl complexes stabilised by 2,6-bis(*N*,*N*′-2,6-diisopropyl-phenyl)acetaldiminopyridine ($^{i\mathrm{Pr}}$BIP) have been selectively prepared by reacting suitable alkylmanganese(II) precursors, such as homoleptic dialkyls $[(MnR_2)_n]$ or the corresponding THF adducts $[\{MnR_2(thf)\}_2]$ with the mentioned ligand. For $R = CH_2CMe_2Ph$ or CH_2Ph, formally Mn^I derivatives are produced, in which one of the two R groups migrates to the 4-position of the central pyridine ring in the $^{i\mathrm{Pr}}$BIP ligand. In contrast, a true dialkyl complex $[MnR_2(^{i\mathrm{Pr}}BIP)]$ can be isolated for $R = CH_2SiMe_3$. In solution, this compound slowly evolves to the corresponding Mn^I monoalkyl derivative. A detailed study of this reaction provides insights on its mechanism, showing that it proceeds through successive alkyl migrations, followed by spontaneous dehydrogenation. Protonation of $[Mn(CH_2SiMe_3)_2(^{i\mathrm{Pr}}BIP)]$ with the pyridinium salt $[H(Py)_2][BAr'_4]$ ($Ar' = 3,5\text{-}C_6H_3(CF_3)_2$) leads to the cationic species $[Mn(CH_2SiMe_3)(Py)(^{i\mathrm{Pr}}BIP)]^+$. Alternatively, the same complex can be produced by reaction of the pyridine complex $[\{Mn(CH_2SiMe_3)_2(Py)\}_2]$ with the protonated ligand salt $[H^{i\mathrm{Pr}}BIP]^+[BAr'_4]^-$. This last reaction allows the synthesis of analogous cationic alkylmanganese(II) derivatives, when precursors of type $[MnR_2(^{i\mathrm{Pr}}BIP)]$ are not available. Treatment of these neutral and cationic $^{i\mathrm{Pr}}$BIP alkylmanganese derivatives with a range of typical cocatalysts (modified methylaluminoxane (MMAO), $B(C_6F_5)_3$, trimethyl or triisobutylaluminum) does not lead to active ethylene polymerisation catalysts.

Keywords: bis(imino)pyridines · manganese · N ligands · olefin polymerization · tridentate ligands

Introduction

In the last ten years, interest in 2,6-bis(imino)pyridine (BIP) complexes has grown steadily. Several examples of such compounds have been known since the 1970s,[1] but wide interest was triggered in 1998, by simultaneous reports from Brookhart[2a] and Gibson[2b] on the capability of iron– and cobalt–BIP complexes, upon treatment with alumoxanes, to catalyse ethylene polymerisation. It was soon discovered that while similar BIP complexes of vanadium[3] or chromium[4] are also catalysts for ethylene polymerisation, analogous manganese derivatives are essentially inactive.[5] In the interim, it has been increasingly recognised that the BIP complexes compose a promising class of homogenous catalysts, not limited to ethylene polymerisation or oligomerisation, but capable of catalysing other reactions as well.[6]

The cause of the catalytic inactivity of Mn–BIP complexes in olefin polymerisation remains unknown. Although it has been suggested that it could be the inefficient activation of $[MnX_2(BIP)]$ complexes with organoaluminum compounds,[5a] it could also be linked to the unique properties of this element in its +2 oxidation state.[7,8] The often unusual structure and behaviour of Mn^{II} organometallic compounds are due to the special stability of their high spin d^5 configuration, which renders the half-filled 3d orbitals nearly unavailable.[8] In contrast, access to empty d orbitals is possible for BIP complexes of other transition metals, owing to the existence of low-lying intermediate spin electronic configurations.[9]

Several research groups have investigated the reactions of BIP complexes of V, Cr, Mn, Fe and Co with alkyllithiums

[a] Dr. C. M. Pérez, Dr. A. Rodríguez-Delgado, Dr. P. Palma, Dr. E. Álvarez, Dr. J. Cámpora
Instituto de Investigaciones Químicas
Departamento de Química Inorgánica
Universidad de Sevilla-Consejo Superior de Investigaciones Científicas
Avenida Américo Vespucio 49, 41092 Sevilla (Spain)
Fax: (+34) 954460565
E-mail: campora@iiq.csic.es

[b] Dr. E. Gutiérrez-Puebla
Instituto de Ciencia de Materiales de Madrid
Consejo Superior de Investigaciones Científicas
Cantoblanco s/n, 28049 Madrid (Spain)

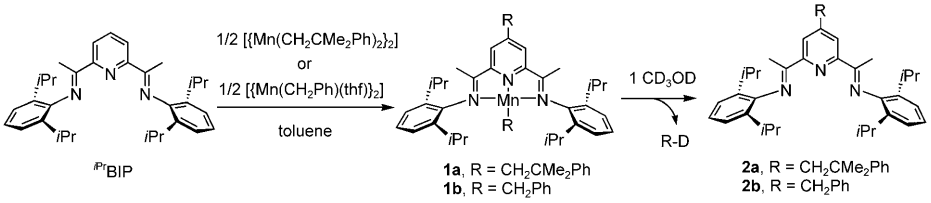
or Grignard reagents to synthesise alkyl complexes relevant to the mechanism of olefin polymerisation.[10–13] These studies unveiled the fascinating reactivity associated to BIP ligands. The outcome of such reactions is usually complex, and straightforward transmetallations are rather exceptional.[11a,13] More often, products arising from apparent reduction of the metal center,[3,4a,5a,13] or from some alteration of the BIP ligand (such as deprotonation,[4a,11e,14] addition of the alkylating reagent to the imine or pyridine moieties[3,4a,11e] or coupling of two ligands to afford dimeric complexes[3,11e,15]) have been observed. In consequence, high-valent alkyl derivatives of type $[MR_n(BIP)]$ ($n>1$; M = transition metal) have been rare until recently. Early studies by Gambarotta showed that manganese is no exception to this behaviour.[3,5a] The treatment of $[MnCl_2(BIP)]$ derivatives with organolithium or organomagnesium reagents leads to mixtures of products, including Mn^{I} or Mn^{0} derivatives, as well as dimeric complexes, arising from intermolecular C–C coupling of the imine functionality.

In our previous work, we have found that ligand exchange reactions provide an efficient mean for the synthesis of various transition metal alkyl complexes. These reactions avoid complications related to potentially reactive ancillary ligands, such as imines. A key requirement for this approach is the availability of suitable alkylmetal precursor complexes. For example, Ni and Pd alkyl derivatives containing α-diimine ligands can be prepared in high yields from the corresponding pyridine dialkyl derivatives $[MR_2(Py)_2]$.[16] Similarly, we reported that alkyliron complexes of the type $[Fe(CH_2SiMe_3)_2(BIP)]$ can be prepared from $[Fe(CH_2SiMe_3)_2(Py)_2]$.[17] In the case of manganese, stable homoleptic alkyls of the type $[(MnR_2)_n]$ are known, which are excellent starting materials for this class of reactions. Copéret has studied the reaction of the bis(neopentyl)manganese with bidentate diimine ligands.[18] Interestingly, these reactions did not afford the expected dialkylMn^{II} complexes, but monoalkylmanganese(II) complexes, arising from alkyl transfer from Mn to the imine ligand. Some time later, we communicated that the reaction of $[\{Mn(CH_2CMe_2Ph)_2\}_2]$ with 2,6-bis(*N,N'*-2,6-diisopropylpropylphenyl)acetaldiminopyridine (^{iPr}BIP) also takes place with the selective transfer of one alkyl group to the pyridine ring,[19] affording a Mn^{I} complex displaying a neophyl substituent at the 4-position of the pyridine ring (see Scheme 1). This reaction is remarkably selective and general and we have been able to use it as part of a practical method for the synthesis of 4-alkyl-BIP ligands. Recently, our group[20] and others[21] have contributed to expand the chemistry of dialkylmanganese complexes that can be used as starting materials for ligand exchange reactions. In this paper, we provide a complete account of the investigation we have carried out on the synthesis of Mn alkyl complexes stabilised by the ^{iPr}BIP ligand, with the final aim of establishing whether these compounds can be converted in active catalysts for olefin polymerisation.

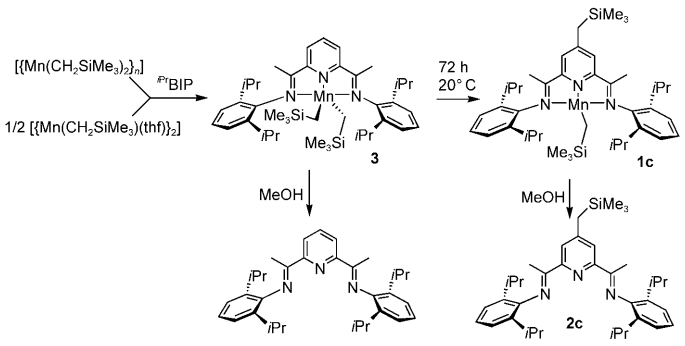
Results and Discussion

Neutral Mn^{I} and Mn^{II} alkyl complexes: As shown in Scheme 1, reaction of $[\{Mn(CH_2CMe_2Ph)_2\}_2]$ with ^{iPr}BIP affords a burgundy red product that has been identified as monoalkyl complex, **1a**.[19] A analogous product, **1b**, was similarly obtained from the reaction of the THF adduct of dibenzylmanganese, $[\{Mn(CH_2Ph)_2(thf)\}_2]$, with the same ligand. The structures of these compounds were established on the basis of analytical data, magnetometry and degradation experiments. Thus, while elemental analyses are consistent with the composition $[MnR_2(^{iPr}BIP)]$, their magnetic moments, 4.9 (**1a**) and 4.8 μ_B (**1b**) (298 K), are too low for typical high-spin Mn^{II} centers, pointing out the presence of only four unpaired electrons. These properties resemble those of the structurally characterised monomethyl complex $[MnMe(^{iPr}BIP)]$, described by Gambarotta.[5a] Both compounds react rapidly with methanol, selectively affording the corresponding 4-alkyl BIP derivatives, **2a** and **2b**. Furthermore, careful measurements showed that **1a** reacts with exactly one equivalent of methanol, releasing one equivalent of the 4-substituted ligand and one of *tert*-butylbenzene, which becomes $[D_1]t$BuPh when CD_3OD is used. These results confirm that compounds **1** contain a single alkyl group bound to the metal center, whilst the other alkyl has been transferred to the pyridine ring of the BIP ligand, as shown in Scheme 1. Analogous monoalkyl derivatives of Fe and Co have also been described in the literature, which according to DFT calculations should be considered metal(II) complexes containing an antiferromagnetically coupled BIP anion radical, rather than true metal(I) compounds.[9,22] This is probably the case for **1a** and **1b** as well.

The presence of a silyl group in the β-position of the R group can enhance the stability of the transition-metal alkyl complexes of the BIP ligands, as compared with analogous derivatives that lack such substituents. For instance, while $[Fe(CH_2SiMe_3)_2(BIP)]$ complexes are stable,[11,17] similar neopentyl derivatives undergo spontaneous Fe–C homolysis affording monoalkyliron complexes.[17f] Thus, in order to throw some light on the mechanism that lead to the formation of complexes **1**, we undertook the synthesis of related trimethylsilylmethyl derivatives (Scheme 2). Both the homoleptic alkyl $[\{Mn(CH_2SiMe_3)_2\}_n]$[20,23] and its THF



Scheme 1.



Scheme 2.

adduct $[\{Mn(CH_2SiMe_3)_2(thf)\}_2]$[20,23] react immediately with $^{i\mathrm{Pr}}$BIP in toluene, affording compound **3** as a dark blue solid. The contrast between its colour and the burgundy-red hue of complexes **1a** and **1b** immediately suggested that **3** would be a different kind of compound. Its magnetic moment at 298 K, 5.3 μ_B, is higher than those of complexes **1** and fully consistent with high-spin Mn^{II} derivative. In addition, unaltered $^{i\mathrm{Pr}}$BIP is recovered when **3** is treated with an excess of methanol, indicating that no alkyl migration had taken place in this case. These observations suggested that this compound might be a genuine Mn^{II} dialkyl complex, which was ultimately confirmed by its crystal structure, shown in Figure 1.

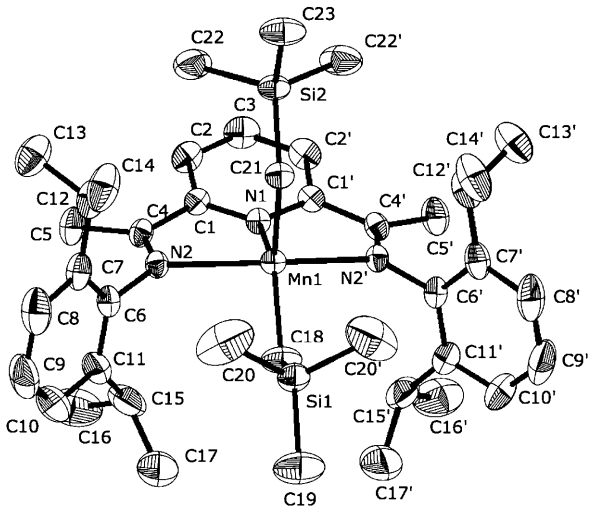
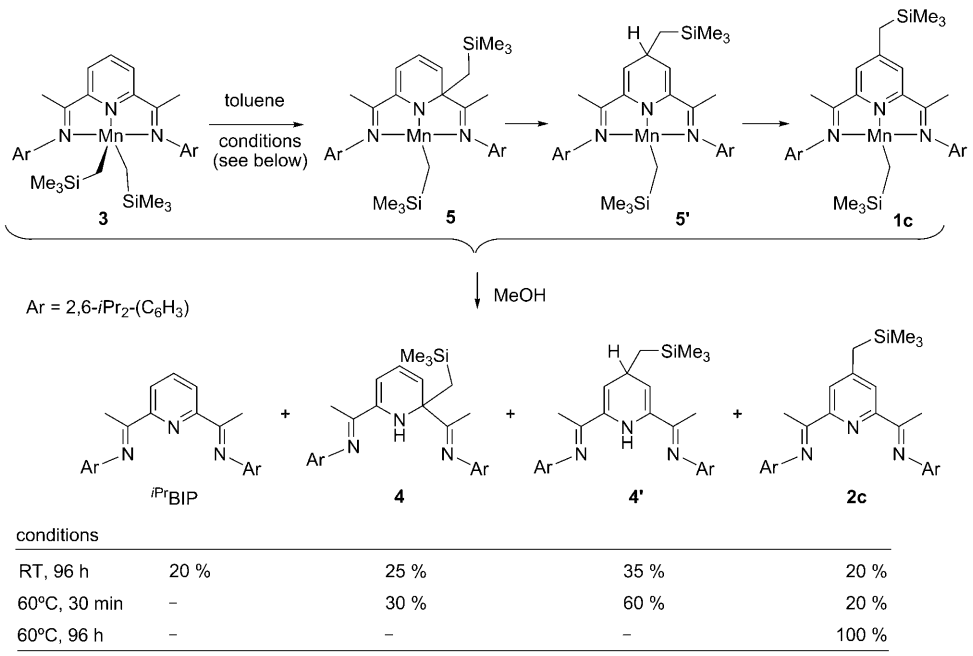


Figure 1. Crystal structure of compound **3**·C_7H_8 (solvent molecule not shown). Selected bond lengths (Å) and angles (°): Mn-C21, 2.169(2); Mn−C18 2.133(2); Mn−N1, 2.2279(17); Mn−N2, 2.4181(12); C1−C4, 1.490(2); C4−N2, 1.277(2); C4−C5, 1.504(2); C18-Mn-C21, 120.93(10); N1-Mn-C18, 133.90(9); N1-Mn-C21, 105.17(7); N2-Mn-N2′, 135.16(6); N1-Mn-N2, 69.16(3).

Complex **3** has a square-pyramidal coordination environment around the Mn atom, with one of the alkyl groups sitting on the apical site, while the other shares the base with the $^{i\mathrm{Pr}}$BIP nitrogen atoms. The molecule has a crystallographically imposed mirror plane that contains the MnR_2 unit and exchanges the two halves of the molecule. Its general configuration resembles that of its Fe analogue, reported by Chirik.[12] In both compounds, the axial M−C bond length is somewhat longer than that of the basal one, although the difference is more significant in the Mn derivative (2.169 vs. 2.133 Å). This suggests that the apical M−C bond could be weak, and this would be consistent with the observed tendency of one of the two M−C bonds to leave the metal center. In addition, some of the Mn−N distances are remarkably long. For example, the Mn−N(imine) bonds are 2.4181(12) Å, which are significantly longer than those in the related $[MnCl_2(^{i\mathrm{Pr}}BIP)]$ complex (2.342(3) Å, av),[5a] and are probably in the limit of what could be considered a covalent Mn−N interaction.

On standing at room temperature for 72 h, the dark blue solutions of **3** gradually turn to burgundy-red. A new compound, **1c**, was isolated from the purple solution in about 20% yield. Its colour and magnetic moment (4.8 μ_B) are similar to those of **1a** and **1b**. As shown in Scheme 2, methanolysis of **1c** affords the corresponding 4-trimethylsilylmethyl substituted BIP ligand **2c**. These observations confirm that, like **1a** and **1b**, **1c** arises from migration of one of the alkyl groups to the 4-position of the BIP pyridine ring. From this conclusion it is reasonable inferring that, in general, formation of compounds of type **1** involves the initial formation of dialkyls $[MnR_2(BIP)]$, which are too unstable to be detected when the alkyl group lacks stabilising α-silyl substituents.

The process leading to the formation of formally Mn^{I} species **1** can be decomposed in two more basic steps: 1) migration of the alkyl group from the metal center to the aromatic ring, and 2) loss of one hydrogen atom. The latter takes place spontaneously in solution, but it is relatively slow at room temperature. Previous investigations[19] showed that when $[MnR_2]$ complexes (R = neophyl, benzyl or allyl) are reacted with BIP ligands and the resulting reaction mixtures are directly quenched with MeOH, not only the 4-alkyl-BIP ligands, but also the corresponding 4-alkyl-2,6-diimino-1,4-dihydropyridine derivatives are obtained. In some cases, such dihydropyridines can represent as much as 80% of the products. The availability of the stable Mn^{II} dialkyl **3** gave us the opportunity to investigate this transformation in more detail, in order to provide some insights on its mechanism. Thus, we carried out a series of experiments in which solutions of **3** were allowed to evolve over different reaction times and temperatures. The products were then quenched with MeOH, and the resulting organic species were analysed by ^{1}H NMR spectroscopy. In the first experiment, we reproduced the conditions that led to the isolation of **1c** by allowing a toluene solution of **3** to stand at room temperature for four days. Quenching the resulting burgundy solution afforded a mixture of four organic products (Scheme 3). The ^{1}H NMR spectrum of this mixture displays signals of two familiar compounds: unaltered $^{i\mathrm{Pr}}$BIP, and the expected 4-trimethylsilylmethyl BIP derivative **2c**, each one representing 20% of the mixture. The other products, **4** and **4′**, were identified with help of their 2D ^{1}H COSY and NOESY spectra.



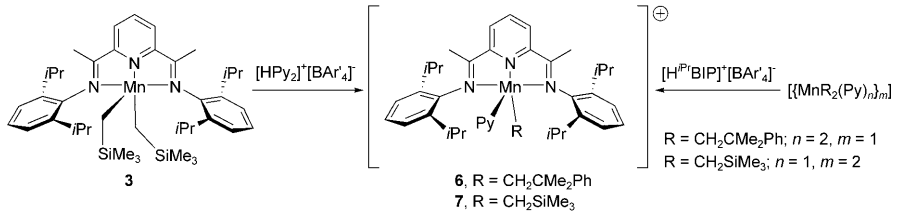
conditions				
RT, 96 h	20 %	25 %	35 %	20 %
60°C, 30 min	–	30 %	60 %	20 %
60°C, 96 h	–	–	–	100 %

Scheme 3.

The major component (35 %) of the mixture, **4′**, gives rise to a diagnostic multiplet at $\delta = 3.62$ ppm, corresponding to the 4-C(R)-*H* signal of a 1,4-dihydropyridine derivative. This signal is coupled to both the alkyl CH_2 and to the 3,3′-pyridine protons, which produce a single resonance at $\delta =$ 5.09 ppm, as expected for a symmetric 1,4-dihydropyridine. In contrast, the central ring of **4** is a non-symmetric 1,2-dihydropyridine derivative with the alkyl ring bound to one of the heterocyclic α-carbon atoms. Consistently, this compound gives rise to a set of three mutually coupled resonances at $\delta = 5.32$, 5.40 and 5.99 ppm, and two different acetaldimino (*Me*-C=N(Ar)) signals. The absence of couplings in the Me_3SiCH_2 methylene signal confirms that it is bound to a quaternary carbon atom. While ^{iPr}BIP and **2c** are evidently formed by the methanolysis of **3** and from **1c**, compounds **4** and **4′** must originate from the Mn^{II}–dihydropyridinate(−1) complexes **5** and **5′** (Scheme 3, top), although these have not been isolated from the reaction mixture, probably due to their high solubility. Notice that this result is consistent with the isolated yield of complex **1c** (ca. 20 %), and implies that the alkyl transfer does not proceed to completion under the conditions of this experiment.

When a solution of **3** is heated at 60 °C, the characteristic colour change from blue to burgundy takes place within a few minutes. After heating for 30 min, methanolysis afforded compounds **4**, **4′** and **2c** in a relative ratio of 3:6:2, but not ^{iPr}BIP, showing that alkyl transfer to the ring is now complete. Thus, under these conditions, migration of the trimethylsilylmethyl group to the pyridine ring is fast, but the intermediates **4** and **4′** still survive for some time. However, these two products disappear when the heating is extended for four days, leaving compound **2c** as the only product after treatment with methanol. The disappearance of **4** and **4′** suggests that the corresponding precursor complexes, **5** and **5′**, are intermediates in the formation of **1c**, as shown in the upper part of Scheme 3. Accordingly, the alkyl group migrates sequentially from the metal centre to the 2-position in the heterocyclic ring, and then to the 4-position. This would be similar to alkyl migrations observed by Copéret for the reaction of dineopentylmanganese with α-diimines.[18] The process concludes with hydrogen loss and aromatisation, producing the final product, **1c**. As discussed previously, it is reasonable to assume that this mechanism operates in the formation of compounds of the type **1** on a general basis. Although in our previous studies, 1,4-dihydropyridines of the type **4′** were obtained in high yields, while analogues of **4** were not observed, this is probably due to the low stability of intermediates of type **5**. It is also possible that the full reaction sequence might involve a sequence of elemental 1,2- rather than 1,3-shifts, but the corresponding intermediates are too unstable to be trapped. It is worth noting here that the migration of the CH_2CMe_2Ph group that leads to **1a** rules out the participation of free radicals, because the neophyl radical is known to rapidly rearranged to the more stable 1,1-dimethyl-2-phenylethyl,[24] and the corresponding 4-R-BIP derivative has not been detected. This consideration supports further the intramolecular nature of the alkyl migration mechanism, although more complex mechanisms involving intermolecular alkyl transfer cannot be entirely ruled out.

Cationic alkyl complexes: Cationic alkyl complexes play an important role in most olefin polymerisation catalyst systems, and it is believed that this is the case for BIP-containing catalysts as well. Some years ago, Chirik studied the reaction of the dialkyl complex $[Fe(CH_2SiMe_3)_2{}^{iPr}BIP]$ with the protic acid $[PhNMeH_2]^+[BPh_4]^-$, which led to the isolation of complexes of type $[Fe(CH_2SiMe_3)(L)(^{iPr}BIP)]^+$.[11] When L is diethyl ether, the cationic iron alkyl behaves as a single-component catalysts for ethylene polymerisation. We decided to prepare similar cationic manganese derivatives, containing pyridine as ancillary ligand (L). For this purpose, have used two different approaches converging in the same type of product (Scheme 4). The first one is analogous to Chirik's route for cationic alkyliron complexes, and consists in reacting **3** with the pyridinium salt $[H(Py)_2]^+[BAr'_4]^-$ ($Ar' = 3,5\text{-}C_6H_3(CF_3)_2$) as a protic acid. The second method



Scheme 4.

involves the reaction of the pyridine complex $[\{Mn(CH_2SiMe_3)_2(Py)\}_2]$ with the protonated ligand $[H^{iPr}BIP]^+[BAr'_4]^-$. The latter is readily prepared in crystalline form, from the ^{iPr}BIP ligand and the acid $[H(OEt)_2]^+[BAr'_4]^-$. Due to its synthetic and structural interest, the crystal structure of $[H^{iPr}BIP]^+[BAr'_4]^-$ was determined (Figure 2). The imonium proton was located bound to nitrogen atom N3, indicating that the imine functionality behaves as a stronger base than the pyridine ring. The neutral C34=N2 group is antipleriplanar with regard to the pyridine C38–N1 bond, which is the preferred configuration of imine groups in free BIP ligands. In contrast, the protonated imine adopts the opposite configuration with the NH facing the pyridine N1 atom, because this allows hydrogen-bonding stabilisation. The imonium proton forms an additional hydrogen bond with F2, one of the fluorine atoms of the tetraarylborate anion. This interaction is probably rather weak, but illustrates the capability of the $BAr'_4{}^-$ ion for weak interactions with H-bond donors.

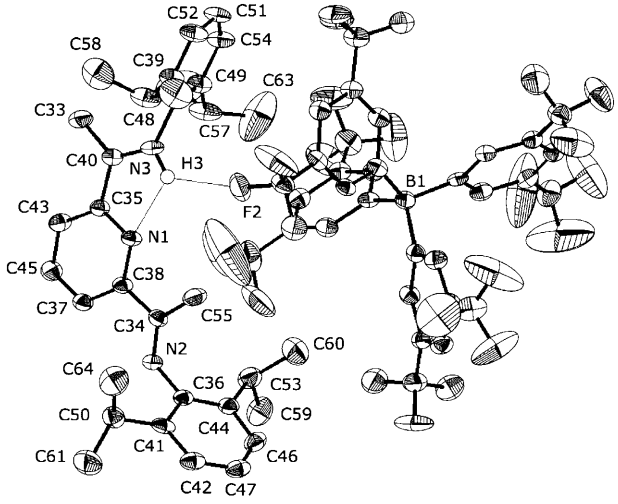


Figure 2. Crystal structure of $[H^{iPr}BIP]^+[BAr'_4]^-$. Selected bond lengths (Å) and angles (°): N3–H3, 0.950(4); H3–N1, 2.04(5); H3–F2, 2.22(5); N3···N1, 2.619(4); N3···F2, 2.906(4); C40–N3, 1.289(4); C34–N2, 1.278(4); N3-H3-N1, 117(2); N3-H3-F2, 128(2).

As expected, the two reactions described in Scheme 4 converge in the formation of the same substance, cationic complex **7**, in 76% and 81% yields, respectively. This compound was isolated as violet material, insoluble in hydrocarbon solvents, expected for an ionic compound. The second route is more general and allows the preparation of stable cationic Mn^{II} derivatives containing "normal" alkyl groups without stabilising β-silyl groups. Thus, complex **6**, the neophyl analogue of **7**, was obtained in 40% yield as violet crystals from $[Mn(CH_2CMe_2Ph)_2(Py)_2]$. Magnetic susceptibilities measured in solution for compounds **6** and **7** at 25°C provide values of μ_{eff} of 5.9 and 6.1 μ_B, respectively, in good agreement with their formulation as high-spin Mn^{II} species. The identity of **6** was confirmed by its crystal structure, shown in Figure 3.

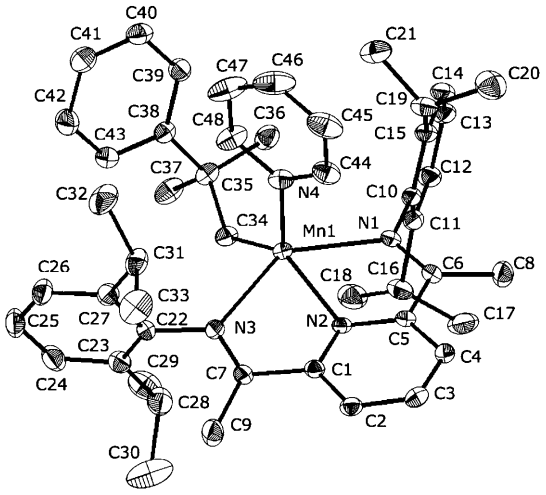


Figure 3. Crystal structure of compound **6** (cationic part). Selected bond lengths (Å) and angles (°): Mn1–C34, 2.1257(18); Mn1–N4, 2.2122(15); Mn1–N2, 2.2323(14); Mn1–N1, 2.3519(14); Mn1–N3, 2.4243(15); C1–C7, 1.495(2); C5–C6, 1.489(2); C6–N1, 1.285(2); C7–N3, 1.283(2); C34-Mn1-N2, 141.35(6); N2-Mn1-N4, 98.20(5); N1-Mn1-N4, 97.56(5); N3-Mn1-N4, 96.66(5); N1-Mn1-N3, 138.60(5)

The cationic fragment of compound **6** exhibits a pentacoordinated manganese atom in approximate square-pyramidal coordination environment, with the ^{iPr}BIP ligand and one of the alkyls occupying three basal positions, as observed for **3**, and the pyridine ligand at the apex. In spite of the positive charge of **6**, metal–ligand bond lengths in the neutral and cationic species are very similar. Thus, the basal Mn–C bond is only marginally shorter in **6** (2.133(2) Å for **3** vs. 2.1257(18) Å for **6**), and the bond to the central pyridine atom (N2) is even slightly longer in the cation. In contrast with **3**, coordination of the ^{iPr}BIP ligand is rather unsymmetrical in **6**, with one of the two Mn–N(imine) bonds, Mn–N3, being almost as long as that of **3**, while the other (Mn–N1) is 0.072 Å shorter. The shortest Mn–N distance in **6** corresponds to the apical pyridine ligand. Interestingly, in the

analogous Fe derivatives $[Fe(R)(L)(^{iPr}BIP)]^+$ ($R = CH_2SiMe_3$, $L = Et_2O$ or THF)[11b] the alkyl group and the neutral L ligand invert their relative positions, with the lying in the basal position and the former occupying the apex.

Attempted ethylene polymerisation: We have shown that complexes of type $[Fe(CH_2SiMe_3)_2(BIP)]$ become active ethylene polymerisation catalysts in the presence of very mild activators, such as trimethylaluminum ($AlMe_3$) or triisobutylaluminum (TIBA) or even $Al(Me)(O\text{-}2,4,6\text{-}C_6H_2\text{-}tBu_3)_2$.[20] The availability of an array of alkylmanganese ^{iPr}BIP complexes provided new opportunities for testing the potential activity of this kind of compounds in olefin polymerisation. Therefore, we carried out a set of ethylene polymerisation tests using neutral **3** and cationic **6** complexes under similar conditions, employing modified methylaluminoxane (MMAO), $AlMe_3$ or $B(C_6F_5)_3$ as activating agents. No catalytic activity was detected in any of these experiments.

Monoalkyl complexes **1** are formally Mn^I derivatives, and thus isoelectronic with catalytically active Fe^{II} derivatives. The 4-alkyl groups in the central ring of these compounds are not expected to perturb their catalytic activity, since the presence of such substituents has no significant effects on the activity of Fe^{II} or Co^{II} catalysts.[25] Thus, they might be promising candidates to generate active ethylene polymerisation catalysts. However, no activity was detected when compound **1b** was tested in the presence of MMAO, $AlMe_3$ or $Al(iBu)_3$ as cocatalysts. This would not be too surprising since if, as previously mentioned, compounds like **1** are actually Mn^{II} complexes containing a monoanionic BIP radical ligand.

Conclusion

In this article we have addressed the questions of whether Mn^{II} alkyl complexes stabilised by BIP ligands are isolable compounds, and whether they can give rise to active olefin polymerisation catalysts. The reaction of suitable dialkylmanganese complexes ,such as homoleptic dialkyls $[(MnR_2)_n]$ or $[\{MnR_2(thf)\}_2]$, with BIP ligands is an efficient methodology for this purpose. Specifically, we investigated the reactions of the ^{iPr}BIP ligand with neophyl (CH_2CMe_2Ph), benzyl and trimethylsilylmethyl manganese alkyls. Only in the last case does this method afford the expected Mn^{II} dialkyl, $[Mn(CH_2SiMe_3)_2(^{iPr}BIP)]$ (**3**), while in the other two, it leads to the formation of formally Mn^I monoalkyl complexes **1a** and **1b**, in which one of the R groups, originally bound to the metal center, has been transferred to the 4-position of the pyridine ring of the BIP ligand. Compound **3** also undergoes this alkyl transfer process, although much more slowly, leading to the monoalkylmanganese derivative **1c**. Detailed studies on this particular transformation allowed the identification of 1,2- and 1,4-dihydropyridinate(−1) complexes **4** and **4′** as intermediates in the alkyl migration process. Accordingly, an intramolecular mechanism involving elemental alkyl migration steps (either 1,3- or 1,2-alkyl shifts), followed by spontaneous hydrogen loss and aromatisation, has been proposed. Compounds **1a** and **1b** are most likely formed through analogous mechanisms, but the corresponding dialkylmanganese intermediates are too unstable to be detected. This behavior resembles the chemistry of the analogous Fe complexes, and thus the ability of the trimethylsilylmethyl group to stabilise high-valent BIP–alkyl complexes appears to be a common feature among first-row transition metal elements.

Cationic Mn^{II} alkyl complexes of type $[Mn(R)(Py)(^{iPr}BIP)]^+$ (complexes **6** and **7**) can be prepared either by protonation of $[Mn(CH_2SiMe_3)_2(^{iPr}BIP)]$ (**3**) with pyridinium tetraarylborate, or by reaction of the salt $[H(^{iPr}BIP)]^+[BAr'_4]^-$ with dialkyl precursors $[\{MnR_2(Py)\}_2]$. In contrast with the neutral dialkyl Mn^{II} complexes, these cationic monoalkyls are thermally stable, even for R groups without stabilising β-silyl groups.

Attempts to generate active ethylene polymerisation catalysts from either neutral Mn dialkyl **3** or from cationic Mn^{II} dialkyl **6** and typical activation agents such as MMAO, $AlMe_3$ or $B(C_6F_5)_3$ have been unsuccessful. It is striking that, in spite of the remarkable analogies in the structure and chemical behaviour of the BIP alkyl derivatives of Fe and Mn, the former give rise to highly active catalysts, while the latter are essentially inactive. The failure of the Mn complexes to catalyse ethylene polymerisation could be due to the high stability of the d^5 electronic configuration of the high-spin Mn^{II} ion, which renders intermediate spin states with empty d orbitals energetically unavailable. This situation prevents the coordination of the olefin monomer and frustrates migratory insertion, the essential step in coordination olefin polymerisation. In spite of being isoelectronic with the Fe^{II}–BIP catalysts, the formally Mn^I complex **1a** proves also inactive in the presence of the above-mentioned co-catalysts. It is very likely that this class of monoalkyl compounds are actually Mn^{II} complexes containing a monoanionic BIP radical ligand, and therefore it is not too surprising that, similarly to **3**, **6** or **7**, they are also catalytically inactive.

Experimental Section

All manipulations were carried out under oxygen-free argon atmosphere, using conventional Schlenck techniques or a nitrogen filled glove box. Solvents were rigorously dried and degassed before using. Methanol was refluxed over sodium methoxide, distilled and kept in a glass ampoule over activated molecular sieves under inert atmosphere. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas. Infrared spectra were recorded on a Bruker Vector 22 spectrometer, and NMR spectra on Bruker 300, 400 and 500 MHz spectrometers. The ^1H and $^{13}C\{^1H\}$ resonances of the solvent were used as the internal standard, but the chemical shifts are reported with respect to TMS. Magnetic susceptibilities were measured at 298 K by Evans' method.[26] Magnetic moments have been calculated from the average values of two independent measurements of the magnetic susceptibility and are corrected for the diamagnetic contributions estimated from Pascal constants.[27]

$MnCl_2$ was purchased from Aldrich Chemical Co. and rigorously dried following a literature method.[28] Pyridine was refluxed over Na, distilled and stored in a gastight ampoule under Ar protected from the light. Stock solutions of the Grignard reagents Mg(R)Cl ($R = CH_2SiMe_3$, CH_2CMe_2Ph and CH_2Ph) were prepared according to conventional procedures. $Mg(CH_2Ph)_2$ was obtained by addition of dioxane (1 equiv) to a solution of $Mg(CH_2Ph)Cl$ in Et_2O, followed by removal of the resulting precipitate by centrifugation. The manganese alkyl precursors $[Mn(CH_2SiMe_3)_2(thf)]$, $[Mn(CH_2SiMe_3)_2(Py)]$, $[\{Mn(CH_2CMe_2Ph)_2\}_2]$, $[Mn(CH_2CMe_2Ph)_2(Py)_2]$, and $[\{Mn(CH_2Ph)_2(thf)\}_2]$, as well as the acid $[H(Py)_2]^+[BAr'_4]^-$ were prepared as described in a precedent publication.[20] The homoleptic trimethylsilylmethyl derivative $[Mn(CH_2SiMe_3)_2]$[29] and the acid $[H(Et_2O)_2]^+[BAr'_4]^-$[30] were obtained as described in literature. The synthesis and spectroscopic properties of compounds **1a**, **2a** and **2b** have been reported before.[18]

Methanolysis of compound 1a: Compound $[\{Mn(CH_2CMe_2Ph)_2\}_2]$[17] (0.280 g, 0.03 mmol) was dissolved in dry C_6D_6 (0.6 mL). To this solution, dry methanol (3 mL, 2 equiv) was added and a brown precipitate appeared. The volatile components of the mixture were transferred under vacuum into a cold trap, and analysed by ^1H, ^{13}C NMR, GC and GC-MS, which showed the presence of equimolar amounts of *t*Bu-Ph and CH_3OH. This indicates that only one equivalent of the latter had been consumed in the reaction. The dry residue was extracted in C_6D_6, filtered and analysed by ^1H and ^{13}C NMR spectroscopy, showing the presence of 4-$(PhCMe_2CH_2)$-$^{i\text{Pr}}$BIP (**2a**)[18] as the only detectable organic component. The same experiment using only one equivalent of CH_3OH led to similar results, but the volatile fraction did not contain significant amounts of the alcohol.

A similar experiment was carried out using CD_3OD. In this case, $PhCMe_2CH_2D$ was detected in the volatile fraction, while the solid residue contained **2a**.

[Mn(CH$_2$Ph)(4-PhCH$_2$-$^{i\text{Pr}}$BIP)] (1b): A solution of $[\{Mn(CH_2Ph)_2(thf)\}_2]$ (0.34 g, 1.1 mmol)[18] in toluene (15 mL) was added to a solution of $^{i\text{Pr}}$BIP (0.48 g, 1 mmol) in toluene (10 mL) that was being stirred at −40 °C. The colour of the mixture turned to dark red within seconds. The stirring was continued for 5 min at this temperture and then for 45 min at room temperature. Volatiles were removed and the resultant oily residue was extracted in hexane (15 mL). The solution was filtered and cooled at −30 °C. A purple microcrystalline precipitate (**1b**) was formed, which was collected by filtration and dried under vacuum. Yield, 0.23 g, 31 %; elemental analysis calcd (%) for $C_{47}H_{56}MnN_3$: C 78.63, H 7.86, N 5.85; found: C 78.52, H 7.99, N 5.84; IR (Nujol mull): $\tilde{\nu}$ = 3060, 1588, 1566, 1492, 1401, 1325, 1309, 1267, 1094, 1057. 971, 790, 744, 698 cm^{-1}; μ_{eff} = 4.8 μ_B

Methanolysis of compound 1b: Compound **1b** (0.033 g) was reacted with two equivalents of methanol as described for the methanolisis of **1a**. Analysis of the volatile components indicated the presence of equimolar amounts of toluene and methanol, while the non-volatile fraction consisted of 4-$(PhCH_2)$-$^{i\text{Pr}}$BIP, (**2b**).[18]

[Mn(CH$_2$SiMe$_3$)$_2$($^{i\text{Pr}}$BIP)] (3)

Method A, from [{Mn(CH$_2$SiMe$_3$)$_2$}$_n$]: A suspension of $[\{Mn(CH_2SiMe_3)_2\}_n]$ (0.30 g, 1.3 mmol) in toluene (15 mL) was added to a stirred suspension of $^{i\text{Pr}}$BIP (0.580 g, 1.2 mmol) in toluene (10 mL) at −40 °C. The colour of the mixture changed gradually from pale orange to dark blue. After 5 min, the cold bath was removed, and the mixture stirred for 30 min at room temperature. The solution was concentrated to about 1/3 of the original volume, and stored at −30 °C. Blue crystals were observed after 24 h. These were collected by filtration and dried in vacuum to afford 0.490 g (57 %) of product **3**.

Method B, from [{Mn(CH$_2$SiMe$_3$)$_2$(thf)}$_2$]: $[\{Mn(CH_2SiMe_3)_2(thf)\}_2]$ (0.900 g, 3 mmol) was dissolved in toluene (15 mL) and reacted with an equimolar amount of $^{i\text{Pr}}$BIP as described above. The same workup afforded 1.210 g (61 % yield) of **3**. Elemental analysis calcd (%) for $C_{41}H_{65}MnN_3Si_2$: C 69.25, H 9.21, N 5.91; found.: C 69.26, H 9.21, N 5.66; IR (Nujol mull): $\tilde{\nu}$ = 1635, 1590 ($^{i\text{Pr}}$BIP); 1260, 871 cm^{-1} ($SiMe_3$); μ_{eff} = 5.9 μ_B.

Methanolysis of 3: Compound **3** (0.100 g, 0.14 mmol) was dissolved in toluene (15 mL). MeOH (5 mL) was added to the dark blue solution at room temperature. The resultant mixture turned brown and a precipitate of the same colour was formed. The suspension was filtered and the resulting dark yellow solution was passed through an Et_3N-doped silica column. The resultant yellow solution was evaporated to dryness, leading to the recovery of 0.060 g (0.12 mmol, 88 %) of $^{i\text{Pr}}$BIP.

[Mn(CH$_2$SiMe$_3$){4-(Me$_3$SiCH$_2$)-$^{i\text{Pr}}$BIP}] (1c): A solution of compound **3** (0.4 mmol) in toluene (30 mL), directly prepared from $[Mn(CH_2SiMe_3)_2(thf)]$ and $^{i\text{Pr}}$BIP was stirred for 72 h at room temperature. During this time, the colour gradually changed from blue to purple. The solution was taken to dryness, and the oily residue was extracted in hexane (25 mL), filtered, concentrated to about 2/3 of its original volume and stored at −30 °C. The product precipitates as a powdery purple solid, which was filtered out and dried in vacuo. Yield 0.860 g, 29 %; elemental analysis calcd (%) for $C_{41}H_{64}MnN_3Si_2$ C 69.35, H 9.08, N 5.92; found: C 68.82, H 9.44, N 5.93; IR (Nujol mull): $\tilde{\nu}$ = 1625, 1590 (4-R-$^{i\text{Pr}}$BIP), 1250, 852 cm^{-1} (ν(Si-C)); μ_{eff} = 4.8 μ_B.

Methanolysis of compound 1c—formation of 4-(Me$_3$SiCH$_2$)-$^{i\text{Pr}}$BIP (2c): Compound **1c** (0.180 g, 0.25 mmol) was treated as described for the methanolysis of **2**, affording 0.12 g of **2c** (84 % yield). ^1H NMR (C_6D_6, 298 K, 300 MHz): δ = −0.11 (s, 9H; CH_2SiMe_3), 1.18 (d, $^3J_{HH}$ = 6.7 Hz, 12H; CH*Me*), 1.24 (d, $^3J_{HH}$ = 6.9 Hz, 12H; CH*Me'*), 1.85 (s, 2H; CH_2SiMe_3), 2.34 (s, 6H; CH_3C=NAr), 2.97 (sept, 4H; $CHMe_2$), 7.17–7.24 (m, 6H; CH_{ar}), 8.45 ppm (s, 2H; *3*-$CH_{ar(py)}$); $^{13}C\{^1H\}$-NMR (C_6D_6, 298 K, 125 MHz): δ = −2.8 (s, CH_2SiMe_3), 16.8 (s, CH_3C=NAr), 23.1, 22.5 (s, $CHMe_2$), 27.0 (s, CH_2SiMe_3), 28.6 (s, $CHMe_2$), 122.1 (s, CH_{ar}), 123.2 (s, CH_{ar}), 123.9 (s, CH_{ar}), 135.5 (s, C_{ar}), 146.9 (s, C_{ar}), 151.1 (s, C_{ar}), 155.0 (s, C_{ar}), 166.8 ppm (s, CH_3C=NAr). ESI MS: *m/z*: 590.4 $[M+Na]^+$.

Monitoring the transformation of 3 into 1c: A dark blue toluene solution of compound **3** (12.7 μmol, 9.0 mg) was stirred in a Young® Teflon tap sealed glass ampoule. After 96 h, the solution, which had turned purple, was treated with excess of anhydrous methanol. Solvents and volatiles were removed from the resultant red-orange solution. An orange oil was isolated, which was then extracted in hexane (3×25 mL), leading, after solvent evaporation, to yellow-orange oily residue This was dissolved in C_6D_6 and analysed by ^1H NMR spectroscopy, showing the presence of four compounds (together with trace amounts (ca. 5 %) of related compounds of unknown structure). The identified compounds are: $^{i\text{Pr}}$BIP (25 %), 4-alkyl-bisiminopyridine (**2c** 21 %), 4-alkyl-bisimino-1,2 dihydropyridine (**4**; 21 %) and 4-alkyl-bisimino-1,4 dihydropyridine (**4′**; 33 %).

*Data for **4***: ^1H NMR (C_6D_6, 298 K, 500 MHz)**:** δ = −0.10 (s, 9H; CH_2SiMe_3), 0.99 (d, $^3J_{HH}$ = 8.5 Hz, 12H; $CHMe_2$), 1.02 (d, $^3J_{HH}$ = 8.5 Hz, 12 H; $CHMe_2$'), 1.85 (m, 2H; CH_2SiMe_3), 1.63 (s, 3H; CH_3C=NAr), 1.57 (s, 3H; CH_3C=NAr), 2.83 (sept, 4H; $CHMe_2$), 5.32 (d, $^3J_{HH}$ = 8.0 Hz, 1H; 3,5-$CH_{ar(py)}$), 5.40 (d, $^3J_{HH}$ = 11.0 Hz, 1H; 3,5-$CH_{ar(py)}$), 5.99 (dd, $^3J_{HH}$ = 11.0, 8.0 Hz 1H; 4-CH 3,5-$CH_{ar(py)}$), 6.38 (s, 1H; N-H) 7.08–7.23 ppm (m, 6H; CH_{ar}); some coupling constants are not included, because they could not be accurately calculated due to signal overlapping.

*Data for **4′***: ^1H NMR (C_6D_6, 298 K, 300 MHz): δ = 0.10 (s, 9H; CH_2SiMe_3), 1.11 (br d, 12H; $CHMe_2$), 1.14 (br d, 12H; $CHMe_2$'), 1.89 (s, 2H; CH_2SiMe_3), 1.74 (s, 6H; CH_3C=NAr), 2.83 (sept, 4H; $CHMe_2$), 3.58 (br q, 1H; 4-CH $CH_{ar(py)}$) 5.08–5.10 (m, 2H; 3,5-$CH_{ar(py)}$) 7.23–7.26 (m, 6H; CH_{ar}), 8.90 ppm (br s, 1H; N-H); some coupling constants are not included, because they could not be accurately calculated due to signal overlapping.

In a second experiment, a Young® Teflon tap sealed NMR tube containing a solution of compound **3** (12.7 μmol, 9.0 mg) in toluene (0.7 mL) was heated at 60 °C in oil bath. The dark blue solution turned dark-red within few minutes. The solution was quenched with an excess of methanol after 30 min at the said temperature. After the above-mentioned organic standard workup, the yellow residue was dissolved in C_6D_6 and analysed by ^1H NMR spectroscopy, showing the presence of signals attributed to compouns **4**, **4′** and **2c** in 26:57:17 ratio and total absence of unsubstituted bisiminopyridine ($^{i\text{Pr}}$BIP). When the same experiment was performed (60 °C) during 96 h, the only product observed is **2c**.

Synthesis of [H$^{i\text{Pr}}$BIP]$^+$[BAr′$_4$]$^-$: A solution of $[H(Et_2O)_2][BAr']_4$ (1.010 g, 1 mmol) in of Et_2O (10 mL) was added dropwise to a stirred

suspension of $^{i\mathrm{Pr}}$BIP (0.480 g, 1 mmol) in Et_2O (20 mL) at −30 °C. The resulting orange solution was stirred for 5 min, and then for additional 1 h at room temperature. The solvent was then evaporated under vacuum. The yellow residue was recrystallised from a 2:1 mixture of diethyl ether and hexane, affording $[H^{i\mathrm{Pr}}BIP]^+[BAr'_4]^-$ as yellow crystals. Yield, 1.010 g, 75%; ^{1}H NMR (CD_2Cl_2, 298 K, 300 MHz): δ = 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 12H; CH*Me*), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 12H; CH*Me'*), 2.52 (s, 6H; C*H*$_3$-C=NAr), 2.64 (sept, $^3J_{HH}$ = 6.8 Hz, 4H; C*H*Me$_2$), 7.33 (m, 6H; C*H*$_{ar}$), 7.55 (s, 4H; C*H*$_{ar}$), 7.72 (brs, 8H; C*H*$_{ar}$), 8.43 (t, J = 8.1 Hz, 1H; *4*-C*H*$_{(py)}$), 8.63 (d, J = 8.1 Hz, 2H; *3*-C*H*$_{(py)}$), 11.58 ppm (s, 1H; N*H*). IR (Nujol mull): $\tilde{\nu}$ = 1637, 1611, 1589 ($H^{i\mathrm{Pr}}BIP^+$) 1277, 1127, 890 cm^{-1} ($BAr'_4{}^-$); elemental analysis calcd (%) for $C_{65}H_{56}BF_{24}N_3$ C 58.00, H 4.19, N 3.12; Found: C 58.04, H 4.00, N 3.13.

[Mn(CH$_2$CMe$_2$Ph)(Py)($^{i\mathrm{Pr}}$BIP)]$^+$[BAr′$_4$]$^-$ (6): The acid $[H^{i\mathrm{Pr}}BIP]^+[BAr'_4]^-$ (1.345 g, 1 mmol) was dissolved in diethyl ether (15 mL), and the solution was added dropwise into a solution of $[Mn(CH_2CMe_2Ph)_2(Py)_2]$[20] (0.500 g, 1.05 mmol) in diethyl ether (15 mL), stirred at −60 °C. The colour of the mixture turned violet. After 5 min, the bath was removed and the mixture was stirred for 30 min at the room temperature. The solvent was removed under vacuum, leaving a violet-coloured foam, which solidified upon washing with hexane (15 mL). This was extracted in diethyl ether (15 mL). The suspension was filtered and hexane was carefully added until slight turbidity. Violet crystals appeared when the solution was allowed to rest at −10 °C. Yield: 0.620 g, 32%; elemental analysis calcd (%) for $C_{80}H_{73}BF_{24}MnN_4$ C 59.60, H 4.56, N 3.48; found: C 58.98, H 4.53, N 3.56; IR (Nujol mull): $\tilde{\nu}$ = 1630, 1603, 1593 (BIP); 1280, 1129, 885 cm^{-1} (BAr′$_4$); μ_{eff} = 6.1 μ_B.

[Mn(CH$_2$SiMe$_3$)(Py)($^{i\mathrm{Pr}}$BIP)]$^+$[BAr′$_4$]$^-$ (7)

*Route A, from compound **3**:* A fine suspension of $[H(Py)_2][BAr'_4]$ (1.020 g, 1 mmol) in toluene (15 mL) was added dropwise to a solution of **3** (0.780 g, 1.10 mmol) in toluene (30 mL) stirred at −40 °C. The mixture turned from dark blue to violet. The stirring was kept 5 min at −40 °C and 25 min at room temperature. Solvents and volatiles were then removed and the violet solid was washed with hexane (15 mL). The resultant solid was taken up in Et_2O (15 mL), filtered, and hexane was added again to the solution until it became slightly turbid. Crystals of **7** appeared after storing the solution overnight at −30 °C. Filtration and drying yielded, 1.190 g, 76%.

Route B, from [{Mn(CH$_2$SiMe$_3$)$_2$(Py)}$_2$]: A solution of the protonated ligand $[H^{i\mathrm{Pr}}BIP]^+[BAr'_4]^-$ (0.910 g, 0.68 mmol) in diethyl ether (15 mL) was dropwise added to a stirred solution of $[\{Mn(CH_2SiMe_3)_2(Py)\}_2]$[21] (0.240 g, 0.39 mmol) in diethyl ether (15 mL), cooled at −60 °C. The colour of the mixture first changed to dark blue and then to violet. Following the same workup described for Route A, 0.950 g (89%) of compound **7** were obtained. Elemental analysis calcd (%) for $C_{74}H_{71}BF_{24}MnN_4Si$: C 56.75, H 4.57, N 3.58; found: C 56.44, H 4.41, N 3.54; IR (Nujol mull): $\tilde{\nu}$ = 1607, 1584 ($^{i\mathrm{Pr}}$BIP); 1279 (SiMe$_3$); 1280, 1129, 889 cm^{-1} (BAr′$_4$); μ_{eff} = 6.0 μ_B.

Attempted ethylene polymerisation: All attempts were carried out in a Fischer–Porter glass reactor equipped with a septum-capped and magnetic stirring. The temperature was fixed at 30 °C with a thermostatic oil bath, and the ethylene pressure was 4 bar. Ethylene consumption was monitored continuously. The reactor was charged with toluene (50 mL), purged with ethylene to displace the original N_2 atmosphere and allowed to stabilise at the working temperature and pressure. Once the toluene was saturated with ethylene at the desired pressure, freshly made solutions containing the catalyst (10 mmol in 2 mL of toluene) and the co-catalyst were successively injected through the septum port. Complexes **3** and **7** were tested in combination with i) MMAO (400 or 1000 equiv); ii) $B(C_6F_5)_3$ (3 equiv); trimethylaluminum (100 or 1000 Equiv); iii) triisobutylaluminum (1000 Equiv); trimethylaluminum + $B(C_6F_5)_3$ (100:1). Compound **1** was tested i) in the absence of co-catalyst; ii) with MMAO (400 or 1000 equiv); iii) triisobutylaluminum (1000 equiv). These experiments proceeded with negligible or no ethylene consumption. In all cases, the solutions remained clear, or developed a slight turbidity.

X-ray crystallography. Crystals coated with dry perfluoropolyether were mounted on a glass fiber and fixed in a cold nitrogen stream (T = 100(2) K) and the Intensity data were collected on a Bruker-Nonius X8 Apex-II CCD diffractometer (**6**) or coated with an epoxy polymer (T = 293(2) K) were collected on a Bruker SMART Apex CCD diffractometer ([HBIP][BAr′$_4$]), both equipped with a $Mo_{K\alpha1}$ radiation (λ = 0.71073 Å) source and graphite monochromator. The data were reduced (SAINT)[31] and corrected for Lorentz polarisation and absorption effects by multiscan method (SADABS)[32]. The structure was solved by direct methods (SIR-2002)[33] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12)[34] minimising $w[F_o^2-F_c^2]^2$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and allowed to ride on the attached carbon atoms with the isotropic temperature factors (U_{iso} values) fixed at 1.2 times (1.5 times for methyl groups) those U_{eq} values of the corresponding carbon atoms. Table 1 contains some more details of the crystallographic measurements. CCDC-773733 (**3**), 773734 ($[H^{i\mathrm{Pr}}BIP]^+[BAr'_4]^-$) and 773735 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal and refinement data.

	3·C_7H_8	[HBIP][BAr′$_4$]	**6**
formula	$C_{48}H_{73}MnN_3Si_2$	$C_{65}H_{56}BF_{24}N_3$	$C_{80}H_{73}BF_{24}N_4Mn$
M_r	803.21	1345.94	1612.17
T [K]	173(2)	293(2)	100(2)
crystal size [mm]	0.5×0.5×0.1	0.5×0.3×0.1	0.4×0.2×0.2
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/m$	$P\bar{1}$	$P2_1/c$
a [Å]	9.2626(3)	14.4268(7)	12.5799(3)
b [Å]	14.4853(6)	14.5529(8)	19.7359(6)
c [Å]	18.5098(8)	17.9210(9)	30.8501(10)
α [°]	90	83.7840(8)	90
β [°]	100.6570(10)	70.1920(9)	90.5860(10)
γ [°]	90	63.2210(10)	90
V [Å^3]	2440.65(17)	3163.7(3)	7658.9(4)
Z	2	2	4
ρ_{calcd} [Mg m^{-3}]	1.093	1.413	1.398
μ [mm^{-1}]	0.352	0.132	0.277
θ range [°]	1.12–30.53	1.57-28.84	1.22-30.52
reflns collected	44726	24866	48014
reflns used	7320	16397	22959
parameters	278	852	1001
R_1 [$I>2\sigma(I)$]	0.0444	0.0729	0.0518
wR^2 (all data)	0.1082	0.2158	0.1499
GOF	1.025	0.998	1.048

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