Synthesis and Reactions of Manganese(II) Dialkyl Complexes Containing Monodentate and Bidentate Nitrogen Ligands

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In this paper we describe the synthesis of Mn(II) dialkyl compounds and their adducts with THF and pyridine. These compounds are useful precursors for the preparation of Mn complexes relevant to catalysis, such as dialkylmanganese(II) derivatives containing chelating nitrogen ligands. In contrast with previously known manganese(II) dialkyls, dibenzylmanganese can not be prepared from MnCl₂ and benzylmanganese chloride due to the formation of insoluble mixed manganesemagnesium compounds. Homoleptic manganese(II) dialkyls are highly sensitive and often quite insoluble owing to their polymeric structure. However, adducts of type MnR_2L or MnR_2L_2 (L = THF, pyridine) are soluble in hydrocarbon solvents and more readily isolated and stored than the homoleptic alkyls compounds. Manganese dialkyls as well as their THF or pyridine adducts react instantly with 2,2'-bipyridyl to afford the corresponding MnR₂(bipy) complexes. Thus, the stabilized dialkylmanganese(II) THF or Py adducts represent a practical alternative to the more reactive but less easily handled homoleptic dialkyl precursors for synthetic purposes. In addition, the reactivity of MnR₂(bipy) derivatives with O₂ and the protic acid [H(OEt₂)][BAr'₄] (Ar' = $3,5-C_6H_3(CF_3)_2$) are described. The former reaction leads to the formation of a mixed-valence Mn(II)/Mn(III) alkyl complex containing a tetranuclear [Mn₄O₂] core.

Introduction

Owing to its central position in the first transition row of the periodic table, manganese is an element with many singular properties.¹ Perhaps because of this circumstance, development of its organometallic chemistry has been slower than that of its congener transition elements.² Thus, although organomanganese(II) alkyls were first prepared in solution by Gilman in the decade of 1930,³ these compounds remained uncharacterized for a long time. Another example of such delay is dimanganese heptacarbonyl, one of the main starting materials in modern organomanganese chemistry, which was not fully characterized until 1954.⁴ Although the organometallic chemistry of manganese has nowadays achieved a degree of development comparable to that of any other transition element, it is still largely limited to compounds in low oxidation states (-1, 0, +1) containing carbonyl or other strongly π -acceptor ligands. Organometallic derivatives in +2 or higher oxidation states continue to be relatively rare, with the exception of manganocene derivatives.⁵ Manganese(II) alkyls have found many applications in organic synthesis as *in situ* generated reagents,⁶ but their study has been hampered by their paramagnetic, NMRsilent character and their extreme sensitivity to air. Simple Mn(II) dialkyls $[MnR_2]_n$ (R = CH₂SiMe₃(1), CH₂CMe₂Ph(2), CH_2CMe_3 ,⁷ as well as their adducts with phosphines, were first reported by Wilkinson between 1976 and 1983. Partial X-ray diffraction data for the homoleptic derivatives showed that these compounds have unusual alkyl-bridged structures, polymeric in the case of 1 and dimeric for 2. Very recently, Mulvey and co-workers have provided full characterization data for 1, confirming Wilkinson's proposal.⁹ Discrete molecular dialkyls are obtained with large R groups.

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For example, monomeric Mn(II) dialkyls, displaying linear R-M-R arrangements, have been observed for very bulky alkyl groups ($\mathbf{R} = CH(SiMe_3)_2$,¹⁰ C(SiMe_3)₃¹¹). Furthermore polymeric MnR₂ molecules of simple alkyls such as 1 can be broken down into readily soluble THF adducts that are convenient starting materials in organometallic synthesis.¹² However, apart from these results, further work on the chemistry of simple Mn(II) dialkyls have only sparsely been reported.1,5

Recent progress on olefin polymerization catalysis has generated a renewed interest in the chemistry of transition metal alkyls and their role in polymerization catalysis.¹³ As previously noted, manganese is in many aspects exceptional when compared to other transition elements. This is also true with regard to its behavior in polymerization catalysis. Very few examples of manganese catalysts for olefin polymeriza-tion have been reported, ¹⁴ in contrast with other first-row transition elements. For example, 2,6-bisiminopyridine complexes of cobalt, iron, chromium, and vanadium give rise to very active ethylene polymerization catalysts on activation with alkylaluminum cocatalysts, but the corresponding manganese complexes do not.¹⁵ Clarifying the reasons for such behavior would contribute to a better understanding of polymerization mechanism, but this task is thwarted by the difficulty of synthesizing suitable alkylmanganese complexes from such ligands.^{15a,16} Most post-metallocene polymerization complexes are based on classic σ -donor imine-based ligands. The synthesis of alkyl complexes containing such ligands is frequently complicated by the tendency of the latter to undergo side reactions with strongly basic or nucleophilic transmetalation reagents.¹⁷ We found that these problems can be avoided to a large extent if, instead of resorting to classic transmetalation reactions involving prebuilt metal halocomplexes containing the ligand of interest, these ligands are reacted with appropriate alkylmetal precursors capable of delivering the "MR_n" fragment. Alkyl complexes supported by labile secondary ligands, such as the pyridine derivatives MR_2Py_2 (M = Ni or Pd, ¹⁸ Fe¹⁹), have

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Figure 1. ORTEP view of compound 2. Selected bond distances (Å) and angles (deg): Mn1-C1, 2.255(2); Mn1-C1', 2.327(2); Mn1-C11, 2.118(2); Mn1-C5, 2.7284(16); Mn1-C10: 2.6389(17); Mn1-Mn1': 2.7286(6); C11-Mn1-C1, 127.73(7); C11-Mn1-C1: 120.01(7); C1'-Mn1-C1: 106.92(6); Mn1-C1-Mn1', 73.08(6); Mn1-C1-C2, 121.00(13); Mn1'-C1-C2, 104.84(11). Symmetry transformations used to generate equivalent atoms ('): -x, -v+1, -z.

proven very useful for this purpose. Manganese homoleptic dialkyls or weakly ligated dialkyl complexes also appear to be ideal precursors for the synthesis of organometallic complexes with reactive nitrogen ligands. In this paper, we describe the synthesis and characterization of different types of manganese dialkyl complexes and preliminary work on their use in the preparation of derivatives containing monodentate and bidentate nitrogen ligands, such as pyridine and bipyridine. In addition, we present some results on the reactivity of MnR₂(bipy) complexes.

Results and Discussion

Homoleptic Manganese(II) Dialkyls and THF Adducts. The homoleptic trimethylsilymethyl (1) and neophyl (R =CH₂CMe₂Ph, 2) dialkyls were prepared as described by Wilkinson, by reaction of MnCl₂ with the suitable Grignard reagents in diethyl ether (eq 1).⁷ Attempts to extend this procedure to the synthesis of dibenzylmanganese led to the formation of a highly insoluble colorless material. However, a pyrophoric yellowish product, sparingly soluble in hot toluene, was isolated in up to 33% yield when, instead of using Mg(CH₂Ph)(Cl), the reaction was carried out with Mg(CH₂Ph)₂ (prepared by addition of 1,4-dioxane to the latter). The IR spectrum of this product shows exclusively absorptions assigned to the benzyl group, while characteristic $\nu(C-O-C)$ bands of coordinated dioxane or diethyl ether (ca. $1000-1200 \text{ cm}^{-1}$) are absent, and therefore we propose that this compound is dibenzylmanganese, 3 (eq 2). Compound 3 is only sparingly soluble in hydrocarbon solvents, and this, combined with its extreme sensitivity to air, prevented us from advancing in its characterization. The insolubility of this compound suggests that it has a polymeric structure in the solid state, as previously shown for 1.^{7a,20}

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In contrast with 1 and 3 compound 2 is readily soluble in hydrocarbon solvents, and this facilitates its isolation as a crystalline solid in good yields (ca. 50%). Although the structure of this compound has been described,⁷ full crystallographic data were not provided, and for this reason we completed the characterization of this interesting molecule (Figure 1). Our results are in full agreement with the previous description. The molecule is a dimer containing two MnR₂ units, bridged by one of the alkyl groups, while the other is coordinated in a terminal fashion. A crystallographic inversion center relates the two MnR₂ fragments. The distance between the manganese atoms, 2.7286(6) Å, is significantly smaller than in some other structurally related Mn(II) dimeric compounds (see below) and even shorter than some typical Mn–Mn bonds (e.g., in $Mn_2(CO)_{10}$, 2.903 Å); therefore a Mn-Mn covalent interaction cannot be easily ruled out. The low magnetic susceptibility ($\mu_{eff} = 3.1 \,\mu_B$ per Mn atom at 293 K) measured for this compound could be argued in favor of such a metal-metal bonding interaction, but probably this is best explained by a strong antiferromagnetic interaction, as Gambarotta^{12a} and Mulvey⁹ have found for related dimeric Mn(II) and polymeric alkyl compounds.

$$MnCl_{2} \xrightarrow{Mg(Cl)R} [MnR_{2}]_{n} + MgCl_{2}$$
(1)

$$R = CH_{2}SiMe_{3}, \infty = (1);$$

$$CH_{2}CMe_{2}Ph, n = 2 (2)$$

$$\operatorname{MnCl}_{2} \xrightarrow{\operatorname{Mg(CH_{2}Ph)_{2}}}_{\operatorname{Et_{2}O}} [\operatorname{Mn}(\operatorname{CH_{2}Ph})_{2}]_{n} + \operatorname{MgCl}_{2} \quad (2)$$

The Mn₂C₂ ring has a trapezoidal shape, with two different Mn-C bond lengths (2.327(2) and 2.255(2) Å). The coordination geometry of the bridging carbon atoms can be compared to a square pyramid, with both manganese centers and the two hydrogen atoms placed on the base and the CMe₂Ph fragment in the apex. This configuration causes the H atoms of the bridging CH₂ to come in close contact with the closest Mn center (ca. 2.2 Å), hinting at the existence of agostic interactions, as previously suggested for [MnR2- $(PR'_3)]_2$ complexes.²⁰ The configuration of the bridging alkyl groups allows secondary interactions between the pendant phenyl rings and each of the manganese atoms. Short contacts are observed between Mn and carbons ipso (C5, 2.7284(16) Å) and ortho (C10, 2.6389(17) Å), and thus the interaction is best described as a η^2 -arene bond. These $Mn \cdots C$ bond distances are very similar to those measured in the zinc π -adduct Zn(C₆F₅)₂(η^2 -C₆H₈), 2.784(2) and 2.6847(15) Å.²¹ The π -arene interaction is also reminiscent of that observed in a family of three-coordinated neutral and cationic Pd-neophyl complexes, where a π -interaction alleviates the coordinative unsaturation of the metal center.²² However, this interaction appears to be significantly weaker in the Mn complex than in the Pd derivatives, as the Pd-C(ipso) distances (2.34–2.39 Å) are significantly shorter, in spite of the larger covalent radius of Pd. The weakness of the Mn π -arene interaction is further confirmed by the nearly planar geometry of the MnC₃ fragment formed by the metal atom and the three σ -bonded carbons, C1, C1', and C11, which is in contrast with the tetrahedral arrangement normally observed in four-coordinated Mn centers. The sum of the three C-Mn-C bonds amounts to 354,7°, equivalent to a pyramidalization degree of only 18.4% in a scale going from 0% for a perfectly planar MnC₃ unit to 100% for a pyramid with three perfectly tetrahedral C-Mn-C angles of 109.5°.

Reactions of MnCl₂ with alkylmagnesium reagents in Et₂O are in general very slow, and this combined with the low solubility of the products (particularly in the cases of 1 and 3) led us to examine the use of THF as solvent (eq 3). Judging from the changes in the appearance of the mixtures, these reactions proceed more rapidly and are completed within a few hours. The binuclear THF adduct of bis-(trimethylsilyl)manganese, 4, was readily isolated as orange crystals in good yield. Although the reaction is apparently also rapid and complete for R = neophyl and benzyl, the products formed are exceedingly soluble in hydrocarbon solvents and reluctant to crystallize. Only after very careful removal of THF under vacuum was a small amount of compound 5, the neophyl analogue of 4, obtained. The corresponding benzyl derivative, 6, could not be isolated in the same way, but was obtained by a somewhat different procedure (see below). The IR spectra of these compounds display intense absorptions at ca. 1020 and 870 cm⁻¹ that are absent in those of the corresponding homoleptic derivatives and hence can be assigned to coordinated THF C-O stretching bands. Crystalline samples of these compounds are moderately soluble in hexane; therefore the difficulties for product isolation when R = neophyl or benzyl suggest that the use of THF as solvent favors the formation of very soluble products, perhaps THF-stabilized monomeric complexes. The crystal structures of 4, 5, and 6 are shown in Figure 2, and Table 1 collects selected bond distances and angles. Although the crystal structure of 4 has been reported previously,¹² we have determined it independently and considered worthwhile including our data here because of their relation with other compounds in this work. As can be seen, the three THF adducts have closely related alkyl-bridged binuclear structures. Effective magnetic moments measured at room temperature (293 K) are $5.2-5.3 \mu_{\rm B}$ per manganese atom, larger than that found for homoleptic 2 but still slightly below 5.9, the spin-only value for five electrons that would be expected for high-spin Mn(II). As pointed out by

$$MnCl_{2} \xrightarrow{2Mg(R)Cl} [MnR_{2}(THF)_{n}] + MgCl_{2}$$

$$R = CH_{2}SiMe_{3} (4); CH_{2}CMe_{2}Ph (5); CH_{2}Ph (6)$$
(3)

Gambarotta for 4, this is due to the noticeable antiferromagnetic coupling of the manganese centers.^{12a}

Compounds **4**–**6** feature two symmetrical $Mn(\mu-R)(R)$ -(THF) units related by a crystallographic inversion center. As found for **2**, Mn_2C_2 cores have rhomboidal shapes with obtuse $C_{Br}-Mn-C_{Br}$ and acute $Mn-C_{Br}-Mn'$ angles (C_{Br} denotes the bridging carbon) and two slightly unequal $Mn-C_{Br}$ distances. The Mn centers occupy a distorted tetrahedral environment, configured by the two bridging and the terminal C atoms and completed by the THF ligand. As compared with **2**, the MnC₃ fragments are less planar in

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Figure 2. Crystal structures of compounds 4 (left), 5 (center), and 6 (right). See Table 1 for selected bond distances and angles. Symmetry transformations used to generate equivalent atoms ('): 4, -x, y+1/2, -z+1/2; 5, -x+2, -y, -z+1; 6, -x+1, -y+1, -z.

 Table 1. Selected Bond Distances and Angles for Binuclear Alkyls



the THF adducts but still rather flat, with pyramidalization degrees of 37%, 34%, and 49% for 4, 5, and 6, respectively. Saturation of the Mn centers by the THF ligand results in the disappearance of any secondary interactions with the alkyl chain. Thus, in contrast with bis(neophyl)manganese 2, the phenyl rings of the THF adduct 5 are removed far away from the metal center. Another difference between 2 and 5 is observed in the more open structure of the latter, as evidenced by the significantly longer $Mn \cdots Mn$ distance (2.7286(6) Å in 2 vs 2.8416(4) Å in 5), probably as a consequence of the increased steric hindrance. However, the most striking dissimilarity between the structures of 2, 4, 5, and 6 is the different coordination geometries of the bridging carbon atom. As noted by Gambarotta,^{12a} the silyl group of compound 4 is almost perfectly aligned with one of the Mn atoms $(Mn'-C_{Br}-Si = 176.0(3)^\circ)$, giving rise to a bipyramidaltrigonal geometry at the CBr center, with the two H atoms and the other Mn atom occupying the equatorial positions. A similar but not as precise alignment is observed in 5 (Mn'- $C_{Br}-C = 166.55(11)^{\circ}$). In 6, the coordination polyhedron of the bridging carbon is more akin to that in 2, although in less



Figure 3. Schematic representation of the bridging alkyl configurations found in compounds 2, 4, 5, and 6.

symmetrical fashion, with one of the two H atoms eclipsing the "long" Mn-C bond. Although at first sight the geometries of the C_{Br} center appear rather unusual for carbon, it can be readily seen that the "short" Mn-C bond is never too far from the normal "tetrahedral" disposition with respect to the H and C/Si substituents. The different configurations of the bridging carbon can be viewed as a result of the relative orientation of the farthest Mn atom with regard to the "short" Mn-C(R)(H)(H) group, as schematically represented in Figure 3. This interpretation suggests that the secondary ("long") Mn···C interaction lacks directional character, which is not too surprising considering the highly ionic character of Mn(II)-C bonds.¹ The relative disposition of the two Mn centers is probably dictated by steric factors or by the influence of the secondary π -interactions as in the case of 2.

We have mentioned that the dibenzylmanganese THF adduct 6 could not be isolated from the reaction mixture obtained by treating MnCl₂ with the benzyl Grignard reagent in diethyl ether. However, while studying the synthesis of [Mn(CH₂Ph)₂] from dibenzylmagnesium and MnCl₂ in Et₂O, we observed that extraction in toluene is greatly helped by the addition of a small amount of THF. This procedure led to the isolation of two products, 6 and a new compound of composition [MnMg(CH₂Ph)Cl₃(THF)₂], 7, in 11% and 25% yield, respectively. The crystal structure of 7 is shown in Figure 4. This compound could be described as an adduct of the (chloro)benzylmanganese "Grignard" Mn(CH₂Ph)Cl with magnesium chloride. The molecule is dimeric, comprising two crystallographically equivalent "Mn(CH₂Ph)Mg-(THF)₂Cl₃" units. Each pair of manganese and magnesium atoms is bridged by two chlorine ligands. The manganese atoms are found in a slightly distorted tetrahedral environment formed by three Cl atoms and the terminal benzyl group, while the octahedral coordination of magnesium is completed by two mutually cis molecules of THF. The molecule resembles a prism lacking two opposite vertexes



Figure 4. Crystal structure of compound 7. Selected bond lengths (Å) and angles (deg): Mn1-C1, 2.1225(14); Mn1-C11, 2.4074(4); Mn1-C12, 2.4954(4); Mn1-C13, 2.4201(4); Mg1-C11, 2.4816(6); Mg1-C12, 2.5785(6); Mg1-O1, 2.0480(11); Mg1-O2, 2.0311(11); C11-Mn1-C12, 91.559(13); C11-Mn1-C13, 101.571(14); C12-Mn1-C13, 90.076(13); C1-Mn1-C11, 122.33(5); C1-Mn1-C12, 115.01(4); C1-Mn1-C13, 126.73(5); Mn1-C1-C2, 108.00(10). Symmetry transformations used to generate equivalent atoms ('): -x+1, -y, -z.

and is strongly reminiscent of the dimeric ethylmagnesium compound $[Mg_2EtCl_3(THF)_3]_2$, reported by Toney and Stucky in 1971.²³ In fact, the distances Mn-Cl and Mg-Cl are very similar, resulting in a very harmonious and symmetrical structure. The effective magnetic moment per manganese atom in this compound at room temperature (5.8 $\mu_{\rm B}$) is very close for the spin-only value for five unpaired electrons, suggesting that magnetic interactions are weak or nonexisting. In spite of the great relevance of "Grignard"-type monoalkylmanganese derivatives in organic synthesis,⁸ only a few derivatives of this kind containing extremely bulky alkyl ligands of the type tris(trialkylsilyl)-methyl have been characterized so far.²⁴ The formation of compounds 6 and 7 in 1:2 ratio suggests that in the reaction of manganese dichloride with Mg(Cl)CH₂Ph in Et₂O an insoluble, possibly a polymeric product of composition " $Mn(R)(Cl) \cdot MgCl_2$ " is strongly favored over the dialkyl MnR₂, as shown in Scheme 1. Because the use of the dibenzylmagnesium reagent limits the amount of chloride available for the formation of this adduct, a fraction of the starting material can be converted into dibenzylmangnese (3), and upon treatment with a nearstoichiometric amount of THF, the two products are converted into the soluble products 6 and 7. Accordingly, the reaction of MnCl₂ with Mg(CH₂Ph)(Cl) in diethyl ether essentially leads, as previously mentioned, to the insoluble material "Mn(R)(Cl)·MgCl2", which on treatment with

THF is converted into 7 in high yield (see Experimental Section).

Pyridine and Bipyridine Mn(II) Dialkyl Complexes. As anticipated, both the homoleptic dialkyls and their THF adducts serve as excellent starting materials for the preparation of different derivatives containing the MnR₂ fragment. Due to our previous results in related chemistry of Ni, Pd, and Fe alkyls, in the first place we were interested in the corresponding pyridine adducts.^{16,17} These compounds can be readily prepared adding pyridine to "MnR₂(THF)_n" solutions, as shown in Scheme 2. This procedure led to the isolation of trimethylsilylmethyl (8) and neophyl (9) adducts as orange- and red-colored solids, respectively. Pyridinestabilized complexes are less sensitive than the corresponding THF adducts and can be stored for long periods of time without signs of decomposition. Analytical data for these two compounds indicate different pyridine contents: while 8 contains one equivalent of pyridine per manganese, 9 has two. This suggests that 9 is a monomer, and 8 is a dimer displaying a hydrocarbyl-bridged structure analogous to that of 4. The crystal structure of the latter, shown in Figure 5, confirmed this proposal. Selected bond distances and angles are included in Table 1. For 9, formation of a dimeric structure probably reflects the somewhat low ability of the comparatively bulky neophyl group to bridge two Mn(II) centers. Wilkinson observed a similar trend for the dialkyls $MnR_2(PR'_3)_2$: These compounds spontaneously lose one phosphine ligand, converting into the corresponding binuclear species $[MnR_2(PR'_3)]_2$, except in the case of the neophyl derivatives.²⁵ In this light, the formation of the monomeric trimethylsilylmethyl complex Mn(CH₂SiMe₃)₂Py₂ from 1 and pyridine, recently reported by Mulvey,18 is not too surprising and suggests that also in this case monomeric and dimeric species are readily exchangeable species.

The structure of compound **8** is very similar to that of the THF adduct **4**. The disposition of the bridging alkyl is the same in the two compounds, and analogous bond distances and angles are very close. The sum of the three C-Mn-C angles is slightly smaller in **8**, leading to a larger degree of pyramidalization of the MnC₃ fragment as compared to **4**. Together with the PMe₃ adduct, described by Wilkinson,^{8a,b} **4** and **8** constitute a series of isostructural complexes of composition [Mn(CH₂SiMe₃)₂L]₂, with L = THF, Py, and PMe₃. The donor capability of L exerts a small but noticeable influence in the pyramidalization degree of the MnC₃ fragment, which increases along the series in the order THF (37%) < Py (49%) < PMe₃ (53%).

The reactivity of homoleptic manganese alkyls toward chelating nitrogen ligands has been seldom explored. Copéret has studied the reaction of bis(neopentyl)manganese, showing that the initially formed $MnR_2(N-N)$ complexes undergo migration of one metal-bound alkyl to the imine ligand.²⁶ We obtained a similar result in the case of reaction of bis(neophyl)manganese **6** with 2,6-bis(imino)pyiridine ligands, which takes place with selective migration of one alkyl group to the pyridine ring, to afford formally Mn(I) alkyl complexes.¹⁹ 2,2'-Bipyridyl is a highly stabilizing ligand and probably less prone than imine derivatives to accept alkyl migrations, but to the best of our knowledge, MnR₂(bipy)

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complexes have not been reported before. Thus, in order to gauge of the potential of different types of alkylmanganese compounds as precursors for the synthesis of stable dialkylmanganese derivatives containing chelating nitrogen ligands, we compared the reactivity of MnR₂ and their THF or pyridine adducts toward bipyridyl (Scheme 3). These reactions proceed in a straightforward manner, affording the bipyridine complexes 10 and 11 in good yields (50-65%), isolated), as dark blue solids. The use of the more reactive precursors such as homoleptic 6 or the THF adduct 4 provides no significant advantage over the pyridine derivatives 8 and 9, which are more easily stored and handled. Actually, isolated yields were slightly improved with the latter. The crystal structure of 11, shown in Figure 6, confirms that this complex is mononuclear with the bipyridyl ligand and the alkyl groups arranged in an approximately tetrahedral structure. The molecule has no symmetry elements, and small differences are observed in the two Mn-C bonds, as well as in the Mn-N. On average, these distances are ca. 2.150 and 2.216 Å, respectively, which can be considered normal for a high-spin Mn(II) center.

In general, alkylmanganese(II) complexes are extremely sensitive to air, but stable products resulting from their reactions with oxygen have not been reported so far. Wilkinson mentions that samples of bis(neophyl)manganese 2 are often stained to a green hue, and he attributed this to an impurity formed by reaction with traces of oxygen. This impurity was detected by ESR, but could not be isolated.⁷ In the course our efforts for growing X-ray quality crystals of 10, we isolated a brown crystalline material, 12. Its structure is shown in Figure 7. It is a tetranuclear oxo-bridged alkyl complex displaying two Mn(R)(bipy) and two MnR₂ units bridged by two μ_3 -oxo units. A large number of inorganic polynuclear complexes containing $[Mn_4(\mu_3-O)_2]$ cores have been synthesized and characterized.²⁷ These compounds have attracted much interest because of their relevance as bioinorganic models for the active center for water oxidation in

Scheme 2







Figure 5. Crystal structure of compound 8. See Table 1 for selected bond distances and angles. Symmetry transformations used to generate equivalent atoms ('): -x+2, -y, -z.



Figure 6. Crystal structure of compound **11**. Selected bond lengths (Å) and angles (deg): Mn1–C11, 2.1518(15); Mn1–C21, 2.1490(17); Mn1–N1, 2.2214(12); Mn1–N2, 2.2099(12); C11–Mn1–C21, 125.19(6); N1–Mn1–N2, 73.60(4).

photosystem II²⁸ and their behavior as molecular magnets.²⁹ However, this is the first time that such an array is observed in an organometallic structure, and it is interesting that this compound has been formed as result of a "natural" oxidation with atmospheric oxygen. Because of the potential interest of

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Figure 7. Top and side views of the crystal structure of compound 12. Selected distances (Å) and angles (deg): Mn1-C11, 2.142(4); Mn2-C15, 2.070(3); Mn2-C19, 2.068(4); Mn1-O1, 1.959(2); Mn2-O1, 1.932(2); Mn2-O1', 1.923(2); Mn1-N1, 2.240(3); Mn1-N2, 2.246(3); C15-Mn2-C19, 92.14(14); C11-Mn1-O1, 121.41(12); N1-Mn1-N2, 73.33(10); O1-Mn2-O1', 84.92(10); Mn2-O1-Mn2', 95.08(10); Mn1-O1-Mn2, 126.65(13); Mn1-O1-Mn2', 136.89(12); Mn2-Mn2', 2.8443(11). Symmetry transformations used to generate equivalent atoms ('): -x+2, -y+1, -z.

this process, we sought a reproducible method for the synthesis of this compound by controlled reaction of **10** with oxygen (eq 4). After a number of attempts, we found that a brown material with the correct elemental analysis is obtained when the latter compound (generated *in situ* from **8** and bipy) is exposed to a stoichiometric amount of O₂ (0.25 O₂ per manganese atom) at -80 °C. The IR spectrum of this substance shows typical absorptions for bipyridyl (1597, 1567 cm⁻¹) and SiMe₃ (1233 and 893 cm⁻¹).

$$Mn(CH_2SiMe_3)_2(bipy) (10) \xrightarrow{1/4 O_2}$$
$$[Mn_2(CH_2SiMe_3)_2(\mu-O)(bipy)]_2(12)$$
(4)

The molecule of 12 contains two symmetrical halves related by a crystallographic inversion center. The four manganese atoms are strictly coplanar, but due to the slightly pyramidal geometry of the bridging O atoms (pyramidalization degree 4.3%), these fall a little above and below the plane. The geometry of the terminal Mn1 is approximately tetrahedral, while Mn2 is intermediate between tetrahedral and square planar. The average oxidation state of manganese atoms is +2.5, but comparison of bond lengths at the Mn1 and Mn2 centers shows significant differences, which suggest that these have well-defined oxidation states of +2and +3, respectively. Thus, the Mn1-C11 bond length (2.148 Å) is similar to the analogous distances in the Mn(II) derivative 11, but Mn2-C15 and Mn2-C19 are appreciably shorter (2.070 and 2.068 Å, respectively), consistent with a smaller covalent radius of Mn2. The Mn2-O1 distances are also somewhat shorter than Mn1-O1. Other metric parameters of the Mn1 center (Mn1-N distances and bond angles in general) also resemble those in 11, while the flattened tetrahedral geometry of Mn2 is precisely as expected for a high-spin tetracoordinated d⁴ center.³⁰ The effective magnetic moment measured in solution for this molecule is very low, 1.6 μ_B per Mn atom at 298 K, which indicates that the four Mn centers have strong antiferromagnetic





couplings, as is usually observed in polynuclear manganese complexes with high *S* numbers.^{27,31}

Due to our interest in olefin polymerization and oligomerization, we decided to attempt the synthesis of potentially active catalysts based on alkylmanganese complexes displaying a coordinative unsaturation or a readily dissociable ligand. Bipyridyl dialkylmanganese complexes provide a good starting point for this purpose, and therefore we investigated the reaction of 11 with protic acids containing the anion $[BAr'_4]^-$ (Ar' = 3,5-C₆H₃(CF₃)₂) (Scheme 4). We anticipated that its reaction with $[H(OEt)_2]^+[BAr'_4]^$ would lead to the coordinatively unsaturated cation [Mn(CH₂CMe₂Ph)(bipy)]⁺, and we desired to ascertain whether such species could be stabilized by a weak intramolecular π -arene interaction similar to that observed in **2**. When a solution of 11 in Et₂O was treated with an equimolar amount of the acid at -60 °C, a rapid color change from blue to red was observed. However, on stirring the mixture at room temperature, the color changed again to pale orange. The only product isolated from this solution was a paramagnetic colorless compound, identified as the ionic complex $[Mn(bipy)_3]^{2+}{[BAr'_4]^{-}}_2$ on the basis of its crystal structure (Figure 8). The structure cation $[Mn(bipy)_3]^{2+}$, typical for a high-spin Mn(II) octahedral complex, has been reported in the literature as a

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Figure 8. Crystal structure of 13 (cationic part).

component of several ionic compounds.³² The color changes observed suggested that the targeted cationic species is in fact generated, but π -bonding does not suffice to stabilize it at room temperature. Therefore, we decided to synthesize a cationic complex of type $[Mn(R)(bipy)(Py)]^+$ containing a relatively strong co-ligand such as pyridine. With this aim, we explored two alternative methods: treating bipyridine dialkyl 11 with pyridinium tetraarylborate, and the reaction of the bis(pyridine) bis(neophyl)manganese 9 with bipyridinium tetraarylborate, as shown in Scheme 4 (right side). Neither of these methods afforded the expected cationic alkyl, but the same product 13 in 51% and 32% yield, respectively. No other products could be isolated from the reaction mixtures. As expected, 13 is obtained in good to excellent yields by reacting 2, bipy, and $[H(OEt)_2]^+[BAr'_4]^-$ in the correct stoichiometric ratio (1:3:2). Again, these results suggest that, although the sought cationic alkylmanganese complexes might have been formed as intermediates in these reactions, they are in fact thermally unstable and spontaneously disproportionate in solution to afford 13 and dialkylmanganese species.

Conclusions

Homoleptic dialkylmanganese compounds $[MnR_2]_n$ and their adducts with labile monodentate ligands such as THF or pyridine constitute very useful reagents for the synthesis of organomanganese(II) derivatives containing other types of coligands. In this paper we have described the synthesis of some of these compounds and evaluated their synthetic potential for the preparation of bipyridylmanganese(II) alkyl derivatives.

In general, homoleptic alkyls $[MnR_2]_n$ are prepared by reaction of Mn(II) chloride with alkylmagnesium reagents in diethyl ether, but for $R = CH_2Ph$ this reaction is complicated by the formation of a highly insoluble material, possibly a polymeric adduct of composition Mn(Cl)(CH₂Ph)·MgCl₂. Reaction of the manganese dialkyls with THF or pyridine leads to the formation of binuclear complexes $[Mn(R)(\mu-R)(THF)]_2$. THF also solubilizes the polymeric material obtained from the reaction of MnCl₂ and Mg(CH₂Ph)Cl, affording the cage-shaped manganese "Grignard" compound [Mn(CH₂Ph)Cl·MgCl₂(THF)₂]₂. Homoleptic dialkyls and their THF adducts display alkyl-bridged binuclear structures. These bridges are not symmetrical: they display "short" and "long" Mn-C distances, and the geometry at the pentacoordinated carbon center varies from approximately square pyramidal to bipyramidal trigonal. This can be described as the result of a nondirectional interaction between a "normal" tetrahedral carbon at a Mn-C(R)(H)(H) unit with a second Mn atom. When the dialkyls are reacted with pyridine, the products can be either binuclear complexes, analogous to the THF adducts, or mononuclear MnR₂Py₂ derivatives. Homoleptic complexes and their THF or pyridine derivatives have a large potential for the synthesis of new organometallic manganese compounds that is still largely underdeveloped. They all react readily with bipyridyl to afford MnR₂(bipy) compounds in similarly good yields. Compared to homoleptic alkyls and their THF adducts, pyridine derivatives have some advantage in practice because of their higher stability, which facilitates handling and allows longer storage periods.

In addition, this work has addressed some aspects of the chemisty of monomuclear $MnR_2(bipy)$ compounds. Reaction of the trimethylsilyl derivative with oxygen under controlled conditions provides an organometallic example of the mixed-valence Mn(II)/Mn(III) compound displaying a Mn_4O_2 core. However, attempts to prepare cationic complexes $MnR(bipy)^+$ were unsuccessful, apparently due to their tendency to diproportionate, leading to the formation of the $[Mn(bipy)_3]^+$ cation.

Experimental Section

All manipulations were carried out under oxygen-free argon atmosphere, using conventional Schlenck techniques or a nitrogen-filled glovebox. Solvents were rigorously dried and degassed before using. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra were recorded on a Bruker Vector 22 spectrometer, and NMR spectra on Bruker DRX 300, 400, and 500 MHz spectrometers. The ¹H and ¹³C-{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.³³ Magnetic moments have been calculated from the average values of two independent measurements of the magnetic susceptibility and were corrected for the diamagnetic contributions estimated from Pascal's constants.³⁴

MnCl₂ was purchased from Aldrich Chemical Co. and rigorously dried following a literature method.³⁵ Pyridine was refluxed over Na, distilled, and stored in an gastight ampule under Ar protected from the light. Stock solutions of the Grignard reagents Mg(R)Cl (R = CH₂SiMe₃, CH₂CMe₂Ph, and CH₂Ph) were prepared according to conventional procedures. The reagent Mg(CH₂Ph)₂ was obtained by addition of 1,4-dioxane (1 equiv) to a solution of Mg(CH₂Ph)Cl in Et₂O, followed by removal of the resulting precipitate by centrifugation. The acid [H(Et₂O)₂]⁺[BAr']⁻ was obtained as described in the literature.³⁶

 $[Mn(CH_2CMe_2Ph)(\mu-CH_2CMe_2Ph)]_2$, **2.** To a vigorously stirred 40 mL Et₂O suspension of MnCl₂ (0.63 g, 5 mmol) at

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-60 °C was added dropwise 10 mL (10 mmol) of a 1 M Et₂O solution of Mg(CH₂CMe₂Ph)Cl. After 5 min, the mixture was allowed to reach room temperature and the stirring was maintained for 48 h at room temperature. Solvents and volatiles were then evaporated at reduced pressure. The residue was extracted with hexane (3 × 50 mL), and after filtration, the green solution was concentrated to five-sixths of its volume. Compound **2** formed pale yellow crystals after cooling to -30 °C, which were collected by filtration, washed with cold hexane, and dried under vacuum. Yield: 0.86 g (53%). Anal. Calcd for C₄₀H₅₂Mn₂: C, 74.76; H, 8.01. Found: C, 74.03; H, 7.92. IR (Nujol mull, cm⁻¹): 3080, 3055, 3010 (ν C–H arom); 2790, 2715 (ν_s and ν_{as} CH₂); 1595, 1575 (Ph). μ_{eff} : 3.1 μ_B .

 $[Mn(CH_2Ph)_2]_n$, **3**. To a suspension of $MnCl_2(0.38 \text{ g}, 3 \text{ mmol})$ in 40 mL of Et₂O, vigorously stirred at -60 °C, was added dropwise 5.7 mL (3 mmol) of a 0.53 M Et₂O solution of Mg(CH₂Ph)₂. After 5 min, the cold bath was removed and the pale green mixture was stirred for 48 h at room temperature. Volatiles were then removed under reduced pressure. The resulting brown oily residue was washed with 20 mL of hexane and extracted with 100 mL of hot toluene (90 °C). Upon filtration, the solution was stored at 4 °C and a pale yellow solid precipitated. After filtration and drying, compound **3** was isolated as a yellow-green solid. Yield: 0.12 g (17%). IR (Nujol mull, cm⁻¹): 3059, 2740, 1590, 1271, 1078, 1037, 793, 750, 700.

[Mn(CH₂SiMe₃)(μ -CH₂SiMe₃)(THF)]₂, 4. A 0.5 M solution of Mg(CH₂SiMe₃)Cl in Et₂O (12 mL, 6 mmol) was added to a stirred suspension of MnCl₂ (0.38 g, 3 mmol) in 30 mL of THF, and the mixture stirred at room temperature for 4 h. The solvent was removed under vacuum, and the residue was extracted with hexane (2 × 30 mL). After filtration, the combined extracts were concentrated and cooled overnight at -30 °C. Compound 4 was isolated as orange crystals in 94% yield (0.85 g). Anal. Calcd for C₂₄H₆₀Mn₂O₂Si₄: C, 47.81; H, 10.03. Found: C, 47.27; H, 9.58. IR (Nujol mull, cm⁻¹): 1237 (δ_{sym} Si-Me); 1029, 864 (ν C-O-C, THF); 824 (δ Si-CH₃). μ_{eff} : 5.3 μ_{B} . [Mn(CH₂CMe₂Ph)(μ -CH₂CMe₂Ph)(THF)]₂, 5. A suspension

of MnCl₂ (0.41 g, 3.3 mmol) in THF (40 mL) was cooled to -78 °C. A 1.0 M solution Mg(CH₂CMe₂Ph)Cl in Et₂O (7.5 mL, 2 equiv), cooled to 0 °C, was slowly added. The suspension immediately turned pale green, evolving to pale brown within a few minutes. The cold bath was removed after 10 min. Following the intial darkening, the solution turned again nearly colorless after 15 min of stirring at room temperature. Stirring was continued for 16 h at room temperature, and no further changes were observed. Solvents and volatiles were evaporated, and the residue was kept under vacuum during 12 h. The oily residue was treated with hexane (60 mL) and centrifuged. The solution was concentrated to one-fourth of its original volume and stored at -20 °C. After 24 h, some orange cubic crystals were observed, which were separated and used directly for X-ray diffraction. IR (Nujol mull, cm⁻¹): 3195, 3085, 3055, ν (C–H); 2770, 2760 (ν_s and v_{as} CH₂); 1600, 1580 (Ph); 1030, 870 (THF).

[Mn(CH₂Ph)(µ-CH₂Ph)(THF)]₂, 6. To a vigorously stirred and cold (-78 °C) suspension of MnCl₂ (0.38 g, 3 mmol) in Et₂O (40 mL) was added dropwise 1 equiv (5.7 mL, 3 mmol) of a 0.53 M Et₂O solution of Mg(CH₂Ph)₂. The mixture was stirred for 48 h at room temperature, and the color turned pale green over this time. The volatiles were evaporated under vacuum, and the brown oily residue was washed with 20 mL of hexane. The resulting solid was filtered and suspended in 40 mL of toluene, and 0.5 mL (6 mmol) of THF was added. The color turned immediately dark green, and after 15 min stirring, the mixture was filtered. The solution was concentrated and stored at -30 °C. Two crops of crystalline solids were obtained by fractional crystallization. The first crop contained 0.12 g of orange crystals corresponding to compound 6 (11% yield). The second fraction consisted of 0.32 g of colorless crystals of 7 (25% yield). A slightly modified procedure led to an increased yield of 6. In this case, the reaction time was extended to 4 days, and the residue was treated with approximately half the amount of THF (0.3 mL, ca. 1 Equiv). The above-described workup procedure produced 0.35 g (38%) of crystals of **6**. IR (Nujol mull, cm⁻¹): 1020, 860 (ν C–O–C, THF). μ_{eff} : 5.2 μ_{B} .

[Mn(CH₂Ph)(Cl)·MgCl₂(THF)₂]₂, 7. MnCl₂ (0.38 g, 3 mmol) was suspended in 40 mL of Et₂O, and the mixture was treated with 6 mL of Mg(CH₂Ph)(Cl) 0.5 M in Et₂O (3 mmol). The mixture was stirred for 48 h at room temperature and turned pale yellow. Volatiles were removed under vacuum, and the oily brown residue was washed with hexane (20 mL). The resulting solid was filtered and suspended in 30 mL of toluene, and 0.5 mL (6 mmol) of THF were added. The mixture turned dark purple. After stirring for 15 min, the solution was filtered off, concentrated, and cooled to -30 °C. Compound 7 was obtained as colorless crystals (0.95 g, 75% yield). Anal. Calcd for C₃₀H₄₆-Cl₆Mg₂Mn₂O₄: C, 43.80; H, 5.51. Found, C, 43.40; H, 5.85. IR (Nujol mull, cm⁻¹): 1025, 880 (ν C–O–C, THF). μ_{eff} : 5.8 μ_{B} .

[Mn(CH₂SiMe₃)py)₂]₂, 8. A 1.4 M Et₂O solution (7.14 mL, 10 mmol) of Mg(CH₂SiMe₃)Cl was added to a suspension of MnCl₂ (0.63 g, 5 mmol) in 40 mL of THF. The mixture was stirred for 4 h at room temperature. Solvent and volatiles were evaporated, and the resultant residue was extracted with hot toluene (40 mL). The suspension was centrifuged, and the solution was treated with 0.4 mL (5 mmol) of dry pyridine. The mixture was stirred for 15 min at the ambient temperature, during which time a yellow precipitate was formed. After solvent removal, the yellow oily residue was extracted with hexane (3 \times 30 mL). After filtration, the combined extracts were concentrated to approximately one-half of their original volume and cooled at -30 °C. Orange crystals 8 were formed after 48 h, yielding 0.94 g (61%). Anal. Calcd for C₂₆H₅₄Mn₂N₂Si₄: C, 50.62; H, 8.82; N, $^{-1}$): 4.54. Found: C, 50.31; H, 8.59; N, 4.49. IR (Nujol mull, cm⁻ 1600 (pyridine), 1235 (δ Si-Me), 816 (δ Si-CH₃). μ_{eff}: 6.0 μ_B.

[Mn(CH₂CMe₂Ph)₂(py)₂], 9. To a vigorously stirred and cold (-60 °C) suspension of MnCl₂ (0.63 g, 5 mmol) in THF (50 mL) were added 10 mL of a 1 M solution of Mg(CH₂CMe₂Ph)Cl (10 mmol) in Et₂O. The resultant suspension was stirred for 5 min before the cold bath was removed. The stirring was continued for 48 h at room temperature. Solvents and volatiles were removed at reduced pressure. The residue was treated with 40 mL of toluene, and the resulting suspension was centrifuged. The solution was then treated with 0.8 mL (10 mmol) of dry pyridine. The mixture became dark red, and it was stirred for 20 min at room temperature and taken to dryness. The residue was extracted with hexane (2 × 50 mL), filtered, and concentrated. Cooling the solution at -30 °C for 16 h afforded 1.04 g of 9 as a crystalline red solid (43% yield). Anal. Calcd for C₃₀H₃₆MnN₂: C, 75.14; H, 7.57; N, 5.84. Found: C, 74.44; H, 7.54; N, 5.55. IR (Nujol mull, cm⁻¹): 1595 (py). μ_{eff} : 5.9 μ_{B} .

[Mn(CH₂SiMe₃)₂(bipy)], 10. Method A, from Compound 4. A solution of compound 4 (0.45 g, 1.50 mmol) in 15 mL of toluene was added dropwise to a solution of 2,2'-bipyridyl (0.23 g, 1.50 mmol) in 15 mL of toluene, stirred at -30 °C. The resulting deep blue mixture was stirred for 5 min at the same temperature, and then the cooling bath was removed. Stirring was continued for 30 min at room temperature, and the solvent was evaporated under vacuum. The dark blue solid residue was washed with 15 mL of hexane and then extracted with 15 mL of Et₂O. The solution was filtered and hexane was added until a slight persistent turbidity was developed. On cooling to -30 °C, the product crystallizes as a dark blue solid (0.30 g, 51% yield).

Method B, from Compound 8. To a solution of 2,2'-bipyridyl (0.29 g, 1.85 mmol) in 15 mL of toluene, stirred at -30 °C was added dropwise a solution of compound 8 (0.61 g, 1.99 mmol) in 15 mL of the same solvent, turning immediately dark blue. The same workup procedure used in method A was applied to obtain 0.480 g of 10 (65% yield). Anal. Calcd for C₁₈H₃₀MnN₂Si₂: C, 56.07; H, 7.84; N, 7.27. Found: C, 55.40; H, 7.47; N, 7.50. IR (Nujol mull, cm⁻¹): 1595, 1575 (bipyridine); 1237 (δ SiMe₃), 855 (δ Si-*CH*₃). μ_{eff} : 5.8 μ_{B} .

[Mn(CH₂CMe₂Ph)₂(bipy)], 11. Method A, from Compound 2. A solution of compound 2 (0.48 g, 1.50 mmol) in 15 mL of toluene was added dropwise to a solution of 2,2'-bipyridyl (0.22 g, 1.40 mmol) in 15 mL of toluene, stirred at -30 °C. The resulting deep blue mixture was stirred for 5 min at the same temperature, and then the cooling bath was removed. Stirring was continued for 30 min at room temperature, and then the solvent was evaporated under vacuum. The solid residue was washed with 10 mL of hexane and then extracted with 10 mL of Et₂O. The solution was filtered and hexane was added until a slight persistent turbidity developed. On cooling to -30 °C, the product crystallizes as a dark blue solid (0.400 g, 60% yield).

Method B, from Compound 9. To a solution of 2,2'-bipyridyl (0.18 g, 1.16 mmol) in 15 mL of toluene, stirred at -30 °C, was added dropwise a solution of compound **9** (0.63 g, 1.26 mmol) in 15 mL of the same solvent, turning immediately dark blue. The same workup procedure used in method A was applied, to obtain 0.350 g of **11** (63% yield). Anal. Calcd for C₃₀H₃₄MnN₂: C, 75.45; H, 7.18; N, 5.87. Found: C, 75.42; H, 6.91; N, 6.00. IR (Nujol mull, cm⁻¹): 1595, 1575 (bipyridine). μ_{eff} : 6.0 μ B.

[Mn₂(CH₂SiMe₃)₃(bipy)(µ-O)]₂, 12. A solution of compound 10 in toluene was generated from 8 (0.41 g, 1.34 mmol) and 2,2'bipyridyl (0.21 g, 1.34 mmol), as described before. The dark blue solution was allowed to stir 30 min at room temperature. The glass stopper of the flask was replaced with a septum, the argon inlet was closed, and the flask was cooled to -80 °C. Oxygen (7.5 mL, 0.33 mmol) was taken into a gastight syringe fitted with a thin needle (i.d. = 0.7 mm) and injected through the septum (partial vacuum inside the flask assisted the gas uptake). The pore left by the needle was sealed with silicone paste and covered with a piece of parafilm. After 5 min, the cooling bath was removed, and the mixture was allowed to stir for 15 min at room temperature. During this time, the color of the solution changed to dark brown. The solvent was evaporated under reduced pressure. Washing with 10 mL of hexane, the brown oily residue solidified. This solid was extracted with 15 mL of diethyl ether, the solution was filtered, and hexane was added until a slight persisting turbidity developed. A brown powder precipited upon cooling to -10 °C overnight, which was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.180 g, 49%. Anal. Calcd for C44H82Mn4N4O2-Si₆: C, 48.60; H, 7.60; N, 5.15. Found: C, 48.69; H, 7.37; N, 5.25. IR (Nujol mull, cm⁻¹): 1595, 1575 (bipy); 1235, 860 (SiMe₃). Average μ_{eff} /Mn atom: 1.6 μ B.

Pyridinium Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, [**HPy**₂]⁺[**BAr'**₄]⁻. 2 mL of dry pyridne was added to solution of [H(Et₂O)₂]⁺[**BAr'**₄]⁻ (0.70 g, 0.69 mmol) in 5 mL of diethyl ether cooled at -20 °C, and the mixture was the allowed to stir at room temperature for 20 min. The solvent was eliminated under reduced pressure. On treatment with 10 mL of hexane, the oily residue converted into a beige solid. The latter was washed with 2 × 10 mL of hexane and dried under vacuum to afford 0.502 g (71%) of the title compound as a beige powder. The ¹H NMR spectrum showed signals of the anion and the cation with relative intensities corresponding to the formula. ¹H NMR (CD₂Cl₂. 400 MHz): δ 7.56 (s, 4H, *p*-H, Ar'); 7.73 (s, 8H, *o*-H, Ar'); 7.89 (br s, 4H, H-3 Py); 8.24 (t, ³J_{HH} = 7.4 Hz, 2H, H-4 Py); 8.84 (br s, 4H, H-2 Py).

Bipyridinium Tetrakis(**3,5-bis**(**trifluoromethyl**)**phenyl**)**borate,** [**Hbipy**]⁺[**BAr'**₄]⁻. A solution of [$H(Et_2O)_2$]⁺[**BAr'**₄]⁻ (1.14 g, 1.12 mmol) in 15 mL of diethyl ether was added to a cooled (-30 °C) solution of 2,2'-bipyridyl (0.17 g, 1.12 mmol) in the same amount of ether. The resulting orange mixture was stirred 5 min in the cooling bath and 30 min at room temperature. After this time, the solvent was eliminated under vacuum, leaving an orange solid residue that was taken up in a minimum amount of ether. Hexane was added carefully until persistent turbidity. The solution was filtered and cooled to -30 °C to afford the product as pale orange crystals. Yield: 0.830 g, 73%. IR (Nujol mull, cm⁻¹): 1630, 1605 (bipy); 1280, 1120, 890 (B-Ar'). ¹H NMR

| S | 9 | 7.toluene | 8 | 11 | 12 | 13 |
|--|-------------------------|---|--|--|--|---|
| $^{48}_{48}M_{68}Mn_2O_2$ | $C_{36}H_{44}Mn_2O_2$ | $C_{37}H_{46}Cl_6Mg_2Mn_2O_4$ | $\mathrm{C}_{26}\mathrm{H}_{54}\mathrm{Mn}_{2}\mathrm{N}_{2}\mathrm{Si}_{4}$ | $\mathrm{C}_{30}\mathrm{H}_{34}\mathrm{MnN}_2$ | $C_{44}H_{82}Mn_4O_2Si_6$ | $C_{94}H_{48}B_2F_{48}MnN_6$ |
| 86.90 | 618.59 | 925.94 | 616.95 | 477.53 | 1087.44 | 2249.94 |
| 73(2) | 100(2) | 100(2) | 293(2) | 173(2) | 100(2) | 100(2) |
| .5 	imes 0.4 	imes 0.3 | 0.3 	imes 0.3 	imes 0.2 | 0.3 	imes 0.3 	imes 0.2 | 0.5 	imes 0.4 	imes 0.3 | 0.5 	imes 0.5 	imes 0.3 | 0.2	imes 0.2	imes 0.1 | $0.3 \times 0.3. \mathrm{x} \ 0.2$ |
| nonoclinic | monoclinic | triclinic | monoclinic | triclinic | triclinic | monoclinic |
| $2_1/n$ | $P2_1/c$ | $P\overline{1}$ | C2/c | $\overline{P1}$ | $P\overline{I}$ | $P2_1/n$ |
| 0.7433(3) | 11.8497(5) | 12.4275(4) | 17.769(2) | 11.1277(9) | 9.709(2) | 13.3914(14) |
| 6.4739(4) | 10.0286(4) | 12.5664(4) | 10.917(2) | 11.1305(9) | 12.922(3) | 52.058(5) |
| 2.5466(3) | 14.0932(5) | 15.9820(6) | 20.009(3) | 12.8196(10) | 12.973(3) | 13.8225(14) |
| 0 | 90 | 89.1610(13) | 90 | 82.4880(13) | 70.641(3) | 06 |
| 02.1320(10) | 110.2040(10) | 86.6790(12) | 110.27(2) | 64.9180(13) | 73.990(3) | 92.438(2) |
| 0 | 90 | 60.8440(10) | 90 | 64.1140(14) | 85.830(3) | 90 |
| 170.95(10) | 1570.71(11) | 2175.73(13) | 3641.1(11) | 1290.90(18) | 1475.7(6) | 9627.4(17) |
| | 2 | 2 | 4 | 5 | 1 | 4 |
| 204 | 1.308 | 1.013 | 1.125 | 1.229 | 1.224 | 1.552 |
| .617 | 0.834 | 1.013 | 0.841 | 0.531 | 0.992 | 0.280 |
| .08 - 30.73 | 2.81 - 30.59 | 1.28 - 30.58 | 3.79 - 31.08 | 1.76 - 28.90 | 2.61 - 38.38 | 2.11-28.76 |
| 7 138 | 21 766 | 30 447 | 12 299 | 8041 | 9876 | 61 995 |
| 588 | 4791 | 13 159 | 5810 | 6644 | 5942 | 22 1 1 8 |
| 51 | 189 | 488 | 262 | 302 | 271 | 1424 |
| .0378 | 0.0277 | 0.0306 | 0.0345 | 0.0332 | 0.0514 | 0.0916 |
| .1037 | 0.0795 | 0.0839 | 0.0691 | 0.0839 | 0.1371 | 0.2296 |
| .019 | 1.058 | 1.025 | 1.033 | 1.056 | 1.020 | 1.036 |
| $\begin{array}{c} 73(2)\\ .5\times0.4\times\\ 2_{1/n}\\ 0.743(3)\\ 0.7433(3)\\ 0.7433(3)\\ 0.7433(4)\\ 0.2.5466(3)\\ 0.2.1320(10)\\ 0.2.1320(10)\\ 170.95(10)\\ 170.95(10)\\ 170.95(10)\\ 0.378\\ 51\\ 1170.95(10)\\ 0.378\\ 0.0378\\ 0.0378\\ 0.019\\ 0.019\end{array}$ | 0.9 0 () 8 | 0.3 $\begin{array}{c} 0.3 \\ 0.3 \\ 0.3 \\ 0.3 \\ 0.3 \\ 0.3 \\ 0.3 \\ 0.3 \\ 0.3 \\ 0.3 \\ 0.3 \\ 0.3 \\ 0.0 \\ 0.3 \\ 0.8 \\ 0.8 \\ 0.8 \\ 0.8 \\ 0.8 \\ 0.8 \\ 0.8 \\ 0.8 \\ 0.8 \\ 0.8 \\ 0.8 \\ 0.8 \\ 0.8 \\ 0.8 \\ 0.8 \\ 0.0 \\ 0$ | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ |

(CD₂Cl₂. 300 MHz): δ 7.56, (s, 4H, *p*-H, Ar'); 7.73 (overlapping signals, 10H, *o*-H, Ar' and CH bipy); 8.28 (m, 4H, 4,4',5,5' CH bipy); 8.72 (d, 2H, ³J_{HH} = 4.8 Hz, 6,6' CH bipy); 12.34 (br s, N-H).

 $[Mn(bipy)_3]^{2+}{[BAr'_4]^-}_2$, 13. Solutions of 2,2'-bipyridyl (0.16 g, 1.05 mmol) and compound 3 (0.110 g, 0.35 mmol) in 10 and 15 mL of Et₂O, respectively, were mixed at room temperature, and the resulting dark blue mixture was stirred for 10 min and then cooled to -60 °C. The acid $[H(Et_2O)_2]^+[BAr'_4]^-$ (0.710 g, 0.70 mmol) was dissolved in 15 mL of Et₂O, and this solution was added dropwise to the former mixture. The color changed from dark blue to purple and then to pale orange. Stirring was continued for 5 and 20 min more at room temperature. The solvent was evaporated, and the residue was washed with hexane (10 mL). The resulting pale orange solid was recrystallized from a 2:1 mixture of CH₂Cl₂ and hexane at -30 °C. The product was obtained as colorless needles. Yield: 0.550 g, 70%. Anal. Calcd for C₉₄H₄₈B₂F₄₈MnN₆: C, 50.18; H,2.15; N, 3.74. Found: C, 50.21; H, 2.20; N, 3.82. IR (Nujol mull, cm⁻¹): 1605, 1580 (bipy); 1280, 1120, 890 (B-Ar'). μ_{eff} : 6.1 μ_{B} .

Reactions of Compound 11 with $[H(Z)_2]^+[BAr'_4]^-(Z = Et_2O$ or Py). A solution of 1 mmol of the corresponding acid $[H(Z)_2]^+[BAr'_4]^-(Z = Et_2O, 1.01 \text{ g}; Py, 1.02 \text{ g})$ in 15 mL of Et_2O was dropwise added to a solution of Mn(CH₂CMe₂Ph)₂-(bipy) (11) (0.49 g, 1.03 mmol) in 15 mL of Et₂O, stirred at $-60 \,^{\circ}C$. The color of the mixture gradually changed from blue to red. After 5 min, the mixture was allowed to warm to room temperature, and the stirring was continued for 15 min. The solvent was evaporated under vacuum, leaving a orange foam, which was washed with 10 mL of hexane. The resulting orange solid was extracted with 10 mL of Et₂O. The solution was filtered, and hexane was added until a slight but persistent

(40) SHELXTL 6.14; Bruker AXS, Inc.: Madison, WI, 2000–2003.

turbidity was attained. Cooling to -10 °C overnight afforded colorless crystals of **13** in ca. 50% yield.

Reaction of Compound 9, $[Hbipy]^+[BAr'_4]^-$. The reaction was carried out similarly to the previous one, using equimolar amounts of Mn(CH₂CMe₂Ph)₂(Py)₂ (9) and the bipyridinium salt. Compound 13 was isolated in 32% yield.

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 X8Apex-II CCD diffractometer (2, 5, 6, 7, 11, 12, and 13). Compounds 4 and 8 were coated with an epoxy polymer (T = 293(2) K), and data were collected on a Bruker SMART Apex CCD diffractometer. Both diffractometers were equipped with a Mo $K_{\alpha 1}$ radiation ($\lambda = 0.71073$ A) source and graphite monochromator. The data were reduced (SAINT)³⁷ and corrected for Lorentz polarization and absorption effects by the multiscan method (SADABS).³⁸ The structure was solved by direct methods (SIR-2002)³⁷ and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12)⁴⁰ minimizing $w[F_o^2 - F_c^2]^2$. All non-hydrogen atoms were re-fined 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 $(U_{\rm iso} \, {\rm values})$ fixed at 1.2 times (1.5 times for methyl groups) the $U_{\rm eq}$ values of the corresponding carbon atoms. Crystal and refinement data for all compounds are summarized in Table 2.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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⁽³⁸⁾ Sheldrick, G. SADABS; Bruker AXS, Inc.: Madison, WI, 1999.
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