# The First Structurally Characterized Homoleptic Aryl-Manganese(III) Compound and the Corresponding Isoleptic and Isoelectronic Chromium(II) Derivative

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*Received March 18, 2005*

The homoleptic organochromium(II) compound $[Mg(THF)_6][Cr^{II}(C_6F_5)_4]$ (**1**) was obtained as an extremely air-sensitive solid by reaction of $[CrCl_2(THF)]$ with $C_6F_5MgBr$. The arylation of $MnBr_2$ under similar conditions proceeded with oxidation of the metal center to give $[Mg(THF)_6][Mn^{III}(C_6F_5)_4]_2$ (**2**). The crystal structures of **1** and **2** (X-ray diffraction) contain the anions $[Cr(C_6F_5)_4]^{2-}$ and $[Mn(C_6F_5)_4]^-$, respectively, both with approximate square-planar (*SP*-4) geometry around the metal center. In the solid state there is no sign of any covalent interaction or ion-pairing between these anions and the virtually octahedral (*OC*-6) $[Mg(THF)_6]^{2+}$ cations. The average $Mn^{III}-C$ distance in **2**, 2.068(4) Å, is slightly shorter than the mean $Cr^{II}-C$ bond length in **1**, 2.158(6) Å, a fact that can be attributed mainly to the different oxidation states of the metal centers in each case. The use of **2** as an initiator itself and as a weakly coordinating anion in Pd-catalyzed polymerization processes of strained olefins has also been assayed.

## Introduction

The inorganic and coordination chemistry of Mn is dominated by chemical species with the metal in oxidation state II.[1] This oxidation state is not uncommon in organomanganese chemistry either; however most organoderivatives of Mn contain the metal in lower oxidation states: 1, 0, or negative values.[2,3] This is mainly due to extensive and continued research carried out for several decades on the chemistry of Mn carbonyl compounds related directly or, at least, formally with the prototypical species $[Mn_2(CO)_{10}]$.[3] The preparation[4] of $[MnCp_2]$ marked a milestone in organomanganese(II) chemistry, but it was the seminal work of G. Wilkinson and co-workers on homoleptic alkyl manganese(II) compounds that made a real breakthrough in this area.[5] A good number of homoleptic σ-organomanganese(II) compounds are currently available, showing different stoichiometries, nuclearities, and global charges, such as $[MnR_2]$ [R = $CH_2CMe_3$,[6] $CH_2$(adamant-1-yl),[7] $C(SiMe_3)_3$,[8] $C_6H_2(CMe_3)_3$-2,4,6[9]], $[Mn_2R_4]$ (R = $CMe_2Ph$),[5] $[Mn_3R_6]$ (R = $C_6H_2Me_3$-2,4,6),[10] $[Mn_4R_8]$ (R = $CH_2CMe_3$),[6] $[\{MnR_2\}_n]$ (R = $CH_2SiMe_3$),[5] $[MnR_3]^-$ (R = Me,[11] Et,[12] ${}^n$Bu,[12] $C_6H_2Me_3$-2,4,6[13,14]), $[Mn_2R_6]^{2-}$ (R = Ph),[13] and $[MnR_4]^{2-}$ (R = Me,[5,15,16] Et, ${}^n$Bu, $CH_2CH_2CMe_3$,[16] $CH_2SiMe_3$,[5,16] $CH_2NC_5H_{10}$,[17] Ph,[16] $C_6H_4Me$-2,[18] alkynyl[19]). In contrast to this well-developed chemistry, the corresponding homoleptic σ-organomanganese(III) derivatives are extremely rare. The only representative of this kind of compound for which the molecular geometry has been unambiguously established is, as far

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as we know, the square-planar (*SP*-4) anion $[Mn^{III}Me_4]^-$.[20] A square-pyramidal (*SPY*-5) structure has been suggested for the anion $[Mn^{III}Me_5]^{2-}$,[15,20] while we are not aware of any structural proposal having been put forward for the metallacyclic anions $[Mn^{III}(CH_2CH_2CH_2CH_2\text{-}\kappa C^1,\kappa C^4)_2]^-$ and $[Mn^{III}(C_6H_4OC_6H_4\text{-}\kappa C^2,\kappa C^{2'})_2]^-$.[21,22] This paucity has been related with the lack of suitable synthetic precursors[20] and, on the other hand, with the tendency of many $Mn^{III}$ compounds to undergo disporportionation into $Mn^{II}$ and $Mn^{IV}$ species. We report now on a reasonably stable tetraarylmanganate(III) salt together with the corresponding isoleptic and isoelectronic chromium(II) derivative.

## Results and Discussion

**Synthesis.** The low-temperature reaction of $[CrCl_2(THF)]$ with $C_6F_5MgBr$ in a 1:1 mixture of $Et_2O$ and THF takes place under full arylation of the metal center (eq 1). Addition of 1,4-dioxane to the reaction medium does not produce the expected removal of the magnesium ions in an efficient way, since the salt $[Mg(THF)_6][Cr^{II}(C_6F_5)_4]$ (**1**) still remains dissolved at −30 °C. From these solutions, complex **1** can be isolated as an extremely air- and moisture-sensitive green solid in moderate yield.

$$[CrCl_2(THF)] + C_6F_5MgBr \xrightarrow{THF/Et_2O} \underset{\mathbf{1}}{[Mg(THF)_6][Cr(C_6F_5)_4]} \quad (1)$$

The reaction of $MnBr_2$ with $C_6F_5MgBr$ under similar conditions proceeds not only with full arylation but also with oxidation of the metal center (eq 2). From the reaction medium, the salt $[Mg(THF)_6][Mn^{III}(C_6F_5)_4]_2$ (**2**) could be isolated as a brown solid in moderate yield.

$$MnBr_2 + C_6F_5MgBr \xrightarrow{THF/Et_2O} \underset{\mathbf{2}}{[Mg(THF)_6][Mn(C_6F_5)_4]_2} \quad (2)$$

The preparation of $Mn^{III}$ derivatives starting from lower-valent precursors (typically $Mn^{II}$ compounds) is well documented. The most common oxidant in such processes is molecular oxygen,[18] but some other oxidation mechanisms have also been reported, such as the reductive coupling of ethylene to give the 1,4-butanediyl ligand present in the oily species $[K(THF)_x][Mn^{III}(CH_2CH_2CH_2CH_2\text{-}\kappa C^1,\kappa C^4)_2]$ or in its pyridine adduct $[K(py)_2][Mn^{III}(CH_2CH_2CH_2CH_2\text{-}\kappa C^1,\kappa C^4)_2(py)]$.[21] The formation of the $Mn^{III}$ complex **2** could also be due to disproportionation of some nondetected perfluorophenyl-manganese(II) intermediate species. In any case, the nature of the oxidation agent enabling eq 2 to proceed is still unclear.

**Characterization.** Compounds **1** and **2** were identified by analytical and spectroscopic methods. Their crystal and molecular structures were also established by X-ray diffraction methods on single crystals of **1**·2THF and **2**·$3C_4H_8O_2$, respectively (crystal data given in Table 1). A selection of interatomic distances and angles for **1** and **2** are collected in Tables 2 and 3, respectively. The crystal lattices of both **1**·2THF and **2**·$3C_4H_8O_2$ are made of separate ions $[Mg(THF)_6]^{2+}$ and

**Table 1. Summary of Crystallographic Data and Structure Refinement for 1·2THF and 2·3C₄H₈O₂**

| | **1**·2THF | **2**·$3C_4H_8O_2$ |
|---|---|---|
| empirical formula | $C_{56}H_{64}CrF_{20}MgO_8$ | $C_{84}H_{72}F_{40}MgMn_2O_{12}$ |
| fw | 1321.38 | 2167.60 |
| $\lambda$ (Å) | 71.073 | 71.073 |
| cryst syst | monoclinic | triclinic |
| space group | $C2/c$ | $P\bar{1}$ |
| $a$ (Å) | 15.848(2) | 13.212(1) |
| $b$ (Å) | 16.147(2) | 13.281(1) |
| $c$ (Å) | 22.643(2) | 14.499(1) |
| α (deg) | 90 | 111.854(2) |
| $\beta$ (deg) | 98.751(2) | 108.778(2) |
| $\gamma$ (deg) | 90 | 92.750(2) |
| $V$ (Å³) | 5727(1) | 2195.0(4) |
| $Z$ | 4 | 1 |
| $d_c$ (g cm$^{-3}$) | 1.533 | 1.640 |
| $F$(000) | 2720 | 2188 |
| $\mu$ (mm$^{-1}$) | 0.330 | 0.440 |
| $\theta$ range (deg) | 1.81−25.08 | 1.80−25.06 |
| index range | $-17 \le h \le 18$<br>$-19 \le k \le 12$<br>$-26 \le l \le 25$ | $-15 \le h \le 11$<br>$-15 \le k \le 15$<br>$-12 \le l \le 17$ |
| no. of reflns collected | 15 263 | 12 971 |
| no. of unique reflns | 5044 ($R_{int}$ = 0.0496) | 7637 ($R_{int}$ = 0.0356) |
| refinement method | full-matrix least-squares on $F^2$ | |
| final $R$ indices [$I > 2\sigma(I)$][a] | $R_1 = 0.0546$,<br>$wR_2 = 0.1125$ | $R_1 = 0.0604$,<br>$wR_2 = 0.1004$ |
| $R$ indices (all data) | $R_1 = 0.1024$,<br>$wR_2 = 0.1218$ | $R_1 = 0.1067$,<br>$wR_2 = 0.1086$ |
| GOF[b] on $F^2$ | 1.037 | 1.031 |

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_c^2)^2]^{1/2}$; $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$; $P = (1/3)\cdot[\max\{F_o^2,0\} + 2F_c^2]$. [b] Goodness-of-fit $= [\sum w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

**Table 2. Selected Interatomic Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for 1·2THF**

| | | Anion | |
|---|---|---|---|
| Cr−C(1) | 2.157(4) | C(1)−Cr−C(1′) | 179.6(2) |
| Cr−C(7) | 2.158(6) | C(1)−Cr−C(7) | 89.8(1) |
| Cr−C(11) | 2.162(5) | C(1′)−Cr−C(7) | 89.8(1) |
| C(1)−C(2) | 1.352(5) | C(1)−Cr−C(11) | 90.2(1) |
| C(2)−F(2) | 1.368(4) | C(1′)−Cr−C(11) | 90.2(1) |
| C(1)−C(6) | 1.391(5) | C(7)−Cr−C(11) | 180.000(1) |
| C(6)−F(6) | 1.365(4) | Cr−C(1)−C(2) | 122.2(3) |
| C(7)−C(8) | 1.367(5) | Cr−C(1)−C(6) | 125.3(3) |
| C(8)−F(8) | 1.372(4) | C(2)−C(1)−C(6) | 112.5(3) |
| C(11)−C(12) | 1.371(5) | Cr−C(7)−C(8) | 124.1(3) |
| C(12)−F(12) | 1.372(4) | C(8)−C(7)−C(8′) | 111.7(5) |
| | | Cr−C(11)−C(12) | 123.7(2) |
| | | C(12)−C(11)−C(12′) | 112.5(5) |
| | | Cation | |
| Mg−O(1) | 2.093(2) | O(1)−Mg−O(2) | 90.20(9) |
| Mg−O(2) | 2.077(2) | O(1)−Mg−O(2′) | 89.80(9) |
| Mg−O(3) | 2.103(3) | O(1)−Mg−O(3) | 89.62(9) |
| O(1)−C(15) | 1.462(4) | O(1)−Mg−O(3′) | 90.38(9) |
| O(1)−C(18) | 1.466(4) | O(2)−Mg−O(3) | 90.9(1) |
| O(2)−C(19) | 1.463(4) | O(2)−Mg−O(3′) | 89.1(1) |
| O(2)−C(22) | 1.453(4) | Mg−O(1)−C(15) | 126.0(2) |
| O(3)−C(23) | 1.462(5) | Mg−O(1)−C(18) | 126.3(2) |
| O(3)−C(26) | 1.467(4) | C(15)−O(1)−C(18) | 107.6(2) |
| | | Mg−O(2)−C(19) | 124.1(2) |
| | | Mg−O(2)−C(22) | 127.2(2) |
| | | C(19)−O(2)−C(22) | 108.6(3) |
| | | Mg−O(3)−C(23) | 125.0(2) |
| | | Mg−O(3)−C(26) | 127.1(2) |
| | | C(23)−O(3)−C(26) | 107.8(3) |

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**Table 3. Selected Interatomic Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $2{\cdot}3C_4H_8O_2$**

| Anions | | | |
|---|---|---|---|
| Mn(1)−C(1) | 2.072(4) | Mn(2)−C(13) | 2.078(4) |
| Mn(1)−C(7) | 2.061(4) | Mn(2)−C(19) | 2.061(4) |
| C(1)−C(2) | 1.372(6) | C(13)−C(14) | 1.374(5) |
| C(2)−F(2) | 1.354(5) | C(14)−F(14) | 1.366(5) |
| C(1)−C(6) | 1.365(5) | C(13)−C(18) | 1.366(5) |
| C(6)−F(6) | 1.350(5) | C(18)−F(18) | 1.358(4) |
| C(7)−C(8) | 1.386(5) | C(19)−C(20) | 1.367(5) |
| C(8)−F(8) | 1.354(5) | C(19)−C(24) | 1.373(5) |
| C(7)−C(12) | 1.371(6) | C(20)−F(20) | 1.367(4) |
| C(12)−F(12) | 1.353(5) | C(24)−F(24) | 1.369(4) |
| C(1)−Mn(1)−C(7) | 89.7(2) | C(13)−Mn(2)−C(19) | 87.5(2) |
| C(1)−Mn(1)−C(7′) | 90.3(2) | C(13)−Mn(2)−C(19′) | 92.5(2) |
| Mn(1)−C(1)−C(2) | 129.3(4) | Mn(2)−C(13)−C(14) | 124.9(3) |
| Mn(1)−C(1)−C(6) | 116.2(3) | Mn(2)−C(13)−C(18) | 121.3(3) |
| C(2)−C(1)−C(6) | 114.5(4) | C(14)−C(13)−C(18) | 113.6(4) |
| Mn(1)−C(7)−C(8) | 124.4(3) | Mn(2)−C(19)−C(20) | 128.3(3) |
| Mn(1)−C(7)−C(12) | 121.1(3) | Mn(2)−C(19)−C(24) | 117.7(3) |
| C(8)−C(7)−C(12) | 114.4(4) | C(20)−C(19)−C(24) | 113.7(4) |

| Cation | | | |
|---|---|---|---|
| Mg−O(1) | 2.085(3) | O(1)−Mg−O(2) | 89.5(1) |
| Mg−O(2) | 2.085(3) | O(1)−Mg−O(2′) | 90.5(1) |
| Mg−O(3) | 2.099(3) | O(1)−Mg−O(3) | 89.2(1) |
| O(1)−C(25) | 1.451(5) | O(1)−Mg−O(3′) | 90.7(1) |
| O(1)−C(28) | 1.462(5) | O(2)−Mg−O(3) | 90.7(1) |
| O(2)−C(29) | 1.458(4) | O(2)−Mg−O(3′) | 89.3(1) |
| O(2)−C(32) | 1.456(5) | Mg−O(1)−C(25) | 126.2(3) |
| O(3)−C(33) | 1.460(5) | Mg−O(1)−C(28) | 125.8(2) |
| O(3)−C(36) | 1.461(4) | C(25)−O(1)−C(28) | 108.0(3) |
| | | Mg−O(2)−C(29) | 125.6(2) |
| | | Mg−O(2)−C(32) | 126.2(2) |
| | | C(29)−O(2)−C(32) | 108.2(3) |
| | | Mg−O(3)−C(33) | 127.5(2) |
| | | Mg−O(3)−C(36) | 125.3(2) |
| | | C(33)−O(3)−C(36) | 107.2(3) |

$[M(C_6F_5)_4]^{q-}$ (**1**, M = Cr, $q = 2$; **2**, M = Mn, $q = 1$) in the appropriate stoichiometric ratio in each case together with interstitial solvent molecules. The six oxygen atoms of the THF ligands in the $[Mg(THF)_6]^{2+}$ cation define a virtually octahedral (*OC*-6) environment for the $Mg^{2+}$ ion. Angles between *cis*-coordinating oxygen atoms do not significantly deviate from 90°, and those between *trans*-coordinating oxygen atoms are exactly 180° because of crystallographically imposed symmetry (inversion center). All the Mg−O distances are in a very narrow range, 2.077(2)−2.103(3) Å, similar to those found in other salts containing the solvated cation $[Mg(THF)_6]^{2+}$.[23] The IR spectra of **1** and **2** contain absorptions of medium to strong intensity assignable to the stretching vibrations of the C−O−C ether link corresponding to the Mg-coordinated THF ligands.[24] Standard patterns are observed for the vibrations associated with the $C_6F_5$ groups,[25] although no absorption could be unambiguously assigned to the X-sensitive vibration modes in the IR spectrum of **2**. In contrast, a band of medium intensity at 765 $cm^{-1}$ was observed in the IR spectrum of **1**, which can be attributed to the referred $C_6F_5$ X-sensitive vibration mode. Aside from this difference of unknown origin, the vibrational behavior of compounds **1** and **2** is quite similar.

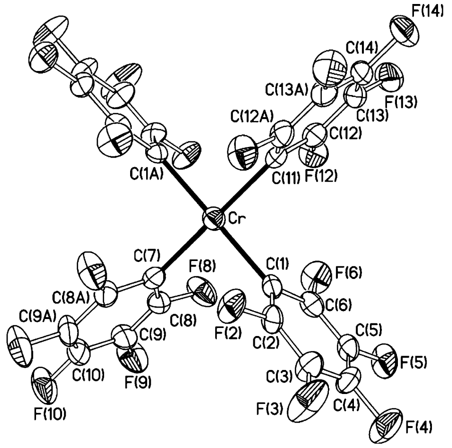

**Figure 1.** Thermal ellipsoid diagram (50% probability) of the $[Cr^{II}(C_6F_5)_4]^{2-}$ anion in $\mathbf{1}{\cdot}2THF$.

The structure of the mononuclear anion $[Cr^{II}(C_6F_5)_4]^{2-}$ as found in $\mathbf{1}{\cdot}2THF$ is shown in Figure 1. The $Cr^{II}$ coordination environment can be described as square-planar (*SP*-4) with no perceptible interligand angular distortions and four virtually identical Cr−C distances (Table 2). The small departure of the $Cr^{II}$ first coordination sphere from ideal *SP*-4 geometry is evidenced by the very low value of continuous shape measure obtained,[26] $S(SP\text{-}4) = 0.005$.[27] The molecule has crystallographically imposed $C_2$ symmetry along the C(7)−Cr−C(11) vector, which also comprises the C(10)−F(10) and C(14)−F(14) segments. The Cr−C($sp^2$) average value, 2.158(6) Å, is shorter than the mean Cr−C($sp^3$) distance found in the mononuclear species $[Li(TMEDA)]_2[Cr^{II}Me_4]$ [2.208(5) Å].[28] Strong cation/anion interactions were observed in the latter compound, where each methyl group is, in fact, acting as an electron-deficient bridge between the Cr center and one of the $Li^+$ ions. This bridging function as well as the different hybridization at the C atom could well justify the longer Cr−C distances observed in this case. In this context, it is interesting to note that the only crystallographically independent Cr−C($sp^2$) bond distance in the related mononuclear aryl species $[Cr^{II}(C_6Cl_5)_4]^{2-}$ was found[29] to be also significantly longer [2.208(3) Å] than in **1**, despite both kinds of C-donor atoms having now the same hybridization. Moreover, the four $C_6F_5$ groups in **1** are roughly perpendicular to the molecular plane (tilt angles: 74.8−88.8°), while in the anion $[Cr^{II}(C_6Cl_5)_4]^{2-}$,

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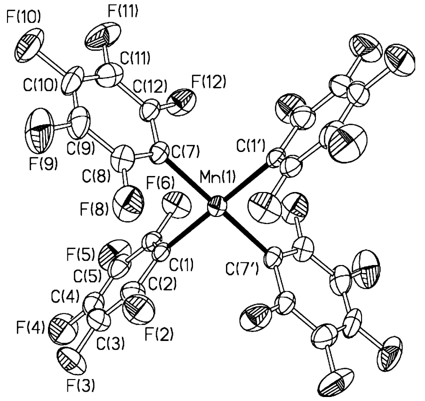

**Figure 2.** Thermal ellipsoid diagram (50% probability) of one of the two crystallographically independent $[Mn^{III}(C_6F_5)_4]^-$ anions in $\mathbf{2}\cdot 3C_4H_8O_2$.

the more sterically demanding $C_6Cl_5$ groups show a higher tilt angle with respect to the molecular plane (68.7°). Both the longer Cr−C distance and the more tilted perhalophenyl groups in $[Cr^{II}(C_6Cl_5)_4]^{2-}$ can be reasonably ascribed to the considerably larger size of Cl vs F given by their corresponding effective van der Waals radii ($r_{vdW}$) in haloaryl compounds: $r_{vdW}(F) = 1.47$ Å vs $r_{vdW}(Cl) = 1.77$ Å.[30] Shorter $Cr-C_6Cl_5$ bonds and less tilted $C_6Cl_5$ rings would probably entail energetically unaffordable Cl···Cl nonbonding interactions between adjacent *ortho*-Cl atoms belonging to neighboring rings.[31] The significance of avoiding such repulsive interactions between *ortho*-substituents for tuning the M−C distance in aryl-metal derivatives can be further illustrated by comparing the Cr−C distances in the homoleptic arylchromate(II) species: $[Li(THF)_2]_2[Cr^{II}(C_6H_2Me_3\text{-}2,4,6)_4]$ [2.255(5) Å] vs $[Li(THF)_2]_2[Cr^{II}Ph_4]$ [mean Cr−C distance: 2.178(3) Å].[32] Note that the Cr−C distance in the later compound bearing unsubstituted phenyl rings is quite similar to that found in our pentafluorophenyl derivative **1** regardless of the sharply different degrees of cation/anion association observed in each case.

The unit cell of $\mathbf{2}\cdot 3C_4H_8O_2$ contains two crystallographically independent $[Mn^{III}(C_6F_5)_4]^-$ anions, one of which is depicted in Figure 2. The structural features of these anions are very similar to those just discussed for the isoleptic and isoelectronic $[Cr^{II}(C_6F_5)_4]^{2-}$ anion with also negligible angular distortions with respect to the ideal *SP*-4 geometry. Continuous shape measure values, *S*(*SP*-4), of 0.001 and 0.048 are obtained respectively for the two crystallographically independent metal centers Mn(1) and Mn(2).[27] The average $Mn^{III}-C$ distance in **2**, 2.068(4) Å, is shorter by ca. 0.09 Å than the mean $Cr^{II}-C$ bond length in **1**, 2.158(6) Å, an observation that can be related to the different oxidation states of the metal centers. On the other hand, similar $Mn^{III}-C$ distances were found in the heteroleptic five-coordinate species $[Mn(C_6H_2Me_3\text{-}2,4,6)Br_2(PMe_3)_2]$ [2.089(8) Å],[18] as well as in the permethylmanganate(III) anion $[Mn^{III}Me_4]^-$ [mean $Mn^{III}-C$ length: 2.078(5) Å].[20] In these examples, the $Mn^{III}-C$ bond length appears to be quite insensitive to the hybridization of the C-donor atoms and to the coordination number. In contrast with the virtually regular *SP*-4 geometry observed for the $[Mn^{III}(C_6F_5)_4]^-$ anion in **2**, the $[Mn^{III}Me_4]^-$ anion showed a significant tetrahedral distortion, as evidenced by the fairly large value of the continuous shape measure parameter, *S*(*SP*-4) = 2.641.[27] This distortion follows a $B_{2u}$ vibrational mode of the ideal square plane, resulting in a $D_{2d}$ spread symmetry.[26c] The structural differences found in the homoleptic organomanganate(III) derivatives $[Mn^{III}R_4]^-$ (R = Me or $C_6F_5$) cannot be assigned to the steric requirements of the organic group. Methyl is usually considered as a nearly spherical substituent with a global[33] van der Waals radius of 2.0 Å and a specific value of $r_{vdW}(C_{aliph}) = 1.70$ Å for the aliphatic C atom.[30] Aryl rings, in contrast, are highly anisotropic groups with an effective thickness of 3.4−3.7 Å.[33] The van der Waals radius assigned to an aromatic C atom is $r_{vdW}(C_{arom}) = 1.77$ Å.[30] Hence, it can be concluded that steric repulsions arising between adjacent Me or perpendicularly arranged aryl groups in *SP*-4 metal complexes might be comparable in magnitude.[34] On the other hand, the different polarity expected for the $Mn^{III}-R$ bond considering the markedly different electron-withdrawing characters of the Me and $C_6F_5$ organic groups might well play an important role in deciding the most energetically favored ground-state molecular geometry in each case. In this context it is interesting to note that the four S-donor atoms in the $[Mn^{III}(\text{toluene-3,4-dithiolato})_2]^-$ anion also define a virtually regular *SP*-4 geometry around the metal center[35] with a value of continuous shape measure, *S*(*SP*-4) = 0.000.[27]

No tendency to dimerize giving metal−metal bonded units was observed either in the $[Mn^{III}(C_6F_5)_4]^-$ or in the $[Cr^{II}(C_6F_5)_4]^{2-}$ anions, both of them having $d^4$ electron configuration. This observation can be attributed, at least in the case of $Cr^{II}$, to the shielding effect of the sterically demanding $C_6F_5$ groups, which would preclude two metal centers from approaching a sufficiently short distance to establish a bonding interaction.

**Polymerization.** Vinyl addition norbornene polymers are typically made using transition metal catalysts.[36] Over the years, we have developed two types of vinyl addition norbornene polymerization initiators: neutral nickel and cationic nickel and palladium complexes. Neutral nickel initiators include complexes containing electron-withdrawing halogenated aryl and labile solvent ligands such as $[Ni(\eta^6\text{-}C_6H_5Me)(C_6F_5)_2]$ and $[Ni\{C_6H_2(CF_3)_3\text{-}2,4,6\}_2(dme)]$.[37] Cationic nickel and palladium catalysts include $\eta^3$-allyl complexes balanced by weakly coordinating anions such as $[PF_6]^-$, $[SbF_6]^-$,

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**Table 4. Polymerization Results[a] of Norbornene-Type Monomers Using 2**

| experiment | monomer | complex | activator | yield | $M_w$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|
| 1 | $^t$BuEsNB | $[\mathrm{Ni}(\eta^6\text{-}\mathrm{C_6H_5Me})(\mathrm{C_6F_5})_2]$ | | 90% | 18 800 | 1.85 |
| 2 | $^t$BuEsNB | **2** | | 0% | | |
| 3 | $^t$BuEsNB | **2** | HBArF | 0% | | |
| 4 | TESNB | *trans*-$[\mathrm{Pd(OAc)_2(P^iPr_3)_2}]$ | LiFABA | 95% | | |
| 5 | TESNB | *trans*-$[\mathrm{Pd(OAc)_2(P^iPr_3)_2}]$ | 2 | 33% | 190 000 | 2.50 |

[a] See Experimental Section for details.

and $[\mathrm{B(C_6F_5)_4}]^-$.[38] In addition, we have found that neutral palladium phosphine complexes in the presence of salts of weakly coordinating anions are excellent initiators for norbornene vinyl addition polymerization.[39]

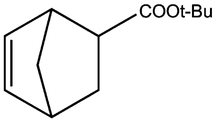
Despite their electron-deficient nature, the reluctance of the $[\mathrm{Mn^{III}(C_6F_5)_4}]^-$ or the $[\mathrm{Cr^{II}(C_6F_5)_4}]^{2-}$ anions to dimerize suggested that these new transition metal anions would not initiate the vinyl addition polymerization of strained olefins themselves. However, they might serve as weakly coordinating anions in the Pd-catalyzed vinyl addition polymerization processes of strained olefins considering their obvious relationship with the widely used tetrahedral (*T*-4) $[\mathrm{B(C_6F_5)_4}]^-$ anion.

We decided to test this theory for one of the two anions synthesized, namely, $[\mathrm{Mn^{III}(C_6F_5)_4}]^-$. First the ability of the anion itself to polymerize a norbornene-type monomer was examined (Table 4). In experiments 1–3, 5-norbornene carboxylic acid *tert*-butyl ester (tBuEsNB) was chosen as a typical norbornene functional monomer. As a control, $[\mathrm{Ni}(\eta^6\text{-}\mathrm{C_6H_5Me})(\mathrm{C_6F_5})_2]$ was used to initiate the polymerization of the ester functional monomer. Under the conditions employed, a 90% yield of polymer was obtained (experiment 1). When the polymerization was repeated but with **2** instead of the nickel complex, no polymer is isolated (experiment 2). An attempt to activate the polymerization by addition of $[\mathrm{H(OEt_2)_2}][\mathrm{B\{C_6H_3(CF_3)_2\text{-}3,5\}_4}]$ (HBArF)[40] also failed (experiment 3). This experiment was carried out in hopes that protonation of the $\mathrm{C_6F_5}$ ligands would occur, eliminating pentafluorobenzene, creating a reactive "$\mathrm{Mn(C_6F_5)}_n$" species in situ akin to $[\mathrm{Ni}(\eta^6\text{-}\mathrm{C_6H_5Me})(\mathrm{C_6F_5})_2]$.

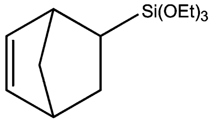
The second set of experiments (4, 5) employed **2** as a weakly coordinating anion in the polymerization of 5-triethoxysilyl-2-norbornene (TESNB). As a control, $[\mathrm{Li(OEt_2)_{2.5}}][\mathrm{B(C_6F_5)_4}]$ (LiFABA) was used in conjunction with *trans*-$[\mathrm{Pd(OAc)_2(P^iPr_3)_2}]$. Under these conditions, a 95% yield of poly(5-triethoxysilyl-2-norbornene) was isolated. When **2** was employed instead of LiFABA, a 33% yield of polymer was obtained.

## Concluding Remarks

A similar structural behavior has been observed for the highly unusual pair of isoleptic and isoelectronic (12-electron) species $[\mathrm{Cr^{II}(C_6F_5)_4}]^{2-}$ and $[\mathrm{Mn^{III}(C_6F_5)_4}]^-$, which have been isolated as their corresponding $[\mathrm{Mg(THF)_6}]^{2+}$ salts. Both anions, in which the metal centers have $d^4$ electron configuration, show rather regular *SP*-4 geometries. The structural comparison is especially reliable because of the absence of significant cation/anion covalent interactions in any of the crystal lattices. This point was not fulfilled in the related permethyl derivatives $[\mathrm{Cr^{II}Me_4}]^{2-}$ and $[\mathrm{Mn^{III}Me_4}]^-$, since different degrees of cation/anion association have always been observed for the methylchromate(II) anion in the different salts for which the molecular structure has been established.[28,41] These often disregarded cation/anion interactions seem to be, at least in the case of $\mathrm{Cr^{II}}$, so important as to determine the formation or breaking of a quadruple metal–metal bond.[28] In the absence of significant cation/anion interactions in the crystal lattices of **1**·2THF and **2**·$3\mathrm{C_4H_8O_2}$, the structures of the $[\mathrm{M(C_6F_5)_4}]^{q-}$ anions (M = Cr, $q = 2$; M = Mn, $q = 1$) are thought to accurately reflect the preferred ground-state geometries in each case. The anion $[\mathrm{Mn^{III}(C_6F_5)_4}]^-$ was shown to be effective as a weakly coordinating anion in the palladium-catalyzed vinyl polymerization of TESNB.



tBuEsNB



TESNB

## Experimental Section

All the synthetic manipulations and operations were carried out under an inert atmosphere (Ar) using Schlenk techniques. Polymerizations were carried out under nitrogen atmosphere using typical drybox techniques. Solvents for synthesis were dried by standard methods. Anhydrous grade solvents were used for polymerization after sparging with nitrogen. Anhydrous $\mathrm{MnBr_2}$ (Riedel-de Haën), TESNB (Gelest), and $^t$BuEsNB (Promerus LLC) were obtained from commercial suppliers and used as received. $[\mathrm{CrCl_2(THF)}]$,[42] $[\mathrm{Ni}(\eta^6\text{-}\mathrm{C_6H_5Me})(\mathrm{C_6F_5})_2]$,[37] *trans*-$[\mathrm{Pd(OAc)_2(P^iPr_3)_2}]$,[39a] HBArF,[40] and $\mathrm{Et_2O}$ solutions of $\mathrm{C_6F_5MgBr}$[43] were prepared according to literature procedures. The $^1$H NMR spectra were recorded on a Bruker AMX-500 NMR spectrometer. Chemical shifts were referenced to internal residual protio solvent resonances and are reported relative to $\mathrm{SiMe_4}$. Polymer molecular weights were determined by GPC according to the following procedure. Approximately 50–60 mg of polymer was dissolved in THF (20 cm$^3$) containing 250 mg of BHT. The solution was filtered through a 0.2 $\mu$m Teflon disposable syringe filter and then injected into the chromatograph. The mobile phase used was THF stabilized with 250

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ppm BHT. The measurements were run on a PL-GPC 50 integrated GPC system from Polymer Laboratories at 40 °C, with a Midas 830 autosampler. The column set used was 2 PLgel 5 $\mu$m Mixed C, plus 1 PL 5 $\mu$m guard column. The data for analysis were acquired using PL Cirrus software, version 2.0. Calibration was obtained using EasiCal polystyrene standards from Polymer Laboratories. The calibration range was $7.5 \times 10^6$ to 580 Da. Elemental analyses were carried out with a Perkin-Elmer 2400-Series II microanalyzer. IR spectra of KBr disks were recorded on a Perkin-Elmer Spectrum One (4000−350 cm$^{-1}$) spectrophotometer.

**Synthesis of [Mg(THF)$_6$][Cr$^{II}$(C$_6$F$_5$)$_4$] (1).** A suspension of [CrCl$_2$(THF)] (1.87 g, 9.61 mmol) in THF (50 cm$^3$) was slowly added to a freshly prepared Et$_2$O solution (50 cm$^3$) of C$_6$F$_5$-MgBr (ca. 48 mmol) precooled at −78 °C. The temperature of the mixture was allowed to rise to 0 °C and further stirred for 3 h at that temperature. After the addition of 1,4-dioxane (30 cm$^3$), the reaction medium was allowed to stand at −30 °C for 2 days. A white precipitate formed, which was removed by filtration. Vacuum evaporation of the solvent from the filtrate gave a green solid, which was identified as **1** (3.4 g, 2.89 mmol, 30% yield). Anal. Calcd (%) for $C_{48}H_{48}CrF_{20}MgO_6$: C 49.0, H 4.1. Found: C 48.5, H 3.75. IR (KBr): $\tilde{\nu}_{max}$/cm$^{-1}$ 2982 (m), 2905 (m), 1633 (w), 1536 (m), 1505 (vs), 1443 (vs), 1255 (m), 1061 (s), 1045 (s), 953 (vs; C$_6$F$_5$: C−F),[25] 863 (s; THF: C−O−C),[24] 765 (m; C$_6$F$_5$: X-sensitive vibr.),[25] 717 (w), 677 (m), 605 (m), 579 (m) and 482 (m).

Single crystals suitable for X-ray diffraction purposes with formula [Mg(THF)$_6$][Cr(C$_6$F$_5$)$_4$]·2THF were obtained by slow diffusion of an Et$_2$O (5 cm$^3$) layer into a solution of 30 mg of **1** in 2 cm$^3$ of THF at −30 °C.

**Synthesis of [Mg(THF)$_6$][Mn$^{III}$(C$_6$F$_5$)$_4$]$_2$ (2).** A freshly prepared Et$_2$O solution (50 cm$^3$) of C$_6$F$_5$MgBr (ca. 26 mmol) was diluted with THF (50 cm$^3$) and cooled to −78 °C. To this solution was added solid MnBr$_2$ (1.12 g, 5.22 mmol), and the resulting suspension was allowed to reach room temperature overnight and then filtered. 1,4-Dioxane (25 cm$^3$) was added to the filtrate, and by allowing this mixture to stand 3 days at −30 °C, a white precipitate formed, which was removed by filtration. Evaporation of the solvent from the filtrate under vacuum gave a brown solid, which was identified as **2** (3.96 g, 2.08 mmol, 40% yield). Anal. Calcd (%) for $C_{72}H_{48}F_{40}MgMn_2O_6$: C 45.4, H 2.5. Found: C 44.8, H 3.1. IR (KBr): $\tilde{\nu}_{max}$/cm$^{-1}$ 2985 (m), 2905 (w), 1634 (m), 1533 (m), 1503 (vs), 1462 (vs), 1368 (w), 1338 (m), 1258 (w), 1180 (w), 1063 (s), 1046 (s), 1016 (m), 955 (vs; C$_6$F$_5$: C−F),[25] and 864 (m; THF: C−O−C).[24]

Single crystals suitable for X-ray diffraction purposes with formula [Mg(THF)$_6$][Mn(C$_6$F$_5$)$_4$]$_2$·3C$_4$H$_8$O$_2$ were obtained by slow diffusion of an Et$_2$O (5 cm$^3$) layer into a solution of 40 mg of **2** in 2 cm$^3$ of THF at −30 °C.

**Polymerization of $^t$BuEsNB.** (a) To a solution of $^t$BuEsNB (2.0 g, 10.3 mmol) in toluene (5.4 cm$^3$) was added [Ni($\eta^6$-C$_6$H$_5$-Me)(C$_6$F$_5$)$_2$] (0.10 g, 0.21 mmol). The glass vial was sealed. After stirring at room temperature for 4 h, the reaction mixture was added dropwise to an excess of MeOH. The precipitated polymer was collected by filtration, washed with MeOH, and dried at 50 °C for 20 h. Yield: 1.8 g (90%). Poly(5-norbornene carboxylic acid *tert*-butyl ester): $M_n$(GPC): 10 200; $M_w$(GPC): 18 800; $M_w$/$M_n$: 1.85. $^1$H NMR (CDCl$_3$): $\delta$ 1.5 [s, b, C(C$\underline{H}_3$)$_3$] and 0.8−3.5 (b, aliphatic norbornene protons).

(b) Under the same conditions as (a), **2** (0.25 g, 0.13 mmol) was added to a toluene solution of $^t$BuEsNB instead of [Ni($\eta^6$-C$_6$H$_5$Me)(C$_6$F$_5$)$_2$]. The reaction mixture was stirred for 4 h. No polymer was obtained after addition of the reaction mixture to MeOH.

(c) Under the same conditions as (b), HBArF (0.41 g, 0.45 mmol) was added to the same mixture and allowed to stir for 4 h. The reaction did not yield any polymer after addition of the reaction mixture to MeOH.

**Polymerization of TESNB.** (a) To a solution of TESNB (4.0 g, 15.6 mmol) in toluene (10 cm$^3$) were added *trans*-[Pd(OAc)$_2$(P$^i$Pr$_3$)$_2$] (8.5 mg, 0.016 mmol) and LiFABA (68.0 mg, 0.078 mmol). The glass vial was sealed and then placed in an oil bath at 65 °C. After stirring for 22 h, the reaction mixture was cooled to ambient temperature and then added dropwise to an excess of MeOH. The precipitated polymer was collected by filtration, washed, and dried at 50 °C for 20 h. Yield: 3.8 g (95%). Poly(5-triethoxy-2-norbornene): $M_n$(GPC): 76 000; $M_w$(GPC): 190 000; $M_w$/$M_n$: 2.50. $^1$H NMR (*o*-dichlorobenzene-*d*$_4$): $\delta$ 4.2−3.7 [b, 6H, Si(OC$H_2$CH$_3$)$_3$] and 3.0−0.5 [b, 18 H, Si(OCH$_2$C$H_3$)$_3$ and aliphatic norbornene protons].

(b) Under the same conditions as in (a), **2** (94.7 mg, 0.050 mmol) was employed as a weakly coordinating anion instead of LiFABA. Yield: 1.3 g (33%).

**X-ray Structure Determinations.** Crystal data and other details of the structure analyses are presented in Table 1. All diffraction measurements were made at 100 K on a Bruker Smart CCD diffractometer using graphite-monochromated Mo Kα radiation. Unit cell dimensions were initially determined from 2147 reflections for **1**·2THF and 888 reflections for **2**·3C$_4$H$_8$O$_2$. For each structure, a full hemisphere of reciprocal space was scanned by 0.3° $\omega$ steps at $\phi$ 0°, 90°, and 180° with the detector at $2\theta = 28°$. The diffraction frames were integrated using the SAINT package[44] and corrected for absorption with SADABS.[45] Lorentz and polarization corrections were applied.

The structures were solved by direct methods and refined using the SHELXL-97 program.[46] All non-hydrogen atoms were assigned anisotropic displacement parameters. The hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times the $U_{iso}$ values of their respective parent atoms. For **1**·2THF, carbon atom C(17) belonging to the [Mg(THF)$_6$]$^{2+}$ cation is disordered over two sets of positions, which were refined with 0.5 partial occupancy. The C−C bond distances involving these two disordered atoms were restrained to be the same. For **2**·3C$_4$H$_8$O$_2$, weak interatomic distances restraints (SADI) were applied on the dioxane solvent molecules. A common set of thermal anisotropic parameters was used for the carbon atoms of dioxane. Full-matrix least-squares refinement of these models against $F^2$ converged to final residual indices given in Table 1. Final difference electron density maps showed no features with significant electron density. CCDC reference numbers: 266541 (**1**·2THF) and 266542 (**2**·3C$_4$H$_8$O$_2$).

**Acknowledgment.** This work has been supported by the Spanish MCYT (DGI)/FEDER (Project BQU2002-03997-CO2-02) and Promerus LLC. We are indebted to Prof. Dr. S. Alvarez (Universitat de Barcelona) for kindly providing values of continuous shape measure as well as for sharing results prior to publication.

**Supporting Information Available:** Crystallographic data of **1**·2THF and **2**·3C$_4$H$_8$O$_2$ (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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