



Reinvestigation of arylmanganese chemistry – Synthesis and molecular structures of $[(\text{thf})_4\text{Mg}(\mu\text{-Cl})_2\text{Mn}(\text{Br})\text{Mes}]$, $[\text{Mes}(\text{thf})\text{Mn}(\mu\text{-Mes})]_2$, and $(\text{MnPh}_2)_\infty$ (Ph = C₆H₅; Mes = mesityl, 2,4,6-Me₃C₆H₂)

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ABSTRACT

The reaction of 2,4,6-trimethylphenylmagnesium bromide (MesMgBr) with manganese(II) chloride in an equimolar ratio yields $[(\text{thf})_4\text{Mg}(\mu\text{-Cl})_2\text{Mn}(\text{Br})\text{Mes}]$ (**1**) with two bridging chloro ligands and a Mn–C bond length of 2.136(5) Å. A molar ratio of 2:1 leads to a metathesis reaction and the formation of $[\text{Mes}(\text{thf})\text{Mn}(\mu\text{-Mes})]_2$ (**2**) with two bridging mesityl groups. Whereas THF-free $[\text{MnMes}_2]_3$ crystallizes as a trimer from toluene solution, the reduced bulkiness of the phenyl groups in $(\text{MnPh}_2)_\infty$ (**3**) leads to the formation of a chain-like structure with Mn–C bond lengths of 2.245(3) Å.

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1. Introduction

Organomanganese compounds are often used in organic synthesis for the preparation of ketones from carbonic acid chlorides. β -Hydride elimination reactions are less favored for these organometallics than for many other organic transition metal compounds. It is also well-known that the Mn–Cp bonding in manganocene exhibits mainly ionic character whereas the metallocenes of the neighbors chromium and iron represent covalent molecules [1]. These properties together with similar ionic radii lead to comparable chemical behavior of manganese(II) and magnesium(II) in many aspects. Several organomanganese compounds of the type $(\text{R}_2\text{Mn})_n$ ($n = \infty$) were characterized by single-crystal X-ray crystallography such as with R as C(Me₂)C₆H₅ ($n = 2$) and CH₂SiMe₃ [2].

The beginning of the arylmanganese chemistry dates back more than 70 years. A mixture of phenylmanganese iodide and diphenylmanganese resulted from the metathesis reaction of phenylmagnesium iodide with anhydrous manganous iodide [3]. Pure diphenylmanganese was prepared from MnI₂ and phenyllithium in diethyl ether [4]. Other diarylmanganese derivatives include examples with 8-dimethylaminonaphthyl [5] and 2-dimethylami-

nometylphenyl groups [6]. The synthesis of $(\text{thf})_2\text{Mn}(\text{C}_6\text{F}_5)_2$ and $(\text{dme})\text{Mn}(\text{C}_6\text{F}_5)_2$ succeeded via a transmetalation reaction of Mn metal with Hg(C₆F₅)₂ in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) [7]. Excess of aryllithium in the metathesis reaction with manganese(II) halides yielded lithium triarylmanganates with aryl groups such as phenyl [8,9], 4-methylphenyl (*para*-tolyl) [8], 2,4,6-trimethylphenyl (mesityl) [9,10] and 4-methoxyphenyl [8]. The molecular structures of these organomanganese compounds are more complex and first crystal structures showed that dimesitylmanganese crystallized from toluene as trimeric Mes–Mn(μ -Mes)₂Mn(μ -Mes)₂MnMes [11,12]. A trinuclear complex was also isolated when two mesityl groups were substituted by an alcoholate derived from glucofuranose [13]. Monomeric diarylmanganese derivatives were obtained with 2,4,6-tri(*tert*-butyl)phenyl [14] and 2,6-bis(2,4,6-trimethylphenyl)phenyl groups [15]. Phenylmanganates also show oligonuclear anions such as $[\text{Mn}_2\text{Ph}_6]^{2-}$ whereas the bulkier mesityl group leads to the formation of mononuclear trimesitylmanganate $[\text{MnMes}_3]^-$ [16]. Furthermore, $[\text{Mn}_2(\mu\text{-Ph})_2]^{2+}$ cations were synthesized and shielded by the counter ions $[\text{BPh}_4]^-$ leading to contact ion pairs [12]. Whereas organic manganese(II) compounds were investigated quite extensively, investigations on organomanganese(III) compounds are far less common. The metathesis reaction of manganese(III) halides with dimesitylmagnesium in the presence of trimethylphosphane and oxygen yielded $[(\text{Mes})\text{MnX}_2(\text{PMe}_3)_2]$

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(X = Cl, Br, I) [17,18]. Bis(2-dimethylaminomethylphenyl)-methylmanganese(III) was obtained via addition of methyl lithium to bis(2-dimethylaminomethylphenyl)manganese(II) and a subsequent oxidation with AgBF_4 [19]. Manganates(III) were stable with pentafluorophenyl groups and Mn–C bond lengths of 2.068 Å were observed for $[\text{Mg}(\text{thf})_6][\text{Mn}(\text{C}_6\text{F}_5)_4]_2$ [20].

Despite the long tradition of the arylmanganese chemistry, the steps of the metathesis reactions were not investigated in detail, even though iodine-containing $[(\text{Et}_2\text{O})\text{Li}(\mu\text{-I})_2\text{Mn}\{\text{C}_6\text{H}_3\text{-2,6-Aryl}\}]$ has already been investigated [21]. Bulky groups at the aryl substituents favor the formation of small aggregation degrees leading to higher solubility in common organic solvents. Whereas diphenylmanganese is known since 70 years [3], its molecular structure is still unknown and should exhibit a higher nuclearity than dimethylmanganese due to the lower shielding degree.

2. Results and discussion

2.1. Synthesis

During the attempt to prepare $[(\text{Mes})_2\text{Mn}]_3$ from manganese(II) chloride and mesitylmagnesium bromide, two yet unknown mesitylmanganese derivatives were isolated. The addition reaction of anhydrous MnCl_2 with MesMgBr in an equimolar ratio in ether yielded heterobimetallic $[(\text{thf})_4\text{Mg}(\mu\text{-Cl})_2\text{Mn}(\text{Br})\text{Mes}] \mathbf{1}$ which can be regarded as an intermediate during the synthesis of $[(\text{Mes})_2\text{Mn}]_3$. Recrystallization from a toluene solution led to the formation of $[(\text{thf})\text{Mn}(\text{Mes})_2]_2 \mathbf{2}$ due to traces of THF during the metathesis reaction, whereas crystals of well-known trinuclear $[\text{Mn}(\text{Mes})_2]_3$ were obtained from recrystallization under strict exclusion of THF.

The metathesis reaction of phenyllithium with manganese(II) iodide in diethyl ether yielded quantitatively diphenylmanganese **3**. Single crystals suitable for X-ray structure determinations were obtained by diffusion of diethyl ether into a saturated THF solution of **3**.

2.2. Molecular structures

The molecular structures of the organomanganese compounds **1** to **3** are displayed in Figs. 1–3. Similar size of the magnesium(II) and manganese(II) cations leads to comparable bond lengths in compound **1**. The metal centers Mg(II) and Mn(II) are bridged by two μ -chloro ligands. The transfer of the bromo and the mesityl groups from Mg to Mn is already complete and the molecule could be regarded as a magnesium(II) chloride adduct at mesitylmanganese bromide. The bridging chlorine atoms show average distances of 2.483 and 2.542 Å for Mn–Cl_b and Mg–Cl_b, respectively. The subscripts b and t distinguish between bridging and terminally bound atoms. With respect to the different coordination numbers of 4 and 6, rather similar ionic radii can be deduced for Mn(II) and Mg(II) which are one of the reasons for comparable chemical reactivities and molecular structures of these elements. Representative examples include $\text{M}(\text{C}_6\text{H}_2\text{-2,4,6-}t\text{Bu}_3)_2$ (M = Mn, Mg [14]), $(\text{MPh}_2)_\infty$ {M = Mn (**1**, this work), Mg [22]}, and isotopic $[(\text{thf})_4\text{Li}][\text{M}(\text{Mes})_3]$ (M = Mn [16], Mg [23]).

Selected structural parameters are compared in Table 1 containing also the coordination number (C.N.) and oxidation state (O.S.) of the manganese atoms. A coordination number of 2 can only be realized for very bulky groups such as $\text{C}_6\text{H}_2\text{-2,4,6-}t\text{Bu}_3$ (Mes^*) [14] and $\text{C}_6\text{H}_2\text{-2,6-Mes}_2$ [15]. From this table several characteristics can be deduced: (I) The Mn–C_b distances to bridging aryl groups are larger than the Mn–C_t bond lengths to terminally bound aryl ligands. This fact can be explained by the formation of M–C_b–M three-center two-electron bonds leading to low M–C bond orders. (II) In neutral manganese complexes the Mn–C distances are smaller

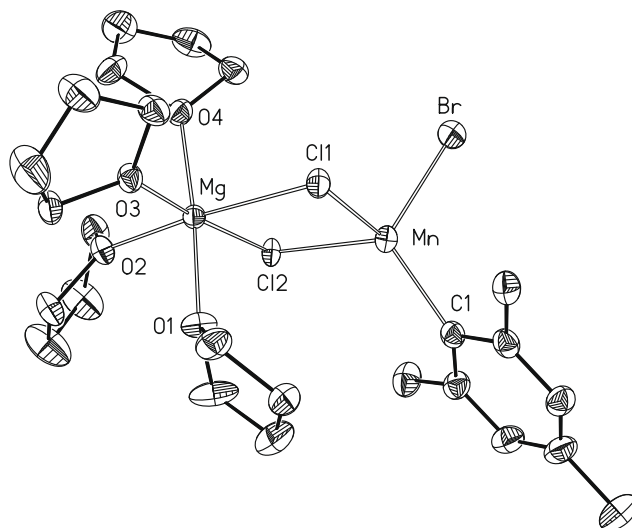


Fig. 1. Molecular structure of $[(\text{Mes})\text{Mn}(\text{Br})(\mu\text{-Cl})_2\text{Mg}(\text{thf})_4] \cdot \text{thf}$ (**1**). Hydrogen atoms and intercalated THF are omitted for clarity reasons. Selected bond distances (Å): Mn–C(1) 2.136(5), Mn–Cl(1) 2.4766(17), Mn–Cl(2) 2.4893(15), Mn–Br 2.5078(12), Mg–O(1) 2.091(4), Mg–O(2) 2.080(4), Mg–O(3) 2.093(4), Mg–O(4) 2.065(4), Mg–Cl(1) 2.526(2), Mg–Cl(2) 2.557(2); selected bond angles (°): Cl(1)–Mn–Cl(2) 88.97(5), C(1)–Mn–Br 113.43(13), Cl(1)–Mn–Br 102.78(5), Cl(2)–Mn–Br 110.10(5), Cl(1)–Mg–Cl(2) 86.41(6), O(4)–Mg–O(1) 173.79(17), O(2)–Mg–O(3) 94.44(15).

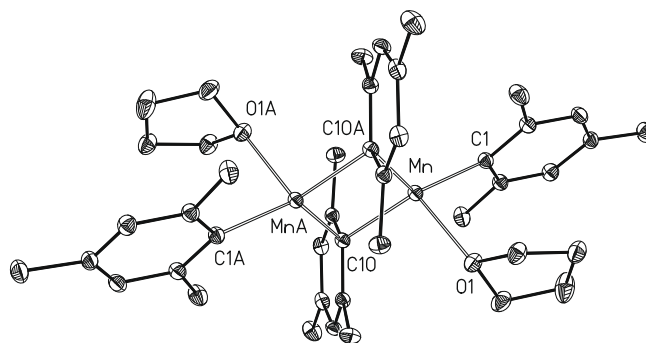


Fig. 2. Molecular structure of $[(\text{thf})(\text{Mes})\text{Mn}(\mu\text{-Mes})_2]_2$ (**2**). Hydrogen atoms are omitted for clarity reasons. Selected bond distances (Å): C(1)–Mn 2.1660(19), C(10)–Mn 2.2921(19), C(10A)–Mn 2.3008(18), Mn–O(1) 2.2467(14), Mn···Mn(A) 2.8628(6). Selected bond angles (°): C(1)–Mn–O(1) 90.83(7), C(1)–Mn–C(10) 122.67(7), C(1)–Mn–C(10A) 126.81(7), C(10)–Mn–C(10A) 102.89(6), O(1)–Mn–C(10) 105.57, O(1)–Mn–C(10A) 102.75, Mn–C(10)–Mn(A) 77.11(6).

than in aryl substituted manganese anions. Higher charge on the metal center leads to additional repulsion between the carbanions and the more electron-rich metal atoms. (III) Aryl–manganese distances depend on the oxidation state of the manganese atom with smaller Mn–C bond lengths for higher oxidation states.

2.3. EPR properties

All organomanganese derivatives are paramagnetic and we were not in the position to record reliable NMR spectra. The EPR spectra of crystalline $[(\text{thf})_4\text{Mg}(\mu\text{-Cl})_2\text{Mn}(\text{Br})\text{Mes}] \cdot \text{thf}$ (**1**) show a strong dependency on the temperature. At 20 °C the characteristic isotropic signal of a mononuclear Mn(II) compound is obtained with a characteristic sextet hyperfine coupling A caused by the ^{55}Mn nucleus ($S = 5/2$, $I = 5/2$, $g = 2.000$, $A(^{55}\text{Mn}) = 8.7 \pm 5$ mT). In the solid state at 20 °C we found two lines at $g = 2.011$ and

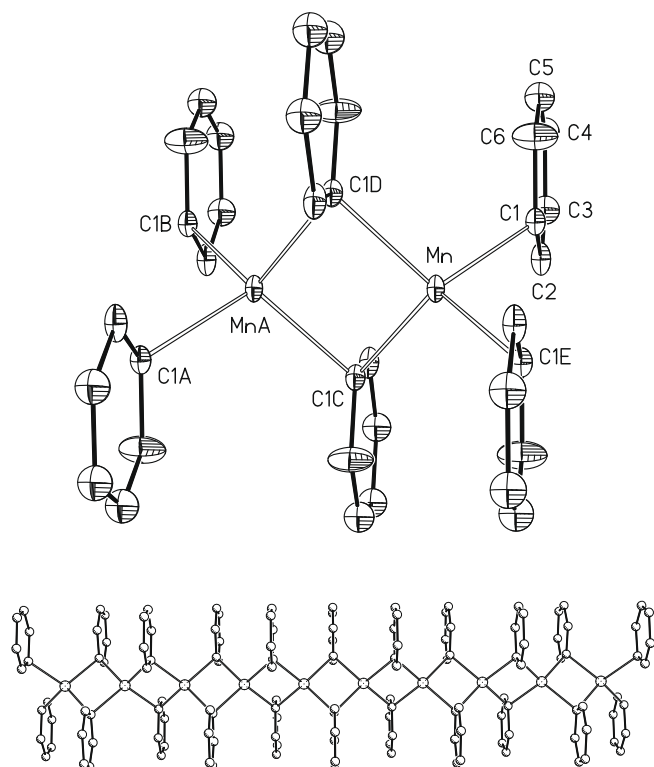


Fig. 3. Molecular structure (at the top) and chain-like structure (at the bottom) of $(\text{MnPh}_2)_\infty$ (**3**). Hydrogen atoms are neglected for clarity reasons. Selected bond distances (Å): C(1)–Mn 2.245(3), Mn···Mn(A) 2.8134(3). Selected bond angles (°): C(1)–Mn–C(1D) 112.07(17), C(1)–Mn–C(1E) 114.16(17), C(1)–Mn–C(1C) 102.41(11), Mn–Mn(A)–Mn(B) 180.0, Mn–C(1)–Mn(A) 77.59(11).

Table 1

Comparison of selected structural parameters of arylmanganese compounds (average values (Å), terminal Mn–C_t and bridging Mn–C_b bonds, Mn–O to bound solvent molecules) with respect to coordination number (C.N.) and oxidation state (O.S.) of the manganese atom.

Compound	C.N.	O.S.	Mn–C _t	Mn–C _b	Mn–O	Lit.
$\text{Mn}(\text{C}_6\text{H}_2\text{-}2,4,6\text{-tBu}_3)_2$	2	2	2.108	–	–	[14]
$\text{Mn}(\text{C}_6\text{H}_2\text{-}2,6\text{-Mes}_2)_2$	2	2	2.095	–	–	[15]
$[\text{Li}(\text{thf})_4]^+[\text{MnMes}_3]^-$	3	2	2.141	–	–	[16]
$\text{MesMn}(\mu\text{-Ph})_2\text{BPh}_2$	3	2	2.066	–	–	[12]
Mn_3Mes_6	3	2	2.122	2.206	–	[12]
	4	2	–	2.331	–	
$[(\text{Et}_2\text{O})_3\text{MnMes}]^+[\text{BPh}_4]^-$	4	2	2.111	–	2.133	[12]
$[\text{Mn}_2(\mu\text{-Ph})_2(\text{BPh}_4)_2]$	4	2	–	2.199	–	[12]
$\text{Li}(\text{thf})_4[\text{Mn}_2\text{Ph}_6]^{2-}$	4	2	2.146	2.285	–	[16]
$[\text{Li}(\text{OEt}_2)_2\text{Mn}_2\text{Ph}_6]$	4	2	2.178	2.255	–	[16]
$[\text{MnPh}_2]_\infty$ (3)	4	2	–	2.245	–	This work
$[\text{Mes}(\text{thf})\text{Mn}(\mu\text{-Mes})_2]_2$ (2)	4	2	2.166	2.292	2.247	This work
$(\text{thf})_4\text{Mg}(\mu\text{-Cl})_2\text{Mn}(\text{Br})\text{Mes}$ (1)	4	2	2.136	–	–	This work
$[\text{Mg}(\text{thf})_6]^{2+}[\text{Mn}(\text{C}_6\text{F}_5)_4]^{2-}$	4	3	2.068	–	–	[20]
$(\text{Mes})\text{MnBr}_2(\text{PMe}_3)_2$	5	3	2.089	–	–	[17,18]

$g = 4.145$. At liquid nitrogen temperature these two signals were recorded with nearly the same g -factors for the frozen THF solution as well as for the solid state. In the frozen THF solution we found at $g = 4.15$ six hyperfine structure lines from ^{55}Mn nucleus ($A(^{55}\text{Mn}) \approx 5.3$ mT). It is well-known [24] that not only for Fe(III) but also for Mn(II) in a strong rhombic distorted crystal field in the presence of a large zero field splitting a signal at a g -factor of approximately 4 can be estimated.

The complex $[\text{Mes}(\text{thf})\text{Mn}(\mu\text{-Mes})_2\text{Mn}(\text{thf})\text{Mes}]$ (**2**) contains two metal centers with a close *trans*-annular Mn···Mn contact

of 2.8134(3) Å. Magnetic measurements at crystalline **2** show an antiferromagnetic coupling of approximately $J = -10 \text{ cm}^{-1}$ so that spin states with total spin $S_T = 0, 1, \dots, 5$ are populated according to the Boltzmann distribution [25]. These spin states lead to different contributions to the EPR-spectra of **2** which were measured in the solid state and in toluene solution at room temperature and at 77 K. We also found many lines in a large field range up to 1 T which could not be assigned to the different spin states.

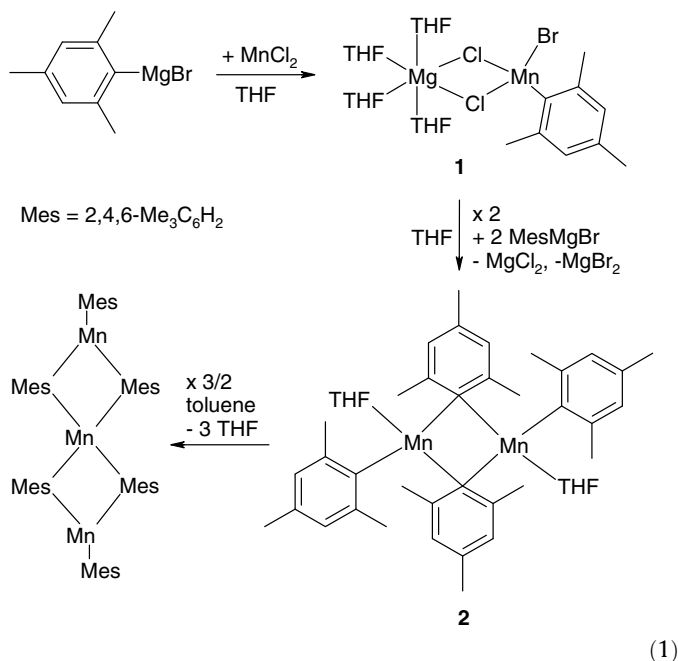
The EPR spectrum of crystalline $(\text{MnPh}_2)_\infty$ (**3**) displays at room temperature and at 77 K a broad Mn(II) signal at $g = 2.007$ with a half height width $\Delta H_{\text{pp}} = 28.0$ mT and 48.6 mT, respectively. Temperature-dependent magnetic measurements show a reduced magnetic moment ($3.43 \mu_B$ bei 20 °C) in comparison to a spin-only value of $5.9 \mu_B$ for five unpaired electrons of Mn(II) at room temperature. This value decreases with decreasing temperature and can be explained by an antiferromagnetic coupling of the manganese atoms in the chain. Treatment of $(\text{MnPh}_2)_\infty$ (**3**) with warm THF and filtration gave a clear solution which showed at room temperature one broad Mn(II) line ($g = 2.001$, $\Delta H_{\text{pp}} = 24.2$ mT). At 77 K we found a signal at $g = 2.006$ ($\Delta H_{\text{pp}} = 24.2$ mT) and an additional band at $g = 4$ consisting of about sixteen lines ($\Delta H_{\text{pp}} = 1.5(\pm 0.5)$ mT, $A = 3.9(\pm 0.4)$ mT). This well-known signal is assigned to a multinuclear manganese cluster in analogy to spectra described elsewhere [26]. Degradation of the chain-like structure of $(\text{MnPh}_2)_\infty$ (**3**) with 1,2-dimethoxyethane (DME) led to the formation of mononuclear complexes which showed in the EPR spectra no lines at $g = 4$ but the common single broad line at $g \approx 2.00$ at room temperature and at 77 K which can be assigned to a mononuclear Mn(II) compound. We interpret these observations in the sense that smaller THF complexes form in THF solution which are responsible for the solubility in this solvent. In similarity to the magnesium chemistry even monomeric molecules such as $[(\text{thf})_2\text{MnMes}_2]$ (in analogy to $[(\text{thf})_2\text{MgPh}_2]$ [22] and $[(\text{thf})_2\text{MgMes}_2]$ [27]) seem likely. For di(*para*-tolyl)magnesium monomeric $[(\text{thf})_2\text{Mg}(p\text{-Tol})_2]$ and dimeric $[(\text{thf})\text{Mg}(p\text{-Tol})_2]_2$ were found at the same time in one crystal [22]. The bidentate chelate base DME mainly leads to the formation of mononuclear complexes $[(\text{dme})\text{MnPh}_2]$.

3. Conclusions

The synthesis of diarylmanganese from the metathesis reaction of mesitylmagnesium bromide with manganese(II) halide proceeds via several intermediates as shown in Eq. (1). Complex **1** is an addition product, however, the aryl group is already transferred from the magnesium to the manganese atom. The harder halogen atoms occupy the bridging positions whereas the soft bromine atom is bound terminally to the manganese atom. A solvent change from THF to toluene leads to the precipitation of the magnesium(II) halides which are insoluble in hydrocarbons. Thorough removal of THF leads to well-known trimeric $[\text{MnMes}_2]_3$. Reduced bulkiness of the aryl groups allows higher aggregation degrees and the formation of polymeric structures as observed for $(\text{MnPh}_2)_\infty$ **3**.

4. Experimental

All experiments were carried out in an inert gas atmosphere, using Schlenk techniques. The solvents were dried over Na/benzophenone and distilled under nitrogen prior to use. EPR spectra were measured on a Bruker spectrometer ESP 300 E. Anhydrous MnCl_2 was prepared from $\text{MnCl}_2(\text{H}_2\text{O})_4$ by reaction with thionylchloride. Anhydrous MnI_2 was prepared from Mn powder and iodine in an ether solution [28].



4.1. [(thf)₄Mg(μ-Cl)₂Mn(Br)Mes] · thf (1)

To a suspension of 6.3 g (50 mmol) MnCl₂ in 20 ml diethyl ether was slowly added a solution of mesitylmagnesium bromide (70 ml, 0.72 M, 50.4 mmol) in diethyl ether. The reaction mixture became warm and started boiling. After the exothermic reaction finished the stirring was continued at ambient temperature overnight. Now the solvent was removed in vacuo and the residue recrystallized from a mixture of THF and toluene. Yield: 25.4 g (71%) of colorless crystals of **1**. Elemental Anal. Calc. for C₂₉H₅₁BrCl₂MgMnO₅ (709.8): Br, 11.26; Cl, 9.99. Found: Br, 11.41; Cl, 10.21%. EPR (THF solution, R.T.): *g* = 2.000, *A*(⁵⁵Mn) = 87(±5) G.

4.2. [Mes(thf)Mn(μ-Mes)₂Mn(thf)Mes] (2)

Sixty milliliters (60.0 mmol) of mesitylmagnesium bromide (1.0 M in THF) were added to a suspension of 3.75 g (29.8 mmol) of MnCl₂ in 10 ml of THF at –78 °C. The brown suspension was warmed to room temperature and stirred overnight. Then the reaction mixture was refluxed for 5 h and 50 ml of dioxane were added. The resulting suspension was stirred overnight and allowed to settle for 2 h. The precipitate was separated and the filtrate evaporated to dryness to give a green solid. The residue was dissolved in warm toluene (40 ml) and all solid materials were carefully removed. Then 5 ml of THF were added. At –20 °C slightly yellow crystals precipitated which also contained a very small amount of brown needles. Yield: 5.7 g (52%) of crystalline **2**. Elemental Anal. Calc. for C₂₂H₃₀MnO, 730.8: Mn, 15.04. Found: Mn, 15.31%. EPR investigations see text.

4.3. (MnPh₂)_∞ (3)

9.1 g (29.47 mmol) of solid MnI₂ were added to a solution of phenyl lithium in diethyl ether (60 ml, 1.0 M, 60.0 mmol) at 0 °C. The color of the reaction mixture changed over yellow to brown. The cooling bath was removed and stirring was continued overnight. The precipitate was removed, washed intensively with diethyl ether and dried in vacuo. Yield: 5.99 g (97%) of pyrophoric brownish yellow powder of Ph₂Mn. Single crystals of diphenyl-

Table 2

Crystal data and refinement details for the X-ray structure determinations of the compounds **1**, **2** and **3**.

Compound	1	2	3
Formula	C ₂₅ H ₄₃ BrCl ₂ MgMnO ₄ · 1/2 C ₄ H ₈ O	C ₄₄ H ₆₀ Mn ₂ O ₂	C ₁₂ H ₁₀ Mn
Formula weight (g mol ⁻¹)	673.71	730.80	209.14
<i>T</i> (°C)	–90(2)	–90(2)	–90(2)
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	P1	P1	Ibam
<i>a</i> (Å)	10.444(2)	8.2176(3)	9.5195(9)
<i>b</i> (Å)	10.923(2)	10.9440(5)	17.9672(16)
<i>c</i> (Å)	16.155(3)	12.1808(4)	5.6268(5)
<i>α</i> (°)	104.57(3)	113.983(2)	90.00
<i>β</i> (°)	94.62(3)	102.836(2)	90.00
<i>γ</i> (°)	100.44(3)	97.847(2)	90.00
<i>V</i> (Å ³)	1738.7(6)	943.71(6)	962.40(15)
<i>Z</i>	2	1	4
<i>ρ</i> (g cm ⁻³)	1.287	1.286	1.443
<i>μ</i> (cm ⁻¹)	17.29	7.05	13.15
Measured data	11897	6383	3901
Data with <i>I</i> > 2σ(<i>I</i>)	4988	3619	436
Unique data (<i>R</i> _{int})	7897/0.0328	4183/0.0313	616/0.1069
w <i>R</i> ² (all data, on <i>F</i> ²) ^a	0.2220	0.1040	0.0980
<i>R</i> ¹ (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0709	0.0393	0.0351
<i>s</i> ^b	1.030	1.019	1.057
Residual density (e Å ⁻³)	1.448/–0.809	0.344/–0.336	0.475/–0.571
Absorption method	Multi-scan	Multi-scan	Multi-scan
Absorption correction	0.7480/0.7976	0.8778/	0.8480/
<i>T</i> min/max	0.9495	0.8976	0.8976
CCDC no.	696024	696025	696026

^a Definition of the *R* indices: *R*¹ = (Σ||*F*_o – |*F*_c||)/Σ|*F*_o| w*R*² = {Σ[w(*F*_o² – *F*_c²)]/Σ[w(*F*_o²)]^{1/2} with *w*⁻¹ = σ²(*F*_o²) + (*aP*)².

^b *s* = {Σ[w(*F*_o² – *F*_c²)]/(*N*_o – *N*_p)^{1/2}.

manganese were obtained by diffusion of diethyl ether into a saturated solution of **3** in THF. Elemental Anal. Calc. for C₁₂H₁₀Mn, 209.1: Mn, 26.27. Found: Mn, 26.09%. *μ*_{eff} = 3.43 μ_B (R.T.). EPR (solid, R.T.): *g* = 2.0085 (broad, see text). EPR investigations see text.

4.4. X-ray structure determinations

Intensity data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz polarization and for absorption effects [29–31]. Crystallographic data as well as structure solution and refinement details are summarized in Table 2. The structures were solved by direct methods (SHELXS [32]) and refined by full-matrix least squares techniques against *F*_o² (SHELXL-97 [33]). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically [33]. XP (SIEMENS Analytical X-ray Instruments, Inc.) and POVRAY were used for structure representations.

Supplementary material

CCDC 696024, 696025 and 696026 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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References

- [1] (a) G.A. Razuvaev, V.N. Latyaeva, *Russ. Chem. Rev.* 34 (1965) 251–267;
(b) K. Oshima, *Sci. Synth.* 2 (2003) 13–89;
(c) R.A. Layfield, *Chem. Soc. Rev.* 37 (2008) 1098–1107.
- [2] R.A. Andersen, E. Carmona-Guzman, J.F. Gibson, G. Wilkinson, *J. Chem. Soc., Dalton Trans.* (1976) 2204–2211.
- [3] H. Gilman, J.C. Bailie, *J. Org. Chem.* 2 (1938) 84–94.
- [4] C. Beermann, K. Clauss, *Angew. Chem.* 71 (1959) 627.
- [5] H. Dreves, *J. Organomet. Chem.* 433 (1992) C1–C3.
- [6] L.E. Manzer, L.J. Guggenberger, *J. Organomet. Chem.* 139 (1977) C34–C38.
- [7] G.B. Deacon, R.S. Dickson, J.L. Latten, B.O. West, *Polyhedron* 12 (1993) 497–500.
- [8] R. Riemenschneider, H.G. Kassahn, *Z. Naturforsch.* 15b (1960) 547–551.
- [9] G. Fiour, G. Cahiez, A. Alexakis, J.F. Normant, *Bull. Soc. Chim. Fr.* (1979) 515–517.
- [10] W. Seidel, I. Bürger, *Z. Chem.* 17 (1977) 31.
- [11] S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, *J. Chem. Soc., Chem. Commun.* (1983) 1128–1129.
- [12] E. Solari, F. Musso, E. Gallo, C. Floriani, N. Re, A. Chiesi-Villa, C. Rozzoli, *Organometallics* 14 (1995) 2265–2276 (Erratum: *Organometallics* 14 (1995) 4030).
- [13] U. Piarulli, C. Floriani, N. Re, G. Gervasio, D. Viterbo, *Inorg. Chem.* 37 (1998) 5142–5148.
- [14] R.J. Wehmschulte, P.P. Power, *Organometallics* 14 (1995) 3264–3267.
- [15] D.L. Kays, A.R. Cowley, *Chem. Commun.* (2007) 1053–1055.
- [16] R.A. Bartlett, M.M. Olmstead, P.P. Power, S.C. Shoner, *Organometallics* 7 (1988) 1801–1806.
- [17] R.J. Morris, G.S. Girolami, *Organometallics* 6 (1987) 1815–1816.
- [18] R.J. Morris, G.S. Girolami, *Organometallics* 10 (1991) 799–804.
- [19] J.L. Latten, R.S. Dickson, G.B. Deacon, B.O. West, E.R.T. Tiekink, *J. Organomet. Chem.* 435 (1992) 101–108.
- [20] J. Forniers, A. Martin, L.F. Martin, B. Menjon, H. Zhen, A. Bell, L.F. Rhodes, *Organometallics* 24 (2005) 3266–3271.
- [21] A.D. Sutton, T. Ngyuen, J.C. Fettingter, M.M. Olmstead, G.J. Long, P.P. Power, *Inorg. Chem.* 46 (2007) 4809–4814.
- [22] P.R. Markies, G. Schat, O.S. Akkerman, F. Bickelhaupt, W.J.J. Smeets, P. van der Sluis, A.L. Spek, *J. Organomet. Chem.* 393 (1990) 315–331.
- [23] S. Kriek, H. Görls, M. Westerhausen, unpublished results (see: S. Kriek, Ph.D. Thesis, Jena/Germany, presumably 2010).
- [24] M.T. Caudle, C.K. Mobley, L.M. Bafaro, R. LoBrutto, G.T. Yee, T.L. Groy, *Inorg. Chem.* 43 (2004) 506–514.
- [25] V.V. Pavlishuk, M. Prushan, A. Addison, *Theor. Exp. Chem.* 41 (2005) 229–234.
- [26] D.H. Kim, R.D. Britt, M.P. Klein, K. Sauer, *J. Am. Chem. Soc.* 112 (1990) 9389–9391.
- [27] K.M. Waggoner, P.P. Power, *Organometallics* 11 (1992) 3209–3214.
- [28] B. Heyn, B. Hipler, G. Kreisel, H. Schreer, D. Walther, *Anorganische Synthesechemie: Ein integriertes Praktikum*, Springer, Berlin, 1986.
- [29] B.V. Nonius, COLLECT, Data Collection Software, Netherlands, 1998.
- [30] Z. Otwinowski, W. Minor, in: C.W. Carter, R.M. Sweet (Eds.), *Methods in enzymology, Macromolecular Crystallography, Part A*, vol. 276, Academic Press, 1997, pp. 307–326.
- [31] SORTAV R.H. Blessing, *Acta Crystallogr., Sect. A* 51 (1995) 33–38.
- [32] G.M. Sheldrick, *Acta Crystallogr., Sect. A* 46 (1990) 467–473.
- [33] G.M. Sheldrick, SHELXL-97 (Release 97-2), University of Göttingen, Germany, 1997.