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Manganese(IV) Corroles with σ-Aryl Ligands

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Abstract. Different pathways for the preparation of organometallic manganese(IV) corroles with σ-aryl ligands have been evaluated. The treatment of a manganese(III) corrole with Grignard reagents PhMgX (X = Cl, Br), followed by aerial oxidation yields oxidized halogenido complexes [(cor)Mn^{IV}X] instead of the anticipated organometallic compounds. Reaction of these halogenido species, especially the bromido compound, with excess Grignard reagents or with lithium aryls results in the formation of the desired σ-aryl compounds *via* salt metatheses. Three examples of this class of rare complexes have been characterized by means of optical and ^{1}H NMR spectroscopy, and in two cases single crystal X-ray diffraction studies have been carried out. In the crystal, the molecular structures of the σ-phenyl- and the σ-(*p*-bromophenyl) derivatives were observed to be very similar, albeit both species pack in different pattern.

Keywords: Manganese; *High-spin* organometallics; Corroles; X-ray diffraction; Porphyrinoids

Introduction

Organometallic porphyrinoid transition metal complexes with σ-bonded alkyl or aryl axial ligands are of interest as model compounds for understanding the functions and relationships of several biological macromolecules [1]. From this viewpoint, a vast amount of data has become available over recent years, but the majority has concerned compounds with iron, cobalt, or rhodium metal ions. The chemical reactivity of this family of compounds has also attracted interest owing to their potential use in the activation of small molecules.

Although porphyrin complexes with organic co-ligands are known for 29 metallic and pseudometallic elements, only one case of a manganese porphyrin with an axial carbene ligand has been described, and the corresponding σ-bonded alkyl complex was postulated only as an intermediate [2]. This result is in agreement with conclusions from the reaction of alkyl or fluoroalkyl radicals with manganese porphyrins [3]. Nonreducing alkyl radicals such as $^{\cdot}CH_3$ exibit a very low reactivity against manganese(III) porphyrins and no evidence has been found for the formation of a [(por)MnR] complex with a lifetime longer than ca. 0.1 ms.

While to the best of our knowledge there is still no definite evidence for the existence of stable σ-bonded organometallic manganese(III) porphyrins, one quite well characterized example of an analogous compound, the σ-phenyl(corrolato)manganese(IV) (**1**) exists in the corrole series (figure 1) [4]. The compound has been thoroughly characterized by crystallographic, spectroscopic and electrochemical means, and a *high-spin* ground state with a $S = 3/2$ Mn^{IV} ion was confirmed for this stable organometallic complex. In the course of our attempts to prepare functional magnetic [5] and other polynuclear materials [6] by rational approaches we became interested in novel building blocks combining kinetic stability and a *high-spin* electronic ground state like **1** [7]. In this contribution we wish to report our recent study toward the preparation of such species and about the successful preparation and structural characterization of halogene functionalized σ-arylmanganese(IV) corroles.

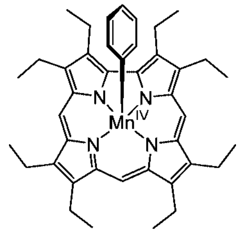

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Fig. 1 Literature precedent [(oec)Mn^{IV}(ph)] (**1**) [4].

Results and Discussion

For our study we have chosen the hexaethyldimethylcorrole ligand (H$_3$hedmc) (**5**) of which a structurally characterized square-planar manganese complex [(hedmc)Mn] (**6**) has been reported [8]. **5** was prepared in two steps from formylpyrrole **2** and dipyrromethane **3** according to the literature as depicted in scheme 1. The insertion of a manganese ion in corroles can in principle be achieved under three different conditions. In the case of **6** and related octaalkyl derivatives literature recommends the cyclization of the biladiene **4** in the presence of excess manganese(II) acetate [9] or the reac-

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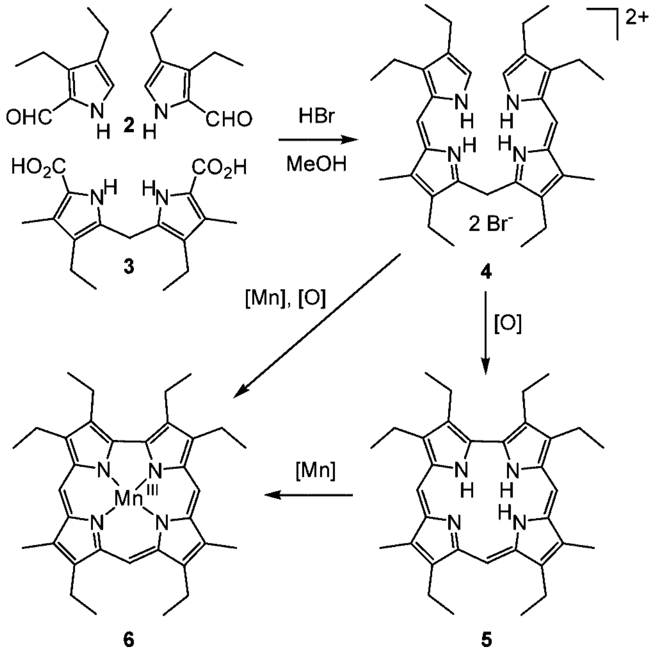
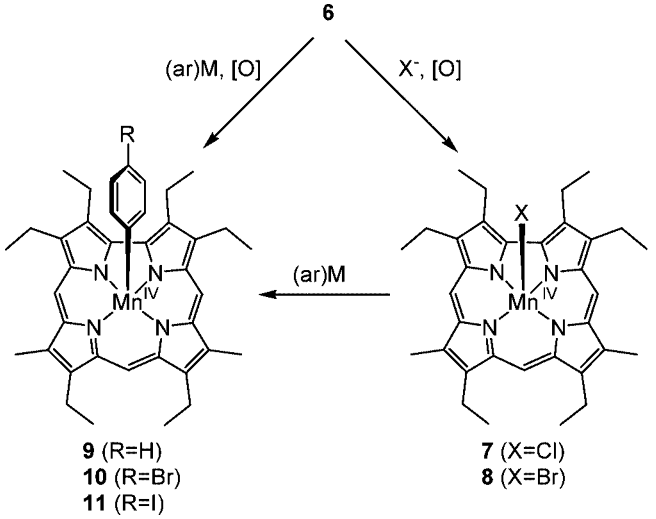
tion of H_3hedmc (**5**) with dimanganesedecacarbonyl, followed by aerial oxidation [10]. In our hands the treatment of the corrole with manganese(II) acetate in hot DMF, preferred method for triarylcorroles, [11] gave the best results and produced the desired manganese corrole **6** in 78 % yield (scheme 1). [(hedmc)Mn] (**6**) was unambigously identified by a comparison of ^{1}H NMR and UV/Vis spectra as well as by high-resolution mass spectrometry.



Scheme 1 Synthesis of corrole (**5**) and manganese(III)corrole (**6**) on different pathways.

The data obtained for **6** are indeed identical to those found in literature [8] and very similar to those of other manganese(III) corroles, that have been described so far [4, 12]. An interesting subject concerning trivalent manganese in the corrole environment is the quest for the proper metal oxidation state. *Paolesse, Boschi* et al. have reported a change from +3 to +2 upon the addition of two intermediately strong axial pyridine ligands, indicated by a change in the optical spectra [8]. A similar behaviour has been the topic of many discussions on related manganese porphyrins before [13]. In general, this behaviour of transition metal ions to reside in oxidation states lower than the formal oxidation state appears particularly typical for metal corroles and has been observed in a number of cases [14]. This so-called non-innocent behaviour [15] of the corrole ligand has, however, not been observed for **6**, and no detailed studies have so far been attempted.

Preparatively, the metal arylation step is in general known within the class of metal corroles using one out of two principal procedures. As detailed in scheme 2 the first procedure contains only one step and utilizes the formation of an −ate complex from (aryl)MgX or (aryl)Li and (cor)M, with successive work-up in air [16]. The other path requires two steps, i.e. the oxidation of the (cor)Mn precursor to a (cor)MX species (X = Cl, Br, I) [4, 11, 12, 17] with concommitant anion metathesis using (aryl)M reagents as described before [4, 18].



Scheme 2 Attempted preparation of arylmanganese(IV)corroles **9**−**11**.

The initial attempts to prepare the desired organometallics via the presumably simpler one-pot route failed. Instead, the treatment of [(hedmc)Mn] (**6**) with phenyllithium, phenylmagnesium chloride, or phenylmagnesium bromide in cold dichloromethane yielded the new halogenido complexes [(hedmc)MnCl] (**7**) and [(hedmc)MnBr] (**8**), respectively, as the only isolable products. Identical derivatives can be obtained easier and in better yields upon simple treatment of **6** with industrial grade dichloromethane (for **7**) or a solution of magnesium bromide dietherate in purified dichloromethane (for **8**). Since no well-formed single crystals could be obtained from the new complexes, their identity had to rely on a comparison of ^{1}H NMR and UV/Vis spectroscopic data with those of analogous [(cor)MnX] precedents in the literature. The most characteristic difference between manganese corroles with the oxidation state +3 (**6**) and +4 (**7** and **8**) is seen in the optical spectra. In the oxidized form the halogenido derivatives display a split soret band with maxima at 350 and 410 nm (**7**) and at 342 and 413 nm (**8**), in addition to markedly less intense Q bands at 586 nm, while the manganese(III) species shows three broad absorptions at 389, 480 and 588 nm with the band at 480 nm being ascribed to a MLCT transition (figure 2).

Applying the two-step procedure indicated in scheme 2 was immediately successful. The treatment of the bromido derivate **8** with phenylmagnesium bromide, followed by aerial oxidation resulted in the formation of the anticipated product [(hedmc)Mn(ph)] (**9**), albeit a seven-fold excess of the Grignard reagent had to apply for a complete transformation. The compound was purified by chromatographic filtration over a silica plug and obtained after evaporation of all volatiles in 99 % yield. This procedure could, in a slightly different way, also be applied for the synthesis of functionalized organometallic manganesecorroles. If instead of the Grignard reagent a preformed mixture of equimolar *n*-BuLi and 1,4-dibromobenzene or 1,4-diiodobenzene [19] in dry THF is used, the functionalized products [(hedmc)Mn(4-BrC_6H_4)] (**10**) and [(hedmc)Mn(4-IC_6H_4)] (**11**) are isolated in 77 % and 38 % yield, respectively, as dark violet powders. Since the aryl substituents of **9-11** are bound in a kinetically inert fashion these three species could be analyzed by HRMS techniques as the M^+ ions and without loss of the axial donor ligands. Again, the reaction can be monitored spectroscopically since optical and nuclear resonance spectra of the new species show very characteristic features distinct from the halogenido complexes **7** and **8** as well as from the manganese(III) derivative **6** (figure 2).

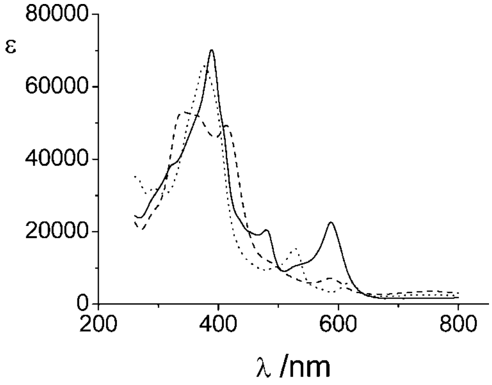


Fig. 2 Optical spectra (ca. 10^{-5} mol/L in CH_2Cl_2) of [(hedmc)Mn] (**6**) (—), [(hedmc)MnBr] (**8**) (–) and [(hedmc)Mn(C_6H_4Br)] (**10**) (···).

Besides the mass spectrometrical analyses and the spectroscopic characterization **9** and **10** could be investigated by single crystal X-ray diffraction studies. Material suitable for the measurements was obtained in both cases by slow evaporation of methanol/dichloromethane solutions. For **9** the molecules pack with Z = 8 in the monoclinic system, space group *C*2/c, while for **10** space group *P*1bar and the triclinic system has been found with Z = 2. The molecular structures and metrical data for the new compounds are presented in figures 3 (**9**) and 4 (**10**).

The bond lengths and angles within the MnN4 coordination units of **9** and **10** are as expected very similar. All Mn-N bonds can be found within the narrow range of 1.883 to 1.907 Å. The N-Mn-N angles in **9** and **10**, that should be rectangular for an undistorted square-planar coordination, are shortened within the bipyrrolic unit to 78.60(15)° and 79.75(11)° and enlarged at the opposite position N2-Mn-N4 to 95.07(15)° and 95.79(11)°, respectively, while the other two angles deviate from 90° by less than 0.6°. The manganese atoms of **9** and **10** are displaced 0.285 and 0.247 Å from the least-squares plane formed by the pyrrole nitrogen atoms and thus display domed square-pyramidal coordination. This value is about 30-40 % smaller than that found for halogenidomanganese(IV)corroles [11, 4, 17]. The tetrapyrrolic macrocycle does not react significantly to the displacement of the central metal atom and is found in both cases in an almost coplanar conformation. The distances between the mean squares planes of the C_{19} ligand backbones and the manganese ions of 0.280 Å (**9**) and 0.183 Å (**10**) are in fact smaller than the Mn-{mean-squares plane-N_4} distances and indicate a slightly convex ligand conformation in both cases.

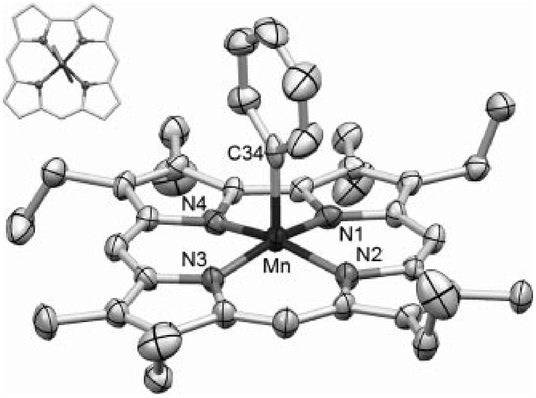


Fig. 3 Molecular structure of **9** (side view) and view on the relative orientation of the phenyl ligand (alkyl groups removed for clarity). Selected bond lengths /Å and -angles /°:

Mn-C34 2.019(5), Mn-N1 1.883(4), Mn-N2 1.905(4), Mn-N3 1.898(4), Mn-N4 1.878(3); N1-Mn-C34 96.97(16), N2-Mn-C34 100.3(2), N3-Mn-C34 99.39(16), N4-Mn-C34 97.6(2), N1-Mn-N2 90.6(2), N1-Mn-N3 161.43(14), N1-Mn-N4 78.60(15), N2-Mn-N3 95.07(15), N2-Mn-N4 160.03(15), N3-Mn-N4 90.53(15).

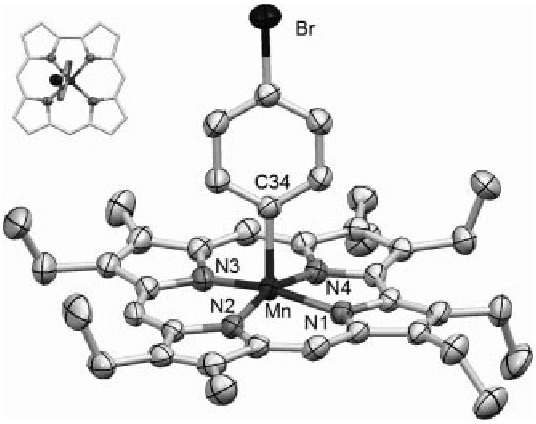


Fig. 4 Molecular structure of **10** (side view) and view on the relative orientation of the C_6H_4Br ligand (alkyl groups removed for clarity). Selected bond lengths /Å and -angles /°:

Mn-C34 2.019(3), Mn-N1 1.891(3), Mn-N2 1.907(2), Mn-N3 1.893(3), Mn-N4 1.901(2); N1-Mn-C34 95.53(12), N2-Mn-C34 95.29(11), N3-Mn-C34 99.69(12), N4-Mn-C34 99.39(11), N1-Mn-N2 90.29(11), N1-Mn-N3 162.99(11), N1-Mn-N4 79.75(11), N2-Mn-N3 95.79(11), N2-Mn-N4 162.95(11), N3-Mn-N4 90.27(11).

The molecular structures of **9** and **10** differ significantly with respect to the aryl ligand situations. As the insets in figure 3 and 4 reveal the planes of the ph and C_6H_4Br ligands are found differently rotated with respect to the MnN_4 coordination unit. This behaviour can be understood on the basis of the electronic structure of the central ion, which should be in a $d_\pi^3 d_\sigma^0$ configuration and therefore allow a rotation of the axial group with almost no barrier. Unexpected, however, is the tilted coordination of the C_6H_4Br ligand of **10** which bends away from a perpendicular orientation by 6.39° (**9**: 1.03°). No obvious electronic or steric argument could explain this finding. A rational for this behaviour was found in different intermolecular interactions as revealed by a comparison of the crystal packings of **9** and **10** (figures 5 and 6).

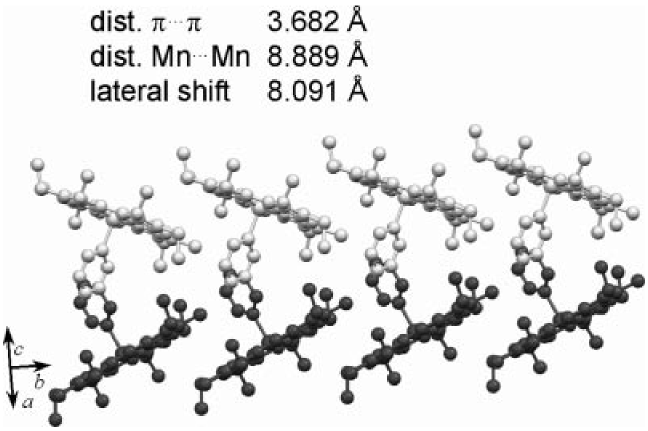


Fig. 5 Chain-like crystal packing pattern of molecules **9**.

For **9**, molecules of identical orientation are arranged in chains with a Mn···Mn distance of 8.889 Å. One identical second chain of molecules **9** displaying a different orientation is located within the van der Waals distance of the first chain (figure 5), and the crystal is build from the uniform association of these double chains with each other. In the local view the next neighbours within this scenario do not influence each other significantly. Although the π···π distance observed between next neighbour molecules of the same chain is as small as 3.682 Å the overlap of the respective macrocycles is small as realized by the lateral shift of 8.091 Å. The contact between the phenyl ligand of one molecule and the alkyl substituents of the neighbour macrocycle thereby becomes sufficiently weak. This results in the finding of an almost undistorted binding of the axial C-donor.

A different situation is present for **10**. In the crystal the bromophenyl derivative forms strongly π-stacked dimers with a Mn···Mn distance of 5.056 Å and a π···π distance of only 3.389 Å, resulting in a largely overlapped structure with a small lateral shift of 3.752 Å. These dimers are than densely packed in independent layers (figure 6). Within these layers the manganese atoms of next neighbour dimers are found in distances of 9.399 Å on one side and of 8.564 Å on the other. The lateral shift, which is a measure for the degree of repulsive interaction between the C_6H_4Br ligand and the alkyl groups of the neighbour molecule, is found at 8.124 Å on the wide side, but at only 7.641 Å at the narrow side. This last distance is insufficient for an undistorted arrangement. The packing forces thus arrange the bromophenyl moieties tightly inbetween two next neighbour dimers and tilt the organometallic ligand from the optimum binding position in the sense of a shear.

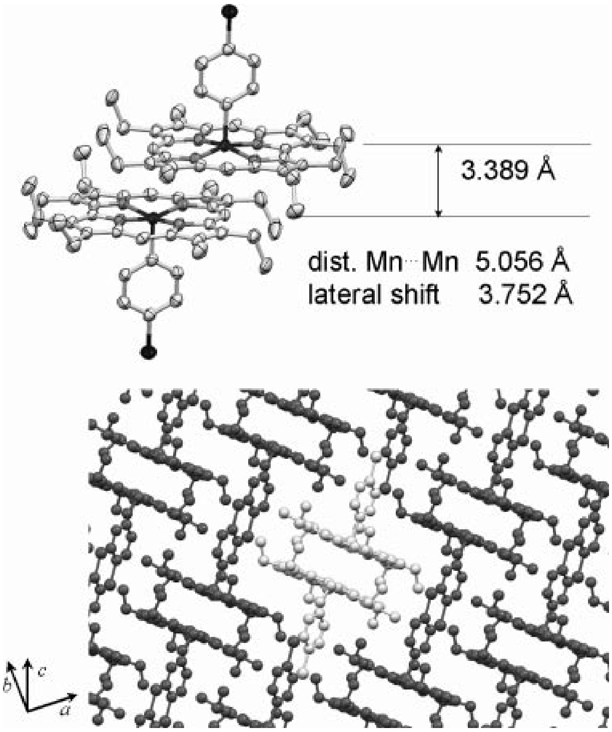


Fig. 6 π-Stacked dimers of **10** (top) and their organization in a layer (bottom).

In summary we have described a general preparative entry for functionalized organometallic manganese(IV) corroles and have characterized the new compounds by spectroscopic and X-ray crystallographic means. Future work will attempt homo- and cross coupling reactions as well as halide-metal exchange studies on the high spin organometallics in order to produce novel building blocks for molecule-based functional materials.

Experimental Section

Materials and Methods: H_3(hedmc) (**5**) [8] and 1,4-diiodobenzene [19] were prepared according to published procedures. All other chemicals were purchased from Aldrich or Merck and used without further purification. Solvents were dried by standard procedures and distilled from appropriate drying agents. ^1H NMR spectra were recorded on Bruker AMX 400 spectrometer. δ values are given relative to residual protio solvent signals. UV/Vis spectra were measured on a Shimadzu UV-1601 PC in concentrations of about 10^{-5} mol L^{-1}. Mass spectra were measured on a VG Tribid or a Varian CH7 (EI), a IonSpec Ultima or a QStar Pulsar i (ESI), or a Bruker Biflex IV instrument (MALDI-TOF). *m/z* values are given for the most abundant isotopes only.

(2,3,8,12,17,18-Hexaethyl-7,13-dimethylcorrolato)manganese(III) [(hedmc)Mn] (6). A solution of H_3(hedmc) (**5**) (200 mg, 0.4 mmol) in dry DMF (60 mL) is heated to 80 °C. Manganese(II) acetate tetrahydrate (490 mg, 2.0 mmol) in DMF (6 mL) are added with vigorous stirring on air. After 3 min the heating source is removed and the mixture is stirred for another 45 min. After cooling in ice the mixture is poored onto diethylether (100 mL) and water (600 mL), and the layers are separated. The aqueous layer is extracted three times with ether (3 × 100 mL), and the combined organic layers are washed once with water (100 mL) and dried with sodium sulfate. Chromatographic purification on basic alumina III with toluene/ether (2:1) and removal of the solvent in vacuo yields the title compound as a blueish-black, fibrous solid. Yield: 170 mg (0.31 mmol, 78 %). − ^{1}**H NMR** (400 MHz, toluene-d_8): δ = 70.8, 39.6, 18.8, 15.5. − **UV/Vis** (toluene): λ /nm = 389, 480, 588. − **HRMS** (EI): *m/z* 546.2572; calcd. for $[\mathrm{C_{33}H_{39}N_4Mn}]^+$: 546.2555.

Chlorido-(2,3,8,12,17,18-hexaethyl-7,13-dimethylcorrolato)manganese(IV)

[(hedmc)MnCl] (7). A solution of [(hedmc)Mn] (**6**) (100 mg, 0.18 mmol) in $\mathrm{CH_2Cl_2}$ (50 mL) is stirred in air for 5 min and filtered on silica with dichloromethane/ether (2:1). After removal of the solvent a dark residue remains. Yield: 103 mg (98 %). The compound is identical to the one formed upon treatment of (**6**) with phenylmagnesium chloride in ether. − ^{1}**H NMR** (400 MHz, $\mathrm{CD_2Cl_2}$): δ = 29.8, 19.4, 16.1, 9.2, −2.5, −10.9. − **UV/Vis** ($\mathrm{CH_2Cl_2}$): λ /nm = 350, 410, 586.

Bromido-(2,3,8,12,17,18-hexaethyl-7,13-dimethylcorrolato)manganese(IV)

[(hedmc)MnBr] (8). A solution of [(hedmc)Mn] (**6**) (100 mg, 0.18 mmol) in $\mathrm{CH_2Cl_2}$ (50 mL) is stirred in air for 5 min. After addition of $\mathrm{MgBr_2 \times Et_2O}$ (253 mg, 1.1 mmol) and further stirring for 5 min the mixture is extracted with water and filtered over silica with dichloromethane/ether (2:1). Removal of the solvent yields a black microcrystalline material. Yield: 110 mg (98 %). The compound is identical to the one formed upon treatment of (**6**) with phenylmagnesium bromide in ether. − ^{1}**H NMR** (400 MHz, $\mathrm{CD_2Cl_2}$): δ = 30.1, 21.5, 16.3, 11.8, −0.2, −8.6. − **UV/Vis** ($\mathrm{CH_2Cl_2}$): λ /nm = 342, 413, 586.

Phenyl-(2,3,8,12,17,18-hexaethyl-7,13-dimethylcorrolato)manganese(IV)

[(hedmc)Mn(ph)] (9). A solution of [(hedmc)MnBr] (**8**) (30 mg, 0.048 mmol) in dry $\mathrm{CH_2Cl_2}$ (25 mL) is treated under an atmosphere of argon dropwise with 6 eq. of PhMgBr in diethylether (0.29 mmol, 0.58 mL of a 0.5 mol $\mathrm{L^{-1}}$ solution). After 3 min the mixture is quenched with water (5 mL), extracted with dichloromethane (50 mL) and filtered on silica. Removal of all volatiles from the eluat yields the title compound as a brownish-red powder. Yield: 34 mg (99 %). − ^{1}**H NMR** (400 MHz, $\mathrm{CD_2Cl_2}$): δ = 76.2, 51.2, 46.5, 27.7, 25.8, 11.1, 4.9, 3.8, 2.8, −50.9. − **UV/Vis** ($\mathrm{CH_2Cl_2}$): λ /nm = 376, 526, 614. − **HRMS** (ESI): *m/z* 623.2946; calcd. for $[\mathrm{C_{39}H_{44}N_4Mn}]^+$: 623.2933.

4-Bromophenyl-(2,3,8,12,17,18-hexaethyl-7,13-dimethylcorrolato)manganese(IV)

[(hedmc)Mn(4-BrC$_6$H$_4$)] (10). 1,4-Dibromobenzene (236 mg, 1.0 mmol) in dry THF (3 mL) is cooled to −78 °C under a blanket of argon and treated with 1 eq. of *n*-BuLi (0.58 mL of a 1.65 mol $\mathrm{L^{-1}}$ solution in *n*-hexane), and the solution is stirred at this temperature for 140 min. A suspension of [(hedmc)MnBr] (**8**) (60 mg, 0.096 mmol) in dry THF (50 mL) is treated at 0 °C with 0.35 mL of this solution and stirred for 3 min, before the next aliquot is added. This operation is repeated 7 times, before the mixture is quenched with water (5 mL), extracted with dichloromethane (25 mL) and filtered over silica. Removal of all volatiles from the eluat yields the title compound as a brownish-red powder. Yield: 52 mg (0.074 mmol, 77 %). − ^{1}**H NMR** (400 MHz, $\mathrm{CD_2Cl_2}$): δ = 76.6, 52.5, 47.7, 28.9, 26.6, 11.5, 5.0, 3.9, 3.8, −26.1. − **UV/Vis** ($\mathrm{CH_2Cl_2}$): λ /nm = 376, 528, 619. − **HRMS** (ESI): *m/z* 701.2034; calcd. for $[\mathrm{C_{39}H_{43}BrN_4Mn}]^+$: 701.2052.

4-Iodophenyl-(2,3,8,12,17,18-hexaethyl-7,13-dimethylcorrolato)manganese(IV)

[(hedmc)Mn(4-IC$_6$H$_4$)] (11). 1,4-Diiodobenzene (330 mg, 1.0 mmol) in dry THF (3 mL) is cooled to −78 °C under a blanket of argon and treated with 1 eq. of *n*-BuLi (0.58 mL of a 1.65 mol $\mathrm{L^{-1}}$ solution in *n*-hexane), and the solution is stirred at this temperature for 210 min. A suspension of [(hedmc)MnBr] (**8**) (60 mg, 0.096 mmol) in dry THF (50 mL) is treated at 0 °C with 0.35 mL of this solution and stirred for 3 min, before the next aliquot is added. This operation is repeated 7 times, before the mixture is quenched with water (5 mL), extracted with dichloromethane (25 mL) and filtered over silica. Removal of all volatiles from the eluat yields the title compound as a brownish-red solid. Yield: 27 mg (0.036 mmol, 38 %). − ^{1}**H NMR** (400 MHz, $\mathrm{CD_2Cl_2}$): δ = 52.6, 47.8, 29.0, 26.6, 11.5, 5.0, 4.0, 3.9, −30.5. − **UV/Vis** ($\mathrm{CH_2Cl_2}$): λ /nm = 376, 525, 618. − **HRMS** (ESI): *m/z* 749.1908; calcd. for $[\mathrm{C_{39}H_{43}IN_4Mn}]^+$: 749.1913.

Collection and Reduction of X-ray Data. Intensity data for **9** and **10** were collected from single crystals at 193(2) K, using a Stoe IPDS-1 X-ray diffractometer. Graphite monochromated Mo Kα radiation (0.71073 Å) was used. The structures were solved by the Patterson method (**9**) or by direct methods (**10**) with SHELXS-97 [20]. Refinements were carried out by full-matrix least-squares techniques against F^2 using SHELXL-97 [21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions. Crystallographic data (excluding structure factors) for the structures reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-651948 and -651949. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(1223) 336-033; E-mail: deposit@cam.ac.uk].

Crystal data for 9: $\mathrm{C_{39}H_{44}MnN_4}$, 623.37, brown needle, crystal size /mm 0.36 × 0.08 × 0.04, monoclinic, space group *C*2/c, a = 32.001(11), b = 8.8888(18), c = 27.391(8) Å, β = 124.24(2)°, V = 6441(4) Å^3, Z = 8, ρ_{calc} = 1.286 g cm^{-3}, μ(Mo-K$_\alpha$) = 0.444 cm^{-1}, $\theta_{\min}$ = 1.80°, $\theta_{\max}$ = 26.00°, 30703 reflections measured, 6273 independent, 2149 observed with $I > 2\sigma(I)$, 404 parameters, 0 restraints, $R1$ $[I > 2\sigma(I)]$ = 0.0461, $R1$ (all data) = 0.1667, $wR2$ (all data) = 0.0822, max./min. peak = 0.328/−0.282 eÅ^{-3}.

Crystal data for 10: $\mathrm{C_{39}H_{43}BrMnN_4}$, 702.62, brown block, crystal size /mm 0.34 × 0.23 × 0.13, triclinic, space group $P\bar{1}$, a = 11.2309(13), b = 12.6237(15), c = 13.1136(16) Å, α = 71.843(14)°, β = 84.285(15)°, γ = 85.048(14)°, V = 1754.8(4) Å^3, Z = 2, ρ_{calc} = 1.330 g cm^{-3}, μ(Mo-K$_\alpha$) = 1.547 cm^{-1}, $\theta_{\min}$ = 2.36°, $\theta_{\max}$ = 26.06°, 17583 reflections measured, 6425 independent, 4387 observed with $I > 2\sigma(I)$, 414 parameters, 0 restraints, $R1$ $[I > 2\sigma(I)]$ =

0.0429, $R1$ (all data) = 0.0667, $wR2$ (all data) = 0.1112, max./min. peak = 0.509/−0.500 eÅ^{-3}.

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