Mono- and Dinuclear High-Spin Half-Sandwich Manganese(II) Complexes Containing Acetylide and TMEDA Ligands

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The d^5 high-spin Mn^{II} half-sandwich complexes $[Mn(C\equiv CR)(MeC_5H_4)(tmeda)]$ (R = $SiMe_3$ **2**; Ph **3**; *t*Bu **4**; $C\equiv CSiMe_3$ **5**; $C\equiv CPh$ **6**; tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) were prepared by the reaction of $[Mn(MeC_5H_4)_2(tmeda)]$ (**1**) with 1 equiv. of the corresponding acetylene or the trimethyltin acetylide. The dinuclear complexes $[Mn(C\equiv C\text{–}C\equiv CSiMe_3)_2(tmeda)]_2$ (**7**) and $[Mn_2(MeCp)_2(\mu_1\text{-}tBuC\equiv C)_2(\mu_1\text{-tmeda})]$ (**8**), which contain Mn–Mn bonds, were synthesized by treating **1** with an excess of $HC\equiv C\text{–}C\equiv CSiMe_3$ or $HC\equiv CtBu$, respectively. Dinuclear complexes of the type $[(MeC_5H_4)(tmeda)MnC\equiv C\text{–}X\text{–}C\equiv CMn(tmeda)(C_5H_4Me)]$ [X = 1,3-C_6H_4 **9**; 1,4-C_6H_4 **10**; 4,4′-$(C_6H_4)_2$ **11**] were obtained by treatment of **1** with 0.5 equiv. of the corresponding acetylides 1,3-$C_6H_4(C\equiv CSnMe_3)_2$, 1,4-$C_6H_4(C\equiv CSnMe_3)_2$ and 4,4′-$(C_6H_4)_2(C\equiv CSnMe_3)_2$ in benzene for 24 h to yield the corresponding dinuclear complexes in very good yields. All the mono- and dinuclear compounds have been characterized by NMR, IR, Raman spectroscopy and elemental analyses. X-ray diffraction studies have been performed on complexes **3** and **5**–**11**. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

Mono- and dinuclear transition metal acetylide complexes offer an interesting perspective for the construction of organometallic systems as molecular-level single-electron devices and the bottom-up construction of miniaturized components capable of performing specific electronic functions. This is an important challenge for many facets of modern chemistry.[1−15] During the last decade several organometallic research groups have focused on the development of facile synthetic routes to $L_mMC_xM'L'_{m'}$ rigid rod transition metal complexes.[2,16−91] Our ongoing interest in such building blocks is devoted to the synthesis and physical properties of molecular species that might function as wires. Specifically, they should consist of an all-carbon chain capped by two redox-active metal termini.[36,46,57,63,74,75] We have sought to explore reactions to prepare mono- and dinuclear precursors containing polyyne ligands. We have already reported some of the results involving manganese centers with strong-field ligands such as phosphanes.[36,46,57,63,74,75] We subsequently decided to synthesize and study the properties of molecules with weak-field ligands, such as tmeda, expecting high-spin configurations of the metal centers.[92−100] In addition to the above reasons, the $L_mMn{-}C_4{-}MnL_m$ systems were selected as target molecules because a build-up of di- and oligonuclear Mn complexes seemed not only to be synthetically feasible by acetylide substitution processes, but also by coupling of $Mn{-}C_2$ units, such as Mn−alkynyl and Mn−vinylidene moieties. These possibilities have been corroborated by recent studies in our group.[36,46,57,74,75,101] For instance, we have published the synthesis of redox-active dinuclear complexes of the type $[\{Mn(dmpe)_2(X)\}_2(\mu\text{-}C_4)]^{n+}$ (X = $C\equiv CH$, $C\equiv C{-}C\equiv CSiMe_3$ and $n = 0{-}2$), which were obtained by an in situ C−C coupling of $[Mn^{III}(dmpe)_2(C\equiv CH)(C\equiv C)]$ units.[74,75,101] We have also previously reported the synthesis and characterization of $[I(dmpe)_2MnC\equiv C{-}C\equiv CMn(dmpe)_2I]^{n+}$ [57] in a preliminary communication and report herein the mononuclear half-sandwich complexes of the type $[(MeC_5H_4)(tmeda)MnC\equiv CR]$ (R = $SiMe_3$, Ph, *t*Bu, $C\equiv CSiMe_3$, $C\equiv CPh$) and dinuclear half-sandwich complexes of the type $[(MeC_5H_4)(tmeda)Mn{-}X{-}Mn(tmeda)(MeC_5H_4)]$ [X = 1,4-$C_6H_4(C\equiv C)_2$, 1,3-$C_6H_4(C\equiv C)_2$, 4,4′-$C_6H_4C_6H_4(C\equiv C)_2$].

The first representatives of the manganocene family — $[MnCp_2]$ and $[Mn(MeC_5H_4)_2]$[102,103] — have been known for around 40 years and their electronic and structural properties have been studied extensively; however, their synthetic potential, in particular with regard to Cp or MeC_5H_4 replacement by other organometallic units, has not been exploited appropriately except for earlier work from our group.[63,104] The mononuclear complexes were obtained by the reaction of $[(MeC_5H_4)_2Mn(tmeda)]$[105,106] with $RC\equiv CR'$ (R′ = H, $SnMe_3$, R = $SiMe_3$, Ph, *t*Bu,

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C≡CSiMe$_3$, C≡CPh) and the corresponding dinuclear systems by treatment of 0.5 equiv. of the bifunctional acetylenes $Me_3SnC≡C-R''-C≡CSnMe_3$ [R″ = 1,4-$C_6H_4(C≡C)_2$,[107–109] 1,3-$C_6H_4(C≡C)_2$,[107–109] or 4,4′-$C_6H_4C_6H_4(C≡C)_2$ [107–109] with $[Mn(MeC_5H_4)_2(tmeda)]$.

Results and Discussion

On the basis of known, facile methylcyclopentadienyl replacements in $[Mn(MeC_5H_4)_2(dmpe)]$,[63,103,105] where one of the methylcyclopentadienyl rings is bound to the manganese center in an η^5 fashion and the other in an η^2 fashion,[103,105] we thought that it should be even easier to replace one of the methylcyclopentadienyl rings in $[Mn(MeC_5H_4)_2(tmeda)]$[106] (**1**), which comprises two η^1-methylcyclopentadienyl rings bound to the manganese center, by an acetylide ligand. Reaction of **1** with 1 equiv. of various acetylenes HC≡CSiMe$_3$ or Me$_3$SnC≡CSiMe$_3$, PhC≡CH or PhC≡CSnMe$_3$, *t*BuC≡CH or *t*BuC≡CSnMe$_3$, Me$_3$SiC≡C−C≡CH, Me$_3$SiC≡C−C≡CSnMe$_3$ or PhC≡C−C≡CSnMe$_3$ yielded, in THF at room temperature for 3 d, the corresponding high-spin d^5 Mn^{II} mononuclear complexes of the type $[(MeC_5H_4)(tmeda)MnC≡CR]$ (R = SiMe$_3$ **2**; Ph **3**; *t*Bu **4**; C≡CSiMe$_3$ **5**; C≡CPh **6**) quantitatively (Scheme 1). The ^1H NMR spectra of complexes **3**, **4** and **6** at 20 °C contain proton resonances for the ring protons of the MeC$_5$H$_4$ group in the high-field region, while for **2** and **5** similar resonances are not present. The only proton resonances that are observed for complexes **2** and **5** are for the SiMe$_3$ protons at δ = 7.3 and 4.8 ppm, respectively. The signals of the methyl and the methylene protons of the tmeda ligand of these complexes are observed between δ = 60 and 110 ppm. The paramagnetic behavior of these complexes apparently influences the relaxation of the ^{15}N nucleus, so that ^{15}N resonances can be observed. The ^{15}N NMR spectra of **3**, **4** and **6** reveal resonances for the tmeda ligand at higher field, at $\delta \approx -75$ to -90 ppm. The proton resonances for the methyl and the methylene protons of the tmeda ligand are absent. The ^1H and ^{15}N NMR spectroscopic data for complexes **2**−**6** are summarized in Table 1.

Table 1. ^1H and ^{15}N NMR spectroscopic data (δ [ppm]) for complexes **2**−**6**

	^{15}N NMR	^1H NMR $CH_3C_5\mathit{H}_4$	 $C\mathit{H}_3C_5H_4$	 CH_2 or CH_3
2	−75.6 (br.)	–[a]	–[a]	–[a]
3	−85.9 (br.)	−27.7	106.5	62.1 (br.)
4	−90.7 (br.)	−19.8	151.0	62.6, 102.1
5	−79.8 (br.)	–[a]	–[a]	–[a]
6	−81.7 (br.)	−10.2	−9.0	–[a]

[a] Not observed.

Raman spectroscopy showed characteristic bands for the ν(C≡C) vibrations for these complexes between 2000 and 2100 cm^{-1}.

The structure of **3** was additionally confirmed by an X-ray diffraction study (Figure 1). A pseudo-tetrahedral coordination of the manganese center was found. The bond

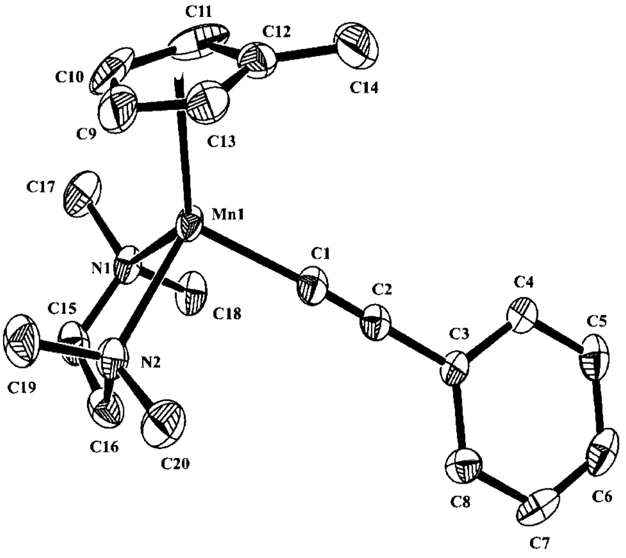
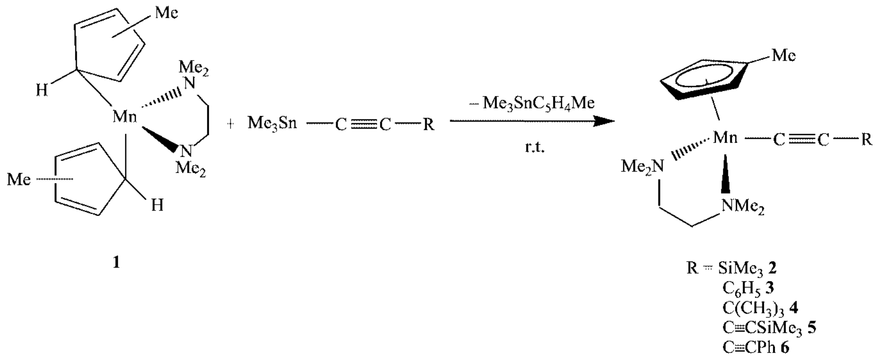


Figure 1. Molecular structure of **3** (30% probability displacement ellipsoids); hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Mn−C1 2.142(2), C1−C2 1.158(3), C2−C3 1.473(3), Mn−MeCp (centroid) 2.5144(2); Mn−C1−C2 176.76(19), C1−C2−C3 179.5(2)



Scheme 1

lengths of 1.158(3) Å and 2.142(2) Å for C1−C2 and Mn−C1, respectively, fall into the range observed for similar kinds of complexes.[63]

The structure of **5** was also confirmed by a single-crystal X-ray diffraction study (Figure 2). The crystals were obtained by cooling the compound in a mixture of pentane and benzene to −30 °C. The solid-state structure reveals a pseudo-tetrahedral coordination of the manganese center. The bond lengths of 1.109(3) Å and 1.203(3) Å for C1−C2 and C3−C4, respectively, confirm the triple-bond nature of these bonds. An X-ray diffraction analysis also confirmed the spectroscopically derived structure of **6** which is related to **5** (Figure 3). The solid-state structure revealed the C1−C2 and C3−C4 bond lengths to be 1.220(3) Å and 1.206(3) Å, respectively.

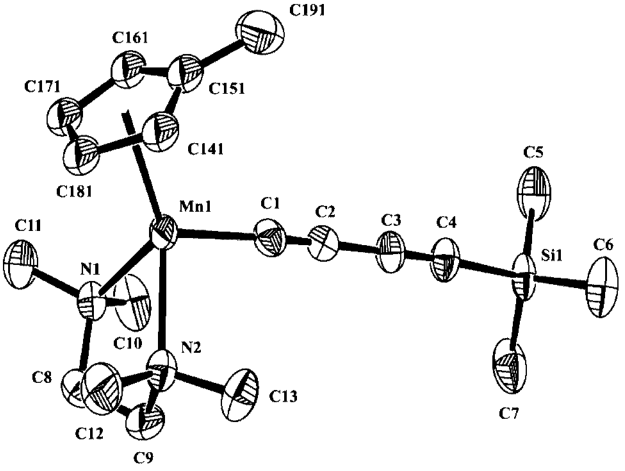


Figure 2. Molecular structure of **5** (30% probability displacement ellipsoids); hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Mn−C1 2.160(2), C1−C2 1.109(3), C2−C3 1.473(3), C3−C4 1.203(3), Mn−MeCp (centroid) 2.4805(5); Mn−C1−C2 176.5(2), C1−C2−C3 178.9(2), C2−C3−C4 179.3(2), C3−C4−Si 176.7(2)

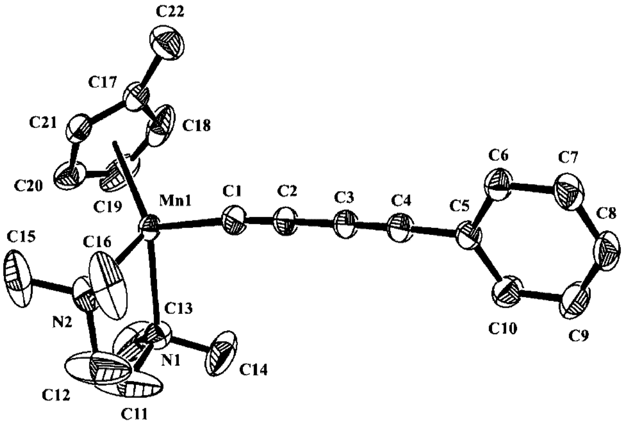
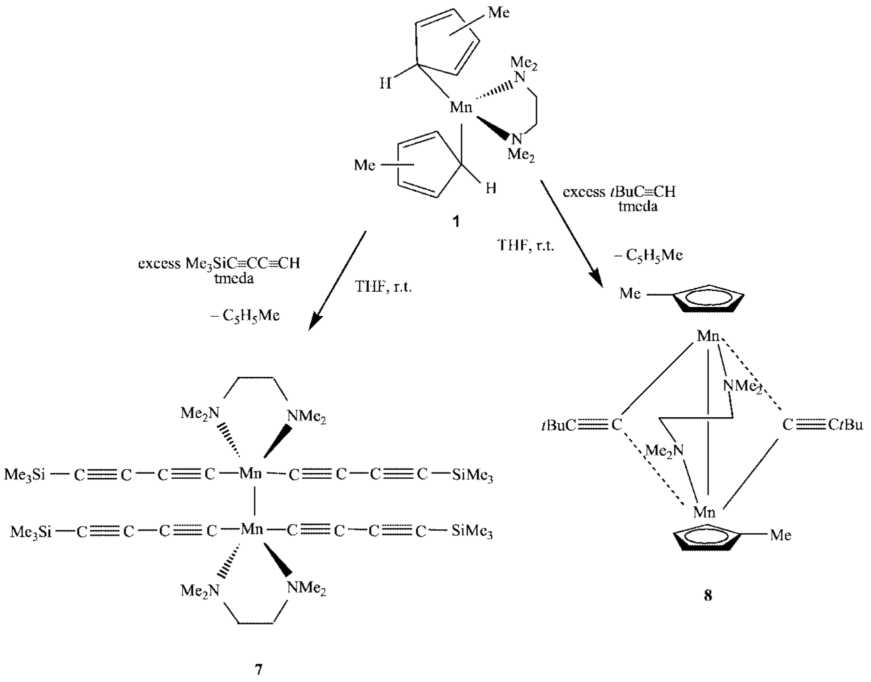


Figure 3. Molecular structure of **6** (30% probability displacement ellipsoids); hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Mn−C1 2.1222(19), C1−C2 1.220(3), C2−C3 1.397(3), C3−C4 1.206(3), Mn−MeCp (centroid) 2.4914(5); Mn−C1−C2 174.98(17), C1−C2−C3 178.3(2), C2−C3−C4 178.7(2), C3−C4−C5 176.0(2)

Both methylcyclopentadienyl rings in **1** could be replaced by using an excess of the acetylene component. Stirring of **1** with $Me_3SiC\equiv C-C\equiv CH$ at room temperature for 5 d yielded the dinuclear complex **7** (Scheme 2). The ^{1}H NMR spectrum of **7** in [D$_8$]toluene at 25 °C shows only a signal for the SiMe$_3$ protons. In the ^{15}N NMR spectrum, the nitrogen atoms of the tmeda ligands are observed as a broad resonance at $\delta = -93.4$ ppm. Characteristic ν(C≡C) vibrations appear in the Raman spectrum at 2154, 2115 and 2001 cm^{-1}. The structure of **7** was confirmed by an X-ray



Scheme 2

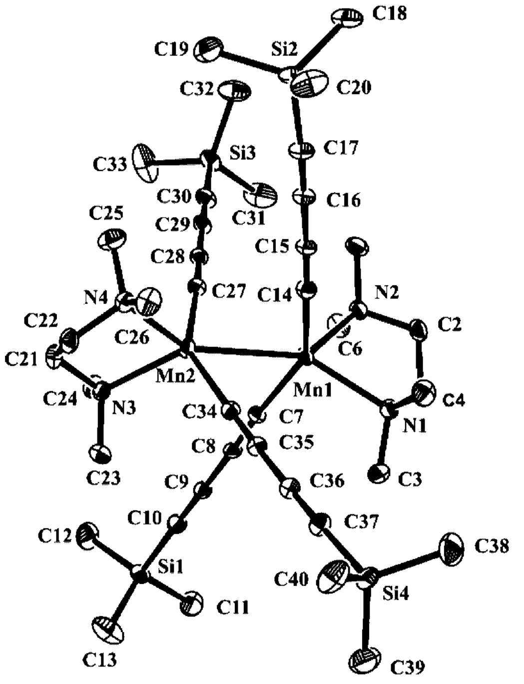


Figure 4. Molecular structure of **7** (30% probability displacement ellipsoids); hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Mn1−Mn2 2.8059(4), Mn1−C7 2.095(2), Mn1−C14 2.088(2), C7−C8 1.212(3), Mn2−C27 2.103(2), Mn2−C34 2.099(2), C27−C28 1.210(3), C8−C9 1.387(3), C9−C10 1.208(3), C14−C15 1.208(3), C15−C16 1.385(3), C16−C17 1.214(3), C28−C29 1.392(3), C29−C30 1.204(3), C34−C35 1.205(3), C35−C36 1.394(3), C36−C37 1.209(3); C7−Mn1−C14 147.43(8), Mn1−C7−C8 175.50(18), Mn1−C14−C15 176.57(19), C27−Mn2−C34 146.09(8), Mn2−C27−C28 173.18(19), Mn2−C34−C35 178.69(19), C7−C8−C9 177.5(2), C8−C9−C10 179.4(3), C27−C28−C29 178.3(2), C28−C29−C30 178.5(2), C9−C10−Si1 178.3(2), C14−C15−C16 177.7(2), C15−C16−C17 179.3(2), C16−C17−Si2 173.2(2), C29−C30−Si3 178.8(2), C34−C35−C36 178.2(2), C35−C36−C37 178.7(2), C36−C37−Si4 176.8(2), C27−Mn2−Mn1 76.11(6), C14−Mn1−Mn2 76.37(2), Mn1−Mn2−C34 70.11(6), Mn2−Mn1−C7 71.08(6)

diffraction analysis (Figure 4). In the solid-state structure a bond length of 2.8059(4) Å was found between the two manganese centers Mn1−Mn2, which is similar to compounds with Mn−Mn single bonds reported earlier, for instance $Mn_2(CO)_{10}$.[110−114] However, we should note that the electron counts for both complexes are different, so that the character of the unique single bond of **7** might also be different. The C7−C8 bond length was observed to be 1.212(3) Å, which is expected for a C≡C bond. The Mn1−C7−C8 unit possesses a bond angle of 175.50(18)°, which shows that this butadiynyl chain is slightly bent, as are the other three C_4 units. The coordination geometry of the Mn centers may thus be derived from a trigonal bipyramid with the tmeda ligand and the neighbouring manganese atom in the equatorial plane and the acetylide moieties in the axial positions [the angle between the planes (Mn2, N3, N4) (Mn2, Mn1, C4) is 84.48(7)°; other related angles between planes have similar values]. The rather acute C7−Mn1−C14 bond angle of 147.43(18)° stresses the fact that the two acetylide units at an Mn center are quite far away from the ideal *trans* position; the reason for this deviation could not be determined. It is supposed that there is an electronic driving force, and one possibility could be a secondary-type interaction between the manganese centers and the metal-adjacent triple bonds. For example, the Mn1−C34 distance of 2.877(2) Å is within the sum of the van der Waals radii and the Mn1−C35 distance of 3.531(2) Å is just about the sum of the van der Waals radii. When an excess of *t*BuC≡CH was used in the reaction with **1**, the unexpected dinuclear complex **8** was obtained (Scheme 2), with η^5-methylcyclopentadienyl rings at each Mn atom. The two manganese centers are bridged by one tmeda ligand and are connected by a presumably ligand-enforced Mn−Mn bond, which was confirmed by an X-ray diffraction study on **8** (Figure 5).

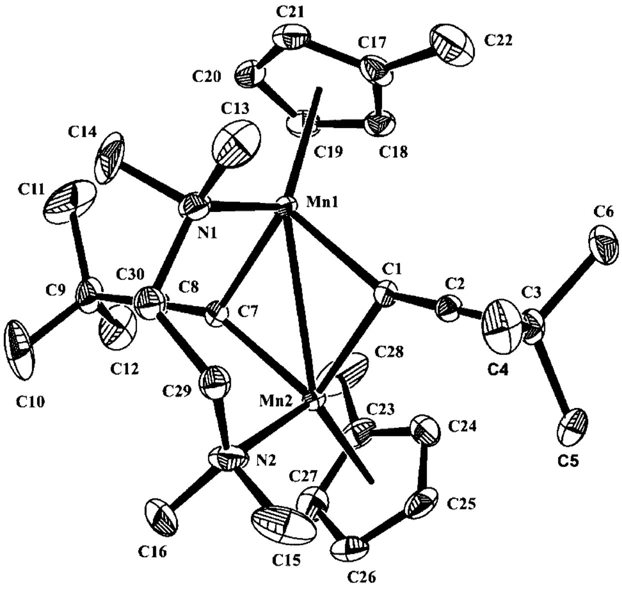
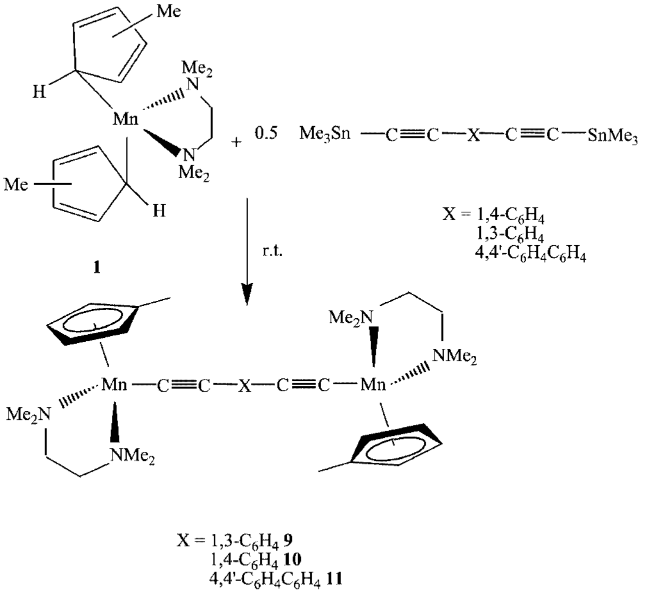


Figure 5. Molecular structure of **8** (30% probability displacement ellipsoids); hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Mn1−Mn2 2.8738(5), Mn1−C1 2.192(2), Mn1−C7 2.220(3), Mn2−C1 2.179(13), Mn2−C7 2.234(3), C1−C2 1.204(3), C2−C3 1.795(3), Mn1−MeCp1 (centroid) 2.491(3), Mn2−MeCp2 (centroid) 2.496(3); C1−Mn1−C7 98.58(9), C1−Mn2−C7 98.69(9), Mn1−C1−C2 152.8(2), Mn2−C7−C8 151.6(2), C1−C2−C3 179.5(3), C7−C8−C9 176.6(3), Mn1−C1−Mn2 80.98(7), C1−Mn1−Mn2 48.49(5), C1−Mn2−Mn1 48.89(5) Mn2−C7−Mn1 81.66(7), C7−Mn1−Mn2 50.14(7), C7−Mn2−Mn1 89.85(7)

The acetylide moiety also bridges the two manganese centers. The ^{1}H NMR spectrum of **8** in [D$_8$]toluene at 30 °C reveals a broad resonance for the methylcyclopentadienyl ring at $\delta = -11.4$ ppm and the corresponding resonances for the *tert*-butyl groups and the methyl and methylene groups of the tmeda ligand, which are observed at low field (δ = 14.2, 34.6 and 65.5 ppm, respectively). The ^{15}N NMR spectrum shows a broad resonance at $\delta = -73.8$ ppm. In the Raman spectrum a band attributed to a ν(C≡C) vibration is observed at 2052 cm^{-1}.

The [Mn(MeC$_5$H$_4$)$_2$(tmeda)] complex **1** is a valuable starting material and allows access to dinuclear complexes bridged by sp-carbon units. Complexes of this type have been widely studied in conjunction with potential molecular-wire applications.[32−35,43−45,50,52,55,56,66,69,70,72,87,115,127a] Complexes **9**, **10** and **11** were obtained by treatment of **1** with 0.5 equiv. of the corresponding acetylenes 1,3-$C_6H_4(C{\equiv}CSnMe_3)_2$, 1,4-$C_6H_4(C{\equiv}CSnMe_3)_2$ or 4,4′-$(C_6H_4)_2(C{\equiv}CSnMe_3)_2$ in benzene for 24 h to afford the corresponding dinuclear complexes in very good yields (Scheme 3). The ^1H NMR spectrum of **9** in [D$_8$]THF at 22 °C reveals two signals for the protons of the cyclopentadienyl rings, both paramagnetically shifted to high field at $\delta = -63.7$ and -45.9 ppm, and a broad resonance in the downfield region at $\delta = 163.3$ ppm. The proton resonance for the tmeda moieties appears at $\delta = 74.2$ ppm, while the aromatic protons are observed as two broad signals at $\delta = 38.6$ and 41.6 ppm. The resonance of the tmeda ligands appears in the ^{15}N NMR spectrum (20 °C) as a broad signal at $\delta \approx -100.4$ ppm. The ^1H NMR spectra of complexes **10** and **11** show significant differences in comparison with that of complex **9**, since only the proton resonances corresponding to the methylcyclopentadienyl rings [$\delta = -8.1$ (**10**) and -24.9 ppm (**11**)] and the aromatic protons [$\delta = 27.2$ (**10**) and 20.7 ppm (**11**)] could be observed.



Scheme 3

The structures of complexes **9**, **10** and **11** were characterized by X-ray diffraction analyses. The solid-state structures of these complexes reveal different types of bonding of the methylcyclopentadienyl groups to the manganese centers. In complex **9** the methylcyclopentadienyl rings are η^3- and η^3-bound (see Supporting Information), whereas in **10** both possess η^2 hapticity (Figure 6); the maximum hapticity of the MeC_5H_4 rings (η^5,η^5) is observed in **11** (Figure 7). These different bonding situations might arise from the fact that the interaction between the methylcyclopentadienyl ring and the manganese center is quite ionic in nature and can therefore not be expressed by localized covalent interactions, but rather by partly localized ionic interactions of the ion-pair type.[100] Based on the ionic bonding, the energetic differences between the various binding modes are expected to be relatively small. Hence, simple packing forces on the order of 1 kcal·mol^{-1} might be just enough to induce different ring slippage modes in otherwise quite related structures. The C≡C bond lengths found in these complexes are similar to compounds already reported in the literature. CV experiments (ca. 0 to +1.5 V) failed to oxidize the complexes **9**, **10** and **11** possessing high-spin d^5-metal centers further.

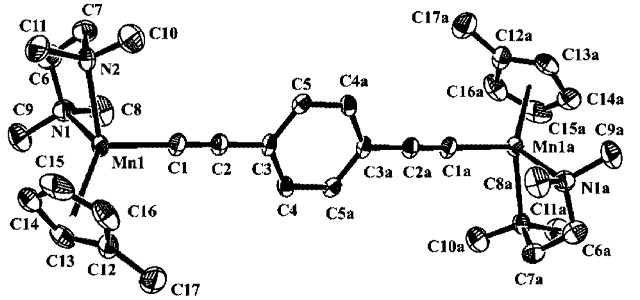


Figure 6. Molecular structure of **10** (30% probability displacement ellipsoids); hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Mn1−C1 2.109(3), C1−C2 1.203(4), C2−C3 1.438(4), Mn1−N1 2.333(3), Mn1−N2 2.269(3); Mn1−C1−C2 177.3(3), C1−C2−C3 179.0(4)

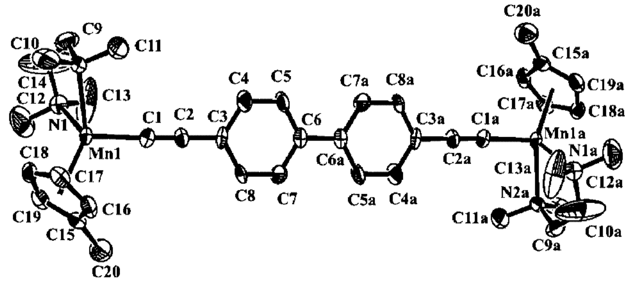


Figure 7. Molecular structure of **11** (30% probability displacement ellipsoids); hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Mn1−C1 2.096(6), C1−C2 1.212(6), C2−C3 1.436(6), C3−C8 1.370(6), C8−C7 1.365(6), C4−C5 1.375(6), C5−C6 1.372(6), C6−C6a 1.488(8), Mn1−Cp (centroid) 2.1524(5); Mn1−C1−C2 177.2(5), C1−C2−C3 178.8(6)

Conclusions

Mono- and dinuclear complexes of polyynes capped by Mn^{II} half-sandwich units were synthesized. A series of these complexes has been structurally characterized showing a variety of different hapticities of the cyclopentadienyl rings. This observation witnesses quite ionic bonding of these rings as would indeed be expected for d^5 high-spin complexes. The manganese centers have a stable electron configuration additionally indicated by the inability to further oxidize them. Based on this we might conclude that the d electrons in the dinuclear complexes **9**−**11** are contracted, which also prevents strong electronic communication of the metal centers. It is therefore suggested that these complexes belong to class I or to the weaker interaction side of class II compounds according to the Robin/Day classification.[127b]

Experimental Section

General: Reagent-grade benzene, toluene, hexane, pentane, diethyl ether and tetrahydrofuran were dried and distilled from sodium benzophenone ketyl prior to use. Dichloromethane was distilled first from P_2O_5, and then prior to use from CaH_2. Literature procedures were used to prepare the following compounds: 1,2-bis(dimethylphosphanyl)ethane (dmpe),[128] $[Mn(MeC_5H_4)_2]$,[102,103] $[Mn(MeC_5H_4)_2(tmeda)]$,[105,106] $Me_3SnC{\equiv}CSiMe_3$,[129] $Me_3SiC{\equiv}C{-}C{\equiv}CH$,[130] $PhC{\equiv}CSnMe_3$, tBuC≡CSnMe₃ → $tBuC{\equiv}CSnMe_3$,[128] $PhC{\equiv}C{-}C{\equiv}CSnMe_3$,[131] and $Me_3SnC{\equiv}C{-}R''{-}C{\equiv}CSnMe_3$ [R'' = 1,4-$C_6H_4(C{\equiv}C)_2$, 1,3-$C_6H_4(C{\equiv}C)_2$, 4,4′-$C_6H_4C_6H_4(C{\equiv}C)_2$].[107–109] nBuLi (1.6 M in hexane) and Me_3SnCl were used as received. All the manipulations were carried out under nitrogen using Schlenk techniques or in a drybox. IR spectra were obtained with a Bio-Rad FTS-45 instrument and the Raman spectra with a Renishaw Ramanscope spectrometer (514 nm). ^1H NMR spectra were measured with a Varian Gemini-2000 at 300 MHz and ^{15}N NMR spectra at 50.70 MHz with a Bruker DRX 500 spectrometer. All NMR spectra of paramagnetic compounds were obtained from concentrated solutions of analytically pure samples. The assignment of the ^1H NMR signals for paramagnetic signals is principally based on the investigations of Köhler et al.[132–134] Chemical shifts for ^1H are given in ppm with respect to the signals for residual solvent protons (^1H) of the deuterated solvents and for ^{15}N related to nitromethane.

Synthesis of $[Mn(\eta^1\text{-}MeC_5H_4)_2(tmeda)]$ (1): A diethyl ether solution (5 mL) of tmeda (116.2 mg, 1.0 mmol) was added to a diethyl ether solution (5 mL) of [Mn(MeCp)₂] → $[Mn(MeCp)_2]$ (213 mg, 1.0 mmol), and the mixture stirred at room temperature for 15 min. The solvent was then evaporated in vacuo and the solid residue was washed with pentane (3 × 5 mL). Colorless crystals of **1** were obtained by crystallizing from a mixture of THF (2 mL) and pentane (20 mL) at −40 °C. Yield 313 mg, 95%. $C_{18}H_{30}MnN_2$ (329.39): calcd. C 65.64, H 9.18, N 8.50; found C 65.36, H 9.41, N 8.45. ^1H NMR ($[D_8]$THF, 300 MHz, 30 °C): $\delta = -39.1$ (br., 8 H, $CH_3C_5H_4$), −3.5 (br., 6 H, $CH_3C_5H_4$), 30.6 (br., 16 H, tmeda) ppm. $^{15}N\{^1H\}$ NMR ($[D_8]$THF, 50.70 MHz, 20 °C): $\delta = -75.7$ (br., tmeda) ppm.

Synthesis of $[Mn(C{\equiv}CSiMe_3)(\eta^5\text{-}MeCp)(tmeda)]$ (2): A THF solution (5 mL) of $Me_3SiC{\equiv}CH$ (98.2 mg, 1.0 mmol) or $Me_3SiC{\equiv}CSnMe_3$ (261 mg, 1.0 mmol) was added to a THF solution (10 mL) of $[Mn(\eta^1\text{-}MeC_5H_4)_2(tmeda)]$, and the mixture stirred at room temperature for 3 d. The solvent was evaporated in vacuo and the solid residue was extracted with 10 mL of pentane. The pentane solution was concentrated to 5 mL, filtered through Celite and crystallized to give pure colorless crystals of **2** at −40 °C (330 mg, 95% yield). $C_{18}H_{30}MnN_2$ (347.48): calcd. C 65.64, H 9.18, N 8.50; found C 65.36, H 9.41, N 8.45. ^1H NMR ($[D_8]$THF, 300 MHz, 30 °C): $\delta = 7.3$ (br., 9 H, $SiMe_3$) ppm. $^{15}N\{^1H\}$ NMR ($[D_8]$THF, 50.70 MHz, 7 °C): $\delta = -75.6$ (br., tmeda) ppm. Raman: $\tilde{\nu} = 2021$ [s, ν(C=C)] cm^{-1}.

Synthesis of $[Mn(C{\equiv}CPh)(\eta^5\text{-}MeCp)(tmeda)]$ (3): A THF solution (5 mL) of $PhC{\equiv}CH$ (102.1 mg, 1.0 mmol) or $PhC{\equiv}CSnMe_3$ (265 mg, 1.0 mmol) was added to a THF solution (10 mL) of $[Mn(\eta^1\text{-}MeC_5H_4)_2(tmeda)]$, and the mixture stirred at room temperature for 3 d. The solvent was evaporated in vacuo and the solid residue was extracted with 5 mL of benzene. The benzene solution was filtered through Celite and crystallized from a mixture of benzene (5 mL) and pentane (20 mL) to give pure yellow crystals of the title compound at −40 °C (341 mg, 97% yield). $C_{20}H_{28}MnN_2$ (351.40): calcd. C 68.36, H 8.03, N 7.97; found C 68.63, H 7.88, N 7.74. ^1H NMR ($[D_8]$THF, 300 MHz, 20 °C): $\delta = -27.7$ (br., 4 H, $CH_3C_5H_4$), 24.9 (br., 5 H, C_6H_5), 62.1 (br., 16 H, tmeda), 106.5 (br., 3 H, $CH_3C_5H_4$) ppm. $^{15}N\{^1H\}$ NMR ($[D_8]$THF, 50.70 MHz, 10 °C): $\delta = -85.9$ (br., tmeda) ppm. Raman: $\tilde{\nu} = 2074$ [s, ν(C=C)] cm^{-1}.

Synthesis of $[Mn(C{\equiv}CtBu)(\eta^5\text{-}MeCp)(tmeda)]$ (4): A THF solution (5 mL) of $tBuC{\equiv}CH$ (82.1 mg, 1.0 mmol) or $tBuC{\equiv}CSnMe_3$ (245 mg, 1.0 mmol) was added to a THF solution (10 mL) of $[Mn(\eta^1\text{-}MeC_5H_4)_2(tmeda)]$, and the mixture stirred at room temperature for 3 d. The solvent was evaporated in vacuo and the solid residue was extracted with 10 mL of pentane. The pentane solution was concentrated to 5 mL, filtered through Celite and crystallized to give pure light-blue crystals of **4** at −40 °C (265 mg, 80% yield). $C_{18}H_{32}MnN_2$ (331.41): calcd. C 65.24, H 9.73, N 8.45; found C 65.60, H 9.70, N 8.56. ^1H NMR ($[D_8]$toluene, 300 MHz, 20 °C): $\delta = -19.8$ (br., 4 H, $CH_3C_5H_4$), 14.5 (br., 9 H, tBu), 62.6, 102.1 (br., 16 H, tmeda), 151.0 (br., 3 H, $CH_3C_5H_4$) ppm. $^{15}N\{^1H\}$ NMR ($[D_8]$THF, 50.70 MHz, 10 °C): $\delta = -90.7$ (br., tmeda) ppm. Raman: $\tilde{\nu} = 2075$ [s, ν(C=C)] cm^{-1}.

Synthesis of $[Mn(C{\equiv}C{-}C{\equiv}CSiMe_3)(\eta^5\text{-}MeCp)(tmeda)]$ (5): A THF solution (5 mL) of $Me_3SiC{\equiv}C{-}C{\equiv}CH$ (122.2 mg, 1.0 mmol) or $Me_3SiC{\equiv}C{-}C{\equiv}CSnMe_3$ (285 mg, 1.0 mmol) was added to a THF solution (10 mL) of $[Mn(\eta^1\text{-}MeC_5H_4)_2(tmeda)]$ (329.4 mg, 1.0 mmol), and the mixture stirred at room temperature for 3 d. The solvent was evaporated in vacuo and the solid residue was washed with pentane (3 × 5 mL). Benzene (5 mL) was added to the pentane solution (5 mL) and the resulting mixture was filtered through Celite and crystallized to give pure light-yellow crystals of complex **5** at −40 °C (357 mg, 96% yield). $C_{19}H_{32}MnN_2Si$ (371.50): calcd. C 65.24, H 9.73, N 8.45; found C 65.60, H 9.70, N 8.56. ^1H NMR ($[D_8]$toluene, 300 MHz, 20 °C): $\delta = 4.8$ (br., 9 H, $SiMe_3$) ppm. $^{15}N\{^1H\}$ NMR ($[D_8]$THF, 50.70 MHz, 10 °C): $\delta = -90.7$ (br., tmeda) ppm. Raman: $\tilde{\nu} = 2075$ [s, ν(C=C)] cm^{-1}.

Synthesis of $[Mn(C{\equiv}C{-}C{\equiv}C{-}Ph)(\eta^5\text{-}MeCp)(tmeda)]$ (6): A THF solution (5 mL) of $PhC{\equiv}C{-}C{\equiv}CSnMe_3$ (290 mg, 1.0 mmol) was added to a THF solution (10 mL) of $[Mn(\eta^1\text{-}MeC_5H_4)_2(tmeda)]$ (329.4 mg, 1.0 mmol), and the mixture stirred at room temperature for 3 d. The solvent was evaporated in vacuo and the solid residue was washed with pentane (3 × 5 mL). THF (5 mL) was added and the mixture filtered through Celite. Diethyl ether (30 mL) was added and light yellow brown crystals of complex **6** were obtained at −40 °C (353 mg, 92% yield). $C_{22}H_{28}MnN_2$ (375.42): calcd. C 70.39, H 7.52, N 7.46; found C 70.52, H 7.46, N 7.13. ^1H NMR ($[D_8]$toluene, 300 MHz, 20 °C): $\delta = -10.2$, −9.0 (br., 4 H, $CH_3C_5H_4$), 15.5 (br., 5 H, C_6H_5) ppm. $^{15}N\{^1H\}$ NMR ($[D_8]$THF, 50.70 MHz, 10 °C): $\delta = -81.7$ (br., tmeda) ppm. Raman: $\tilde{\nu} = 2174$ (s), 2022 [s, ν(C=C)] cm^{-1}.

Synthesis of $[Mn(C{\equiv}C{-}C{\equiv}CSiMe_3)_2(tmeda)]_2$ (7): A THF solution (5 mL) containing an excess of $Me_3SiC{\equiv}C{-}C{\equiv}CH$ (1.22 g, 10 mmol) was added to a THF solution (10 mL) of $[Mn(\eta^1\text{-}MeC_5H_4)_2(tmeda)]$ (329.4 mg, 1.0 mmol), and the mixture stirred at room temperature for 5 d. The solvent was evaporated in vacuo and the solid residue was washed with pentane (3 × 5 mL). The olive-green solid was dissolved in toluene (5 mL) and pentane (30 mL) was added to obtain olive-green crystals of complex **7** at −40 °C (871 mg, 95% yield). $C_{40}H_{68}Mn_2N_2Si_2$ (827.23): calcd. C

58.08, H 8.29, N 6.77; found C 58.26, H 8.35, N 6.89. ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 3.0 (s, 18 H, SiMe$_3$) ppm. ^{15}N{^{1}H} NMR ([D$_8$]toluene, 50.70 MHz, 10 °C): δ = −93.4 (br., tmeda) ppm. Raman: $\tilde{\nu}$ = 2154 (s), 2115 (s), 2001 [s, ν(C=C)] cm^{-1}.

Synthesis of [Mn$_2$(MeCp)$_2$(μ_1-tmeda)(μ_1-*t*BuC≡C)$_2$] (8): A THF solution (5 mL) containing an excess of *t*BuC≡CH (821.5 mg, 10 mmol) was added to a THF solution (10 mL) of [Mn(η^1-MeC$_5$H$_4$)$_2$(tmeda)] (659 mg, 2.0 mmol), and the mixture stirred at room temperature for 5 d. The solvent was evaporated in vacuo and the solid residue was washed with pentane (3 × 5 mL). The olive-green solid was dissolved in benzene (5 mL) and pentane (30 mL) was added to obtain olive-green crystals of complex **8** at −40 °C (383 mg, 70% yield). C$_{30}$H$_{48}$Mn$_2$N$_2$ (546.60): calcd. C 65.92, H 8.85, N 5.13; found C 66.21, H 8.64, N 5.03. ^{1}H NMR ([D$_8$]toluene, 300 MHz, 30 °C): δ = −11.4 (br., 8 H, CH$_3$C$_5$*H*$_4$), 14.2 (s, 18 H, *t*Bu), 34.6, 65.5 (br., 16 H, tmeda) ppm. ^{15}N{^{1}H} NMR ([D$_8$]toluene, 50.70 MHz, 20 °C): δ = −73.8 (br., tmeda) ppm. Raman: $\tilde{\nu}$ = 2052 [s, ν(C=C)] cm^{-1}.

Synthesis of [{(η^3-MeCp)(tmeda)Mn}$_2$(μ-1,3-C$_6$H$_4$(C≡C)$_2$] (9): A benzene solution (10 mL) of 1,3-C$_6$H$_4$(C≡CSnMe$_3$)$_2$ (452 mg, 1.0 mmol) was added to a benzene solution (20 mL) of [Mn(η^1-MeC$_5$H$_4$)$_2$(tmeda)] (659 mg, 2.0 mmol), and the mixture stirred at room temperature for 24 h. The solvent was evaporated in vacuo and the solid residue was washed with pentane (3 × 5 mL). The olive-green solid was dissolved in toluene (5 mL) and pentane (30 mL) was added to obtain light-orange crystals of complex **9** at −30 °C (469 mg, 75% yield). C$_{34}$H$_{50}$Mn$_2$N$_4$ (624.68): calcd. C 65.37, H 8.07, N 8.97; found C 65.08, H 8.44, N 8.68. ^{1}H NMR ([D$_8$]THF, 300 MHz, 30 °C): δ = −62.9 (br., 4 H, CH$_3$C$_5$*H*$_4$), −44.9 (br., 4 H, CH$_3$C$_5$*H*$_4$), 34.5 (br., 2 H, C$_6$H$_4$), 41.3 (br., 2 H, C$_6$H$_4$), 77.0 (br., 16 H, tmeda), 161.5 (br., 3 H, C*H*$_3$C$_5$H$_4$) ppm. ^{15}N{^{1}H} NMR ([D$_8$]THF, 50.70 MHz, 20 °C): δ = −100.4 (br., tmeda) ppm. Raman: $\tilde{\nu}$ = 2067 [s, ν(C=C)] cm^{-1}.

Synthesis of [{(η^1-MeCp)(tmeda)Mn}$_2$(μ-1,4-C$_6$H$_4$(C≡C)$_2$] (10): A benzene solution (10 mL) of 1,4-C$_6$H$_4$(C≡CSnMe$_3$)$_2$ (452 mg, 1.0 mmol) was added to a benzene solution (20 mL) of [Mn(η^1-MeC$_5$H$_4$)$_2$(tmeda)] (659 mg, 2.0 mmol), and the mixture stirred at room temperature for 24 h. The solvent was evaporated in vacuo and the solid residue was washed with pentane (3 × 5 mL). The olive-green solid was redissolved in toluene (5 mL) and pentane (30 mL) was added to obtain light-orange crystals of the title compound at −30 °C (500 mg, 80% yield). C$_{34}$H$_{50}$Mn$_2$N$_4$ (624.68): calcd. C 65.37, H 8.07, N 8.97; found C 65.51, H 8.11, N 8.61. ^{1}H NMR ([D$_8$]THF, 300 MHz, 30 °C): δ = −8.8 (br., 8 H, CH$_3$C$_5$*H*$_4$), 27.2 (br., 4 H, C$_6$H$_4$) ppm. ^{15}N{^{1}H} NMR ([D$_8$]THF, 50.70, 20 °C): δ = −71.3 (br., tmeda) ppm. Raman: $\tilde{\nu}$ = 2071 [s, ν(C=C)] cm^{-1}.

Synthesis of [{(η^5-MeCp)(tmeda)Mn}$_2${μ-4,4′-(C$_6$H$_4$)$_2$(C≡C)$_2$}] (11): A benzene solution (10 mL) of 4,4-(C$_6$H$_4$)$_2$(C≡CSnMe$_3$)$_2$ (528 mg, 1.0 mmol) was added to a benzene solution (20 mL) of [Mn(η^1-MeC$_5$H$_4$)$_2$(tmeda)] (659 mg, 2.0 mmol), and the mixture stirred at room temperature for 24 h. The solvent was evaporated in vacuo and the solid residue was washed with pentane (3 × 5 mL). The olive-green solid was redissolved in toluene (5 mL) and pentane (30 mL) was added to obtain light-orange crystals of complex **11** at −30 °C (500 mg, 80% yield). C$_{34}$H$_{50}$Mn$_2$N$_4$ (624.68): calcd. C 65.37, H 8.07, N 8.97; found C 65.51, H 8.11, N 8.61. ^{1}H NMR ([D$_8$]THF, 300 MHz, 30 °C): δ = −8.8 (br., 8 H, CH$_3$C$_5$*H*$_4$), 27.2 (br., 4 H, C$_6$H$_4$) ppm. ^{15}N{^{1}H} NMR ([D$_8$]THF, 50.70 MHz,

Table 2. Crystallograhic details for **3** and **5−7**

	3	5	6	7
Empirical formula	C$_{20}$H$_{28}$MnN$_2$	C$_{19}$H$_{32}$MnN$_2$Si	C$_{22}$H$_{28}$MnN$_2$	C$_{20}$H$_{34}$MnN$_2$Si$_2$
Formula mass	351.38	371.50	375.40	413.61
Color	yellow block	pale yellow block	yellow block	olive-green plate
Crystal size [mm]	0.30 × 0.52 × 0.51	0.53 × 0.58 × 0.73	0.28 × 0.40 × 0.72	0.26 × 0.41 × 0.52
T [K]	183(2)	183(2)	183(2)	183(2)
λ(Mo-K_α) [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/a$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a [Å]	13.0770(9)	10.0023(10)	11.4503(8)	12.9613(4)
b [Å]	11.4899(9)	11.8147(7)	16.0633(10)	29.8420(11)
c [Å]	13.6328(10)	19.0675(12)	12.0656(8)	12.9613(4)
β [°]	102.489(8)	90	112.112(8)	90.056(7)
V [Å^3]	1999.9(3)	2253.3(3)	2056.0(2)	5013.3(3)
Z	4	4	4	8
$\rho_{\text{calcd.}}$ [g·cm^{-3}]	1.167	1.095	1.213	1.096
μ [mm^{-1}]	0.661	0.640	0.648	0.627
F(000)	748	796	796	1768
Transmission range	0.8471−0.7555	0.7794−0.7135	0.8412−0.6702	0.8560−0.7807
θ range [°]	$6.02 \le 2\theta \le 60.92$	$5.74 \le 2\theta \le 60.68$	$6.24 \le 2\theta \le 60.66$	$4.44 \le 2\theta \le 56.04$
Measured reflections	20820	25415	21358	39994
Unique reflections	5973	6693	6116	11802
$I > 2\sigma(I)$ reflections	2985	4339	4120	9231
Parameters	213	219	231	472
Gof (for F^2)	1.026	1.140	1.096	1.078
R_1 [$I > 2\sigma(I)$],[a] R_1 (all data)	0.0410, 0.0898	0.0367, 0.0667	0.0426, 0.0682	0.0344, 0.0472
wR_2 [$I > 2\sigma(I)$],[b] wR_2 (all data)	0.0730, 0.0784	0.0573, 0.0598	0.1040, 0.1101	0.0637, 0.0653
$\Delta\rho_{\text{max/min}}$	0.548/−0.448	0.455/−0.458	0.569/−0.588	0.423/−0.263

[a] $R1 = \Sigma(F_o - F_c)/\Sigma F_o$; $I > 2\sigma(I)$. [b] $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

Table 3. Crystallographic details of **8−11**

	8	**9**	**10**	**11**
Empirical formula	$C_{30}H_{48}Mn_2N_2$	$C_{171}H_{240}Mn_8N_{16}$	$C_{34}H_{50}Mn_2N_4$	$C_{40}H_{54}Mn_2N_4$
Molecular mass	546.58	2959.31	624.66	700.75
Color	olive-green block	olive-green block	yellow plate	yellow plate
Crystal size [mm]	0.22 × 0.25 × 0.26	0.26 × 0.45 × 0.57	0.05 × 0.30 × 0.39	0.06 × 0.13 × 0.25
T [K]	183(2)	183(2)	173(2)	173(2)
λ(Mo-K_α) [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a [Å]	14.1396(11)	14.4364(10)	7.7597(7)	7.9877(6)
b [Å]	14.0700(7)	18.3976(14)	15.2611(11)	11.9903(9)
c [Å]	15.6110(10)	16.2726(16)	14.5355(13)	20.5803(18)
β [°]	95.988(9)	90.573(10)	98.399(10)	100.599(10)
V [Å^3]	3088.8(3)	4321.7(6)	1702.9(2)	1937.4(3)
Z	4	1	2	2
$\rho_{\text{calcd.}}$ [g·cm^{-3}]	1.175	1.137	1.218	1.201
μ [mm^{-1}]	0.836	0.615	0.768	0.683
F(000)	1168	1578	664	744
Transmission range	0.8635−0.8027	0.7707−0.6799	0.9641−0.7524	0.9660−0.8194
θ range [°]	$6.00 \le 2\theta \le 60.70$	$4.36 \le 2\theta \le 51.94$	$5.34 \le 2\theta \le 55.78$	$3.94 \le 2\theta \le 51.82$
Measured reflections	36111	36990	14209	11833
Unique reflections	8653	7999	4045	3604
$I > 2\sigma(I)$ reflections	4263	2050	1920	1464
Parameters	303	262	186	213
Gof (for F^2)	0.908	1.302	1.024	0.840
R_1 [$I > 2\sigma(I)$],[a] $R1$ (all data)	0.0378, 0.0913	0.1503, 0.2700	0.0383, 0.0981	0.0559, 0.1380
wR_2 [$I > 2\sigma(I)$],[b] wR_2 (all data)	0.0539, 0.0577	0.3464, 0.3728	0.0567, 0.0596	0.0760, 0.0837
$\Delta\rho_{\text{max/min}}$	0.531/−0.540	0.890/−0.619	0.288/−0.707	0.665/−0.686

[a] $R1 = \Sigma(F_o - F_c)/\Sigma F_o$; $I > 2\sigma(I)$. [b] $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

20 °C): $\delta = -71.3$ (br., tmeda) ppm. Raman: $\tilde{\nu} = 2071$ [s, ν(C≡C)] cm^{-1}.

X-ray Diffraction Studies on 3 and 5−11: Crystals of **3** and **5−11**, protected in hydrocarbon oil, were selected for the X-ray experiments using a polarizing microscope. They were mounted on the tip of a glass fibre and immediately transferred to the goniometer of an imaging plate detector system (Stoe IPDS diffractometer), where they were cooled to 183(2) K [**10** and **11** 173(2) K] using an Oxford Cryogenic System. The crystal−image distances were set to 50 mm (**3**, **5**, **6**, and **8**), 60 mm (**7** and **10**), and 70 mm (**9** and **11**) (θ_{max} = 30.46, 30.34, 30.33, 30.35, 28.02, 27.89, 25.97 and 25.91° for **3** and **5−11**, respectively). The φ-rotation (**3**, **6**) or φ-oscillation (**5**, **7−11**) scan modes were applied according to the diffraction power of the measured crystals. For the cell-parameter refinements 7998 (**5**), 8000 (**3**, **6−10**) or 4287 (**11**) reflections were selected out of the whole limiting spheres. A total of 20820 (**3**), 25415 (**5**), 21358 (**6**), 39994 (**7**), 36111 (**8**), 36990 (**9**), 14209 (**10**), and 11833 (**11**) diffraction intensities were collected,[135] of which 5973, 6693, 6116, 11802, 8653, 7999, 4045, and 3604, respectively, were unique (R_{int} = 0.0618, 0.0504, 0.0524, 0.0424, 0.0762, 0.1014, 0.0932, and 0.1190 for **3** and **5−11**, respectively) after data reduction. Numerical absorption corrections[136] based on 16, 20, 12, 19, 15, 22, 6, and 6 crystal faces, respectively, were applied with FACEitVIDEO and XRED.[135] The structures were solved by direct methods (**5**) and by the Patterson method (for the other seven compounds) using the program SHELXS-97.[137] Interpretation of the difference Fourier maps, preliminary plot generations and checking for higher symmetry were performed with PLATON[138] and the implemented program LEPAGE.[139] All heavy atoms were refined (SHELXL-97)[140] using anisotropic displacement parameters, except for disordered atoms in the structures of **5**, **8**, and **9**, which were refined isotropically. The positions of the H atoms were calculated after each refinement cycle (riding model). Structural plots (Figures 1−7) were generated using ORTEP. Further crystallographic data and refinement results are presented in Tables 2 and 3, and Table S1 in the Supporting Information (see also the footnote on the first page of this article). It is noteworthy to mention the difficulties in performing a rapid preparation of the crystals in the protecting oil. Some crystals deteriorated relatively fast at room temperature, and in these cases a Peltier element was used at 253 K to save the crystals during the preparation under polarized light. For the intensity measurements of crystals of **5** and **6** a collimator with 0.80 mm diameter had to be used (see Table 2). For compound **7** two measurements were necessary (the last measurement with 37 h measuring time) to determine that the metrically tetragonal unit cell belongs to the Laue class $P2/m$ (space group $P2_1/c$). Furthermore, a twin refinement with ratio 1:3 was successfully performed using the twin matrix (001, 0−10, −100) for this structure. A detailed description of structure solution and refinement is given in the CIF file of **7**. Compound **9** most probably belongs to a modulated structure type: four very weak intensity peaks were observed between the strong reflection intensities in one reciprocal direction (modulo5). The weak reflections were not used for the unit-cell determination. Application of programmes DISPLA, XYZ, RECIPE, INDEX and CELL[135] resulted in space group $P21/c$. The structure was solved without difficulties; however, anisotropic refinement showed many non-hydrogen atoms to have non-positive definite displacement parameters or indicated many split atomic positions. Thus, most of the atoms were refined with isotropic displacement parameters. It should be noted that only about 25% of the intensity data were observed [$I > 2\sigma(I)$]. Additionally, for a disordered toluene solvent molecule with very large isotropic displacement parameters the site occupation factors were fixed at estimated values of 1/4. For this reason compound **9** has a Z value of 1 and the enlarged chemical formula as given in Table 3. Finally, 45 distance restraints had to be used to stabilize the refinement. The structures of **10** and **11** possess centres of inversion that coincide with crystallographic inversion centres, thus only one half of each complex needed to be refined, resulting in Z values of 2 ($Z' = 1/2$). The crystals of compound **11** were very sensitive to mechanical touch. Due to the thin plate-like crystal (0.25 × 0.13 × 0.06 mm) and the necessity to seal the susceptible crystal of fair quality into a thin-walled glass capillary including protecting oil, the background intensities increased drastically. The centering procedure introduced systematic errors that were probably added to the measured intensity data. Only about 40% of these data were considered observed, which explains the relatively high R_{int} (11.9%) and $R\sigma(I)$ (21.65%) values. The reliability factors of the final refinement [$R1 = 5.59\%$ and $wR2 = 8.37\%$ (all data)] are acceptable, and the standard uncertainties for C−C bond lengths range between 0.005 Å and 0.009 Å, which can be considered as an acceptable result. CCDC-226222 to -226229 (**3**, **5**−**11**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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