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Synthesis and Characterization of Mononuclear and Dinuclear Manganese Bis-acetylide Complexes

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Abstract. The symmetric d^5 *trans*-bis-alkynyl complexes $\{Mn[(Me)_2P(CH_2)_nP(Me)_2]_2(C{\equiv}CC_6H_4R)_2\}$ (n = 2, R = -C≡CTIPS (**2a**); n = 3, R = -C≡CTIPS (**2b**); n = 2, R = F (**4**); n = 3; -C≡CTIPS) were prepared by the reaction of $[Mn(dmpe)_2Br_2]$ with two equivalents of the corresponding acetylide $LiC{\equiv}CC_6H_4R$ (R = F, -C≡CTIPS). The reaction of compounds **2a**, **2b** and **4** with $[Cp_2Fe][PF_6]$ yielded the corresponding d^4 complexes $\{Mn[(Me)_2P(CH_2)_nP(Me)_2]_2(C{\equiv}CC_6H_4R)_2\}[PF_6]$ (n = 2, R = -C≡CTIPS, [**2a**]$^+$; n = 3, R = -C≡CTIPS, [**2b**]$^+$; n = 2, R = F, [**4**]$^+$; n = 3; -C≡CTIPS). The unsymmetrically substituted *trans*-iodo-alkynyl complex $[IMn(dmpe)_2(C{\equiv}CC_6H_4\text{-}C{\equiv}CTIPS)]$ (**5**) was obtained by treating MeCpMn(dmpe)I with one equivalent of $H\text{-}C{\equiv}CC_6H_4\text{-}C{\equiv}CTIPS$ in the presence of dmpe. Deprotection of the TIPS group with TBAF gave complex $[IMn(dmpe)_2(C{\equiv}CC_6H_4C{\equiv}CH)]$ (**6**) in 94 % yield. The neutral dinuclear complexes Mn^{II}/Mn^{II} compounds $\{[Mn((Me)_2P(CH_2CH_2)P(Me)_2)_2(C{\equiv}CC_6H_4R)]_2(\mu\text{-}C_4)\}$ (R = H, Me, n-pentyl, F) were prepared by the direct reaction of $\{[Mn((Me)_2P(CH_2CH_2)P(Me)_2)_2I]_2(\mu\text{-}C_4)\}$ with the corresponding $LiC{\equiv}CC_6H_4R$ (R = H, n-pentyl, F). These Mn^{II}/Mn^{II} dinuclear compounds were further oxidized to the mixed-valent complexes and the dicationic complexes using $[Cp_2Fe][PF_6]$. All complexes have been characterized by NMR, IR, and Raman spectroscopy. X-ray diffraction studies were carried out on complexes **1c**, **2a**, **4**, [**4**]$^+$, and **6**.

Introduction

The development of molecular devices requires the preparation of functional materials with suitable properties [1−3]. π-Conjugated "conducting" units containing electrochemically active transition-metal end groups, such as $L_mM\text{-}(C{\equiv}C)_n\text{-}ML_m$ are basic constituents for electronic materials [4−6]. Research into the synthesis and electronic properties of metal alkynyl complexes and polymers continues to develop as a key area of organometallic chemistry [7−17]. Owing to its high stability, ease of functionalization, and well-defined electrochemistry, transition-metal units have been widely used as redox-active centers that are linked together with a wide variety of structural units such as saturated and unsaturated carbon bridges, delocalized fused rings, and polymeric and dendritic backbones [18−56]. In particular, their rigid rod architectures and conjugated backbones have been studied in the field of linear and non-linear optics, liquid crystallinity, and photovoltaic cells [24, 25]. We expect that electronic properties of materials with low energy work functions could be reasonably satisfied by molecular units with electron-rich phosphane substituted manganese end groups and a C_4-spacer [26−29]. In addition to the above reasons, the $L_mMn{-}C_4{-}MnL_m$ systems were selected as target molecules, because a build-up of Mn-di- and oligonuclears seemed to be synthetically feasible by acetylide substitution processes [27]. We have shown through our recent studies that systems of the type $L_mMn{-}C_4{-}MnL_m$ can be achieved by coupling of Mn-C_2 units, such as Mn-alkynyl and Mn-vinylidene moieties. 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 = I, C≡CH, $C{\equiv}C{-}C{\equiv}CSiMe_3$ and n = 0−2), which were either obtained by the reaction of two equivalents of [IMn(MeCp)(dmpe)] [dmpe = 1,2-bis(dimethylphosphanyl)ethane] with $Me_3Sn{-}C_4{-}SnMe_3$ and dmpe and subsequent acetylide substitution, or by an in situ C−C coupling of $[Mn^{III}(dmpe)_2(C{\equiv}CH)(C{\equiv}C)]$ units similar to the Eglinton and McCrae oxidative coupling of acetylenic compounds [26−29]. We had earlier suggested from DFT calculations and experimental evidence that the terminal end group (X) in these kind of complexes $\{[Mn(dmpe)_2(X)]_2(\mu\text{-}C_4)\}^{n+}$ (X = I, C≡CH, $C{\equiv}C{-}C{\equiv}CSiMe_3$ and n = 0−2), have less bearing or influence on the communication between the two metal centers [27]. However, the functionality and reactivity of the terminal end groups does matter considering the fact of further utilizing these molecules for the build up of longer oligonuclear and attaching these molecules to electrode surfaces for single-molecule conductivity measurements [44].

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The solubility of these dinuclear complexes is very much influenced by the substituents on the phosphorus ligand and also on the terminal end groups. Additionally, the substituents on the phosphorus atom have an effect on the redox properties of these kind $[Mn(dmpe)_2(C{\equiv}CSiR_3)X]^+$ of molecules [27]. This insight propelled us to gain access to new dinuclear complexes bearing end groups of the type -C≡C−R (R = H, Me, *n*-pentyl, F).

Results and Discussion

Complexes of the type ML_2X_2 (M = Mn, L = dmpe, X = Br, I) are valuable starting materials for the synthesis of bis-acetylide complexes by simple addition of lithium acetylides [57−59]. It is well known from previous studies that substituents on the phosphorus ligands have a significant effect on the redox properties [27]. Hence the manganese complexes **1b** and **1c** bearing a dmpp [dmpp = 1,3-bis(dimethylphosphanyl)propane] ligand were synthesized starting from manganese iodide or manganese bromide. Both complexes were isolated in excellent yields. The ^{1}H NMR spectrum of **1b** showed broad resonances for the protons in a more downfield region at around 40.9 (PCH_2), 32.4 $[P(CH_3)_2]$, 11.6 (PCH_2CH_2) ppm than the **1c** complexes which had resonances at 18.9 and 4.6 ppm for the methylene and methyl protons. The structure of complex **1c** was unequivocally established by an X-ray diffraction study (Figure 1).

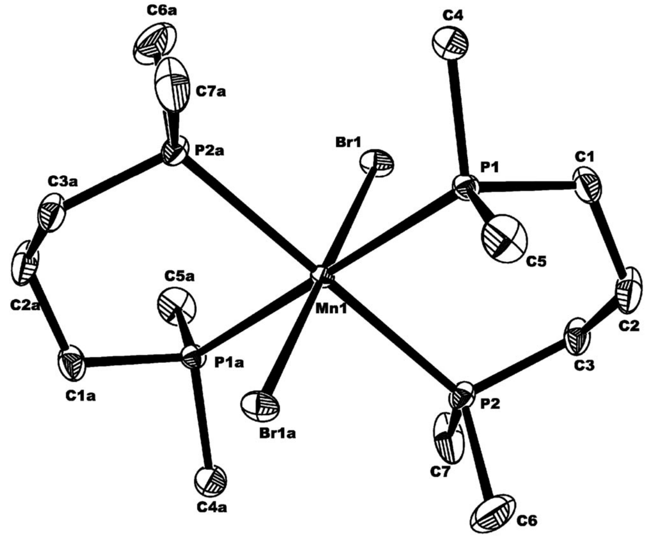
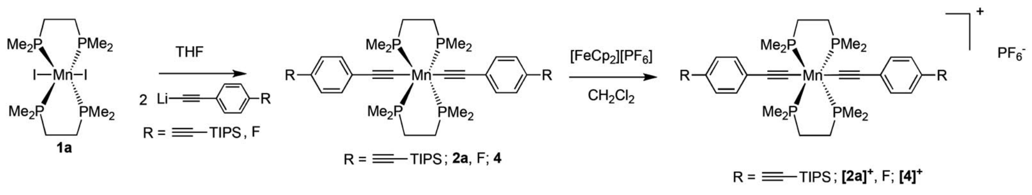


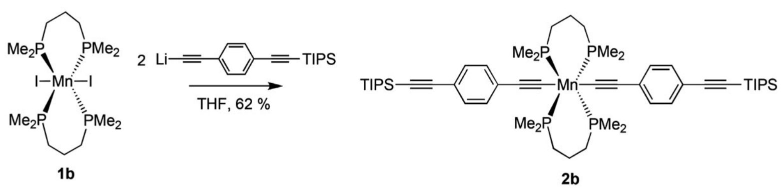
Figure 1. Molecular structure of **1c** with displacement ellipsoids drawn at the 50 % probability level (all hydrogen atoms are omitted for clarity). The atoms labeled with the suffix a are generated by the symmetry operation (−*x*, 1−*y*, −*z*). Selected bond lengths /Å and angles /°: Mn1−Br1 2.6512(5), Mn1−P1 2.6718(11); Br1−Mn1−Br1a 180.0, Br1−Mn1−P1 87.38.

Paramagnetic d^5 *trans*-bis-alkynyl manganese compounds $[Mn((Me)_2P(CH_2)_nP(Me)_2)_2(C{\equiv}CC_6H_4R)_2]$ [$n = 2$, R = -C≡CTIPS, (**2a**); $n = 3$, R = -C≡CTIPS (**2b**); $n = 2$, R = F (**4**)] can be prepared by the reaction of $\{Mn[(Me)_2P(CH_2)_nP(Me)_2]_2I_2\}$ ($n = 2$, **1a**; $n = 3$, **1b**) with two equivalents of LiC≡CR (R = -C≡CTIPS, R = F) (Scheme 1, 2). Similar kinds of complexes were obtained by two other methods by the reaction of $[MnCp_2]$ (Cp = C_5H_5, C_5H_4Me) with two equivalents of $EC{\equiv}CSiR_3$ (E = H, $SnMe_3$) in the presence of dmpe or by SiR_3 metathesis [27, 28]. However, the yields were far better using the former method. All the derivatives **2a**, **2b** and **4** are soluble in nonpolar solvents such as pentane, Et_2O etc. The ^{1}H NMR spectra of **2a** and **2b** showed a broad signal at 17.6 and −2.8 ppm for the aromatic protons. The protons of the dmpe and dmpp in **2a** and **2b** appeared as a broad signal at −15.6. These values are characteristic for these types of low spin d^5 complexes. The Si*i*Pr$_3$ groups of **2a** and **2b** were identified as broad resonances at 1.3 ppm.

The structure of complexes **2a** (Figure 2) and **4** (Figure 3) was established by X-ray diffraction studies. Complex **2a** crystallizes either in an orthorhombic (**2a-1**) or in a triclinic (**2a-2**) system. Figure 2 shows the molecular structure of **2a-1**. The metal exhibits a pseudo-octahedral coordination with both acetylide ligands in *trans* positions, and the four



Scheme 1.



Scheme 2.

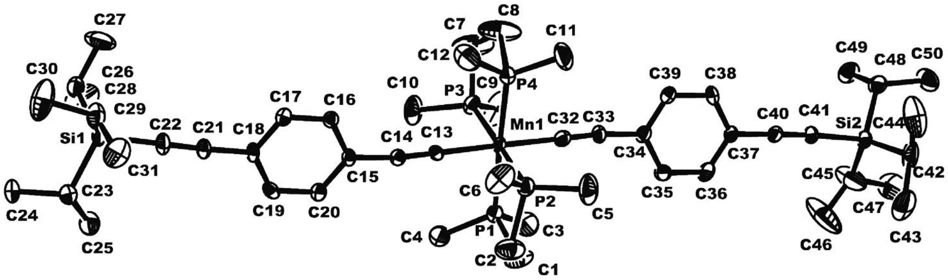


Figure 2. Molecular structure of **2a-1** with displacement ellipsoids drawn at the 30 % probability level (all hydrogen atoms are omitted for clarity). Selected bond lengths /Å and angles /°: Mn1−C13 1.985(5), Mn1−C32 1.999(6), C13−C14 1.182(6), C21−C22 1.209(6), C32−C33 1.184(7), C40−C41 1.202(6), C22−Si1 1.854(6), C41−Si2 1.854(6); C32−Mn1−C13 179.0(3).

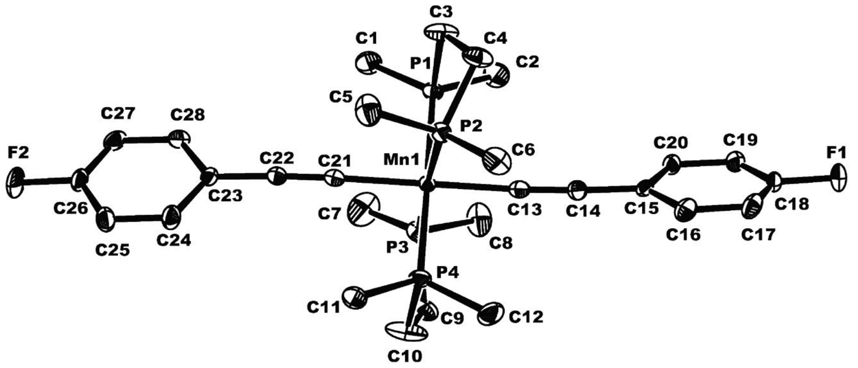


Figure 3. Molecular structure of **4** with displacement ellipsoids drawn at the 30 % probability level (all hydrogen atoms are omitted for clarity). Selected bond lengths /Å and angles /°: Mn1−C13 1.952(3), C13−C14 1.227(4), C21−C22 1.217(4); C13−Mn1−C21 179.84(15).

phosphorous atoms defining an equatorial plane. The C≡C bond in **2a-1** is 1.182(6) Å for C13−C14 and 1.184(7) Å for C32−C33 similar to that found in related complexes [27].

Compounds **2a** and **4** were treated with $[FeCp_2][PF_6]$ to give the oxidized complexes $[\mathbf{2a}]^+$ and $[\mathbf{4}]^+$ in high yields. The ^1H NMR spectrum of $[\mathbf{2a}]^+$ showed a significant shift in the resonances of the phenyl protons to 39.9 and −58.3 and of methyl and methylene protons to −29.1 and −38.6 ppm, respectively. The solid-state structure of $[\mathbf{4}]^+$ was also determined by an X-ray diffraction study (Figure 4).

The deprotection of the TIPS group in $[\mathbf{2a}]^+$ with $[Bu_4N]F^-$ (5 % H_2O) gave the neutral Mn^{II} compound **3a** in 60 % yield (Scheme 3). The ^1H NMR spectrum revealed resonances characteristic of the acetylide protons at δ = 2.51 as a singlet. The resonances for the aromatic protons and dmpe protons appear at 17.0 and −2.9 ppm and −14.8 ppm, respectively. These signals are characteristic for paramagnetic Mn^{II} complexes [29]. This complex is unique in the sense that it has two reactive end groups that can be

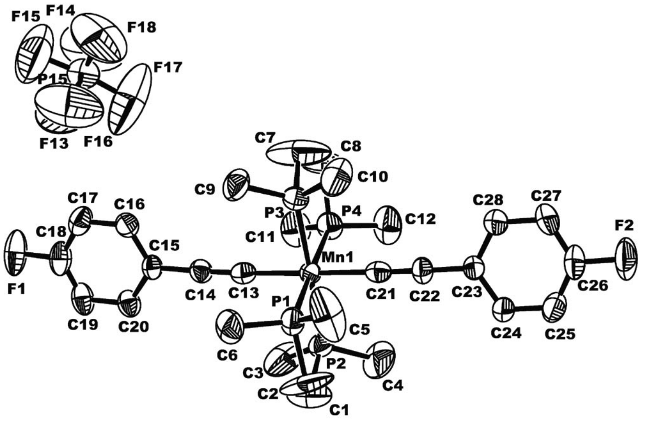
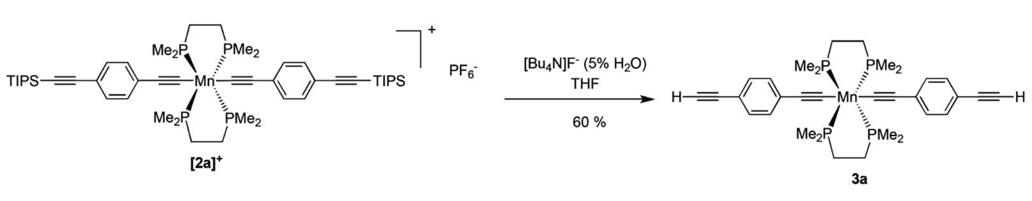


Figure 4. View of the molecular structure of one of the three crystallographically independent molecules of $[\mathbf{4}]^+$ with displacement ellipsoids drawn at the 30 % probability level (all hydrogen atoms are omitted for clarity). Selected average bond lengths /Å and angles /°: Mn1−C_α 1.943, C_α−C_β 1.229; C_α−Mn1−C_α 178.0.



Scheme 3.

further used to access oligonuclears in a precise fashion. Compound **3a** was oxidized to the Mn^{III} using $[FeCp_2][PF_6]$ in 92 % yield.

Thus far, we had described the synthesis of unsymmetrically substituted *trans*-bis-alkynyl manganese complexes using manganese vinylidene complexes as starting materials. Another seemingly convenient route for obtaining the required asymmetrically substituted Mn^{II} *trans*-bis-alkynyl manganese complexes might be envisaged as the stepwise substitution of dihalo complexes $[Mn(dmpe)_2X_2]$(X = Br, I) through the intermediacy of appropriate monoacetylide species *trans*-$[Mn(dmpe)_2(X)(C{\equiv}CR)]$ (X = Br, I; R = H, SiR_3) [27]. However, these *trans*-halo-alkynyl manganese compounds could not be prepared by this route; all attempts invariably led to ligand proportionation with mixtures of the corresponding $[Mn(dmpe)_2X_2]$ (X = Br, I) and $[Mn(dmpe)_2(C{\equiv}CR)_2]$ complexes.

As an alternative, conversion of the complex $[Mn(MeC_5H_4)(dmpe)I]$ with $H{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}CTIPS$ and dmpe was considered, which indeed yielded the expected d^5 paramagnetic *trans*-iodo-alkynyl compound $[Mn(dmpe)_2(C{\equiv}CC_6H_4{-}C{\equiv}CTIPS)]$ (**5**) isolated as a pure red brown solid in 73 % yield. The ^1H NMR spectrum of **5** in C_6D_6 shows resonances at = 18.9 and −1.6 ppm for the aromatic protons and broad signal at −17.2 ppm for the methyl and methylene protons of the dmpe. Further reaction of **5** with TBAF (5 % H_2O) yielded the alkyne terminated compound $[Mn(dmpe)_2(C{\equiv}C{-}C_6H_4{-}C{\equiv}CH)]$ (**6**) in 94 % yield (Scheme 4). The structure of **5** was confirmed by single-crystal X-ray diffraction (Figure 5). The manganese center is in a pseudo-octahedral environment, with the alkynyl and iodo ligands in a *trans* arrangement. The C13−C14 and Mn−C13 distances of 1.212(4) and 1.937(3) Å and the Mn−I distance of 2.7198(4) Å compare well with the corresponding parameters found for related $[Mn(dmpe)_2(alkynyl)_2]$ species and the Mn−C13−C14 angle [178.9(3)°] is practically linear as in numerous other $L_nM{-}C{\equiv}CR$ arrangements [26−29].

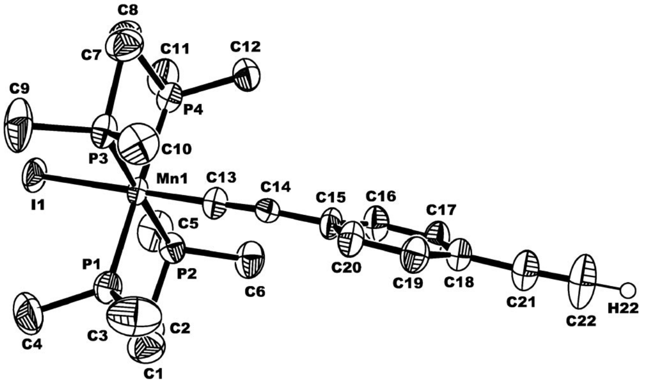
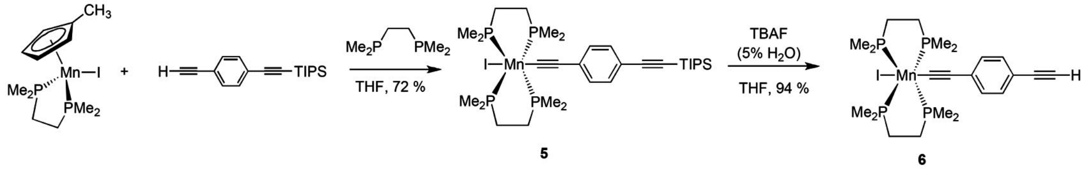


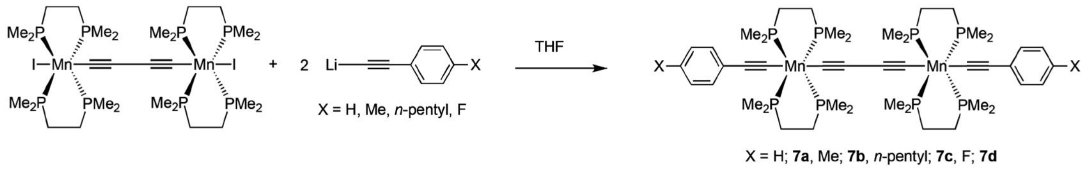
Figure 5. Molecular structure of **6** with displacement ellipsoids drawn at the 50 % probability level (all hydrogen atoms except H22 are omitted for clarity). Selected bond lengths /Å and angles /°: Mn1−C13 1.905(5), I1−Mn1 2.7296(8), C13−C14 1.218(5), C21−C22 1.194(9); C3−Mn1−I1 176.73(16), C14−C13−Mn1 176.3(4).

Preparation of [Mn]−C_4-[Mn] rigid-rod species: We reported the carbon−carbon coupling of two molecules of $[Mn(dmpe)_2(C{\equiv}CH)][PF_6]$ establishing a dinuclear Mn−C_4−Mn unit [27]. In this paper, we utilized simple metathesis reaction involving addition of various lithium acetylides to the I−Mn−C_4−Mn−I fragment thereby developing dinuclear complexes with different end groups (Scheme 5). Addition of two equivalents of the $LiC{\equiv}CC_6H_4X$ (X = H, Me, *n*-pentyl, F) to $\{[Mn(dmpe)_2I]_2(\mu\text{-}C_4)\}$ gave in good yields the corresponding alkyne terminated dinuclear complexes $\{[Mn(dmpe)_2(C{\equiv}CC_6H_4X)]_2(\mu\text{-}C_4)\}$ [X = H (**7a**); Me (**7b**); *n*-pentyl (**7c**); F (**7d**)]. The ^1H NMR spectrum of the compounds **7a−d** show broad resonances between 15 to 16 ppm and −4 to −5 ppm for the aromatic protons. The signals for the dmpe protons appear between −15 and −16 ppm. In a quantitative fashion, the paramagnetism of complexes **7a−d** was confirmed by the temperature dependence of the ^1H NMR spectra. The chemical shifts in the temperature range −70 to 20 °C follow Curie-Weiss behavior.

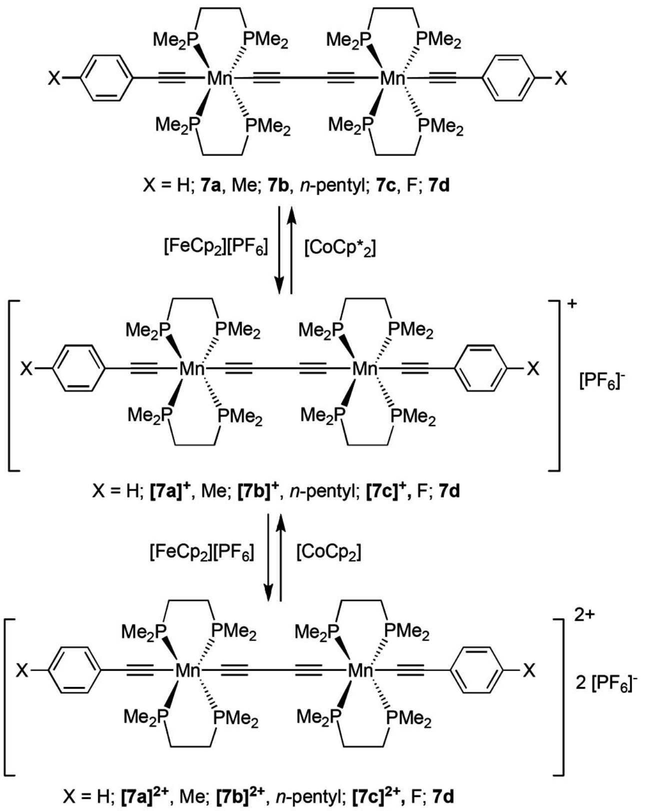
The redox-active neutral compounds **7a−d** can be oxidized further to the corresponding mixed-valent complexes $[\mathbf{7a{-}d}]^+$ and the dicationic species $[\mathbf{7a{-}d}]^{2+}$ applying one



Scheme 4.



Scheme 5.



Scheme 6.

or two equivalents of $[Cp_2Fe][PF_6]$ (Scheme 6). Both the mono- and dicationic complexes are soluble in only polar solvents such as THF and CH_2Cl_2. In striking contrast to the diamagnetic $Mn^{III}-C_4-Mn^{III}$ compounds reported earlier with silylacetylenyl end groups [26, 27], the ^{1}H NMR spectra of **[7a−d]**$^{2+}$ displayed paramagnetic resonances with shifted downfield aromatic protons and shifted upfield protons of the dmpe ligand in comparison with the mixed-valent complexes [**7a**−**d**]$^+$ and the neutral species [**7a**−**d**].

Conclusions

A series of Mn^{II} and Mn^{III} symmetric complexes of the type $\{Mn[(Me)_2(CH_2)_x(Me)_2]_2(C\equiv CC_6H_4R)_2\}^{n+}$ (X = 2, 3; R = -C≡CTIPS; F; *n* = 0, 1) has been prepared. The reaction of the symmetrically substituted *trans*-bis-alkynyl d^4 manganese complexes produce with one equivalent of TBAF the desilylated complex $\{Mn[(Me)_2P(CH_2)_2P(Me)_2]_2(C\equiv CC_6H_4-C\equiv CH)_2\}$. The asymmetric *trans*-iodoalkynyl complex $\{IMn[(Me)_2(CH_2)_2(Me)_2]_2(C\equiv CC_6H_4-C\equiv CTIPS)\}$ which is obtained by the reaction of $(CH_3C_5H_4Mn(dmpe)I)$ with $HC\equiv CC_6H_4-C\equiv CTIPS$ and dmpe, reacts with TBAF to yield the corresponding alkyne terminated complex $\{IMn[(Me)_2P(CH_2CH_2)P(Me)_2]_2(C\equiv CC_6H_4-C\equiv CH)\}$. Dinuclear manganese complexes were prepared in a straightforward fashion by the reaction of $\{[Mn(dmpe)_2I]_2(\mu\text{-}C_4)\}$ with $LiC\equiv CC_6H_4R$. All these complexes exhibit characteristic paramagnetic behaviour. The obtained mononuclear monofunctionalized acetylide manganese complexes are envisaged to be valuable starting materials for the construction of trinuclear or oligonuclear compounds.

Experimental Section

General: All operations were carried out under nitrogen using Schlenk and vacuum-line techniques or in a glove box, model MB-150 B-G. The following solvents were dried and purified by distillation under nitrogen before use, employing appropriate drying/deoxygenating agents: tetrahydrofurane (Na/benzophenone), toluene (sodium), CH_2Cl_2 (P_2O_5, with filtration through active Alox). IR spectra were obtained with a Bio-Rad FTS instrument. Raman spectra were recorded with a Renishaw Ramanscope spectrometer (514 nm). EPR measurements were made with MPMS-5 S and PPMS-6000 instruments. ^{1}H NMR spectra were recorded with Unity 300 or Varian Gemini 200 spectrometers at 300 or 200 MHz, respectively. ^{1}H NMR chemical shifts are reported in ppm units with respect to the signals of residual protons in the solvents and referenced to TMS. C and H elemental analysis were carried on with a LECO CHN-932 microanalyzer.

{*trans*-Bis[1,2-bis(dimethylphosphanyl)propane]diiodomanganese(II)}, [MnI$_2$(dmpp)$_2$] (1b): Anhydrous MnI_2 (618 mg, 2.00 mmol) was suspended in THF (20 mL) and dmpp (657 mg, 4.00 mmol) was added. The reaction mixture was stirred for 12 h after which the resulting colorless solution was filtered through Celite and the solvents were evaporated under vacuum to give a colorless powder. Crystallization at −30 °C in THF gave single crystals suitable for a X-ray diffraction study. Yield 1.24 g (1.94 mmol, 96 %). $C_{14}H_{36}I_2MnP_4$ (637.08): calcd. C 26.39, H 5.70; found C 26.54, H 5.62. **^{1}H NMR** ([D$_8$]THF, 200 MHz, 19 °C): δ = 40.9 (s, 8 H, PCH_2), 32.4 [s, 24 H, $P(CH_3)_2$], 11.6 (s, 4 H, PCH_2CH_2).

{*trans*-Bis[1,2-bis(dimethylphosphanyl)propane]dibromomanganese(II)}, [MnBr$_2$(dmpp)$_2$] (1c): dmpp (657 mg, 4.00 mmol) was added to $MnBr_2\cdot 2THF$ (718 mg, 2.00 mmol) in THF (20 mL). The reaction mixture was stirred for 12 h after which the resulting colorless solution was filtered through Celite and the solvents were evaporated under vacuum to give a colorless powder. Crystallization at −30 °C in THF gave single crystals suitable for a X-ray diffraction study. Yield. 1.03 g (1.90 mmol, 95 %). $C_{14}H_{36}Br_2MnP_4$ (543.08): calcd. C 30.96, H 6.68; found C 30.66, H 6.91. **^{1}H NMR** ([D$_8$]THF, 200 MHz, 20 °C): δ = 18.9 [s, 32 H, $(CH_3)_2PCH_2$], 4.6 (s, 4 H, PCH_2CH_2).

{*trans*-Bis[1,2-bis(dimethylphosphanyl)ethane]bis[(4-(triisopropylsilyl)ethynyl)phenylethynyl]manganese(II)}, {[TIPS−C≡C−C$_6$H$_4$−C≡C]$_2$(dmpe)$_2$Mn} (2a): Butyllithium (1.6 M) in hexane (625 µL, 1.00 mmol) was added to $TIPS-C\equiv C-C_6H_4-C\equiv C-H$ (282.5 mg, 1.00 mmol) in THF (15 mL). The reaction mixture was slowly warmed to room temperature, before being cooled to −30 °C. After 30 min the cooled solution of $TIPS-C\equiv C-C_6H_4-C\equiv C-Li$ was added dropwise to $[Mn^{I}_2(dmpe)_2]$ (304 mg, 0.50 mmol) in THF (10 mL) at −30 °C. The reaction mixture was stirred at room temperature for 1 h and was evaporated under vacuum to yield a red brown solid. The solid was extracted with pentane (5 × 10 mL), filtered through Celite and the solvent was evaporated under vacuo to give a solid. Yield 449 mg (0.489 mmol, 98 %). Crystallization at −30 °C in pentane gave single crystals suitable for an X-ray diffraction study.

$C_{50}H_{82}MnP_4Si_2$ (918.19): calcd. C 65.40, H 9.00; found C 65.23, H 8.74. **^{1}H NMR** ($[D_8]$THF, 200 MHz, 20 °C): δ = 17.2 (s, 4 H, Ar*H*$_m$), 1.2 {s, 6 H, Si[C*H*(CH$_3$)$_2$]$_3$}, 1.08 {s, 36 H, Si[CH(C*H*$_3$)$_2$]$_3$}, −3.0 (s, 4 H, Ar*H*$_o$), −14.7 [s, 32 H, C*H*$_2$P(C*H*$_3$)$_2$]. **Raman**: ν(TIPS−*C≡C*) = 2147 (m), ν(*C≡C*−Mn) = 2022 (m), ν(*C=C*)$_{\text{Ar}}$ = 1591 (vs), ν(*C=C*)$_{\text{Ar}}$ = 1171 (s), ν(*P−C*) = 946 (m), ν(HC=*CH*)$_{\text{Ar}}$ = 836 (m), ν(*Mn−C*) = 650 (m), ν(*Mn−P*) = 345 (s) cm^{-1}. **IR** (KBr): ν(*C−H*) = 2942 (s), 2902 (s), 2864 (s), ν(TIPS−*C≡C*) = 2146 (m), ν(*C≡C*−Mn) = 1998 (vs), ν(*C=C*)$_{\text{Ar}}$ = 1589 (s), ν(*P−C*) = 995 (w), 936 (s), δ(HC=*CH*)$_{\text{Ar}}$ = 835 (s) cm^{-1}.

{*trans*-Bis[1,2-bis(dimethylphosphanyl)propane]bis[(4-triisopropylsilylethynyl)phenylethynyl]manganese(II)}, {[TIPS−C≡C−C_6H_4−C≡C]$_2$(dmpp)$_2$Mn} (2b): Butyllithium (1.6 M) in hexane (625 µL, 1.00 mmol) was added to 1-ethynyl-4-(triisopropylsilyl)ethynylbenzene (283 mg, 1.00 mmol) in THF (15 mL) at −30 °C. The reaction mixture was slowly warmed to room temperature, before being cooled again to −30 °C. After 30 min the cooled TIPS−C≡C−C_6H_4−C≡C−Li was added dropwise to [Mn$^{\text{I}}{}_2$(dmpp)$_2$] (319 mg, 0.50 mmol) in THF (10 mL) at −30 °C. The reaction mixture was stirred at room temperature for 1 h and was evaporated under vacuo to yield a red brown solid. The solid was extracted with pentane (5 × 10 mL), filtered through Celite and the solvent was evaporated under vacuum to give a dark red solid. Yield 304 mg (0.321 mmol, 64 %). $C_{52}H_{86}MnP_4Si_2$ (946.24): calcd. C 66.00, H 9.16; found C 65.71, H 8.91. **^{1}H NMR** (C_6D_6, 200 MHz, 22 °C): δ = 17.6 (s, 4 H, Ar*H*$_m$), 1.3 {s, 6 H, Si[C*H*(CH$_3$)$_2$]$_3$}, 1.10 {s, 36 H, Si[CH(C*H*$_3$)$_2$]$_3$}, −2.8 (s, 4 H, Ar*H*$_o$), −15.6 [s, 32 H, C*H*$_2$P(C*H*$_3$)$_2$]. **IR** (KBr): ν(*C−H*) = 2940 (s), 2903 (s), 2863 (s), ν(TIPS−*C≡C*) = 2142 (m), ν(*C≡C*−Mn) = 1992 (s), ν(*C=C*)$_{\text{Ar}}$ = 1586 (vs), δ(*CH*$_2$) = 1410 (m), ν(*P−C*) = 994 (w), 933 (s), δ(*HC=CH*)$_{\text{Ar}}$ = 831 (vs) cm^{-1}.

{*trans*-Bis[1,2-bis(dimethylphosphanyl)ethane]-bis[(4-triisopropylsilylethynyl)phenylethynyl]manganese(III)} Hexafluorophosphate, {[TIPS−C≡C−C_6H_4−C≡C]$_2$(dmpe)$_2$Mn}[PF$_6$], [2a]$^+$: Compound **2a** (275 mg, 0.30 mmol) and [Cp$_2$Fe][PF$_6$] (100 mg, 0.30 mmol) were added to CH$_2$Cl$_2$ (10 mL) and the reaction mixture was stirred at room temperature for 30 min. Afterwards, the solvent was removed under vacuo, was washed with pentane (8 × 5 mL) and subsequently with diethyl ether (3 × 5 mL). The remaining solid was dissolved in THF (15 mL), filtered through Celite and the solvents were evaporated under vacuum to give a dark green solid. Yield 309 mg (0.291 mmol, 97 %). $C_{50}H_{82}F_6MnP_5Si_2$ (1063.15): calcd. C 56.49, H 7.77; found C 56.70, H 7.49. **^{1}H NMR** ($[D_8]$THF, 200 MHz, 22 °C): δ = 39.9 (s, 4 H, Ar*H*$_m$), 1.14 {s, 42 H, Si[C*H*(C*H*$_3$)$_2$]$_3$}, −29.1 (s, 8 H, PC*H*$_2$), −38.6 [s, 24 H, P(C*H*$_3$)$_2$], −58.3 (s, 4 H, Ar*H*$_o$). ***((≤Author: please check spectroscopic data.))*** **^{19}F NMR** ($[D_8]$THF, 188.16 MHz, 20 °C): δ = −75.8 (d, $^1J_{\text{FP}}$ = 714 Hz, 6 F, P*F*$_6$). **^{31}P NMR** (CD$_2$Cl$_2$, 80.95 MHz, 22 °C): δ = −143.9 (sept, $^1J_{\text{PF}}$ = 716 Hz, 1 P, *P*F$_6$). **Raman**: ν(TIPS−*C≡C*) = 2147 (w), ν(*C≡C*−Mn) = 2030 (vs), ν(*C=C*)$_{\text{Ar}}$ = 1589 (vs), ν(*C=C*)$_{\text{Ar}}$ = 1171 (s), ν(HC=*CH*)$_{\text{Ar}}$ = 837 (w), ν(*Mn−C*) = 652 (w), ν(*Mn−P*) = 340 (w) cm^{-1}. **IR** (KBr): ν(*C−H*) = 2942 (s), 2864 (s), ν(TIPS−*C≡C*) = 2152 (m), ν(*C≡C*−Mn) = 2033 (m), ν(*C=C*)$_{\text{Ar}}$ = 1626 (m), ν(*P−C*) = 996 (w), 944 (s), δ(HC=*CH*)$_{\text{Ar}}$ = 838 (s) cm^{-1}.

{*trans*-Bis[1,2-bis(dimethylphosphanyl)ethane]-bis[(4-ethynyl)phenylethynyl]manganese(II)}, {[HC≡C−C_6H_4−C≡C]$_2$ (dmpe)$_2$Mn} (3a): TBAF (1 M) in THF (5 % H$_2$O, 0.2 mL, 0.2 mmol) was added to **[2a]**$^+$ (213 mg, 0.2 mmol) in THF (15 mL) at room temp. The reaction mixture was stirred at that temperature for 1 h during which the color changed from deep green to dark red. The solvent was evaporated under vacuum to give a solid. The solid was washed with diethyl ether (10 mL) and extracted with toluene (3 × 5 mL) and filtered through Celite. The solvent was evaporated to give a red brown solid. Yield 75 mg (0.124 mmol, 62 %). $C_{32}H_{42}MnP_4$ (605.51): calcd. C 63.47, H 6.99; found C 63.15, H 7.31. **^{1}H NMR** ($[D_8]$THF, 200 MHz, 22 °C): δ = 17.0 (s, 4 H, Ar*H*$_m$), 2.31 (s, 2 H, C≡C*H*), −2.9 (s, 4 H, Ar*H*$_o$), −14.8 [s, 32 H, C*H*$_2$P(C*H*$_3$)$_2$]. **Raman**: ν(H−*C≡C*) = 2100 (m), ν(*C≡C*−Mn) = 2010 (m), ν(*C=C*)$_{\text{Ar}}$ = 1593 (vs), ν(*C=C*)$_{\text{Ar}}$ = 1166 (s), ν(*P−C*) = 948 (m), ν(HC=*CH*)$_{\text{Ar}}$ = 816 (m), ν(*Mn−C*) = 649 (m), ν(*Mn−P*) = 342 (s) cm^{-1}. **IR** (KBr): ν(*H−C*≡C) = 3308 (m), ν(*C−H*) = 2962 (m), 2902 (m), ν(H−*C≡C*) = 2100 (w), ν(*C≡C*−Mn) = 1992 (vs), ν(*C=C*)$_{\text{Ar}}$ = 1589 (s), ν(*P−C*) = 941 (m), δ(HC=*CH*)$_{\text{Ar}}$ = 841 (m) cm^{-1}.

{*trans*-Bis[1,2-bis(dimethylphosphanyl)ethane]-bis[(4-ethynyl)phenylethynyl]manganese(III)} Hexafluorophosphate, {[HC≡C−C_6H_4−C≡C]$_2$(dmpe)$_2$Mn}[PF$_6$], [3a]$^+$: CH$_2$Cl$_2$ (10 mL) was added to **3a** (182 mg, 0.30 mmol) and [Cp$_2$Fe][PF$_6$] (100 mg, 0.30 mmol) and the reaction mixture was stirred for 30 min. The color changed from deep red to dark green during this time. The reaction mixture was evaporated under vacuo and washed with pentane (8 × 5 mL) and ether (3 × 5 mL). The solid was extracted with THF (15 mL), filtered through Celite and the solvents were evaporated under vacuum to give a green solid. Yield 207 mg (0.276 mmol, 92 %). $C_{32}H_{42}F_6MnP_5$ (750.47): calcd. C 51.21, H 5.64; found C 51.34, H 5.91. **^{1}H NMR** ($[D_8]$THF, 200 MHz, 20 °C): δ = 39.7 (s, 4 H, Ar*H*$_m$), −26.4 (s, 2 H, C≡C*H*), −29.4 (s, 8 H, PC*H*$_2$), −38.7 [s, 24 H, P(C*H*$_3$)$_2$], −58.2 (s, 4 H, Ar*H*$_o$). **Raman**: ν(H−*C≡C*) = 2152 (w), ν(*C≡C*−Mn) = 2037 (vs), ν(*C=C*)$_{\text{Ar}}$ = 1593 (vs), ν(*C=C*)$_{\text{Ar}}$ = 1174 (s), ν(HC=*CH*)$_{\text{Ar}}$ = 840 (w), ν(*Mn−P*) = 337 (w) cm^{-1}. **IR** (KBr): ν(*H−C*≡C) = 3306 (m), ν(*C−H*) = 2950 (s), 2883 (s), ν(H−*C≡C*) = 2160 (m), ν(*C≡C*−Mn) = 2035 (m), ν(*C=C*)$_{\text{Ar}}$ = 1619 (m), ν(*P−C*) = 998 (w), 947 (m), δ(HC=*CH*)$_{\text{Ar}}$ = 844 (vs) cm^{-1}.

{*trans*-Bis[1,2-bis(dimethylphosphanyl)ethane]-bis(fluorophenylethynyl)manganese(II)}, {[FC_6H_4C≡C]$_2$(dmpe)$_2$Mn} (4a): Butyllithium (1.6 M) in hexane (1.5 mL, 2.40 mmol) was added to *para*-fluorophenylacetylene (288 mg, 2.40 mmol) in THF (15 mL) at −30 °C. The reaction mixture was slowly warmed to room temperature, before being cooled to −30 °C. The cooled Li−C≡CC_6H_4F was added dropwise to [Mn$^{\text{I}}{}_2$(dmpe)$_2$] (609 mg, 1.00 mmol) in THF (15 mL) at −30 °C. The reaction mixture was stirred at room temperature for 2 h and the solvent was evaporated under vacuo to yield a red brown solid. The solid was extracted with diethyl ether and (3 × 5 mL) and filtered through Celite. Evaporation of ether fraction under vacuo resulted in an oil, which was washed with 10 mL of pentane and filtered through Celite. The solid over the Celite was extracted with toluene (3 × 5 mL). Evaporation of the toluene fraction under vacuum resulted in a solid. Crystallization at −30 °C in diethyl ether gave single crystals suitable for a X-ray diffraction study. Yield 542 mg (0.913 mmol, 91 %). $C_{28}H_{40}F_2MnP_4$ (593.45): calcd. C 56.67, H 6.79; found C 56.82, H 6.87. **^{1}H NMR** (C_6D_6, 200 MHz, 22 °C): δ = 16.4 (s, 4 H, Ar*H*$_m$), −5.7 (s, 4 H, Ar*H*$_o$), −14.8 [s, 32 H, C*H*$_2$P(C*H*$_3$)$_2$]. **^{19}F NMR** (C_6D_6, 188.16 MHz, 22 °C): δ = −104.2 (s, 2 F, Ar*F*). **IR** (ATR): ν(*C−H*) = 2965 (w), 2900 (m), ν(*C≡C*) = 2004 (s), ν(*C=C*)$_{\text{Ar}}$ = 1493 (s), ν(*C−F*) = 1216 (s), 1198 (s), ν(*P−C*) = 923 (s), δ(HC=*CH*)$_{\text{Ar}}$ = 827 (s) cm^{-1}.

{*trans*-Bis[1,2-bis(dimethylphosphanyl)ethane]-bis(fluorophenylethynyl)manganese(III)} Hexafluorophosphate, $\{[\mathrm{FC_6H_4C{\equiv}C}]_2(\mathrm{dmpe})_2\mathrm{Mn}\}[\mathrm{PF_6}]$, $[\mathbf{4a}]^+$: Compound **4** (297 mg, 0.50 mmol) was oxidized with $[\mathrm{Cp_2Fe}][\mathrm{PF_6}]$ (165 mg, 0.50 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL). The reaction mixture was stirred at room temperature for 1 h, after which the solvent was evaporated under vacuo to give a solid. The solid was washed with ethyl ether (5 × 10 mL) followed by extraction with THF (10 mL). The extract was filtered through Celite and the solvents were evaporated under vacuum to give a dark violet solid. Yield 365 mg (0.494 mmol, 99 %). Crystallization at −30 °C in $\mathrm{CH_2Cl_2}$ gave single crystals suitable for a X-ray diffraction study. $\mathrm{C_{28}H_{40}F_8MnP_5}$ (738.41): calcd. C 45.54, H 5.46; found C 45.19, H 5.31. ^{1}**H NMR** ($\mathrm{CD_2Cl_2}$, 300 MHz, 22 °C): δ = 35.3 (s, 4 H, ArH_m), −29.3 (s, 8 H, PCH_2), −38.7 (s, 24 H, PCH_3), −58.2 (s, 4 H, ArH_o). ^{19}**F NMR** ($\mathrm{CD_2Cl_2}$, 282.33 MHz, 22 °C): δ = −75.8 (d, $^1J_{\mathrm{FP}}$ = 712 Hz, 6 F, PF_6), −105.2 (s, 2 F, ArF). ^{31}**P NMR** ($\mathrm{CD_2Cl_2}$, 121.47 MHz, 22 °C): δ = −144.2 (sept, $^1J_{\mathrm{PF}}$ = 707 Hz, 1 P, PF$_6$). **IR** (ATR): $\nu(C{-}H)$ = 2961 (w), 2898 (m), $\nu(C{\equiv}C)$ = 2034 (s), $\nu(C{=}C)_{\mathrm{Ar}}$ = 1527 (s), $\nu(C{-}F)$ = 1214 (s), 1201 (s), $\nu(P{-}C)$ = 930 (s), $\delta(\mathrm{HC{=}}CH)_{\mathrm{Ar}}$ = 828 (s) cm^{-1}.

{*trans*-Bis[1,2-bis(dimethylphosphanyl)ethane]-[4-(triisopropylsilylethynyl)]phenylethynyl-iodomanganese(II)}, $\{[\mathrm{TIPS{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C}](\mathrm{dmpe})_2\mathrm{MnI}\}$ (5): $\mathrm{TIPS{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}H}$ (283 mg, 1.00 mmol) was added to [MeCpMn(dmpe)I] (411 mg, 1.00 mmol) dissolved in THF (20 mL). The reaction mixture was stirred for 30 min at room temperature and dmpe (150 mg, 1.00 mmol) was further added. The reaction mixture was stirred at room temperature for additional 6 h resulting in an intense red colored solution. The reaction mixture was evaporated under vacuum and the resulting residue was extracted with pentane (5 × 10 mL) until the solution was colorless. The pentane extract was filtered through Celite and the solvents evaporated under vacuum to give a red brown solid. Yield 557 mg (0.729 mmol, 73 %). $\mathrm{C_{31}H_{57}IMnP_4Si}$ (763.61): calcd. C 48.76, H 7.52; found C 48.41, H 7.80. ^{1}**H NMR** ($\mathrm{C_6D_6}$, 200 MHz, 22 °C): δ = 18.9 (s, 2 H, ArH_m), 1.31 {s, 3 H, Si[CH(CH$_3$)$_2$]$_3$}, 1.14 {s, 18 H, Si[CH(CH_3)$_2$]$_3$}, −1.6 (s, 2 H, ArH_o), −17.2 [s, 32 H, CH_2P(CH_3)$_2$]. **IR** (ATR): $\nu(C{-}H)$ = 2940 (m), 2889 (m), 2867 (m), $\nu(\mathrm{TIPS{-}}C{\equiv}C)$ = 2137 (m), $\nu(C{\equiv}C{-}\mathrm{Mn})$ = 2001 (s), $\nu(C{=}C)_{\mathrm{Ar}}$ = 1592 (s), $\nu(P{-}C)$ = 992 (w), 940 (s), $\delta(\mathrm{HC{=}}CH)_{\mathrm{Ar}}$ = 845 (s) cm^{-1}.

{*trans*-Bis[1,2-bis(dimethylphosphanyl)ethane]-(4-ethynyl)phenylethynyl-iodo-manganese(II)}, $\{[\mathrm{H{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C}](\mathrm{dmpe})_2\mathrm{MnI}\}$ (6): Tetrabutylammonium fluoride (0.4 mL of 1 M, $\mathrm{Bu_4NF}$; TBAF) in THF (5 % $\mathrm{H_2O}$) was added to **5** (305 mg, 0.40 mmol) in THF (10 mL). The reaction mixture was stirred at room temperature for 2 h and the solvents were evaporated under vacuum to yield a solid residue. The solid residue was first washed with pentane and extracted with ethyl ether (2 × 5 mL). The ether extract was filtered through Celite and the solvents were evaporated under vacuum to give a solid. Yield 238 mg (0.392 mmol, 98 %). Crystallization at −30 °C in THF gave single crystals suitable for an X-ray diffraction study. $\mathrm{C_{22}H_{37}IMnP_4}$ (607.27): calcd. C 43.51, H 6.14; found C 43.65, H 5.88. ^{1}**H NMR** ([D$_8$]THF, 200 MHz, 22 °C): δ = 18.1 (s, 2 H, ArH_m), 2.32 (s, 1 H, CCH), −3.1 (s, 2 H, ArH_o), −17.1 [s, 32 H, CH_2P(CH_3)$_2$]. **IR** (ATR): $\nu(H{-}C{\equiv}\mathrm{C})$ = 3312 (m), $\nu(C{-}H)$ = 2959 (m), 2906 (m), $\nu(\mathrm{H{-}}C{\equiv}C)$ = 2104 (w), $\nu(C{\equiv}C{-}\mathrm{Mn})$ = 1996 (s), $\nu(C{=}C)_{\mathrm{Ar}}$ = 1593 (s), $\nu(P{-}C)$ = 949 (m), $\delta(\mathrm{HC{=}}CH)_{\mathrm{Ar}}$ = 837 (m) cm^{-1}.

{Bis-[*trans*-bis(1,2-bis(dimethylphosphanyl)ethane)phenylethynylmanganese(II/II)]-(μ-1,3-butadiyne)}, $\{[(\mathrm{PhC{\equiv}C})(\mathrm{dmpe})_2\mathrm{Mn}]_2(\mu\text{-}\mathrm{C{\equiv}C{-}C{\equiv}C})\}$ (7a): Lithium phenylacetylide (0.40 mmol), synthesized from phenylacetylene (39 mg, 0.40 mmol) and 1.6 M Butyllithium in hexane (250 μL, 0.40 mmol) at −30 °C, in THF (15 mL) was added to $\{[\mathrm{Mn(dmpe)_2I}]_2(\mu\text{-}\mathrm{C_4})\}$ (101 mg, 0.10 mmol) in THF and the reaction mixture was stirred at room temperature for 6 h. The solvent was evaporated under vacuum to give a brown solid. The solid was washed with pentane (3 × 10 mL) extracted with diethyl ether (3 × 5 mL) and filtered through Celite. The deep red solution was evaporated under vacuum to give a red solid. Yield 82 mg (0.085 mmol, 85 %). $\mathrm{C_{44}H_{74}Mn_2P_8}$ (960.72): calcd. C 55.01, H 7.76; found C 55.10, H 7.78. ^{1}**H NMR** ($\mathrm{C_6D_6}$, 200 MHz, 20 °C): δ = 16.8 (s, 4 H, ArH_m), −0.3 (s, 2 H, ArH_p), −4.1 (s, 4 H, ArH_o), −15.0 [s, 64 H, P(CH_3)$_2$, PCH_2].

{Bis-[*trans*-bis(1,2-bis(dimethylphosphanyl)ethane)phenylethynylmanganese(II/III)]-(μ-1,3-butadiyne)} Hexafluorophosphate, $\{[(\mathrm{PhC{\equiv}C})(\mathrm{dmpe})_2\mathrm{Mn}]_2(\mu\text{-}\mathrm{C{\equiv}C{-}C{\equiv}C})\}[\mathrm{PF_6}]$, $[\mathbf{7a}]^+$: $[\mathrm{Cp_2Fe}][\mathrm{PF_6}]$ (17 mg, 0.051 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was added to **7a** (50 mg, 0.052 mmol) at room temperature whilst stirring. After a few minutes, the color of the reaction mixture changed to green. The reaction mixture was evaporated under vacuum and the solid was washed with diethyl ether (5 × 10 mL). The solid was extracted with THF and filtered through Celite. The solvent was evaporated under vacuum to give a deep green solid. Yield 53 mg (0.048 mmol, 94 %). $\mathrm{C_{44}H_{74}F_6Mn_2P_9}$ (1105.69): calcd. C 47.80, H 6.75; found C 47.49, H 6.54. ^{1}**H NMR** ([D$_8$]THF, 200 MHz, 20 °C): δ = 28.7 (s, 4 H, ArH_m), −22.1 (s, 16 H, PCH_2), −26.5 [s, 50 H, P(CH_3)$_2$, ArH_p], −31.9 (s, 4 H, ArH_o).

{Bis-[*trans*-bis(1,2-bis(dimethylphosphanyl)ethane)phenylethynylmanganese(III/III)]-(μ-1,3butadiyne)} Bis(hexafluorophosphate), $\{[(\mathrm{PhC{\equiv}C})(\mathrm{dmpe})_2\,\mathrm{Mn}]_2(\mu\text{-}\mathrm{C{\equiv}C{-}C{\equiv}C})\}[\mathrm{PF_6}]_2$, $[\mathbf{7a}]^{2+}$: To **7a** (50 mg, 0.052 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL), $[\mathrm{Cp_2Fe}][\mathrm{PF_6}]$ (34.4 mg, 0.104 mmol) was added and the reaction mixture was stirred 30 min at room temp. The solvent was evaporated under vacuum and washed with diethyl ether (5 × 10 mL), filtered and further washed with a small amount of THF (5 mL). The violet product was extracted with a 1/1 mixture of THF/$\mathrm{CH_2Cl_2}$ (10 mL), filtered through Celite and the solvents were evaporated under vacuum to yield a violet solid. Yield 58 mg (0.046 mmol, 89 %). $\mathrm{C_{44}H_{74}F_{12}Mn_2P_{10}}$ (1250.65): calcd. C 42.26, H 5.96; found C 42.17, H 6.04. ^{1}**H NMR** ($\mathrm{CD_3CN}$, 200 MHz, 20 °C): δ = 36.6 (s, 4 H, ArH_m), −29.2 (s, 16 H, PCH_2), −38.5 [s, 48 H, P(CH_3)$_2$], −52.7 (s, 2 H, ArH_p), −56.9 (s, 4 H, ArH_o).

{Bis-[*trans*-bis(1,2-bis(dimethylphosphanyl)ethane)(methyl)phenylethynylmanganese(II/II)]-(μ-1,3-butadiyne)}, $\{[(\mathrm{CH_3C_6H_4C{\equiv}C})(\mathrm{dmpe})_2\mathrm{Mn}]_2(\mu\text{-}\mathrm{C{\equiv}C{-}C{\equiv}C})\}$ (7b): Lithium-*para*-(methyl)phenylacetylide (0.40 mmol) in THF (15 mL), [which was synthesized from *para*-(methyl) phenylacetylene (46 mg, 0.40 mmol) und 1.6 M butyllithium in hexane (250 μL, 0.40 mmol) at −30 °C], was added to $[\{\mathrm{Mn(dmpe)_2I}\}_2(\mu\text{-}\mathrm{C_4})]$ (101 mg, 0.10 mmol) and the reaction mixture was stirred for 6 h. The solvent was evaporated under vacuum and washed with pentane (3 × 10 mL). The solid was extracted with diethyl ether (3 × 5 mL) and filtered through Celite. The deep red solution was evaporated under vacuum to give a dark red solid. Yield 83 mg (0.084 mmol, 84 %). $\mathrm{C_{46}H_{78}Mn_2P_8}$ (988.78): calcd. C 55.88, H 7.95; found C 55.69, H 7.82. ^{1}**H NMR** ($\mathrm{C_6D_6}$, 200 MHz, 20 °C): δ = 16.2 (s, 4 H, ArH_m), 0.9 (s, 6 H, ArCH_3), −4.3 (s, 4 H, ArH_o), −15.1 [s, 64 H, P(CH_3)$_2$, PCH_2].

{Bis-[*trans*-bis(1,2-bis(dimethylphosphanyl)ethane)(methyl)phenylethynylmanganese(II/III)]-(μ-1,3-butadiyne)} Hexafluorophosphate, $\{[(\mathrm{CH_3C_6H_4C{\equiv}C})(\mathrm{dmpe})_2\mathrm{Mn}]_2(\mu\text{-}\mathrm{C{\equiv}C{-}C{\equiv}C})\}[\mathrm{PF_6}]$, $[\mathbf{7b}]^+$:

$[Cp_2Fe][PF_6]$ (17 mg, 0.051 mmol) was added to **7b** (50 mg, 0.051 mmol) in CH_2Cl_2 (10 mL). After a few minutes, the color of the reaction mixture turned to green. The solvent was evaporated under vacuum and washed with diethyl ether (5 × 10 mL) to remove ferrocene. The solid was extracted with THF, filtered through Celite and the solvents were evaporated under vacuum to give a deep green solid. Yield 53 mg (93 %). $C_{46}H_{78}F_6Mn_2P_9$ (1133.74): calcd. C 48.73, H 6.93; found C 48.58, H 6.69. **^{1}H NMR** ($[D_8]$THF, 200 MHz, 20 °C): δ = 28.1 (s, 4 H, ArH_m), 0.8 (s, 6 H, ArCH_3), −21.9 (s, 16 H, PCH_2), −26.3 [s, 48 H, P(CH_3)$_2$], −32.2 (s, 4 H, ArH_o).

{Bis-[*trans*-bis(1,2-bis(dimethylphosphanyl)ethane)(methyl)phenylethynylmanganese(III/III)]-(μ-1,3-butadiyne)} Bis(hexafluorophosphate), $\{[(CH_3C_6H_4C{\equiv}C)(dmpe)_2Mn]_2(\mu\text{-}C{\equiv}C{-}C{\equiv}C)\}[PF_6]_2$, $[7b]^{2+}$: $[Cp_2Fe][PF_6]$ (34 mg, 0.104 mmol) was added to **7b** (51 mg, 0.052 mmol) in CH_2Cl_2 (10 mL) and the reaction mixture was stirred at room temperature for 30 min. The solvent was evaporated under vacuum and the solid was washed with diethyl ether (5 × 10 mL) to remove ferrocene. Further, the solid was washed with THF (5 mL), extracted with a THF/DCM mixture and filtered through Celite. Afterwards, the solvent was evaporated under vacuum to give a violet solid. Yield 64 mg (0.050 mmol, 96 %). $C_{46}H_{78}F_{12}Mn_2P_{10}$ (1278.71): calcd. C 43.21, H 6.14; found C 43.00, H 5.95. **^{1}H NMR** (CD_3CN, 200 MHz, 20 °C): δ = 34.3 (s, 4 H, ArH_m), 0.9 (s, 6 H, ArCH_3), −29.3 (s, 16 H, PCH_2), −38.5 [s, 48 H, P(CH_3)$_2$], −57.1 (s, 4 H, ArH_o).

{Bis-[*trans*-bis(1,2-bis(dimethylphosphanyl)ethane)(*n*-pentyl)phenylethynylmanganese(II/II)]-(μ-1,3-butadiyne)}, $\{[(CH_3(CH_2)_4C_6H_4\text{-}C{\equiv}C)(dmpe)_2Mn]_2(\mu\text{-}C{\equiv}C{-}C{\equiv}C)\}$ (7c): Lithium-(*n*-pentyl)phenylacetylide (0.40 mmol) in THF (15 mL) [synthesized from (*n*-pentyl)phenylacetylene (52 mg, 0.40 mmol) and 1.6 M butyllithium (250 μL, 0.40 mmol)], was added to $[\{Mn(dmpe)_2I\}_2(\mu\text{-}C_4)]$ (101 mg, 0.10 mmol) in THF (10 mL) at −30 °C and the reaction mixture was stirred at room temperature for 6 h. The reaction mixture was evaporated under vacuum; the resulting residue was extracted with pentane (3 × 10 mL) and filtered through Celite. The dark red solution was cooled to −30 °C to give dark red crystals. Yield 90 mg (0.082 mmol, 82 %). $C_{54}H_{94}Mn_2P_8$ (1100.99): calcd. C 58.91, H 8.61; found C 58.56, H 8.43. **^{1}H NMR** (C_6D_6, 200 MHz, 20 °C): δ = 16.2 (s, 4 H, ArH_m), 0.98−1.42 [m, 22 H, Ar(CH_2)$_4$CH_3], −4.0 (s, 4 H, ArH_o), −14.9 [s, 64 H, P(CH_3)$_2$, PCH_2].

{Bis-[*trans*-bis(1,2-bis(dimethylphosphanyl)ethane)-(*n*-pentyl)phenylethynylmanganese(II/III)]-(μ-1,3-butadiyne)} Hexafluorophosphate, $\{[(CH_3(CH_2)_4C_6H_4\ C{\equiv}C)(dmpe)_2Mn]_2(\mu\text{-}C{\equiv}C{-}C{\equiv}C)\}[PF_6]$, $[7c]^+$: $[Cp_2Fe][PF_6]$ (17 mg, 0.051 mmol) was added to **7c** (57 mg, 0.052 mmol) in CH_2Cl_2 (10 mL), and the reaction mixture was stirred for a few minutes. After the solvent was evaporated, the residue was washed with diethyl ether (5 × 10 mL) and the solid was extracted with THF. The THF extract was filtered through Celite and evaporated to give a solid. Yield 62 mg (0.050 mmol, 96 %). $C_{54}H_{94}F_6Mn_2P_9$ (1245.95): calcd. C 52.05, H 7.60; found C 52.00, H 7.56. **^{1}H NMR** ($[D_8]$THF, 200 MHz, 20 °C): δ = 28.5 (s, 4 H, ArH_m), 0.79−1.38 [m, 22 H, Ar(CH_2)$_4$CH_3], −22.2 (s, 16 H, PCH_2), −26.6 [s, 48 H, P(CH_3)$_2$], −32.8 (s, 4 H, ArH_o).

{Bis-[*trans*-bis(1,2-bis(dimethylphosphanyl)ethane)(*n*-pentyl)phenylethynylmanganese(III/III)]-(μ-1,3-butadiyne)} Bis(hexafluorophosphate), $\{[(CH_3(CH_2)_4C_6H_4C{\equiv}C)(dmpe)_2Mn]_2(\mu\text{-}C{\equiv}C{-}C{\equiv}C)\}\text{-}[PF_6]_2$, $[7c]^{2+}$: $[Cp_2Fe][PF_6]$ (34 mg, 0.104 mmol) was added to **7c** (57 mg, 0.052 mmol) in CH_2Cl_2 (10 mL) and stirred at room temperature for 30 min. The solvent was evaporated under vacuo, washed with diethyl ether (5 × 10 mL) and a small amount of THF (5 mL). The resulting violet product was extracted with a THF/DCM mixture and filtered through Celite. The solvent was evaporated under vacuum to give a violet solid. Yield 68 mg (0.049 mmol, 94 %). $C_{54}H_{94}F_{12}Mn_2P_{10}$ (1390.92): calcd. C 46.63, H 6.81; found C 46.39, H 6.63. **^{1}H NMR** (CD_3CN, 200 MHz, 20 °C): δ = 35.1 (s, 4 H, ArH_m), 0.90−1.52 [m, 22 H, Ar(CH_2)$_4$CH_3], −29.1 (s, 16 H, PCH_2), −38.4 [s, 48 H, P(CH_3)$_2$], −56.9 (s, 4 H, ArH_o).

{Bis-[*trans*-bis(1,2-bis(dimethylphosphanyl)ethane)(fluoro)phenylethynylmanganese(II/II)]-(μ-1,3-butadiyne)}, $\{[(FC_6H_4C{\equiv}C)\text{-}(dmpe)_2Mn]_2(\mu\text{-}C{\equiv}C{-}C{\equiv}C)\}$ (7d): Lithium(*para*-fluorophenyl)acetylide (0.32 mmol), synthesized in situ from *para*-fluorophenylacetylene (38 mg, 0.32 mmol) and 1.6 M Butyllithium (200 μL, 0.32 mmol) at −30 °C, in THF (15 mL) was added to $[\{Mn(dmpe)_2I\}_2(\mu\text{-}C_4)]$ (108 mg, 0.11 mmol) in THF and the reaction mixture was stirred at room temperature for 3 h. The solvent was evaporated under vacuum to a brown solid, which was washed with pentane (3 × 10 mL) extracted with diethyl ether (2 × 5 mL) and filtered through Celite. The solvent was evaporated under vacuum to give a red brown solid. Yield 70 mg (0.070 mmol, 64 %). $C_{44}H_{72}F_2Mn_2P_8$ (996.71): calcd. C 53.02, H 7.28; found C 52.91, H 7.20. **^{1}H NMR** (C_6D_6, 200 MHz, 20 °C): δ = 16.4 (s, 4 H, ArH_m), −5.7 (s, 4 H, ArH_o), −13.8 (s, 16 H, PCH_2), −15.1 [s, 48 H, P(CH_3)$_2$].

{Bis-[*trans*-bis(1,2-bis(dimethylphosphanyl)ethane)(fluoro)phenylethynylmanganese(II/III)]-(μ-1,3-butadiyne)} Hexafluorophosphate, $\{[(FC_6H_4C{\equiv}C)(dmpe)_2Mn]_2(\mu\text{-}C{\equiv}C{-}C{\equiv}C)\}[PF_6]$, $[7d]^+$: $[Cp_2Fe][PF_6]$ (17 mg, 0.051 mmol) was added to **7d** (52 mg, 0.052 mmol) in CH_2Cl_2 (10 mL) and the reaction mixture was stirred at room temperature for 30 min. After the solvent was evaporated under vacuum, the residue was washed with diethyl ether (5 × 10 mL) to remove ferrocene. The solid was extracted with THF, filtered through Celite and the solvent was evaporated to give a dark green solid. Yield 56 mg (0.049 mmol, 96 %). $C_{44}H_{72}F_8Mn_2P_9$ (1141.67): calcd. C 46.29, H 6.36; found C 46.42, H 6.31. **^{1}H NMR** ($[D_8]$THF, 200 MHz, 20 °C): δ = 27.2 (s, 4 H, ArH_m), −21.8 (s, 16 H, PCH_2), −26.0 [s, 48 H, P(CH_3)$_2$], −33.3 (s, 4 H, ArH_o).

{Bis-[*trans*-bis(1,2-bis(dimethylphosphanyl)ethane)(fluoro)phenylethynylmanganese(III/III)]-(μ-1,3-butadiyne)} Bis(hexafluorophosphate), $\{[(FC_6H_4C{\equiv}C)(dmpe)_2Mn]_2(\mu\text{-}C{\equiv}C{-}C{\equiv}C)\}[PF_6]_2$, $[7d]^{2+}$: $[Cp_2Fe][PF_6]$ (34 mg, 0.104 mmol) was added to **7d** (52 mg, 0.052 mmol) in CH_2Cl_2 (10 mL) and the reaction mixture was stirred at room temperature for 30 min. Afterwards, the solvent was evaporated under vacuum and the residue was washed with diethyl ether (5 × 10 mL) to remove ferrocene. The violet solid was extracted with CH_2Cl_2, filtered through Celite and the solvents were evaporated under vacuum to give the title compound. yield 60 mg (0.047 mmol, 90 %). $C_{44}H_{72}F_{14}Mn_2P_{10}$ (1286.63): calcd. C 41.07, H 5.64; found C 41.28, H 5.63. **^{1}H NMR** (CD_3CN, 200 MHz, 20 °C): δ = 34.6 (s, 4 H, ArH_m), −29.0 (s, 16 H, PCH_2), −38.3 [s, 48 H, P(CH_3)$_2$], −56.7 (s, 4 H, ArH_o).

Crystal Structure Determinations: Suitable crystals of **1c**, **2a-1**, **2a-2**, **4**, $[\mathbf{4}]^+$ and **6** were mounted on the tip of a glass fiber using polybutene oil as protecting agent. The crystals were cooled to 183(2) K (**1c**, **2a-1**, **4** and **6**), 153(2) K (**2a-2**) or 297(2) K ($[\mathbf{4}]^+$) by an Oxford cryogenic system. Totals of 43025, 56255, 75402, 54578, 116947 and 29044 reflections were collected [61] for **1c**, **2a-1**, **2a-2**,

4, [**4**]$^+$ and **6** and resulted in 3697 (R_{int} = 0.077), 16424 (R_{int} = 0.177), 23018 (R_{int} = 0.141), 5332 (R_{int} = 0.122), 29657 (R_{int} = 0.070) and 6586 (R_{int} = 0.056) unique reflections, respectively. Numerical absorption corrections [62] based on 23, 9, 9, 6, 8 and 17 crystal faces, respectively, were applied with FACEitVIDEO and XRED [61]. The structures were solved by direct methods using the program SHELXS-97 [63]. The full-matrix least-squares refinements (based on F^2) were carried out with SHELXL-97 [63]. The plots of the structures were generated by using ORTEP [64].

The small size of the plate-like crystals of **2a-1**, **2a-2** and [**4**]$^+$ resulted in low diffraction power, only 21 % to 25 % of the unique intensity reflections were considered observed by criterion $I > 2\sigma(I)$ in spite of high generator power and long exposure time of the image plate contributing to the relatively high R_{int}, R_σ, and wR and R_1 values. Crystallographic details are presented in Table 1 and in the deposited CIF files. The absolute structure parameter [65] was finally refined to −0.01(3). Crystals of **6** were found to be all twinned when examined by using a polarizing microscope. A twin

Table 1. Summary of the X-ray diffraction studies of **1c**, **2a-1**, **2a-1**, **4**, [**4**]$^+$ and **6**.

	1c	**2a-1**	**2a-2**
Empirical formula	$C_{14}H_{36}Br_2MnP_4$	$C_{50}H_{82}MnP_4Si_2$	$C_{50}H_{82}MnP_4Si_2$
Formula weight /g·mol^{-1}	543.07	918.16	918.16
Temperature /K	183(2)	183(2)	153(2)
Wavelength /Å	0.71073	0.71073	0.71073
Crystal system, space group	orthorhombic, *Pbca*	orthorhombic, $P2_12_12_1$	triclinic, $P\bar{1}$
a /Å	13.290(2)	15.0234(10)	11.0365(17)
b /Å	13.6837(16)	15.4419(7)	19.435(3)
c /Å	13.475(2)	23.4842(11)	20.336(3)
α /°	90	90	105.930(18)
β /°	90	90	97.968(18)
γ /°	90	90	90.255(18)
Volume /Å^3	2450.6(6)	5448.1(5)	4149.7(12)
Z, density (calcd.) /Mg·m^{-3}	4, 1.472	4, 1.119	3, 1.102
Absorbtion coefficient /mm^{-1}	4.055	0.434	0.427
F(000)	1100	1980	1485
Crystal size /mm	0.42 × 0.32 × 0.31	0.21 × 0.18 × 0.07	0.28 × 0.17 × 0.04
θ Range /°	2.62 to 30.42	2.71 to 30.47	2.88 to 30.53
Reflections collected	43025	56255	75402
Reflections unique	3697 [R_{int} = 0.077]	16424 [R_{int} = 0.177]	23018 [R_{int} = 0.141]
Completeness to *θ* /%	99.4	99.2	90.8
Max/min transmission	0.3617/0.2833	0.9754/0.9244	0.9814/0.9084
Data/restraints/parameters	3697/0/101	16424/10/514	23018/2/802
Goodness-of-fit on F^2	0.780	0.473	0.560
Final R_1 and wR_2 indices [$I > 2\sigma(I)$]	0.0507, 0.113	0.0413, 0.0667	0.0508, 0.0951
R_1 and wR_2 indices (all data)	0.0933, 0.121	0.2166, 0.1136	0.2150, 0.1265
	4	[**4**]$^+$	**6**
Empirical formula	$C_{28}H_{40}F_2MnP_4$	$C_{28}H_{40}F_8MnP_5$	$C_{22}H_{37}IMnP_4$
Formula weight /g·mol^{-1}	593.42	738.39	607.24
Temperature /K	183(2)	297(2)	183(2)
Wavelength /Å	0.71073	0.71073	0.71073
Crystal system, space group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$
a /Å	12.3182(18)	12.5139(8)	9.1395(5)
b /Å	13.6885(15)	21.0539(15)	13.0655(7)
c /Å	18.935(3)	23.0029(14)	23.2824(15)
α /°	90	107.594(7)	90
β /°	108.889(17)	105.814(7)	99.239(7)
γ /°	90	99.765(8)	90
Volume /Å^3	3020.9(7)	5344.4(8)	2744.1(3)
Z, density (calcd.) /Mg·m^{-3}	4, 1.305	6, 1.377	4, 1.470
Absorbtion coefficient /mm^{-1}	0.677	0.654	1.846
F(000)	1244	2280	1228
Crystal size /mm	0.21 × 0.20 × 0.14	0.40 × 0.36 × 0.08	0.39 × 0.36 × 0.27
θ Range /°	2.72 to 25.00	2.80 to 30.55	2.64 to 28.08
Reflections collected	54578	116947	29044
Reflections unique	5332 [R_{int} = 0.122]	29657 [R_{int} = 0.070]	6586 [R_{int} = 0.056]
Completeness to *θ* /%	99.9	90.5	94.7
Max/min transmission	0.9335/0.8528	0.9525/0.7978	0.6881/0.5496
Data/restraints/parameters	5332/0/332	29657/6/1162	6586/0/252
Goodness-of-fit on F^2	0.678	0.680	0.912
Final R_1 and wR_2 indices [$I > 2\sigma(I)$]	0.0339, 0.0655	0.0620, 0.1442	0.0567, 0.1523
R_1 and wR_2 indices (all data)	0.0668, 0.0690	0.1699, 0.1676	0.0761, 0.1606

The unweighted *R*-factor is $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$; $I > 2\,\sigma(I)$ and the weighted *R*-factor is $wR_2 = \{\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2\}^{1/2}$.

crystal of a suitable size was carefully cut to obtain a single crystal for the X-ray measurement. The structure was solved and successfully refined ($R = 4.7\,\%$) however, atom C14 were finally observed as non-positive definite, indicating that the structural model may be wrong, and a large residual electron density peak of 5.43 $e \cdot Å^{-3}$ near atom C14 could not be interpreted as a chemically meaningful result. A check for higher symmetry with PLATON [66] resulted in a new orthorhombic unit cell [$a = 9.1395(5)$, $b = 13.0665(7)$, $c = 114.903(8)$ Å] based on the transformation matrix [−1 0 0, 0 −1 0, 2 0 5]. Structure solutions with the heavy atoms manganese, phosphorous and iodine were obtained with typical atom positions of superstructure arrangements or for modulated structures but could not be refined successfully. As a consequence, the structure was re-refined in the accepted monoclinic space group $P2_1/c$ using shift-limiting restraints until the displacement parameters of the carbon atom C14 get close to the non-positive-definite warning. In the last stage of the refinement, the coordinates and anisotropic displacement parameters of C14 were fixed.

It was accidentally found that compound **2a** crystallizes in both orthorhombic (**2a-1**) and triclinic (**2a-2**) crystal systems. Both dimorphs **2a-1** and **2a-2** present rather similar geometric parameters for the Mn−C and C≡C bonds of the central units in structures (average values of 1.993 and 1.183 Å for **2a-1**, and 1.952 and 1.201 Å for **2a-2**). Remarkable differences are observed concerning the number Z' of complexes in the asymmetric unit of the cells in **2a-2** and [**4**]$^+$, $Z' = 1.5$ and 3, respectively. In compound **2a-2**, one complex is on a general position and one half complex with the Mn atom on an inversion centre, which results in three complexes in the triclinic unit cell. In the crystal structure of [**4**]$^+$, three symmetry-independent manganese molecules with two independent counterions PF_6^- and two half PF_6^- ions on special positions are observed, formally $Z' = 3$, but altogether seven molecular units had to be refined, and the number of molecules in the unit cell is formally six.

Crystallographic data (excluding structure factors) for the structures given in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-713976−713979 (**1c-4**), and CCDC-631119 ([**4**]$^+$), and CCDC-713980 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, [Fax: (+44) 1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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