New Access to Homodinuclear Half-Sandwich Vinylidenemanganese Complexes

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The d^6 low-spin Mn^I half-sandwich dinuclear complexes of the type $[\{Mn(MeC_5H_4)(R_2PCH_2CH_2PR_2)=C=C(SnMe_3)\}_2\{X\}]$ (X = {μ-1,4-C_6H_4}, R = Me, **2a**; X = {μ-1,4-C_6H_4}, R = Et, **2b**; X = {μ-1,3-C_6H_4}, R = Me, **3a**; X = {μ-1,3-C_6H_4}, R = Et, **3b**; X = {μ-4,4-C_6H_4-C_6H_4}, R = Me, **4a**; X = {μ-4,4-C_6H_4-C_6H_4}, R = Et, **4b**; X = {μ-1,4-C_4H_2S}, R = Me, **5a**; X = {μ-1,4-C_4H_2S}, R = Et, **5b**) were obtained by the treatment of $[Mn(C_5H_4Me)(\eta^6\text{-cycloheptatriene})]$ with 0.5 equiv. of the corresponding acetylene $Me_3Sn–C≡C–X–C≡C–SnMe_3$ (X = {μ-1,4-C_6H_4}, {μ-1,3-C_6H_4}, {μ-4,4-C_6H_4-C_6H_4}, {μ-1,4-C_4H_2S}) and $R_2PCH_2CH_2PR_2$ (R = Me, Et) at 50 °C for 12 h to yield the corresponding dinuclear complexes in very good yields. These dinuclear tin-substituted vinylidene complexes were further treated with an excess of MeOH to give the corresponding dinuclear parent vinylidene complexes of the type $[\{Mn(MeC_5H_4)(R_2PCH_2CH_2PR_2)=C=C(H)\}_2\{X\}]$ (X = {μ-1,4-C_6H_4}, R = Me, **6a**; X = {μ-1,4-C_6H_4}, R = Et, **6b**; X = {μ-1,3-C_6H_4}, R = Me, **7a**; X = {μ-1,3-C_6H_4}, R = Et, **7b**; X = {μ-4,4-C_6H_4-C_6H_4}, R = Me, **8a**; X = {μ-4,4-C_6H_4-C_6H_4}, R = Et, **8b**). All dinuclear compounds were characterised by NMR and IR spectroscopy and elemental analysis. X-ray diffraction studies were performed on complexes **2b**, **3a**, **4a** and **6a**.
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Introduction

Carbon-rich organometallics containing rigid, π-conjugated chains are of increasing interest due to their uses in the synthesis of unsaturated organic species,[1–4] organometallic polymers[5] and π-conjugated di- or multimetallic systems.[3,6–24] In particular, the dinuclear transition metal acetylide complexes offer an interesting perspective for the build-up of organometallic systems as molecular-level single-electron devices and the bottom-up construction of miniaturised components capable of performing specific electronic functions.[8–20] Our ongoing interest in such building blocks is devoted to the synthesis and physical properties of molecular species which might function as wires. Specifically, they should consist of an all-carbon chain capped by two redox-active metal termini.[6–17] We sought to explore reactions of dinuclear vinylidene precursor complexes which would ultimately lead to polyyne ligand containing complexes. We recently reported the chemistry and reactivity of Mn^{II} and Mn^{III} half-sandwich $Me_2PCH_2CH_2PMe_2$ (dmpe) alkynyl complexes and their conversion to (vinylidene)Mn^I species.[21,23,24] The first conclusion of this study was that vinylidene complexes gained considerable stability through the presence of the bis(dimethylphosphanyl)ethane ligand (dmpe) in comparison with the reported CO-substituted species $[Mn(Cp)L^1L^2(C=CR_2)]$ ($L^1 = L^2$ = CO, PR'_3 or L^1 = CO, $L^2 = PR'_3$).[25] Although the dinuclear complexes with the CO ligands were reported earlier,[26] these complexes are not expected to possess low-energy work functions which is an important property required for the molecules to function as molecular wires.[23] In contrast, the complexes bearing electron-donating phosphane ligands can be expected to possess suitable electronic properties, i.e. a low energy work function. Similar types of dinuclear vinylidene complexes have been reported with terminal ends capped by various other transition metals such as Ru,[17b] Rh[27] or Fe.[7] We herein report access to new dinuclear half-sandwich complexes of the type $[\{Mn(MeC_5H_4)(R_2PCH_2CH_2PR_2)=C=C(H)\}_2\{X\}]$ (R = Me, Et) (X = {μ-1,4-C_6H_4}, {μ-1,3-C_6H_4} and {μ-4,4-C_6H_4-C_6H_4}). It has been demonstrated by other groups that similar types of dinuclear vinylidene complexes can serve as valuable starting materials for obtaining access to dinuclear acetylide complexes.

Results and Discussion

A common method for obtaining vinylidene complexes is to make use of the high propensity of terminal acetylide derivatives to rearrange into vinylidene compounds.[28–36] Such principal possibilities have been corroborated by recent studies by our group.[18–23] For such a process to be initiated in half-sandwich Mn^I chemistry, we believed the complex $[Mn(C_5H_4Me)(\eta^6\text{-cycloheptatriene})]$ (**1**)[37] would be an excellent starting material, since facile cycloheptatriene exchange could be expected to occur with electron donating ligands such as phosphanes or acetylenes.[38,39] Further reactivity with disubstituted tin acetylides was anticipated, thus leading to the desired dinuclear vinylidene species.

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The reaction of [Mn(C_5H_4Me)(η^6-cycloheptatriene)] (**1**) with 0.5 equiv. of $Me_3Sn–C{\equiv}C–X–C{\equiv}C–SnMe_3$ (X = {μ-1,4-C_6H_4}, {μ-1,3-C_6H_4}, {μ-4,4-C_6H_4-C_6H_4},[40–42] {μ-1,4-C_4H_2S}) and $R_2PCH_2CH_2PR_2$ (R = Me, Et) at 50 °C for 12 h gave the corresponding vinylidene complexes of the type [{Mn(MeC_5H_4)($R_2PCH_2CH_2PR_2$)=C=C($SnMe_3$)}$_2$-{X}] (X = {μ-1,4-C_6H_4}, R = Me, **2a**; X = {μ-1,4-C_6H_4}, R = Et, **2b**; X = {μ-1,3-C_6H_4}, R = Me, **3a**; X = {μ-1,3-C_6H_4}, R = Et, **3b**; X = {μ-4,4-C_6H_4-C_6H_4}, R = Me, **4a**; X = {μ-4,4-C_6H_4-C_6H_4}, R = Et, **4b**; X = {μ-1,4-C_4H_2S}, R = Me, **5a**; X = {μ-1,4-C_4H_2S}, R = Et, **5b**) in quantitative yields (Scheme 1).

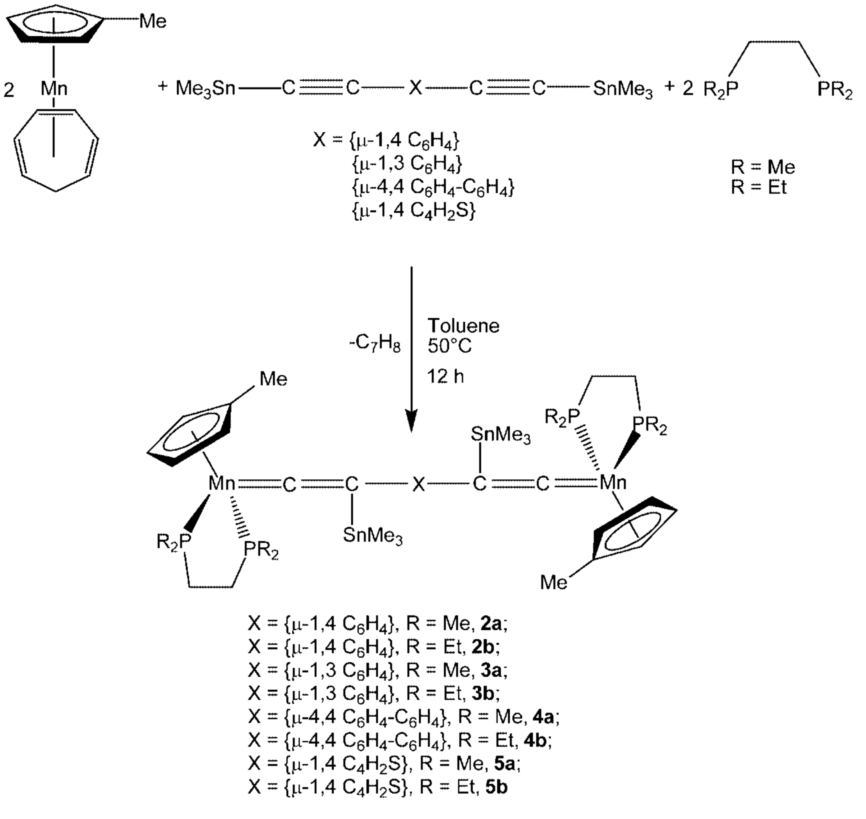
These reactions appear to require the initial formation of (alkyne)Mn species.[25] However, NMR studies of the reactions carried out in the temperature range of –70 to 20 °C did not reveal any intermediates. The ^{13}C NMR spectra of complexes **2**–**5** show the C_α and the C_β resonances between δ = 326–330 and 110–140 ppm, respectively. The ^{31}P NMR resonances appear at $\delta \approx$ 95 ppm for complexes **2a**–**5a** and are thus comparable with those observed for the related [Mn($C_5H_4R^1$)($Me_2PCH_2CH_2PMe_2$)(=C=CR^2H)] complexes.[24,38,39] However, for complexes **2b**–**5b** a downfield shift to $\delta \approx$ 115 ppm was observed in the ^{31}P NMR spectra. The resonances corresponding to the trimethyltin groups were observed in the ^{119}Sn NMR spectra as triplets at $\delta \approx$ –30 ppm. The ^{31}P, ^{119}Sn and ^{13}C NMR spectroscopic data for the complexes **2**–**5** are summarised in Table 1.

The structure of **2b** was additionally confirmed by an X-ray diffraction study (Figure 1). A pseudo-tetrahedral coordination environment of the manganese centre was revealed. The bond lengths of 1.763(4) Å and 1.345(2) Å for Mn–C11 and C11–C12, respectively, confirm the double-bond character of these bonds. The observed C12–Sn bond length of 2.159(4) Å is similar to that found in the mononuclear vinylidene complexes already reported.[38,39] The bond angles for Mn–C11–C12 and C11–C12–C13 were found to be 175.7(3)° and 125.8(4)°, respectively.

Table 1. $^{31}P\{^1H\}$, $^{119}Sn\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopic data for compounds **2**–**5**

Compound	^{31}P NMR ($R_2PCH_2CH_2PR_2$) δ (ppm)	^{119}Sn NMR ($SnMe_3$) δ (ppm)	^{13}C NMR Mn=C_α=C_β	Mn=C_α=C_β
2a	94.9 (s)	–30.2 (t)	329.6 (t)	129.1
2b	115.0 (s)	–27.4 (t)	326.3 (t)	129.9
3a	94.3 (s)	–29.8 (t)	328.5 (t)	129.1
3b	115.0 (s)	–29.8 (t)	328.5 (t)	129.1
4a	93.0 (s)	–17.1 (t)	330.5 (t)	129.1
4b	113.5 (s)	–29.2 (t)	328.0 (t)	142.3
5a	93.7 (s)	–27.5 (t)	328.5 (t)	110.1
5b	115.1 (s)	–26.3 (t)	326.8 (t)	141.1

X-ray diffraction analysis confirmed the spectroscopically derived structures of **3a** and **4a** which are closely related to that of **2b** (Figures 2 and 3). The solid-state structures indicated the Mn–C_α and C_α–C_β bond lengths to be 1.769(4) and 1.299(6) Å, and 1.744(4) and 1.358(5) Å, for **3a** and **4a**, respectively. These values confirm the double-bond nature in these vinylidene complexes.



Scheme 1.

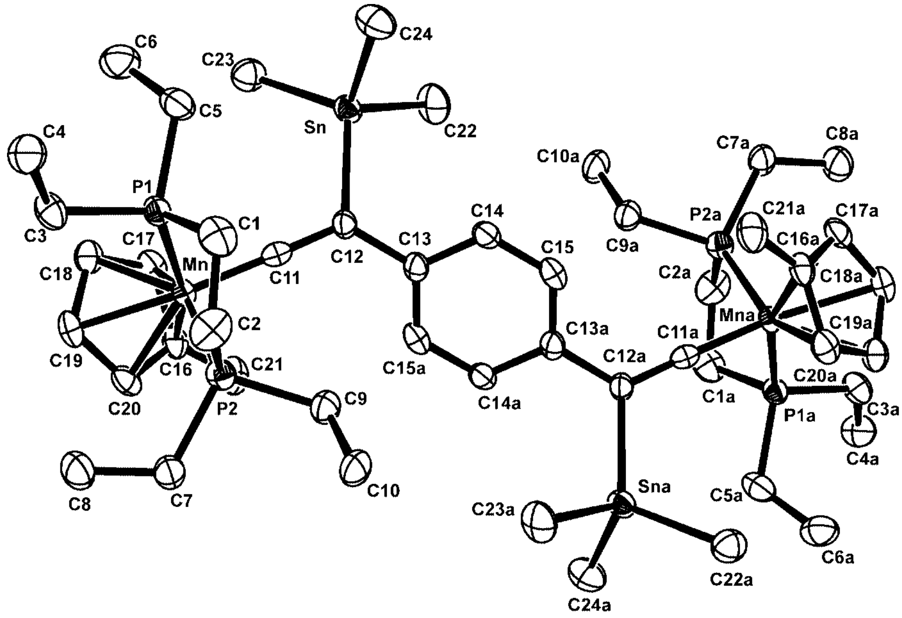


Figure 1. Molecular structure of **2b**; the symmetry operator *a* = –*x*, 2 – *y*, 1 – *z* represents a centre of inversion in the middle of the benzene ring; the ellipsoids are at the 30% probability level and the hydrogen atoms are omitted for clarity; selected bond lengths [Å] and bond angles [°]: Mn–C11 1.763(4), C11–C12 1.345(5), C12–Sn 2.159(4), C12–C13 1.486(6), C13–C14 1.402(5), C14–C15 1.390(6), Mn–Cg1 1.7885(6); C12–C11–Mn 175.7(3), C11–C12–Sn 118.3(3), C13–C12–Sn 115.1(2), C11–C12–C13 125.8(4), P1–Mn–P2 83.59(5)

Complexes **2**–**4** were further transformed into their corresponding parent vinylidene species of the type [{Mn(MeC$_5$H$_4$)(R$_2$PCH$_2$CH$_2$PR$_2$)=C=C(H)}$_2${X}] (X = {μ-1,4-C$_6$H$_4$}, R = Me, **6a**; X = {μ-1,4-C$_6$H$_4$}, R = Et, **6b**; X = {μ-1,3-C$_6$H$_4$}, R = Me, **7a**; X = {μ-1,3-C$_6$H$_4$}, R = Et, **7b**; X = {μ-4,4-C$_6$H$_4$-C$_6$H$_4$}, R = Me, **8a**; X = {μ-4,4-C$_6$H$_4$-C$_6$H$_4$}, R = Et, **8b**) by treatment with an excess of MeOH for 2 h (Scheme 2). However, complexes **5a** and **5b** decomposed upon treatment either with MeOH or tbaf (5% H$_2$O). The ^{1}H NMR spectra of these complexes revealed charac-

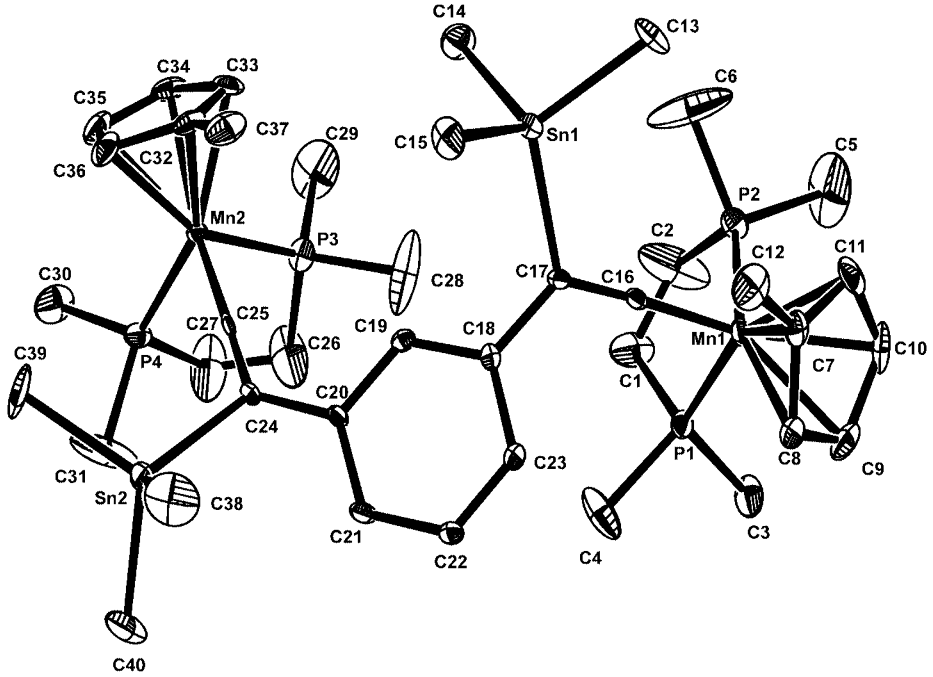


Figure 2. Molecular structure of **3a**; the ellipsoids are at the 30% probability level and the hydrogen atoms are omitted for clarity; selected bond lengths [Å] and bond angles [°]: Mn1–C16 1.769(4), C16–C17 1.299(6), C17–Sn1 2.161(4), C17–C18 1.481(6), C18–C19 1.392(5), C19–C20 1.418(5), Mn1–Cg1 1.8062(7), Mn2–Cg2 1.8045(7); C17–C16–Mn1 176.0(4), C16–C17–C18 124.2(4), C16–C17–Sn1 119.0(2), C17–C18–C19 122.5(4), C23–C18–C17 120.0(3)

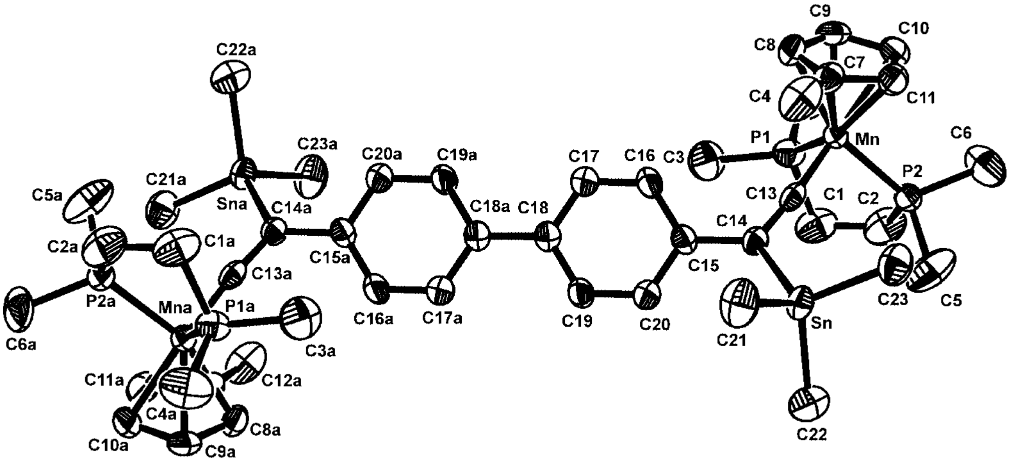
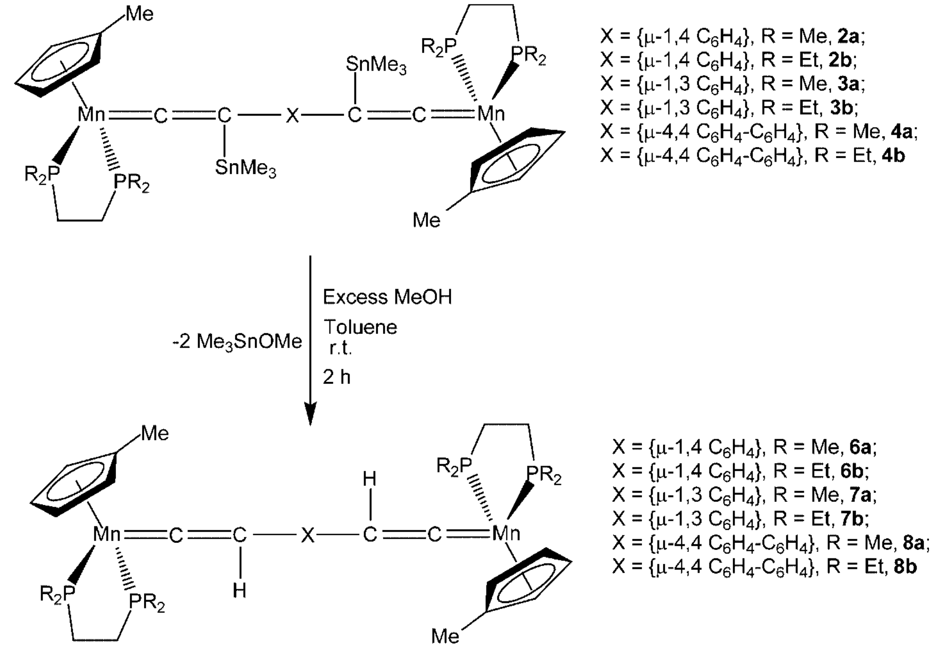


Figure 3. Molecular structure of **4a**; the symmetry operator $a = 2 - x, 1 - y, 1 - z$ represents a centre of inversion in the middle of the biphenyl bond; the ellipsoids are at the 30% probability level and the hydrogen atoms are omitted for clarity; selected bond lengths [Å] and bond angles [°]: Mn–C13 1.744(4), C13–C14 1.358(5), C14–Sn 2.154(4), C14–C15 1.490(5), C15–C16 1.397(5), C16–C17 1.368(5), C17–C18 1.393(5), Mn1–Cg1 1.8055(5); C14–C13–Mn 174.1(13), C13–C14–C15 123.0(3), C13–C14–Sn 117.7(3), C14–C15–C16 122.7(3), C14–C15–C20 122.5(3)

teristic triplet resonances at $\delta \approx 6.0$ ppm with ${}^4J_{P,H}$ values of 8.4 Hz. The ^{13}C NMR spectra of complexes **2**–**5** show the C_α and the C_β resonances further downfield between $\delta = 325$–350 and 130–140 ppm, respectively, in comparison with the tin derivatives. The ^{31}P NMR resonances appear at $\delta \approx 97$ ppm for complexes **6a**–**8a** and are thus comparable with those observed for the related $[Mn(C_5H_4R^1)(Me_2PCH_2CH_2PMe_2)(=C=CR^2H)]$ complexes.[24,38,39] However, the ^{31}P NMR resonances for complexes **6b**–**8b** were observed further downfield at $\delta \approx 114$ ppm. The ^{31}P NMR and ^{13}C NMR spectroscopic data for complexes **6**–**8** are summarised in Table 2.

Table 2. $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopic data for compounds **6**–**8**

Compound	^{31}P NMR ($R_2PCH_2CH_2PR_2$) δ (ppm)	^{13}C NMR δ (ppm) $Mn{=}C_\alpha{=}C_\beta$	$Mn{=}C_\alpha{=}C_\beta$
6a	96.1 (s)	325.4 (t)	133.9
6b	114.5 (s)	327.4 (t)	133.9
7a	94.9 (s)	343.4 (t)	141.3
7b	114.2 (s)	341.9 (t)	140.4
8a	94.5 (s)	342.2 (t)	139.9
8b	115.1 (s)	345.5 (t)	140.2



Scheme 2.

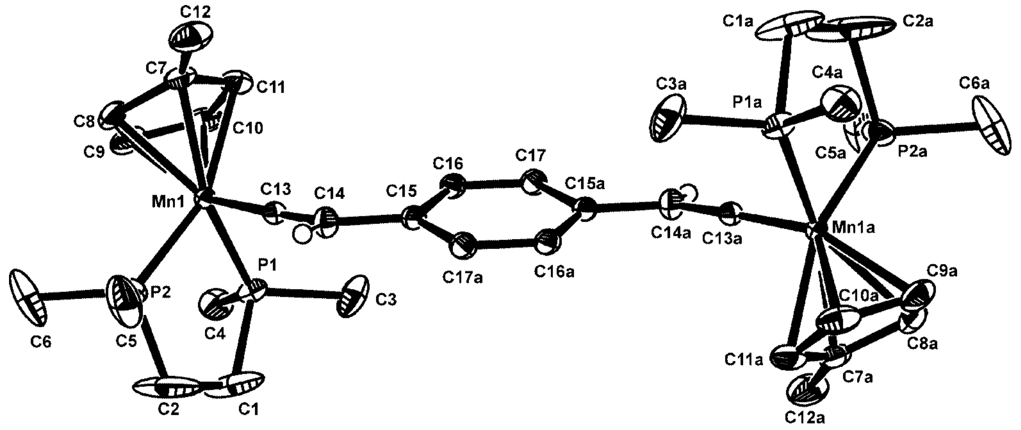


Figure 4. Molecular structure of **6a**; the symmetry operator $a = 2 - x, 2 - y, 1 - z$ represents a centre of inversion in the middle of the benzene ring; the ellipsoids are at the 30% probability level and selected hydrogen atoms are omitted for clarity; selected bond lengths [Å] and bond angles [°]: Mn(1)–C(13) 1.746(2), C(13)–C(14) 1.340(3), C(14)–C(15) 1.466(3), C(1)–C(2) 1.354(5), C(15)–C(16) 1.403(3), Mn1–Cg1 1.7769(3); C(14)–C(13)–Mn(1) 175.09(19), C(13)–C(14)–C(15) 127.8(2), C(14)–C(15)–C(16) 123.1(2), C(5)–P(2)–C(6) 99.17(16), C(3)–P(1)–Mn(1) 120.44(11)

The structure of **6a** was also confirmed by an X-ray diffraction study (Figure 4). A pseudo-tetrahedral coordination environment for each manganese centre was found. The bond lengths of 1.746(4) Å and 1.340(3) Å for Mn1–C13 and C13–C14, respectively, are similar to those found for the previous complexes **2b**, **3a** and **4a** and confirm the double-bond character of these bonds. The bond angles for Mn–C13–C14 and C13–C14–C15 were found to be 175.09(19)° and 127.8(2)°. The latter bond angle suggests that the bending is less pronounced in comparison with the tin derivative.

Conclusions

New dinuclear vinylidenetin complexes and the parent vinylidene complexes capped by Mn^I half-sandwich units have been synthesised. A series of these complexes has been structurally characterised. These complexes offer further possibilities for gaining access to the corresponding dinuclear acetylide complexes.

Experimental Section

X-ray Diffraction Studies on 2b, 3a, 4a and 6a: Single-crystal X-ray diffraction data were collected at measurement temperatures of 183(2) K for **2b** and **4a**, and 153(2) K for **3a** and **6a** using an imaging plate detector system (Stoe IPDS) with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). A total of 200, 167, 154 and 200 images were exposed at constant times of 3.0, 5.0, 2.6 and 2.5 min per image for the structures of **2b**, **3a**, **4a** and **6a**.[43] The crystal-to-image distances were set to 50 mm for **3a**, **4a** and **6a** and to 60 mm for **2b** (θ_{max} range: 27.90–30.46°). φ-oscillation (**2b** and **3a**) and rotation modes (**4a** and **6a**) were chosen for the increments of 1.5, 1.2, 1.3 and 1.3° per exposure in each case. Total exposure times were 21, 24, 14 and 22.4 h. The intensities were integrated using a dynamic peak profile analysis and an estimated mosaic spread (EMS) check was performed to prevent overlapping intensities. For the cell parameter refinements, 8000 reflections with intensities $I > 6\sigma(I)$ were selected out of the whole limiting spheres for the four structures. A total of 18043, 53927, 29813 and 13632 reflections were collected of which 5603, 13101, 7610 and 4830 were unique after performing absorption corrections and data reductions (R_{int} = 8.79, 11.04, 8.02 and 3.92%). For the numerical absorption corrections of **2b**, **3a**, **4a** and **6a**, the numbers of indexed crystal faces used were 9, 10, 6 and 10.[44] All measurement procedures were performed using the stoe IPDS software.[43] The measurement temperatures were controlled by an Oxford cryogenic system. It should be noted that the structures of **2b**, **4a** and **6a** have crystallographically imposed inversion symmetry (see Figure 1, Figure 3 and Figure 4). The structures were solved with the unique data sets using the Patterson method of the program SHELXS-97.[45] The structures were refined with the program SHELXL-97.[46] The programs PLATON and PLUTON[47] were used to check the results of the X-ray analyses and also for the completion of the structures by checking the different electron density calculations. Relevant crystallographic data are collected in Table 3.

Preparations

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 from CaH_2 prior to use. Literature procedures were used to prepare the following compounds: 1,2-bis(dimethylphosphanyl)ethane (dmpe),[48] 1,2-bis(diethylphosphanyl)ethane (depe),[48] [Mn(η^5-MeC_5H_4)(η^6-cycloheptatriene)],[37] $Me_3Sn{-}C{\equiv}C{-}X{-}C{\equiv}C{-}SnMe_3$ (X = {μ-1,4-C_6H_4}, {μ-1,3-C_6H_4}, {μ-4,4-C_6H_4-C_6H_4},[40–42] {μ-1,4-C_4H_2S}). *n*BuLi (1.6 M in hexane), MeLi·LiBr (1.5 M in diethyl ether) and Me_3SnCl were used as received. All manipulations were carried out under nitrogen using Schlenk techniques or in a drybox. IR spectra were obtained with a Bio-Rad FTS-45 instrument. NMR spectra were measured with a Varian Gemini-2000 spectrometer at 300 MHz for ^1H and 121.5 MHz for $^{31}P\{^1H\}$ and with a Bruker DRX-500 spectrometer the frequencies were 125.8 MHz for $^{13}C\{^1H\}$ and 186.5 MHz for ^{119}Sn. Chemical shifts for ^1H and ^{13}C NMR spectra are given in ppm with respect to the solvent signals. $^{31}P\{^1H\}$ NMR spectra were referenced to 98% external H_3PO_4 and the $^{119}Sn\{^1H\}$ NMR spectra are relative to $SnBu_4$.

[{Mn(MeC_5H_4)($Me_2PCH_2CH_2PMe_2$)=C=C($SnMe_3$)}$_2$(μ-1,4-C_6H_4)] (2a): To a toluene solution (10 mL) of [Mn(MeC_5H_4)(η^6-cycloheptatriene)] (50 mg, 0.22 mmol) was added a toluene solution

Table 3. Crystallographic details of **2b**, **3a**, **4a** and **6a**

	2b	**3a**	**4a**	**6a**
Empirical formula	$C_{48}H_{84}Mn_2P_4Sn_2$	$C_{40}H_{68}Mn_2P_4Sn_2$	$C_{46}H_{72}Mn_2P_4Sn_2$	$C_{34}H_{52}Mn_2P_4$
Colour	Red plate	Red elongated block	Red-orange plate	Red block
Formula mass [g mol^{-1}]	1132.29	1020.08	1096.18	694.52
Crystal size [mm]	0.24 × 0.20 × 0.12	0.12 × 0.07 × 0.06	0.20 × 0.12 × 0.05	0.23 × 0.22 × 0.14
T [K]	183(2)	153(2)	183(2)	153(2)
λ(Mo-K_α) [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a [Å]	9.5069(16)	14.9180(8)	10.3548(8)	8.3499(7)
b [Å]	9.8993(16)	17.8972(11)	15.9512(9)	8.3784(7)
c [Å]	14.425(2)	18.1653(10)	15.9948(13)	14.4569(11)
α [°]	104.729(18)	90	90	79.513(10)
β [°]	96.130(19)	108.609(6)	106.259(9)	80.926(10)
γ [°]	97.78(2)	90	90	63.470(9)
V [Å^3]	1286.6(4)	4596.4(5)	2536.2(3)	886.41(12)
Z	1	4	2	1
$\rho_{calcd.}$ [g·cm^{-3}]	1.461	1.474	1.435	1.301
μ [mm^{-1}]	1.594	1.776	1.615	0.914
F(000)	582	2072	1116	366
Transmission range	0.6157–0.8188	0.8326–0.9386	0.7581–0.9257	0.8837–0.9383
2θ range [°]	$4.90 < 2\theta < 55.80$	$5.14 < 2\theta < 60.70$	$5.46 < 2\theta < 60.92$	$5.48 < 2\theta < 60.50$
Measured reflections	18043	53927	29813	13632
Unique reflections	5603	13101	7610	4830
$I > 2\sigma(I)$ reflections	3790	5652	3291	3623
Parameters	261	448	252	186
Gof (for F^2)	0.973	0.718	0.759	1.052
$R_1[I > 2\sigma(I)]$, R_1(all data)[a]	0.0345, 0.0598	0.0338, 0.1070	0.0356, 0.0901	0.0411, 0.0588
$wR_2[I > 2\sigma(I)]$, wR_2(all data)[a]	0.0734, 0.0794	0.0562, 0.0635	0.0556, 0.0594	0.1033, 0.1109
$\Delta\rho_{max/min}$ [e·Å^{-3}]	0.719/–1.166	0.819/–1.192	0.735/–0.489	1.230/–1.174
hkl range	–12/12, –13/13, –18/18	–21/21, –25/25, –25/25	–14/14, –22/22, –22/22	–11/11, –11/11, –20/20

[a] $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$; $I > 2\sigma(I)$; $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.

(10 mL) of dmpe (33 mg, 0.22 mmol) and $Me_3Sn–C{\equiv}C–C_6H_4–C{\equiv}C–SnMe_3$ (50mg, 0.11 mmol). The solution was stirred at 50 °C for 3 h to give a dark red solution. The solvent was removed under vacuum to afford a dark red solid. Then the solid was extracted with diethyl ether and filtered through Celite. The ether fraction was concentrated to give an orange red precipitate. Crystallisation from ether at –35 °C gave single orange-red crystals. Yield: 104 mg, 93%. ^1H NMR ([D$_8$]THF, 300 MHz, 20 °C): δ = 6.75 (4 H, C_6H_5), 4.26 (4 H, C_5H_4Me), 4.00 (4 H, C_5H_4Me), 1.98 (6 H, C_5H_4Me), 1.72 (4 H, PCH_2), 1.61 (4 H, PCH_2), 1.22 (24 H, P[CH_3]$_2$), –0.07 ppm (18 H, $SnMe_3$). $^{13}C\{^1H\}$ NMR ([D$_8$]THF, 125.8 MHz, 20 °C): δ = 329.6 (t, $^2J_{P,C}$ = 35 Hz, Mn-C_α), 136.7 (s, C_i-Ph), 129.1 (m, = C_β), 129.4 (s, 2 C, C_i-C_5H_4Me), 122.2 (s, C_6H_5), 120.5 (s, C_6H_5), 120.2 (s, C_6H_5), 83.9 (s, 4 C, C_5H_4Me), 81.3 (s, 4 C, C_5H_4Me), 32.1 (4 C, PCH_2), 24.5 (PCH_2), 21.9 (P[CH_3]$_3$), 14.8 (P[CH_3]$_3$), –6.1 ($SnMe_3$) ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]THF, 121.5 MHz, 20 °C): δ = 94.9 (s, 4 P) ppm. ^{119}Sn NMR ([D$_8$]THF, 186.5 MHz, 20 °C): δ = –30.2 (t, J = 76 Hz) ppm. IR (CH_2Cl_2, 20 °C): $\tilde{\nu}$ = 1544 [ν(C=C)], 1552 [ν(C=C)] cm^{-1}. $C_{40}H_{68}Mn_2P_4Sn_2$ (1020.15): calcd. C 47.09, H 6.71; found C 47.08, H 6.74.

[{Mn(MeC$_5$H$_4$)(Et$_2$PCH$_2$CH$_2$PEt$_2$)=C=C(SnMe$_3$)}$_2$(μ-1,4-C$_6$H$_4$)] (2b): The same procedure as for **2a** was applied using [Mn(MeC$_5$H$_4$)(η^6-cycloheptatriene)] (50 mg, 0.22 mmol), depe (45 mg, 0.22 mmol) and 1,4-$C_6H_4(C{\equiv}C–SnMe_3)_2$ (50 mg, 0.11 mmol). Yield: 115 mg, 94%. ^1H NMR (C_6D_6, 300 MHz, 20 °C): δ = 7.09 (4 H, C_6H_5), 4.53 (4 H, C_5H_4Me), 3.97 (4 H, C_5H_4Me), 2.22 (6 H, C_5H_4Me), 1.82 (4 H, PCH_2), 1.23 (4 H, PCH_2), 1.58 (4 H, PCH_2CH_3), 1.46 (4 H, PCH_2CH_3), 0.98 (6 H, PCH_2CH_3), 0.67 (6 H, PCH_2CH_3), 0.35 (18 H, $SnMe_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.8 MHz, 20 °C): δ = 326.3 (t, $^2J_{P,C}$ = 30.5 Hz, Mn-C_α), 136.7 (s, C_i-Ph), 129.9 (m, = C_β), 119.4 (s, 2 C, C_i-C_5H_4Me), 96.3 (s, C_6H_5), 120.5 (s, C_6H_5), 81.9 (s, 4 C, C_5H_4Me), 79.3 (s, 4 C, C_5H_4Me), 30.8 (PCH_2), 22.2 (PCH_2), 21.8 (PCH_2CH_3), 19.7 (PCH_2CH_3), 14.5 (s, $C_5H_4CH_3$), –7.1 ($SnMe_3$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz, 20 °C): δ = 115.0 (s, 4 P) ppm. ^{119}Sn NMR (C_6D_6, 186.5 MHz, 20 °C): δ = –27.4 (t, J = 76.0 Hz) ppm. IR (CH_2Cl_2, 20 °C): $\tilde{\nu}$ = 1545 [ν(C=C)], 1553 [ν(C=C)] cm^{-1}. $C_{48}H_{84}Mn_2P_4Sn_2$ (1132.37): calcd. C 50.91, H 7.47; found C 50.61, H 7.66.

[{Mn(MeC$_5$H$_4$)(Me$_2$PCH$_2$CH$_2$PMe$_2$)=C=C(SnMe$_3$)}$_2$(μ-1,3-C$_6$H$_4$)] (3a): The same procedure as for **2a** was applied using [Mn(MeC$_5$H$_4$)(η^6-cycloheptatriene)] (50 mg, 0.22 mmol), dmpe (33 mg, 0.22 mmol) and $Me_3Sn–C{\equiv}C–C_6H_4–C{\equiv}C–SnMe_3$ (50 mg, 0.11 mmol). Yield: 100 mg, 92%. ^1H NMR ([D$_8$]THF, 300 MHz, 20 °C): δ = 6.76 (1 H, C_6H_5), 6.62 (2 H, C_6H_5), 6.41 (1 H, C_6H_5), 4.27 (4 H, C_5H_4Me), 4.01 (4 H, C_5H_4Me), 1.99 (6 H, C_5H_4Me), 1.73 (4 H, PCH_2), 1.63 (4 H, PCH_2), 1.23 (24 H, P[CH_3]$_3$), 0.1 (18 H, $SnMe_3$) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]THF, 125.8 MHz, 20 °C): δ = 328.5 (t, $^2J_{P,C}$ = 30 Hz, Mn-C_α), 143.1 (s, C_i-Ph), 129.1 (m, =C_β), 125.4 (s, 2 C, C_i-C_5H_4Me), 122.2 (s, C_6H_5), 118.5 (s, C_6H_5), 98.2 (s, C_6H_5), 83.9 (s, 4 C, C_5H_4Me), 81.3 (s, 4 C, C_5H_4Me), 32.1 (4 C, PCH_2), 24.5 (PCH_2), 21.9 (P[CH_3]$_3$), 14.8 (P[CH_3]$_3$), –8.1 ($SnMe_3$) ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]THF, 121.5 MHz, 20 °C): δ = 94.3 (s, 4 P) ppm. ^{119}Sn NMR ([D$_8$]THF, 186.5 MHz, 20 °C): δ = –29.8 (t, J = 77.0 Hz). IR (CH_2Cl_2, 20 °C): $\tilde{\nu}$ = 1545 [ν(C=C)], 1556 [ν(C=C)] cm^{-1}. $C_{40}H_{68}Mn_2P_4Sn_2$ (1020.15): calcd. C 47.09, H 6.71; found C 47.08, H 6.74.

[{Mn(MeC$_5$H$_4$)(Et$_2$PCH$_2$CH$_2$PEt$_2$)=C=C(SnMe$_3$)}$_2$(μ-1,3-C$_6$H$_4$)] (3b): The same procedure as for **2a** was applied using

$[Mn(MeC_5H_4)(\eta^6\text{-cycloheptatriene})]$ (50 mg, 0.22 mmol), depe (45 mg, 0.22 mmol) and 1,3-$C_6H_4(C{\equiv}C–SnMe_3)_2$ (50 mg, 0.11 mmol). Yield: 120 mg, 98%. ^{1}H NMR ([D$_8$]THF, 300 MHz, 20 °C): δ = 6.76 (1 H, C_6H_5), 6.62 (2 H, C_6H_5), 6.41 (1 H, C_6H_5), 4.27 (4 H, C_5H_4Me), 4.01 (4 H, C_5H_4Me), 1.99 (6 H, C_5H_4Me), 1.82 (4 H, PCH_2), 1.23 (4 H, PCH_2), 1.58 (4 H, $PC\mathit{H}_2CH_3$), 1.46 (4 H, $PC\mathit{H}_2CH_3$), 0.98 (6 H, $PCH_2C\mathit{H}_3$), 0.67 (6 H, $PCH_2C\mathit{H}_3$), 0.1 (18 H, $SnMe_3$) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]THF, 125.8 MHz, 20 °C): δ = 328.5 (t, $^2J_{P,C}$ = 30 Hz, Mn-C_α), 143.1 (s, C_i-Ph), 129.1 (m, =C_β), 125.4 (s, 2 C, C_i-C_5H_4Me), 122.2 (s, C_6H_5), 118.5 (s, C_6H_5), 98.2 (s, C_6H_5), 83.9 (s, 4 C, C_5H_4Me), 81.3 (s, 4 C, C_5H_4Me), 30.8 ($P\mathit{C}H_2$), 22.2 ($P\mathit{C}H_2$), 21.8 ($P\mathit{C}H_2CH_3$), 19.7 ($PCH_2\mathit{C}H_3$), 14.5 (s, $C_5H_4\mathit{C}H_3$), –7.1 ($SnMe_3$) ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]THF, 121.5 MHz, 20 °C): δ = 115.0 (s, 4 P) ppm. ^{119}Sn NMR ([D$_8$]THF, 186.5 MHz, 20 °C): δ = –29.8 (t, J = 75.0 Hz) ppm. IR (CH_2Cl_2, 20 °C): ṽ = 1549 [ν(C=C)], 1558 [ν(C=C)] cm^{-1}. $C_{48}H_{84}Mn_2P_4Sn_2$ (1132.37): calcd. C 50.91, H 7.47; found C 50.56, H 7.32.

$[\{Mn(MeC_5H_4)(Me_2PCH_2CH_2PMe_2)=C=C(SnMe_3)\}_2\{\mu\text{-}4,4\text{-}(C_6H_4)_2\}]$ (4a): The same procedure as for **2a** was applied using $[Mn(MeC_5H_4)(\eta^6\text{-cycloheptatriene})]$ (50 mg, 0.22 mmol), dmpe (33 mg, 0.22 mmol) and $Me_3Sn–C{\equiv}C–C_6H_4–C_6H_4–C{\equiv}C–SnMe_3$ (58 mg, 0.11 mmol). Yield: 105 mg, 91%. ^{1}H NMR ([D$_8$]THF, 300 MHz, 20 °C): δ = 7.28 (m, 4 H, C_6H_5), 7.02 (m, 4 H, C_6H_5), 4.28 (4 H, C_5H_4Me), 4.03 (4 H, C_5H_4Me), 1.97 (6 H, C_5H_4Me), 1.72 (4 H, PCH_2), 1.61 (4 H, PCH_2), 1.23 (24 H, $P(CH_3]_3$), 0.09 (18 H, $SnMe_3$) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]THF, 125.8 MHz, 20 °C): δ = 330.5 (t, $^2J_{P,C}$ = 35 Hz, Mn-C_α), 143.3 (s, C_i-Ph), 135.8 (s, C_6H_5), 133.2 (s, 2 C, C_i-C_5H_4Me), 129.1 (m, =C_β), 125.4 (s, C_6H_5), 118.1 (s, C_6H_5), 83.4 (s, 4 C, C_5H_4Me), 81.3 (s, 4 C, C_5H_4Me), 32.05 (4 C, PCH_2), 24.5 (PCH_2), 21.9 ($P[CH_3]_3$), 14.8 ($P[CH_3]_3$), –6.1 ($SnMe_3$) ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]THF, 121.5 MHz, 20 °C): δ = 93.0 (s, 4 P) ppm. ^{119}Sn NMR ([D$_8$]THF, 186.5 MHz, 20 °C): δ = –17.1 (t, J = 77.0 Hz) ppm. IR (CH_2Cl_2, 20 °C): ṽ = 1545 [ν(C=C)], 1553 [ν(C=C)] cm^{-1}. $C_{46}H_{72}Mn_2P_4Sn_2$ (1096.25): calcd. C 50.39, H 6.61; found C 50.47, H 6.39.

$[\{Mn(MeC_5H_4)(Et_2PCH_2CH_2PEt_2)=C=C(SnMe_3)\}_2\{\mu\text{-}4,4\text{-}(C_6H_4)_2\}]$ (4b): The same procedure as for **2a** was applied using $[Mn(MeC_5H_4)(\eta^6\text{-cycloheptatriene})]$ (50 mg, 0.22 mmol), dmpe (45 mg, 0.22 mmol) and 4,4-$(C_6H_4)_2(C{\equiv}C–SnMe_3)_2$ (58 mg, 0.11 mmol). Yield: 125 mg, 96%. ^{1}H NMR ([D$_8$]THF, 300 MHz, 20 °C): δ = 7.31 (m, 4 H, C_6H_5), 6.98 (m, 4 H, C_6H_5), 4.48 (4 H, C_5H_4Me), 4.02 (4 H, C_5H_4Me), 2.08 (6 H, C_5H_4Me), 1.89 (4 H, PCH_2), 1.73 (4 H, PCH_2), 1.43 (4 H, $PC\mathit{H}_2CH_3$), 1.14 (4 H, $PC\mathit{H}_2CH_3$), 1.02 (6 H, $PCH_2C\mathit{H}_3$), 0.92 (6 H, $PCH_2C\mathit{H}_3$), 0.11 (18 H, $SnMe_3$) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]THF, 125.8 MHz, 20 °C): δ = 328.0 (t, $^2J_{P,C}$ = 35 Hz, Mn-C_α), 142.3 (m, =C_β), 138.4 (s, C_i-Ph), 135.8 (s, C_6H_5), 133.2 (s, 2 C, C_i-C_5H_4Me), 125.4 (s, C_6H_5), 118.1 (s, C_6H_5), 83.4 (s, 4 C, C_5H_4Me), 81.3 (s, 4 C, C_5H_4Me), 30.8 ($P\mathit{C}H_2$), 22.2 ($P\mathit{C}H_2$), 21.8 ($P\mathit{C}H_2CH_3$), 19.7 ($PCH_2\mathit{C}H_3$), 14.5 (s, $C_5H_4\mathit{C}H_3$), –8.3 ($SnMe_3$) ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]THF, 121.5 MHz, 20 °C): δ = 113.5 (s, 4 P) ppm. ^{119}Sn NMR ([D$_8$]THF, 186.5 MHz, 20 °C): δ = –29.2 (t, J = 75.1 Hz) ppm. IR (CH_2Cl_2, 20 °C): ṽ = 1544 [ν(C=C)], 1559 [ν(C=C)] cm^{-1}. $C_{54}H_{88}Mn_2P_4Sn_2$ (1208.46): calcd. C 53.66, H 7.33; found C 53.77, H 7.36.

$[\{Mn(MeC_5H_4)(Me_2PCH_2CH_2PMe_2)=C=C(SnMe_3)\}_2(\mu\text{-}1,4\text{-}C_4H_2S)]$ (5a): The same procedure as for **2a** was applied using $[Mn(MeC_5H_4)(\eta^6\text{-cycloheptatriene})]$ (50 mg, 0.22 mmol), dmpe (33 mg, 0.22 mmol) and $Me_3Sn–C{\equiv}C–C_4H_2S–C{\equiv}C–SnMe_3$ (37 mg, 0.11 mmol). Yield: 105 mg, 94%. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C): δ = 6.36 (4 H, C_6H_5), 4.36 (4 H, C_5H_4Me), 3.95 (4 H, C_5H_4Me), 2.18 (6 H, C_5H_4Me), 1.59 (4 H, PCH_2), 1.32 (12 H, $P[CH_3]_2$), 1.24 (4 H, PCH_2), 0.85 (12 H, $P[CH_3]_2$), 0.41 (18 H, $SnMe_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.8 MHz, 20 °C): δ = 328.5 (t, $^2J_{P,C}$ = 32.3 Hz, Mn-C_α), 139.7 (s, C_i-C_4H_2S), 120.2 (s, C_4H_2S), 110.1 (m, =C_β), 97.3 (s, 2 C, C_i-C_5H_4Me), 83.9 (s, 4 C, C_5H_4Me), 81.5 (s, 4 C, C_5H_4Me), 31.8 (2 C, PCH_2), 23.7 (2 C, PCH_2), 23.7 ($P[CH_3]_3$), 21.7 ($P[CH_3]_3$), 15.3 (2 C, C_5H_4Me), –6.2 ($SnMe_3$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz, 20 °C): δ = 93.7 (s, 4 P) ppm. ^{119}Sn NMR (C_6D_6, 186.5 MHz, 20 °C): δ = –27.5 (t, J = 72.0 Hz) ppm. IR (CH_2Cl_2, 20 °C): ṽ = 1545 [ν(C=C)], 1553 [ν(C=C)] cm^{-1}. $C_{38}H_{66}Mn_2P_4Sn_2S$ (1026.18): calcd. C 44.47, H 6.48; found C 44.59, H 6.74.

$[\{Mn(MeC_5H_4)(Et_2PCH_2CH_2PEt_2)=C=C(SnMe_3)\}_2(\mu\text{-}1,4\text{-}C_4H_2S)]$ (5b): The same procedure as for **2a** was applied using $[Mn(MeC_5H_4)(\eta^6\text{-cycloheptatriene})]$ (50 mg, 0.22 mmol), depe (45 mg, 0.22 mmol) and 1,4-$C_4H_2S(C{\equiv}C–SnMe_3)_2$ (37 mg, 0.11 mmol). Yield: 120 mg, 94%. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C): δ = 6.35 (4 H, C_6H_5), 4.61 (4 H, C_5H_4Me), 4.01 (4 H, C_5H_4Me), 2.31 (6 H, C_5H_4Me), 1.59 (4 H, PCH_2), 1.32 (8 H, $P[CH_2CH_3]_2$), 1.32 (8 H, $P[CH_2CH_3]_2$), 1.02 (12 H, $P[CH_3]_2$), 0.73 (4 H, PCH_2), 0.48 (18 H, $SnMe_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.8 MHz, 20 °C): δ = 326.8 (t, $^2J_{P,C}$ = 32.3 Hz, Mn-C_α), 141.1 (m, =C_β), 120.9 (s, C_i-C_4H_2S), 109.4 (s, C_4H_2S), 97.4 (s, 2 C, C_i-C_5H_4Me), 82.9 (s, 4 C, C_5H_4Me), 79.8 (s, 4 C, C_5H_4Me), 30.8 ($P\mathit{C}H_2$), 22.2 ($P\mathit{C}H_2$), 21.8 ($P\mathit{C}H_2CH_3$), 19.7 ($PCH_2\mathit{C}H_3$), 14.5 (s, $C_5H_4\mathit{C}H_3$), –6.2 ppm ($SnMe_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz, 20 °C): δ = 115.1 ppm (s, 4 P). ^{119}Sn NMR (C_6D_6, 186.5 MHz, 20 °C): δ = –26.3 (t, J = 72.0 Hz). IR (CH_2Cl_2, 20 °C): ṽ = 1548 [ν(C=C)], 1554 [ν(C=C)] cm^{-1}. $C_{38}H_{66}Mn_2P_4Sn_2S$ (1138.40): calcd. C 44.47, H 6.48; found C 44.59, H 6.74.

$[\{Mn(MeC_5H_4)(Me_2PCH_2CH_2PMe_2)=C=C(H)\}_2(\mu\text{-}1,4\text{-}C_6H_4)]$ (6a): To a toluene solution (10 mL) of $[\{Mn(MeC_5H_4)(dmpe)=C=C(SnMe_3)\}_2(\mu\text{-}1,4\text{-}C_6H_4)]$ (120 mg, 0.17 mmol) was added an excess of methanol. The solution was stirred at room temperature for 2 h to give a dark red solution. The solvent was removed under vacuum to afford a dark red solid which was washed with pentane. The solid was extracted with toluene and filtered through Celite. The toluene fraction was concentrated to give an orange-red precipitate. Crystallisation from a mixture of tetrahydrofuran/ether at –35 °C gave single orange-red crystals. Yield: 105 mg, 90%. ^{1}H NMR ([D$_8$]toluene, 300 MHz, 20 °C): δ = 7.15 (4 H, C_6H_5), 5.91 (2 H, $^4J_{P,H}$ = 8.4 Hz, = C[H]), 4.30 (4 H, C_5H_4Me), 3.86 (4 H, C_5H_4Me), 1.93 (6 H, C_5H_4Me), 1.49 (4 H, PCH_2), 1.11 (12 H, $P(CH_3]_2$), 1.02 (4 H, PCH_2), 0.74 (12 H, $P[CH_3]_2$) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]toluene, 125.8 MHz, 20 °C): δ = 325.4 (t, $^2J_{P,C}$ = 37.5 Hz, Mn-C_α), 133.9 (m, =C_β), 132.3 (s, C_i-Ph), 129.4 (s, 2 C, C_i-C_5H_4Me), 123.1 (s, C_6H_5), 122.3 (s, C_6H_5), 121.9 (s, C_6H_5), 84.1 (s, 4 C, C_5H_4Me), 80.4 (s, 4 C, C_5H_4Me), 31.2 (2 C, PCH_2), 23.5 (2 C, PCH_2), 21.1 ($P[CH_3]_3$), 14.8 ($P[CH_3]_3$) ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]toluene, 121.5 MHz, 20 °C): δ = 96.1 (s, 4 P) ppm. IR (CH_2Cl_2, 20 °C): ṽ = 1545 [ν(C=C)], 1553 [ν(C=C)] cm^{-1}. $C_{34}H_{52}Mn_2P_4$ (694.54): calcd. C 58.79, H 7.54; found C 58.95, H 7.43.

$[\{Mn(MeC_5H_4)(Et_2PCH_2CH_2PEt_2)=C=C(H)\}_2(\mu\text{-}1,4\text{-}C_6H_4)]$ (6b): The same procedure as for **6a** was applied using $[\{Mn(MeC_5H_4)(depe)=C=C(SnMe_3)\}_2(\mu\text{-}1,4\text{-}C_6H_4)]$ (120 mg, 0.10 mmol). Yield: 80 mg, 98%. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C): δ = 7.28 (4 H, C_6H_5), 5.91 (2 H, $^4J_{P,H}$ = 12.9 Hz, =C[H]), 4.51 (4 H, C_5H_4Me), 4.05 (4 H, C_5H_4Me), 2.17 (6 H, C_5H_4Me), 1.89 (4 H, PCH_2), 1.73 (4 H, PCH_2), 1.43 (4 H, $PC\mathit{H}_2CH_3$), 1.14 (4 H, $PC\mathit{H}_2CH_3$), 1.02 (6 H, $PCH_2C\mathit{H}_3$), 0.92 (6 H, $PCH_2C\mathit{H}_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.8 MHz, 20 °C): δ = 327.4 (t, $^2J_{P,C}$ = 37.5 Hz, Mn-C_α), 133.9 (m, =C_β), 132.3 (s, C_i-Ph), 129.4 (s, 2 C,

C_i-C_5H_4Me), 123.1 (s, C_6H_5), 122.3 (s, C_6H_5), 121.9 (s, C_6H_5), 84.1 (s, 4 C, C_5H_4Me), 80.4 (s, 4 C, C_5H_4Me), 30.8 (PCH$_2$), 22.2 (PCH$_2$), 21.8 (PCH$_2$CH$_3$), 19.7 (PCH$_2$$CH_3$), 14.5 (s, $C_5H_4CH_3$) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz, 20 °C): δ = 114.5 (s, 4 P) ppm. IR (CH_2Cl_2, 20 °C): $\tilde{\nu}$ = 1548 [ν(C=C)], 1555 [ν(C=C)] cm^{-1}. $C_{42}H_{68}Mn_2P_4$ (806.76): calcd. C 62.52, H 8.49; found C 62.31, H 8.45.

[{Mn(MeC$_5$H$_4$)(Me$_2$PCH$_2$CH$_2$PMe$_2$)=C=C(H)}$_2$(μ-1,3-C$_6$H$_4$)] (7a): The same procedure as for **6a** was applied using [{Mn(MeC$_5$H$_4$)(dmpe)=C=C(SnMe$_3$)}$_2$(μ-1,3-C$_6$H$_4$)] (120 mg, 0.17 mmol). Yield: 105 mg, 90%. ^{1}H NMR ([D$_8$]toluene, 300 MHz, 20 °C): δ = 7.31 (1 H, C_6H_5), 7.25 (1 H, C_6H_5), 7.13 (2 H, C_6H_5), 6.01 (2 H, $^4J_{P,H}$ = 8.4 Hz, =C[H]), 4.42 (4 H, C_5H_4Me), 3.99 (4 H, C_5H_4Me), 2.07 (6 H, C_5H_4Me), 1.59 (4 H, PCH$_2$), 1.24 (12 H, P[CH$_3$]$_2$), 1.18 (4 H, PCH$_2$), 0.80 (12 H, P[CH$_3$]$_2$) ppm. ^{13}C{^{1}H} NMR ([D$_8$]toluene, 125.8 MHz, 20 °C): δ = 343.4 (t, $^2J_{P,C}$ = 37.5 Hz, Mn-C_α), 141.3 (m, =C_β), 132.3 (s, C_i-Ph), 122.4 (s, 2 C, C_i-C_5H_4Me), 123.1 (s, C_6H_5), 118.4 (s, C_6H_5), 116.7 (s, C_6H_5), 84.1 (s, 4 C, C_5H_4Me), 80.4 (s, 4 C, C_5H_4Me), 31.3 (2 C, PCH$_2$), 23.8 (2 C, PCH$_2$), 21.7 (P[CH$_3$]$_3$), 14.8 (P[CH$_3$]$_3$) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz, 20 °C): δ = 94.9 (s, 4 P) ppm. IR (CH_2Cl_2, 20 °C): $\tilde{\nu}$ = 1549 [ν(C=C)], 1558 [ν(C=C)] cm^{-1}. $C_{34}H_{52}Mn_2P_4$ (694.54): calcd. C 58.79, H 7.54; found C 58.95, H 7.43.

[{Mn(MeC$_5$H$_4$)(Et$_2$PCH$_2$CH$_2$PEt$_2$)=C=C(H)}$_2$(μ-1,3-C$_6$H$_4$)] (7b): The same procedure as for **6a** was applied using [{Mn(MeC$_5$H$_4$)(depe)=C=C(SnMe$_3$)}$_2$(μ-1,3-C$_6$H$_4$)] (190 mg, 0.17 mmol). Yield: 120 mg, 90%. ^{1}H NMR ([D$_8$]toluene, 300 MHz, 20 °C): δ = 7.31 (1 H, C_6H_5), 7.25 (1 H, C_6H_5), 7.13 (2 H, C_6H_5), 6.08 (2 H, $^4J_{P,H}$ = 8.4 Hz, =C[H]), 4.51 (4 H, C_5H_4Me), 4.05 (4 H, C_5H_4Me), 2.17 (6 H, C_5H_4Me), 1.89 (4 H, PCH$_2$), 1.73 (4 H, PCH$_2$), 1.43 (4 H, PCH_2CH$_3$), 1.14 (4 H, PCH_2CH$_3$), 1.02 (6 H, PCH$_2$CH_3), 0.92 (6 H, PCH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR ([D$_8$]toluene, 125.8 MHz, 20 °C): δ = 341.9 (t, $^2J_{P,C}$ = 37 Hz, Mn-C_α), 140.4 (m, =C_β), 132.3 (s, C_i-Ph), 122.4 (s, 2 C, C_i-C_5H_4Me), 123.1 (s, C_6H_5), 118.4 (s, C_6H_5), 116.7 (s, C_6H_5), 84.1 (s, 4 C, C_5H_4Me), 80.4 (s, 4 C, C_5H_4Me), 30.8 (PCH$_2$), 22.2 (PCH$_2$), 21.8 (PCH$_2$CH$_3$), 19.7 (PCH$_2$$CH_3$), 14.5 (s, $C_5H_4CH_3$) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz, 20 °C): δ = 114.2 (s, 4 P) ppm. IR (CH_2Cl_2, 20 °C): $\tilde{\nu}$ = 1545 [ν(C=C)], 1553 [ν(C=C)] cm^{-1}. $C_{42}H_{68}Mn_2P_4$ (806.76): C 58.79, H 7.54; found C 58.89, H 7.89.

[{Mn(MeC$_5$H$_4$)(Me$_2$PCH$_2$CH$_2$PMe$_2$)=C=C(H)}$_2$(μ-4,4-(C$_6$H$_4$)$_2$)] (8a): The same procedure as for **6a** was applied using [{Mn(MeC$_5$H$_4$)(dmpe)=C=C(SnMe$_3$)}$_2${μ-4,4-(C$_6$H$_4$)$_2$}] (120 mg, 0.10 mmol). Yield: 70 mg, 92%. ^{1}H NMR ([D$_8$]toluene, 300 MHz, 20 °C): δ = 7.67 (m, 4 H, C_6H_5), 7.42 (m, 4 H, C_6H_5), 6.00 (2 H, $^4J_{P,H}$ = 7.9 Hz, =C[H]), 4.42 (4 H, C_5H_4Me), 3.95 (4 H, C_5H_4Me), 2.06 (6 H, C_5H_4Me), 1.56 (4 H, PCH$_2$), 1.20 (24 H, P[CH$_3$]$_3$), 1.05 (4 H, PCH$_2$), 0.79 (24 H, P[CH$_3$]$_3$) ppm. ^{13}C{^{1}H} NMR ([D$_8$]toluene, 125.8 MHz, 20 °C): δ = 342.2 (t, $^2J_{P,C}$ = 34.7 Hz, Mn-C_α), 139.9 (m, =C_β), 135.4 (s, C_i-Ph), 133.2 (s, C_6H_5), 126.7 (s, 2 C, C_i-C_5H_4Me), 126.2 (s, C_6H_5), 120.4 (s, C_6H_5), 84.6 (s, 4 C, C_5H_4Me), 80.3 (s, 4 C, C_5H_4Me), 30.8 (4 C, PCH$_2$), 23.3 (PCH$_2$), (P[CH$_3$]$_3$), 14.6 (P[CH$_3$]$_3$) ppm. ^{31}P{^{1}H} NMR ([D$_8$]toluene, 121.5 MHz, 20 °C): δ = 94.5 (s, 4 P) ppm. IR (CH_2Cl_2, 20 °C): $\tilde{\nu}$ = 1547 [ν(C=C)], 1553 [ν(C=C)] cm^{-1}. $C_{40}H_{56}Mn_2P_4$ (770.64): calcd. C 62.34, H 7.32; found C 62.47, H 7.39.

[{Mn(MeC$_5$H$_4$)(Et$_2$PCH$_2$CH$_2$PEt$_2$)=C=C(H)}$_2${μ-4,4-(C$_6$H$_4$)$_2$}] (8b): The same procedure as for **6a** was applied using [{Mn(MeC$_5$H$_4$)(depe)=C=C(SnMe$_3$)}$_2${μ-4,4-(C$_6$H$_4$)$_2$}] (130mg, 0.10 mmol). Yield: 82 mg, 95%. ^{1}H NMR ([D$_8$]toluene, 300 MHz, 20 °C): δ = 7.68 (m, 4 H, C_6H_5), 7.38 (m, 4 H, C_6H_5), 6.00 (2 H, $^4J_{P,H}$ = 8.4 Hz, =C[H]), 4.52 (4 H, C_5H_4Me), 4.03 (4 H, C_5H_4Me), 2.16 (6 H, C_5H_4Me), 1.73 (4 H, PCH$_2$), 1.66 (4 H, PCH$_2$), 1.43 (4 H, PCH_2CH$_3$), 1.14 (4 H, PCH_2CH$_3$), 1.02 (6 H, PCH$_2$CH_3), 0.92 (6 H, PCH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR ([D$_8$]toluene, 125.8 MHz, 20 °C): δ = 345.5 (t, $^2J_{P,C}$ = 34.7 Hz, Mn-C_α), 140.2 (m, =C_β), 136.3 (s, C_i-Ph), 133.2 (s, C_6H_5), 127.8 (s, 2 C, C_i-C_5H_4Me), 123.2 (s, C_6H_5), 120.2 (s, C_6H_5), 83.1 (s, 4 C, C_5H_4Me), 80.4 (s, 4 C, C_5H_4Me), 30.8 (PCH$_2$), 22.2 (PCH$_2$), 21.8 (PCH$_2$CH$_3$), 19.7 (PCH$_2$$CH_3$), 14.5 (s, $C_5H_4CH_3$) ppm. ^{31}P{^{1}H} NMR ([D$_8$]toluene, 121.5 MHz, 20 °C): δ = 115.1 (s, 4 P) ppm. IR (CH_2Cl_2, 20 °C): $\tilde{\nu}$ = 1546 [ν(C=C)], 1559 [ν(C=C)] cm^{-1}. $C_{48}H_{52}Mn_2P_4$ (862.69): calcd. C 66.82, H 6.07; found C 66.93, H 6.04.

X-ray Crystallography: 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-239735, -239736, -239737 and -239738. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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