

Synthetic Access to Half-Sandwich Manganese C₄ Cumulenic Complexes

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The vinylalkynyl complexes $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{R}'')_2\text{PCH}_2\text{CH}_2\text{PR}'')_2(=\text{C}=\text{CSnPh}_3\text{C}\equiv\text{CSnPh}_3)$ (**5**, **6**) were obtained in good yields by treatment of $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\eta^6\text{-cycloheptatriene})$ ($\text{R}' = \text{H}$ (**1a**), Me (**1b**)) with 1 equiv of $\text{Ph}_3\text{SnC}\equiv\text{CC}\equiv\text{CSnPh}_3$ and $\text{R}'')_2\text{PCH}_2\text{CH}_2\text{PR}'')_2$ ($\text{R}'' = \text{CH}_3$ (dmpe), C_2H_5 (depe)). The theoretically characterized (DFT) C₄ cumulenic species $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{R}'')_2\text{PCH}_2\text{CH}_2\text{PR}'')_2\{\text{C}=\text{C}=\text{C}=\text{C}(\text{SnPh}_3)_2\}$ (**7**, **8**) were obtained by photolysis of the tin-substituted vinylalkynyl complexes **5** and **6**. Subsequently **7** and **8** could be converted into the parent cumulenic species $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{R}'')_2\text{PCH}_2\text{CH}_2\text{PR}'')_2\{\text{C}=\text{C}=\text{C}=\text{C}(\text{H})_2\}$ (**9**, **10**) by reacting complexes **7** and **8** with TBAF (5% H₂O) at -40°C . The difference in the thermodynamic stabilities between the complexes **7** and **8** and complexes **9** and **10** was traced by DFT calculations using $\text{Mn}(\text{C}_5\text{H}_5)(\text{dHpe})\{\text{C}=\text{C}=\text{C}=\text{C}(\text{SnMe}_3)_2\}$ (**4-H**) and $\text{Mn}(\text{C}_5\text{H}_5)(\text{dHpe})\{\text{C}=\text{C}=\text{C}=\text{CH}_2\}$ (**9-H**) as model complexes. Treatment of the vinylalkynyl complex with an excess of MeOH led to the formation of a dinuclear complex with a C₈ chain between two manganese centers. The cumulenic complexes and the vinylalkynyl complexes were characterized by NMR and vibrational spectroscopy and elemental analyses. An X-ray diffraction study has been performed on complex **4b**.

Introduction

The chemistry of metallacumulenes $\text{M}(=\text{C})_m\text{CR}_2$ is of considerable interest from several perspectives.^{1,2} In the context of materials science, π -conjugated linear $(=\text{C})_m$ moieties fundamentally allow communication between metal centers and remote functional groups, and potential applications as nonlinear optical materials and molecular wires have been advocated.^{3–7} Metallacumulenes also represent an interesting class of metal–carbon multiple-bond compounds for the study of the bonding interactions in $\text{M}(=\text{C})_m\text{CR}_2$, particularly with regard to the degree of π -bonding/ π -back-bonding interaction^{8–24} and π -delocalization effects. In addition to the theoretical interest in such complexes, the high

degree of unsaturation in metallacumulene complexes $\text{L}_m\text{M}(=\text{C})_m\text{CR}_2$ has also become a challenge for preparative endeavors.^{20,25,26,27–30} Metallacumulenes with $m =$

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1, 2 (vinylidenes or allenylidenes) are very common and have been well studied during the last few years.^{10,11,14,24,31–44} Complexes with $m = 4$ are less common, but some examples of such complexes are known.^{45–50} However, species with a four-carbon chain ($m = 3$) appear to be of extraordinarily low stability and therefore have been accessed only rarely. Recently, Werner's group has prepared the first stable neutral C_4 metallacumulene compound containing a $Ir=C=C=C=CPh_2$ unit⁵¹ and also have later reported reactivity studies of this complex.^{8,9} Furthermore, in situ preparations of cationic species containing a $[Ru=C=C=C=CRH]^+$ fragment have been reported: $R = H$ by Bruce^{48,49} and $R \neq H$ by Dixneuf⁵² and Winter.^{45,47,52,53} The $Ru(=C)_4$ species were quite short-lived, preventing spectroscopic characterization. Lapinte's group managed to stabilize a peculiar complex containing an $Fe(=C)_4$ cumulenic motif by attaching an $FeCp^*(CO)_2$ moiety to the terminal carbon atom of the cumulenic chain.⁵⁰

Recently, we reported the synthesis of novel half-sandwich manganese(I) vinylidene systems which undergo facile oxidative coupling and the reverse reductive decoupling, which might be utilized in electron storage devices.⁵⁴ A first conclusion of this and other earlier studies^{55–57} was that vinylidene complexes gained considerable stability through the presence of the bis-(dimethylphosphino)ethane ligand (dmpe) in comparison with the reported CO-substituted species $Mn(Cp)L^1L^2$.

($C=CR_2$), where $L^1 = L^2 = CO$ or $L^1 = CO$, $L^2 = PR_3$. Our interest in this area has focused also on the preparation of redox-active di- or polynuclear organometallic complexes containing manganese (end) groups, and we consequently sought to utilize the stability and electron richness of dmpe-substituted half-sandwich Mn^I moieties for the buildup of molecular redox wires.⁵⁸ A major route to dinuclear metal systems bearing cumulene bridges utilizes coupling processes of the appropriate mononuclear species.^{10,59–71} Previously, we have communicated a facile route to C_4 monometallacumulenes and the first spectroscopic observation of the parent butatrienyldiene. These results provided the impetus to further investigate the influence of the substituents both on the phosphorus atoms and on the tin atoms with respect to the stability and reactivity of the C_4 monometallacumulenes and vinyl alkynyl complexes.

Results and Discussion

An already established method to obtain vinylidene complexes makes use of the high propensity of terminal acetylene derivatives to rearrange to vinylidene compounds.^{11,14,28–30,32,35,36,47,72} For such a process to be initiated in the realm of half-sandwich Mn^I chemistry, we thought the complexes $Mn(C_5H_4R')(\eta^6\text{-cycloheptatriene})$ ($R' = H$ (**1a**), Me (**1b**))⁷³ would be excellent starting materials, due to the labile character of the Mn–heptatriene interaction. Facile ligand exchange with donating ligands, such as phosphines and acetylenes, was expected to occur as previously reported.^{54,57} Conversions with tin mono- or disubstituted acetylenes led to the desired vinylidene species. The reaction of $Mn(C_5H_4R')(\eta^6\text{-cycloheptatriene})$ ($R' = Me$ (**1b**)) with $Me_3SiC\equiv C\equiv CSnMe_3$ and $R''_2PCH_2CH_2PR''_2$ ($R'' = Me$, dmpe) gave the corresponding vinylidene species $Mn(C_5H_4R')(dmpe)(=C=CSnMe_3C\equiv CSiMe_3)$ ($R' = Me$ (**2b**)) in about 98% yield (Scheme 1). This reaction required the initial formation of a Mn–alkyne species.⁷² How-

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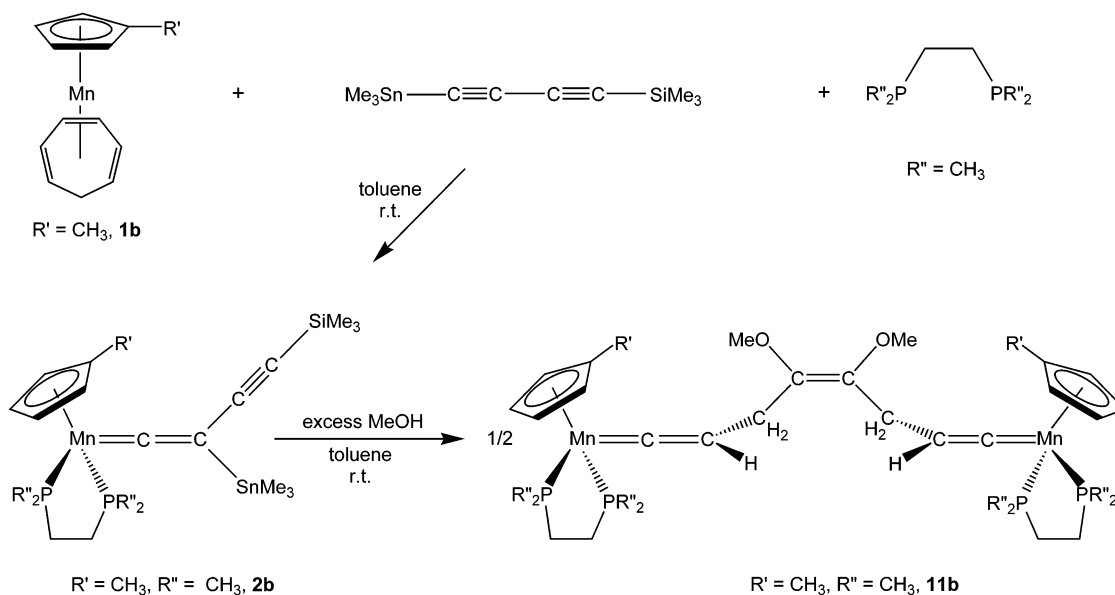
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Scheme 1

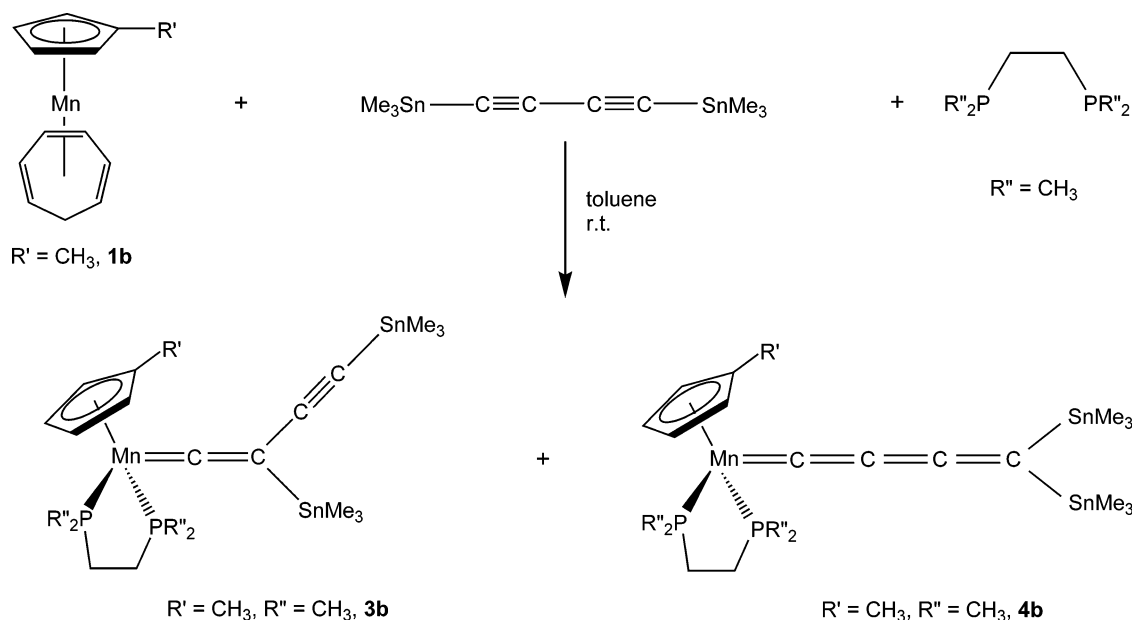


ever, NMR studies of the reaction carried out in the range of -70 to $+20$ °C did not reveal any intermediate. Spectroscopic studies also confirmed the observation that only the SnMe_3 group migrates to the C_β atom of the vinyl alkynyl chain. The ^{13}C NMR spectrum of **2b** shows the C_α and C_β resonances at 329.5 and 91.8 ppm, respectively. The ^{31}P NMR resonances appear at 93.9 ppm. These data are comparable to those which were obtained for the related $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{dmpe})(=\text{C}=\text{CRH})$ complexes.^{60,62,63} The ^{119}Sn NMR spectrum of species **2b** shows a triplet corresponding to the $C_{\text{sp}^2}\text{-Sn}$ bond at -17.5 ppm with $^4J(^{31}\text{P}, ^{119}\text{Sn}) \approx 69$ Hz, and the ^{29}Si NMR spectrum revealed a singlet for $C_{\text{sp}^3}\text{-Si}$ at -23.5 ppm.

The photolysis of compound **2b** led to decomposition, and the conversion to the corresponding cumulenyl complex could not be observed. We thought then to replace the SiMe_3 group with a SnMe_3 group. Treatment of $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\eta^6\text{-cycloheptatriene})$ ($R' = \text{Me}$ (**1b**)) with

1 equiv of $R''_2\text{PCH}_2\text{CH}_2\text{PR}''_2$ ($R'' = \text{Me}$, dmpe) and $\text{Me}_3\text{SnC}\equiv\text{CC}\equiv\text{CSnMe}_3$ at room temperature for 2 h gave a mixture of complexes containing the vinyl alkynyl complex $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{dmpe})(=\text{C}=\text{CSnMe}_3\text{C}\equiv\text{CSnMe}_3)$ ($R' = \text{Me}$ (**3b**)) and the corresponding cumulenyl complex $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{dmpe})(=\text{C}=\text{C}=\text{C}=\text{C}(\text{SnMe}_3)_2)$ ($R' = \text{Me}$ (**4b**)) in a ratio of 4:1 (Scheme 2). The mixture could not be separated; however, spectroscopic characterization of these complexes was possible. The ^{13}C NMR spectrum of the mixture shows C_α and C_β at 265.9 and 115.8 ppm for **3b** and at 332.4 and 131.6 ppm for **4b**. The C_δ and C_γ resonances of **4b** were observed at 127.4 and 139.9 ppm. The ^{31}P NMR resonances show two singlets at 92.2 ppm (**3b**) and 93.8 ppm (**4b**). The ^{119}Sn NMR spectrum of the reaction mixture shows three signals: two signals for **3b** comprising a triplet and a singlet corresponding to the $C_{\text{sp}^2}\text{-Sn}$ at -7.2 ppm with $^6J(^{31}\text{P}, ^{119}\text{Sn}) \approx 69$ Hz and the $C_{\text{sp}^3}\text{-Sn}$ at -66.8 ppm. A triplet was observed for **4b** at 7.3 ppm with $^4J(^{31}\text{P}, ^{119}\text{Sn})$

Scheme 2



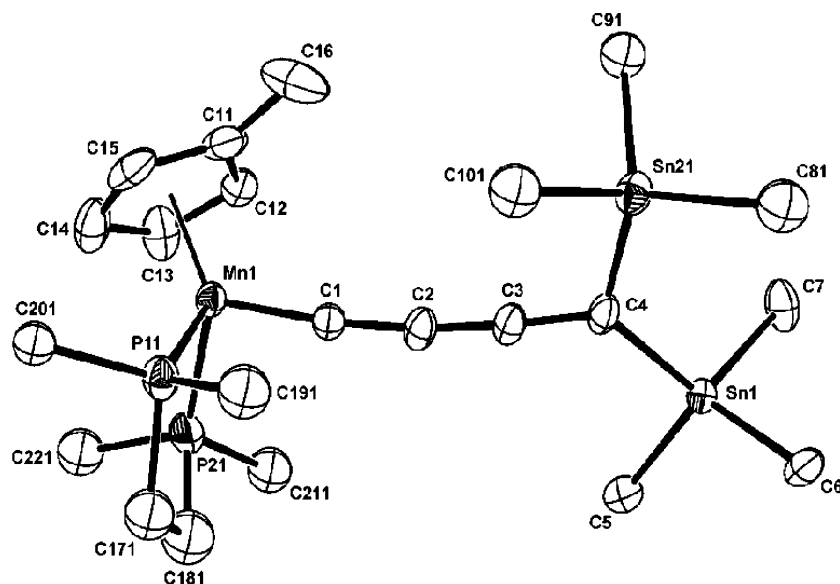


Figure 1. Molecular structure of **4b** (30% probability displacement ellipsoids). The dmpe ligand and one of the SnMe₃ groups appeared to be disordered, and only selected parts are shown for clarity. Selected bond lengths (Å) and angles (deg): Mn1–C1 = 1.735(8), C1–C2 = 1.312(11), C2–C3 = 1.257(12), C3–C4 = 1.325(12), C4–Sn1 = 2.102(9), C4–Sn21 = 2.057(13), C4–Sn22 = 2.357(14); Mn1–C1–C2 = 174.3(9), C1–C2–C3 = 172.3(11), C2–C3–C4 = 175.9(13), C3–C4–Sn1 = 122.5(10), C3–C4–Sn21 = 110.1(8), C3–C4–Sn22 = 117.9(8).

≈ 61 Hz. The complete transformation of **3b** to **4b** could not be accomplished, since the mixture starts to decompose under photolytic or thermal conditions.

Crystals of **4b** were obtained from the mixture in pentane at –30 °C. The unsaturated carbon chain slightly deviates from linearity, as shown for instance by the Mn–C1⋯C4 bond angle of 168.2° (Figure 1). The Mn=C bond distance of 1.735(4) Å is comparable to those found in other Mn–vinylidene complexes.^{54–57,60} The two internal C=C double bonds of 1.312(11) and 1.257(12) Å are shorter than the external bond with 1.325(12) Å. A similar behavior was reported for the mentioned Ir–C₄ cumulenic species and for the Mn–C₄ with SnPh₃ groups.^{8,9,51,57} Despite the fact that the disordered SnMe₃ group disrupts the analysis of the structural parameters, it is interesting to notice that the two bond angles C3–C4–Sn1 and C3–C4–Sn21 are surprisingly different, with values of 122.5(10) and 110.1(8)°, respectively. The same kind of difference has already been observed in one of our recent paper⁵⁷ for the similar complex Mn(C₅H₅)(dmpe)(=C=C=C=C(SnPh₃)₂), for which the C–C–Sn bond angles were 122.6(3) and 112.0(3)°.

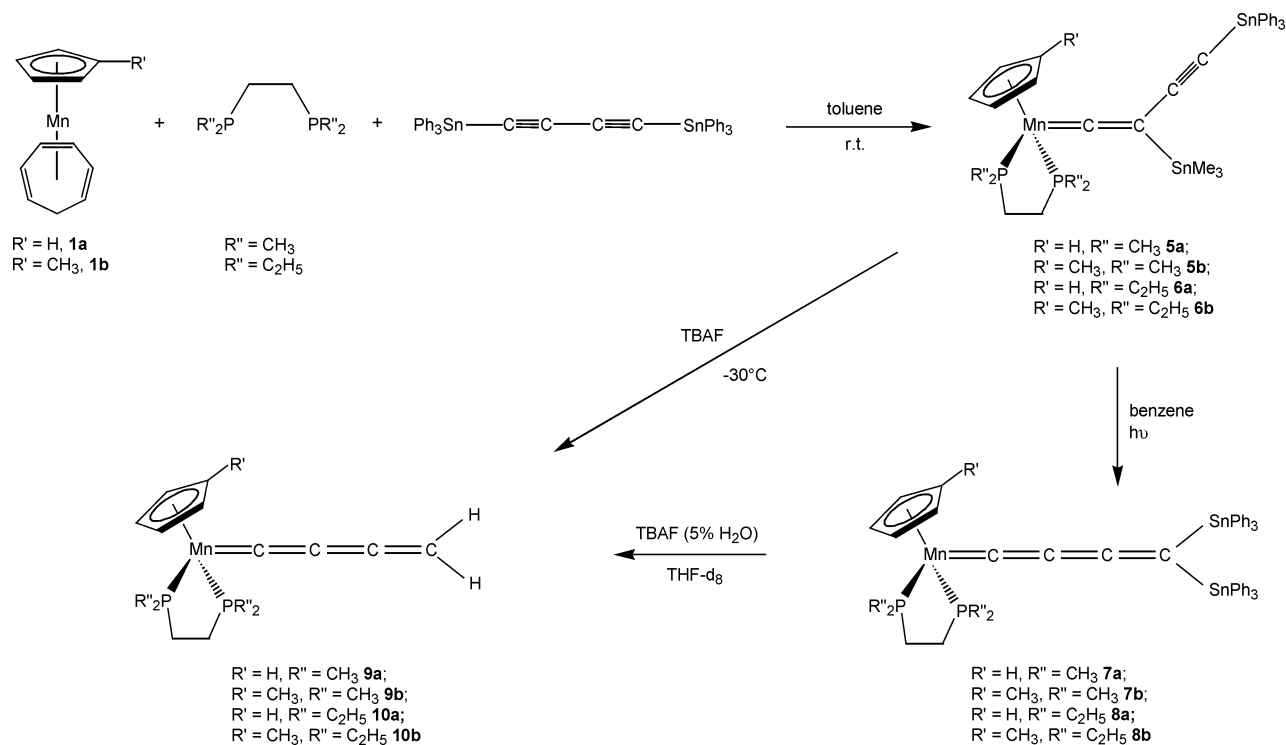
The obtained reaction mixtures of the trimethyltin-substituted complexes **3** and **4** could not be separated. Therefore, Mn(C₅H₄R')(7^b-cycloheptatriene) (R' = H (**1a**), Me (**1b**)) was treated with 1 equiv of the triphenyltin-substituted butadiyne Ph₃SnC≡CC≡CSnPh₃ and R''₂PCH₂CH₂PR''₂ (R'' = CH₃ (dmpe), C₂H₅ (depe)), which afforded the corresponding vinylidene species Mn(C₅H₄R')(R''₂PCH₂CH₂PR''₂)(=C=C(SnPh₃)C≡CSnPh₃) (R' = H, R'' = CH₃, **5a**; R' = CH₃, R'' = CH₃, **5b**; R' = H, R'' = C₂H₅, **6a**; R' = CH₃, R'' = C₂H₅, **6b**) in about 98% yield (Scheme 3). The ¹³C NMR spectrum of **5** shows the C_α and C_β atoms around 328 and 114 ppm, respectively. The ³¹P NMR resonances appear at 93.8 ppm (**5a**) and 92.8 ppm (**5b**). These data are comparable to those which were obtained for the related Mn–(C₅H₄R')(dmpe)(=C=CRH) complexes.^{54,57,60} However,

the ³¹P NMR resonances for complexes **6a** and **6b** were observed further downfield at 109.8 and 111.6 ppm, respectively. The ¹¹⁹Sn NMR spectra of species **5** show two signals which appear at higher field in comparison to those of the analogues **2b** and **3b**. A triplet corresponding to C_{sp}²–Sn at –130 ppm (**5a**) and –132 ppm (**5b**) with ⁴J(³¹P, ¹¹⁹Sn) ≈ 77 Hz and a singlet for C_{sp}–Sn at –162 ppm for both **5a** and **5b** were observed.

When toluene solutions of **5** and **6** were irradiated at 20 °C using a 125 W medium-pressure mercury lamp, the C_{sp}²–Sn bonds were activated and subsequent transformations into the remarkably stable C₄ cumulenic species **7** and **8** were observed. Complexes **7** and **8** were isolated as green solids in approximately 80% yield. The ¹³C NMR spectra of the species **7** exhibit four resonances for the C₄ cumulenic chain as follows (ppm): 266.5 (**7a**), 267.5 (**7b**) (Mn=C₁); 130.8 (**7a**), 131.6 (**7b**) (=C₂=); 124.8 (**7a**), 121.4 (**7b**) (=C₃=); 140.0 (**7a**), 139.9 (**7b**) (=CSn₂). The ³¹P NMR spectrum exhibits a resonance at 91.8 ppm (**7a**) and 91.6 ppm (**7b**) slightly shifted to higher field in comparison with the value obtained for species **5**. The ¹¹⁹Sn NMR spectra display one triplet for the two Sn nuclei at around –125 ppm (t, ⁶J(³¹P, ¹¹⁹Sn) = 64 Hz).

Complexes **7** and **8** constitute an example of C₄ metallacumulene species with main-group-metal substituents as end groups, which were assumed to be reactive and were expected to be readily removable. Indeed, deprotection of species **7** and **8** was accomplished with tetrabutylammonium fluoride (TBAF). The parent C₄ cumulenic species Mn(C₅H₄R')(R''₂PCH₂CH₂PR''₂){=C=C=C=CH₂} (R' = H, R'' = CH₃, **9a**; R' = CH₃, R'' = CH₃, **9b**; R' = H, R'' = C₂H₅, **10a**; R' = CH₃, R'' = C₂H₅, **10b**) were formed by selective replacement of the terminal SnPh₃ moieties. They were unstable above –5 °C and were therefore characterized in solution at –40 °C. The presence of the terminal CH₂ group in **9** and **10** was confirmed by (¹H, ¹³C) correlation, ¹³C-DEPT, and ¹H{³¹P} decoupling NMR experiments. The CH₂ protons appear at 1.93 ppm as a triplet with

Scheme 3



$^6J(^1\text{H}, ^{31}\text{P}) = 2.0$ Hz. The ^{13}C chemical shifts for compounds **7–10** have been assigned under the assumption that the $(^{13}\text{C}, ^{31}\text{P})$ coupling constants decrease with increasing coupling pathway in the linear C_4 chain. The ^{13}C NMR spectrum shows four signals corresponding to the cumulenic carbon chain as follows (ppm): 281.8 (**9a**), 280.8 (**9b**) ($\text{Mn}=\text{C}_1$); 158.7 (**9a**), 157.9 (**9b**) ($=\text{C}_2=$); 141.0 (**9a**), 140.2 (**9b**) ($=\text{C}_3=$); 44.4 (**9a**), 44.3 (**9b**) ($=\text{CH}_2$). The cationic complexes containing the fragment $[\text{Ru}=\text{C}=\text{C}=\text{C}=\text{CH}_2]^+$ were reported earlier by Bruce⁷ in 1996; however, their existence could only be made plausible by reactivity studies analyzing the follow-up complexes. Compounds **9** and **10** are the first examples of complexes with $[\text{M}=\text{C}=\text{C}=\text{C}=\text{CH}_2]$ units which structures have been fully established by NMR spectroscopy in solution. At higher temperatures (-5 °C and above) compounds **9** and **10** decompose to a mixture of as yet unidentified compounds.

The reaction of complex **2b**, **5**, or **6** with 1 equiv of TBAF (5% H_2O) at -30 °C in $\text{THF-}d_8$ instantaneously led also to the formation of complexes **9** and **10**. Although this reaction should pass through the parent vinyl alkynyl intermediate, the thermodynamically stable product seems to be the cumulenic complex, in comparison to the former, due to the faster rate of the 1,2-proton shift. However, the reaction of **2b** with an excess of MeOH led to a dinuclear complex **11b** of the type $[(\text{C}_5\text{H}_4\text{R}')(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2)\{\text{Mn}=\text{C}=\text{C}(\text{H})=\text{CH}_2=\text{C}(\text{OCH}_3)\}]_2$ ($\text{R}' = \text{CH}_3$, $\text{R}'' = \text{CH}_3$), formed in high yield (90%) by coupling. ^1H NMR in toluene- d_8 shows a triplet at 5.40 ppm with $^3J_{\text{P-H}} = 25$ Hz corresponding to the proton attached to C_β , and two resonances were observed at 3.5 and 3.92 ppm for the protons of the C_δ atom, as they are diastereotopic. The ^1H NMR spectrum also revealed a singlet resonance for the methoxy group attached to C_γ at 3.34 ppm. The ^{13}C NMR shows characteristic resonances for C_α and C_β at 339.5 and 117.9 ppm, respectively. However, the other two diag-

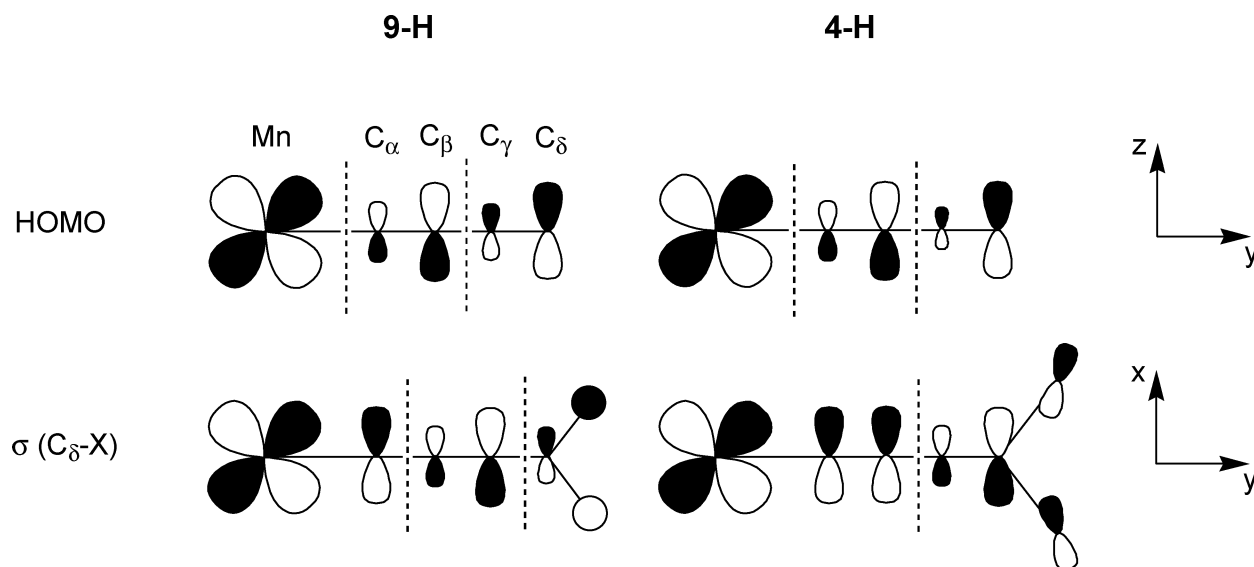
nostic resonances were observed at 69.9 ppm for C_δ and 162.5 ppm for C_γ . The ^{31}P NMR spectrum revealed a singlet at 94.2 ppm. ^{13}C NMR, C–H correlation, long-range C–H, DEPT, and NOE experiments confirmed the **11b** to be a dimer and gave also a clear indication of a cis arrangement of the two OMe groups. The formation of complex **11b** involves a 2 + 2 cycloaddition reaction followed by a rearrangement process, leading to the coupling product. Similar kinds of coupling reactions have been reported by other groups.^{10,74} However, the exact mechanism still remains to be elucidated.

Theoretical Results. The unique structures and the stabilities of complexes **4** and the relative instability of **9** and **10** were a challenge to study these by DFT calculations, which were carried out on the model complexes $\text{Mn}(\text{C}_5\text{H}_5)(\text{dHpe})\{\text{C}=\text{C}=\text{C}=\text{C}(\text{SnMe}_3)_2\}$ (**4-H**) and $\text{Mn}(\text{C}_5\text{H}_5)(\text{dHpe})\{\text{C}=\text{C}=\text{C}=\text{CH}_2\}$ (**9-H**). The MO analysis shows that the HOMO's are π -type orbitals, which have similar shapes and energies and clearly imply strong Mn–chain interactions (Chart 1). However, the HOMO's of **4-H** and **9-H** cannot account for the differences in stability of **4** and **9**, since no participation of tin or H orbital character is observed.

The stabilizing effect of the tin groups of complex **4-H** in comparison with **9-H** is seen in the shape and energy of a MO in the HOMO region of **4-H**, displaying a bonding interaction in the xy plane between the carbon chain and $\text{C}_\delta/\sigma_{\text{p}}(\text{Sn})$. It is energetically stabilized (about 1.3 eV) relative to its counterpart in **9-H**. The excellent donor properties of the energetically high-lying tin σ orbitals allow out-of-phase Sn– C_δ –Sn σ -type orbital character to be mixed into a π function of the cumulenic system in a bonding and therefore stabilizing way (Chart 1 and Figure 2). For complex **9-H** the corre-

(74) Rigaut, S.; Le Pichon, L.; Daran, J. C.; Touchard, D.; Dixneuf, P. H. *Chem. Commun.* **2001**, 1206–1207.

Chart 1



sponding C_8H_2 σ -type orbital character is at much lower energies, which leads to significant contributions of four-electron destabilizing interactions with filled π orbitals. Overall this electronic destabilization is assumed to be the cause for the instability of the series of parent compounds **4**.

The surprising difference of about 10° observed in the X-ray structure of **4b** and in the already reported complex $Mn(C_5H_5)(dmpe)(=C=C=C=C(SnPh_3)_2)$ ⁵⁷ for the terminal bond angles C3–C4–Sn has also been investigated with DFT calculations. The optimized geometry of the model complex **4-H** led to a symmetric ground-state structure with C–C–Sn bond angles of about 118° . Assuming that the formation of the cumulenic complex involves the radical intermediate $Mn(C_5H_5)(dmpe)(-C\equiv C-C\equiv C-SnPh_3)^*$ from the vinylidene species, the recoordination of the radical group $SnPh_3^*$ can occur on the C_γ atom with an electron π -type orbital perpendicularly to the $Mn-C\equiv C\equiv C-SnPh_3$ linear chain. Apparently not much rehybridization occurs then at C_γ . To simulate this rearrangement at its extreme, we performed a linear transit calculation starting from a

geometry for **4-H** characterized by one C–C–Sn bond angle fixed at $\alpha = 170^\circ$; the other C–C–Sn bond angle β and the rest of the geometry were fully optimized. The bending hypersurface with the degree of freedom α showed a relatively flat region in the range of 118 – 140° ($\Delta E < 3.5$ kcal/mol). Furthermore, the energy difference between the fully optimized symmetric geometry ($\alpha = \beta = 118.2^\circ$) and the geometry simulating the X-ray structure ($\alpha_{fixed} = 125^\circ$; $\beta_{calcd} = 114.6^\circ$) was only 0.4 kcal/mol. These observations, therefore, support the possibility of **4-H** to adopt a distorted geometry around C_γ . This distortion could be additionally interpreted in terms of a second-order Jahn–Teller effect with HOMO–LUMO mixing.⁷⁵ An attempt to deprotect the vinylidene complex $Mn(C_5H_4Me)(dmpe)(=C=C-SnMe_3-C\equiv C-SiMe_3)$ (**2b**) by replacement of the tin and silicon groups by hydrogens with tetrabutylammonium fluoride at $-30^\circ C$ leads directly to the cumulenic species $Mn(C_5H_4Me)(dmpe)\{-C=C=C=CH_2\}$ (**9b**), and the formation of the expected vinylidene structure was not observed.

While the $Mn(C_5H_4Me)(dmpe)\{-C=C=CHC\equiv CH\}$ species seems to be undetectable at $-30^\circ C$ on the reaction

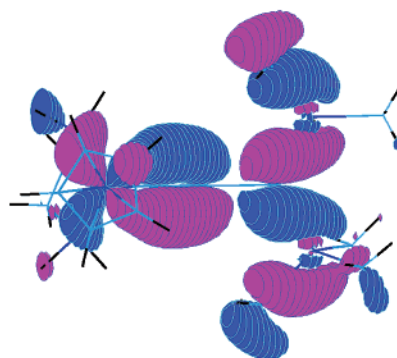
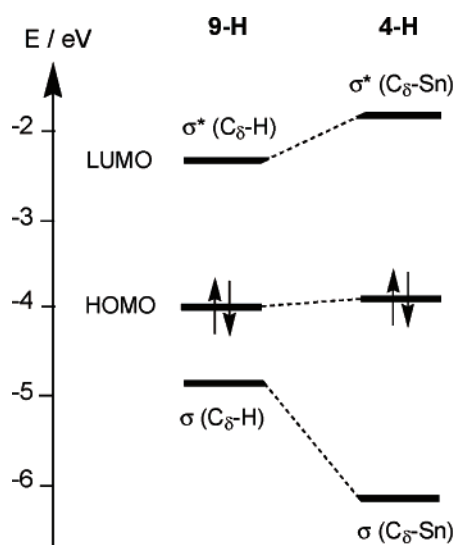


Figure 2. (a, left) Energy levels of frontier molecular orbitals for model complexes **4-H** and **9-H**. (b, right) Calculated occupied MO $\sigma(C_8-Sn)$ of **4-H** showing the bonding interactions between C_8 and the terminal tin groups (Molder¹⁸ plot).

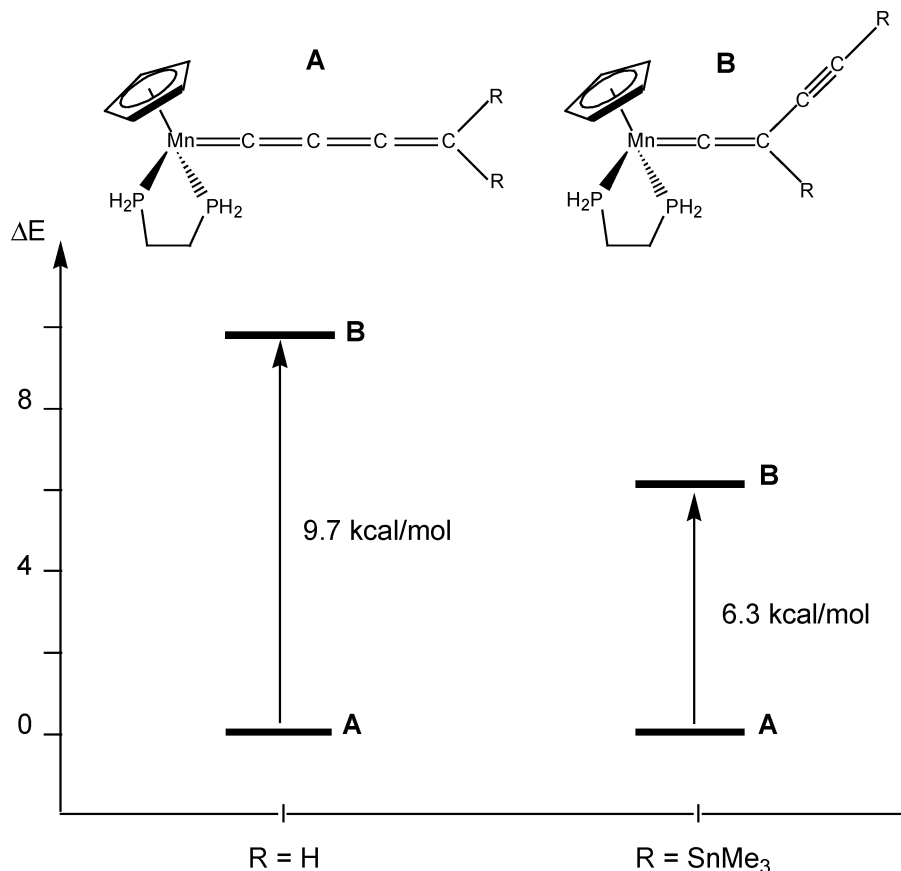


Figure 3.

scale, the corresponding tin-substituted vinylidene complexes **5** and **6** are thermodynamically stable enough to be fully characterized at room temperature. Then, both isomeric structures have been theoretically investigated with the simplified models $\text{Mn}(\text{C}_5\text{H}_5)(\text{dHpe})\{\text{C}_4(\text{SnMe}_3)_2\}$ and $\text{Mn}(\text{C}_5\text{H}_5)(\text{dHpe})\{\text{C}_4\text{H}_2\}$ in terms of total bonding energies. Whatever the substituent R is, H or SnMe_3 , the cumulene species (**A**) are favored over the vinylidene structures (**B**) (Figure 3) but the energy difference between the **A** and **B** isomers in the case of tin substitution is clearly smaller (6.3 kcal/mol) compared to that for complexes with $R = \text{H}$ (9.7 kcal/mol). This calculated thermodynamic destabilization of the vinylidene species when H groups are involved argue for a strong driving force for its rearrangement into the cumulene structure.

On the basis of the DFT calculations we reported earlier⁵⁴ on the oxidative $\text{C}-\text{C}$ coupling of the $(\text{C}_5\text{H}_4\text{Me})(\text{dmpe})\text{Mn}\{\text{C}=\text{C}\text{R}^1\text{R}^2\}$ mononuclear species ($\text{R}^1 = \text{R}^2 = \text{H}$; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Ph}$), we wish to speculate about the possibility of our C_4 cumulene complex to dimerize into a C_8 dinuclear product by oxidation. The mononuclear cationic radical model compound $[\mathbf{9-H}]^{\bullet+}$ has been fully optimized with a spin-unrestricted formalism and the computed spin densities of $+0.88\alpha$, $+0.31\alpha$, and $+0.35\alpha$ located at the manganese and the C_β and C_γ atoms, respectively, indicate a high probability of finding the unpaired electron on the terminal carbon atom of the C_4 chain. The single-point calculations, including a model for solvation effects performed on the gas-phase

geometries of the mononuclear cationic radical system and the $\text{C}-\text{C}$ coupled dinuclear dicationic product, led to a dimerization energy ΔE of $+6.0$ kcal/mol ($\Delta E = E_{\text{dimer}} - 2E_{\text{monomer}}$). When these results are compared with those of the previous study on the analogous C_2 oxidatively induced dimerization $2(\text{C}_5\text{H}_4\text{Me})(\text{dHpe})\text{Mn}\{\text{C}=\text{CH}_2\}^{\bullet+} \leftrightarrow (\text{C}_5\text{H}_4\text{Me})(\text{dHpe})\text{Mn}\{\text{C}\equiv\text{CCH}_2\text{CH}_2\text{C}\equiv\text{C}\}\text{Mn}(\text{dHpe})(\text{C}_5\text{H}_4\text{Me})^{2+}$,⁵⁴ it appears clearly that the formation of the dinuclear dicationic C_8 product is not thermodynamically favored. Indeed, the spin density on the terminal carbon atom is slightly smaller ($+0.35\alpha$ vs $+0.37\alpha$) compared to that on the C_2 cumulenyl cationic radical complex and the formation of the dicationic C_8 dimer is endothermic by 6.0 kcal/mol, while that of the C_4 dimer was previously found to be exothermic by -24.2 kcal/mol, leading to a stable product that was characterized spectroscopically and crystallographically. Nevertheless, a dimerization reaction has been brought to a successful conclusion to **11b** by starting from the vinylidene species **2b** with an excess of MeOH , which was already discussed in the earlier context.

Conclusions

We have gained synthetic access to the new vinylalkynyl complexes $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2)\text{C}=\text{C}=\text{CSnPh}_3\text{C}\equiv\text{CSnPh}_3$ (**5** and **6**), which were further converted to the corresponding cumulenyl complexes $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2)\{\text{C}=\text{C}=\text{C}=\text{C}(\text{SnPh}_3)_2\}$ by photolysis. The parent cumulenyl species $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2)\{\text{C}=\text{C}=\text{C}=\text{C}(\text{H})_2\}$ (**9**, **10**) were obtained by reacting complexes **7** and **8** with

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TBAF (5% H₂O) and has been observed and spectroscopically characterized. The difference in the thermodynamic stabilities between these two complexes Mn(C₅H₄R')(R''₂PCH₂CH₂PR''₂){=C=C=C=C(SnPh₃)₂} and Mn(C₅H₄R')(R''₂PCH₂CH₂PR''₂){=C=C=C=CH₂} has been traced. On the basis of a DFT analysis, the unexpected high stability of the tin-substituted manganese butatrienylienes has been explained, which revealed the energetically high lying and thus strongly electron donating σ orbitals of R₃Sn groups to be the decisive factor. The reaction of the vinylalkynyl complex Mn(C₅H₄R')(R''₂PCH₂CH₂PR''₂)(=C=C(SnMe₃)-C≡CSnMe₃) with MeOH led to a dinuclear complex. Since the C₄ fragment capped by half-sandwich end groups tend to couple and form dinuclear complexes, these systems might prove to be very useful precursors for gaining access to dinuclear systems bridged by long carbon chains.

Experimental Section

General Considerations. 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 P₂O₅ and then prior to use from CaH₂. Literature procedures were used to prepare the following compounds: 1,2-bis(dimethylphosphino)ethane (dmpe),⁷⁸ 1,2-bis(diethylphosphino)ethane (depe),⁷⁸ (η^5 -MeCp)Mn(η^6 -cycloheptatriene),⁷³ Me₃SnC≡CC≡CSnMe₃,⁷⁹ Me₃-SnC≡CC≡CSiMe₃,⁷⁹ and Ph₃SnC≡CC≡CSnPh₃.⁷⁹ *n*-BuLi (1.6 M in hexane), MeLi·LiBr (1.5 M in diethyl ether), Me₃SnCl, and Ph₃SnCl were used as received. All the manipulations were carried out under a nitrogen atmosphere using Schlenk techniques or a drybox. IR spectra were obtained on a Bio-Rad FTS-45 instrument. NMR spectra were measured on a Varian Gemini-2000 spectrometer at 300 MHz for ¹H and 121.5 MHz for ³¹P{¹H} and on a Bruker-DRX-500 spectrometer at 125.8 MHz for ¹³C{¹H} and 186.5 MHz for ¹¹⁹Sn, respectively. Chemical shifts for ¹H and ¹³C are given in ppm relative to the solvent signals; the ³¹P{¹H} NMR spectra were referenced to 98% external H₃PO₄ and the ¹¹⁹Sn{¹H} NMR spectra to SnBu₄.

X-ray Crystallographic Studies. The structure was solved by the Patterson method (SHELXS-97).⁷⁶ Due to the poor crystal quality the *R* values are relatively high. The bis-(dimethylphosphino)ethane ligand and one of the trimethyltin groups appeared to be disordered. They were refined with EADP options and part instruction of SHELXL-97.⁷⁷ A total of 36 distance restraints (DFIX for P–C and C–C and SAME for Sn–C) were applied to stabilize the structure model during the refinement. The positions of all H atoms were calculated after each refinement cycle. The disordered carbon atoms were refined with isotropic displacement parameters. The ratio of the disordered parts was refined to about 67:32. It should be noted that 46% of the non-hydrogen atoms of the structure are involved in positional disorder. Empirical absorption correction did not improve the data set; *R* values were larger than those for the refinement without absorption correction. The shape of the crystal did not allow a numerical absorption correction, because crystal faces could not be observed. Crystallographic details are given in Table 1.

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Table 1. Crystallographic Details of 4b

empirical formula	C ₂₂ H ₄₁ MnP ₂ Sn ₂
color	green needle
<i>M_r</i> (g·mol ⁻¹)	659.81
cryst size (mm)	0.20 × 0.11 × 0.09
<i>T</i> (K)	183(2)
λ (Mo K α) (Å)	0.710 73
cryst syst	triclinic
space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.9783(8)
<i>b</i> (Å)	11.9034(11)
<i>c</i> (Å)	12.5535(10)
α (deg)	83.108(10)
β (deg)	75.397(9)
γ (deg)	83.059(10)
<i>V</i> (Å ³)	1426.1(2)
<i>Z</i>	2
ρ (calcd) (g cm ⁻³)	1.537
μ (mm ⁻¹)	2.291
<i>F</i> (000)	656
2 θ range (deg)	5.42 < 2 θ < 60.42
no. of measd rflns	16 705
no. of unique rflns	7698
no. of rflns with <i>I</i> > 2 σ (<i>I</i>)	3646
no. of params	261
GOF (for <i>F</i> ²)	0.860
R1: <i>I</i> > 2 σ (<i>I</i>), all data	0.0692, 0.1311
wR2: <i>I</i> > 2 σ (<i>I</i>), all data	0.1854, 0.2368
$\Delta\rho$ (max, min)	1.769, -1.551

$$^a R1 = \sum(F_o - F_c)/\sum F_o, I > 2\sigma(I); wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}.$$

[(MeC₅H₄)Mn(dmpe)=C=C(SnMe₃)C≡C(SiMe₃)] (2b).

To a toluene solution (10 mL) of (MeC₅H₄)Mn(η^6 -cycloheptatriene) (100 mg, 0.45 mmol) was added a toluene solution (10 mL) of dmpe (70 mg, 0.45 mmol) and Me₃SiC≡CC≡CSnMe₃ (130 mg, 0.45 mmol). 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 oil. Yield: 220 mg, 94%. Anal. Calcd for C₁₉H₃₁MnP₂SiSn (523.30): C, 43.62; H, 5.97. Found: C, 43.43; H, 5.48. ¹H NMR (THF-*d*₈, 300 MHz, 20 °C; δ): 4.28 (2H, C₅H₄), 3.96 (2H, C₅H₄), 1.88 (3H, C₅H₄CH₃), 1.88 (6H, PCH₃), 1.84 (2H, PCH₂), 1.24 (2H, PCH₂), 1.21 (6H, PCH₃), 0.09 (9H, SnMe₃), -0.06 (9H, SiMe₃). ³¹P{¹H} NMR (THF-*d*₈, 121.5 MHz, 20 °C; δ): 93.9 (s, 2P). ¹³C{¹H} NMR (THF-*d*₈, 125 MHz, 20 °C; δ): 329.5 (m, 1C, Mn-C_o), 97.9 (1C, C_i, C₅H₄Me), 91.8 (1C, m, =C β), 108.1 (C≡CSi), 91.1 (C≡CSn), 85.1 (2C, C₅H₄), 80.8 (2C, C₅H₄), 30.6 (2C, PCH₂), 23.3 (2C, PCH₃), 14.8 (1C, C₅H₄CH₃), 21.0 (2C, PMe₃), 1.5 (3C, Si(CH₃)₃), -7.5 (3C, Sn(CH₃)₃). ¹¹⁹Sn NMR (THF-*d*₈, 186.4 MHz, 20 °C; δ): -17.5 (1Sn, t, ⁴J_{P-Sn} = 69 Hz). ²⁹Si NMR (THF-*d*₈, 99.3 MHz, 20 °C; δ): -23.5 (1Si, (SiCH₃)₃). IR (CH₂-Cl₂, 20 °C; cm⁻¹): 1988 ν (C≡C), 1947 ν (C≡C), 1598 ν (C=C), 1550 ν (C=C).

[(MeC₅H₄)Mn(dmpe)=C=C(SnMe₃)C≡C(SnMe₃)] (3b).

To a toluene solution (10 mL) of (MeC₅H₄)Mn(η^6 -cycloheptatriene) (1b; 100 mg, 0.45 mmol) was added a toluene solution (10 mL) of dmpe (70 mg, 0.45 mmol) and Me₃Sn-C≡C-C≡C-SnMe₃ (170 mg, 0.45 mmol). The solution was stirred at room temperature for 2 h to give a dark red solution. The solvent was removed vacuum to afford a dark red green solid containing mixture of two compounds **3b** and **4b**. ¹H NMR (THF-*d*₈, 300 MHz, 20 °C; δ): 4.48 (2H, C₅H₄), 3.92 (2H, C₅H₄), 2.0 (3H, C₅H₄CH₃), 1.71 (2H, PCH₂), 1.27 (6H, PCH₃), 1.24 (2H, PCH₂), 0.59 (6H, PCH₃), 0.09 (9H, SnMe₃), 0.07 (9H, SnMe₃) ³¹P{¹H}-NMR (THF-*d*₈, 121.5 MHz, 20 °C; δ): 92.2 (s, 2P). ¹³C{¹H} NMR (THF-*d*₈, 125 MHz, 20 °C; δ): 265.9 (m, 1C, Mn-C_o), 115.8 (1C, m, =C β), 98.3 (1C, C_{ipso}(C₅H₄Me)), 89.9 (C≡C), 86.7 (C≡C-Sn), 85.2 (2C, C₅H₄), 80.8 (2C, C₅H₄), 30.6 (2C, PCH₂), 23.3 (2C, PCH₃), 22.4 (1C, C₅H₄CH₃), 21.0 (2C, PMe₃), -7.3 (3C, Sn(CH₃)₃), -7.5 (3C, Sn(CH₃)₃). ¹¹⁹Sn NMR (THF-*d*₈, 186.4 MHz, 20 °C; δ): -7.2 (t, 69 Hz), -66.8 (s). IR (CH₂-

Cl₂, 20 °C; cm⁻¹): 1988 ν(C≡C), 1947 ν(C≡C), 1598 ν(C=C), 1550 ν(C=C).

[(MeC₅H₄)Mn(dmpe)=C=C=C=C(SnMe₃)₂] (4b). The pentane solution of the mixture was concentrated in vacuo and cooled to -30 °C to obtain green crystals of **4b**. ¹H NMR (THF-*d*₆, 300 MHz, 20 °C; δ): 4.31 (2H, C₅H₄), 3.98 (2H, C₅H₄), 1.98 (br, 2H, PCH₂), 1.93 (s, 3H, C₅H₄CH₃), 1.17 (br, 14H, PCH₂ and PCH₃). ³¹P{¹H} NMR (THF-*d*₆, 121.5 MHz, 20 °C; δ): 93.8 (s, 2P). ¹³C{¹H} NMR (THF-*d*₆, 125 MHz, 20 °C; δ): 332.4 (1C, C₁), 139.9 (1C, C₄), 131.6 (1C, C₂), 121.4 (1C, C₃), 100.2 (C₅H₄, C_{ipso}), 85.2 (2C, C₅H₄), 80.0 (2C, C₅H₄), 30.0 (2C, m, PCH₂), 22.3 (2C, PCH₃), 21.4 (1C, C₅H₄CH₃), 20.0 (2C, PCH₃), -7.5 (6C, Sn(CH₃)₃). ¹¹⁹Sn NMR (THF-*d*₆, 20 °C; δ): 7.3 (t, J_{PSn} = 61 Hz). IR (CH₂Cl₂, 20 °C; cm⁻¹): 1594 ν(C=C), 1552 ν(C=C).

[(C₅H₅)Mn(dmpe)=C=C(SnPh₃)C=C(SnPh₃)] (5a). To a toluene solution (10 mL) of (C₅H₅)Mn(η⁶-cycloheptatriene) (100 mg, 0.45 mmol) was added a toluene solution (10 mL) of dmpe (70 mg, 0.45 mmol) and Ph₃SnC≡CC≡CSnPh₃ (330 mg, 0.45 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 of **5a**. Yield: 450 mg, 98%. Anal. Calcd for C₅₁H₅₁MnP₂Sn₂ (1018.25): C, 60.16; H, 5.05. Found: C, 60.46; H, 5.08. ¹H NMR (C₆D₆, 300 MHz, 20 °C; δ): 7.93 (m, 12H, C₆H₅), 7.70 (m, 18H, C₆H₅), 4.13 (5H, C₅H₅), 1.72 (2H, PCH₂), 1.28 (6H, PCH₃), 1.16 (2H, PCH₂), 0.57 (6H, PCH₃). ³¹P{¹H} NMR (C₆D₆, 121.5 MHz, 20 °C; δ): 93.8 (s, 2P). ¹³C{¹H} NMR (C₆D₆, 125 MHz, 20 °C; δ): 327.5 (m, 1C, Mn-C_ω), 141.0 (3C, C_i, C₆H₅), 139.5 (3C, C_i, C₆H₅), 137.8 (12C, C₆H₅), 137.3 (12C, C₆H₅), 114.8 (m, 1C, =C_β), 91.8 (1C, C≡C), 88.0 (1C, C≡CSn(C₆H₅)), 83.8 (5C, C₅H₅), 30.8 (2C, PCH₂), 23.5 (2C, PCH₃), 21.3 (2C, PCH₃). ¹¹⁹Sn NMR (C₆D₆, 186.4 MHz, 20 °C; δ): -130 (t, 77.0 Hz), -162 (s). IR (CH₂Cl₂, 20 °C; cm⁻¹): 1986 ν(C≡C), 1949 ν(C≡C), 1595 ν(C=C), 1550 ν(C=C).

[(MeC₅H₄)Mn(dmpe)=C=C(SnPh₃)C=C(SnPh₃)] (5b). To a toluene solution (10 mL) of (MeC₅H₄)Mn(η⁶-cycloheptatriene) (100 mg, 0.45 mmol) was added a toluene solution (10 mL) of dmpe (70 mg, 0.45 mmol) and Ph₃SnC≡CC≡CSnPh₃ (330 mg, 0.45 mmol). 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 of **5b**. Yield: 455 mg, 98%. Anal. Calcd for C₅₂H₅₃MnP₂Sn₂ (1032.28): C, 60.50; H, 5.17. Found: C, 60.20; H, 5.34. ¹H NMR (C₆D₆, 300 MHz, 20 °C; δ): 7.95 (m, 12H, C₆H₅), 7.69 (m, 18H, C₆H₅), 4.15 (2H, C₅H₄), 3.74 (2H, C₅H₄), 2.01 (3H, C₅H₄CH₃), 1.71 (2H, PCH₂), 1.27 (6H, PCH₃), 1.24 (2H, PCH₂), 0.59 (6H, PCH₃). ³¹P{¹H} NMR (C₆D₆, 121.5 MHz, 20 °C; δ): 92.8 (s, 2P). ¹³C{¹H} NMR (C₆D₆, 125 MHz, 20 °C; δ): 328.2 (m, 1C, Mn-C_ω), 141.0 (3C, C_{ipso}, Ph), 139.3 (3C, C_i, Ph), 137.6 (12C, C₆H₅), 137.1 (12C, C₆H₅), 115.8 (1C, m, =C_β), 98.3 (1C, C_{ipso}, C₅H₄-Me), 89.9 (C≡C), 86.7 (C≡CSn), 85.2 (2C, C₅H₄), 80.8 (2C, C₅H₄), 30.6 (2C, PCH₂), 23.3 (2C, PCH₃), 22.4 (1C, C₅H₄CH₃), 21.0 (2C, PCH₃). ¹¹⁹Sn NMR (C₆D₆, 186.4 MHz, 20 °C; δ): -132 (t, 77.0 Hz), -162 (s). IR (CH₂Cl₂, 20 °C; cm⁻¹): 1988 ν(C≡C), 1947 ν(C≡C), 1598 ν(C=C), 1553 ν(C=C).

[(C₅H₅)Mn(depe)=C=C(SnPh₃)C=C(SnPh₃)] (6a). To a toluene solution (10 mL) of (C₅H₅)Mn(η⁶-cycloheptatriene) (100 mg, 0.45 mmol) was added a toluene solution (10 mL) of depe (90 mg, 0.45 mmol) and Ph₃SnC≡CC≡CSnPh₃ (330 mg, 0.45 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. Yield: 450 mg, 98%. Anal. Calcd for C₅₅H₆₉MnP₂Sn₂ (1084.44): C, 60.91; H, 6.4. Found: C, 60.56; H, 6.08. ¹H NMR (C₆D₆, 300 MHz, 20 °C; δ): 7.95 (m, 12H, C₆H₅), 7.65 (m, 18H, C₆H₅), 4.23 (5H, C₅H₅), 1.72 (2H, PCH₂), 1.60 (6H, PCH₂CH₃), 1.38 (2H, PCH₂), 1.09 (6H, PCH₂CH₃), 0.68 (6H, PCH₂CH₃), 0.63 (6H, PCH₂CH₃). ³¹P{¹H} NMR (C₆D₆, 121.5 MHz, 20 °C; δ): 113.9 (s, 2P). ¹³C{¹H} NMR (C₆D₆, 125 MHz, 20 °C; δ): 331.4 (m, 1C, Mn-C_ω), 141.0 (3C, C_{ipso}, C₆H₅), 139.5 (3C, C_{ipso}, C₆H₅), 137.8 (12C, C₆H₅), 137.3 (12C, C₆H₅), 114.6 (m, 1C, =C_β), 91.6 (1C, C≡C), 87.8 (1C, C≡CSn(C₆H₅)), 83.6 (5C, C₅H₅), 26.3 (2C, PCH₂), 25.2 (2C, PCH₂), 23.96 (2C, PCH₂CH₃), 14.9 (1C, C₅H₄CH₃), 9.47 (PCH₂CH₃). ¹¹⁹Sn NMR (C₆D₆, 186.4 MHz, 20 °C; δ): -133.5 (t, 77.0 Hz), -164.2 (s). IR (CH₂Cl₂, 20 °C; cm⁻¹): 1988 ν(C≡C), 1947 ν(C≡C), 1592 ν(C=C), 1550 ν(C=C).

CH₃), 9.47 (PCH₂CH₃). ¹¹⁹Sn NMR (C₆D₆, 186.4 MHz, 20 °C; δ): -131.2 (t, 77.0 Hz), -164.5 (s). IR (CH₂Cl₂, 20 °C; cm⁻¹): 1985 ν(C≡C), 1949 ν(C≡C), 1594 ν(C=C), 1550 ν(C=C).

[(MeC₅H₄)Mn(depe)=C=C(SnPh₃)C=C(SnPh₃)] (6b). To a toluene solution (10 mL) of (MeC₅H₄)Mn(η⁶-cycloheptatriene) (100 mg, 0.45 mmol) was added a toluene solution (10 mL) of depe (90 mg, 0.45 mmol) and Ph₃SnC≡CC≡CSnPh₃ (330 mg, 0.45 mmol). 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 of **51**. Yield: 475 mg, 98%. Anal. Calcd for C₅₆H₆₁MnP₂Sn₂ (1088.38): C, 61.79; H, 5.64. Found: C, 61.60; H, 5.31. ¹H NMR (C₆D₆, 300 MHz, 20 °C; δ): 7.94 (m, 12H, C₆H₅), 7.67 (m, 18H, C₆H₅), 4.32 (2H, C₅H₄), 3.79 (2H, C₅H₄), 2.27 (3H, C₅H₄CH₃), 1.77 (2H, PCH₂), 1.60 (6H, PCH₂CH₃), 1.38 (2H, PCH₂), 1.09 (6H, PCH₂CH₃), 0.68 (6H, PCH₂CH₃), 0.63 (6H, PCH₂CH₃). ³¹P{¹H} NMR (C₆D₆, 121.5 MHz, 20 °C; δ): 112.87 (s, 2P). ¹³C{¹H} NMR (C₆D₆, 125 MHz, 20 °C; δ): 332.2 (m, 1C, Mn-C_ω), 141.0 (3C, C_i, Ph), 139.3 (3C, C_{ipso}(Ph)), 137.6 (12C, C₆H₅), 137.1 (12C, C₆H₅), 115.8 (1C, m, =C_β), 98.3 (1C, C_{ipso}(C₅H₄Me)), 89.9 (C≡C), 86.7 (C≡CSn), 85.2 (2C, C₅H₄), 80.8 (2C, C₅H₄), 26.3 (2C, PCH₂), 25.2 (2C, PCH₂), 23.96 (2C, PCH₂CH₃), 14.9 (1C, C₅H₄CH₃), 9.47 (PCH₂CH₃). ¹¹⁹Sn NMR (C₆D₆, 186.4 MHz, 20 °C; δ): -133.5 (t, 77.0 Hz), -164.2 (s). IR (CH₂Cl₂, 20 °C; cm⁻¹): 1988 ν(C≡C), 1947 ν(C≡C), 1592 ν(C=C), 1550 ν(C=C).

[(C₅H₅)Mn(dmpe)=C=C=C=C(SnPh₃)₂] (7a). A benzene solution (20 mL) of (C₅H₅)Mn(dmpe)=C=C(SnPh₃)C=C(SnPh₃) (80 mg, 0.08 mmol) was irradiated for 5 h using a 125 W medium-pressure mercury lamp. After the solvent was removed, the residue was extracted with diethyl ether. The diethyl ether solution was concentrated in vacuo and cooled to -30 °C to obtain green crystals of **7a**. Yield: 65 mg, 80%. Anal. Calcd for C₅₁H₅₁MnP₂Sn₂ (1018.25): C, 60.15; H, 5.04. Found: C, 60.21; H, 5.30. ¹H NMR (THF-*d*₆, 300 MHz, 20 °C; δ): 7.39 (m, 12H, C₆H₅), 7.17 (m, 18H, C₆H₅), 4.41 (s, 5H, C₅H₅), 1.95 (br, 2H, PCH₂), 1.14 (br, 14H, PCH₂ and PCH₃). ³¹P{¹H} NMR (THF-*d*₆, 121.5 MHz, 20 °C; δ): 90.7 (s). ¹³C{¹H} NMR (THF-*d*₆, 125 MHz, 20 °C; δ): 266.5 (1C, C₁), 140.0 (1C, C₄), 130.8 (1C, C₂), and 124.8 (1C, C₃), 84.0 (5C, C₅H₅), 31.3 (2C, m, PCH₂), 22.4 (2C, PCH₃), 20.5 (2C, PCH₃). ¹¹⁹Sn NMR (THF-*d*₆, 20 °C; δ): -125.6 (t, J_{PSn} = 64 Hz). IR (CH₂Cl₂, 20 °C; cm⁻¹): 1595 ν(C=C), 1548 ν(C=C).

[(MeC₅H₄)Mn(dmpe)=C=C=C=C(SnPh₃)₂] (7b). A benzene solution (20 mL) of (MeC₅H₄)Mn(dmpe)=C=C(SnPh₃)C=C(SnPh₃) (80 mg, 0.08 mmol) was irradiated for 5 h using a 125 W medium-pressure mercury lamp. After the solvent was removed, the residue was extracted with Et₂O. The Et₂O solution was concentrated in vacuo and cooled to -30 °C to obtain green crystals of **7b**. Yield: 65 mg, 80%. Anal. Calcd for C₅₂H₅₃MnP₂Sn₂ (1032.18): C, 60.50; H, 5.17. Found: C, 60.72; H, 5.27. ¹H NMR (THF-*d*₆, 300 MHz, 20 °C; δ): 7.40 (m, 12H, C₆H₅), 7.16 (m, 18H, C₆H₅), 4.50 (2H, C₅H₄), 3.97 (2H, C₅H₄), 1.95 (br, 2H, PCH₂), 1.93 (s, 3H, C₅H₄CH₃), 1.17 (br, 14 H, PCH₂ and PCH₃). ³¹P{¹H} NMR (THF-*d*₆, 121.5 MHz, 20 °C; δ): 91.6 (s, 2P). ¹³C{¹H} NMR (THF-*d*₆, 125 MHz, 20 °C; δ): 267.5 (1C, C₁), 139.9 (1C, C₄), 131.6 (1C, C₂) and 121.4 (1C, C₃), 100.2 (C₅H₄, C_{ipso}), 85.2 (2C, C₅H₄), 80.0 (2C, C₅H₄), 30.0 (2C, m, PCH₂), 22.3 (2C, PCH₃), 21.4 (1C, C₅H₄CH₃), 20.0 (2C, PCH₃). ¹¹⁹Sn NMR (THF-*d*₆, 20 °C; δ): -122.0 (t, J_{PSn} = 65.0 Hz). IR (CH₂Cl₂, 20 °C; cm⁻¹): 1594 ν(C=C), 1552 ν(C=C).

[(C₅H₅)Mn(depe)=C=C=C=C(SnPh₃)₂] (8a). A benzene solution (20 mL) of (C₅H₅)Mn(depe)=C=C(SnPh₃)C=C(SnPh₃) (80 mg, 0.07 mmol) was irradiated for 5 h using a 125 W medium-pressure mercury lamp. After the solvent was removed, the residue was extracted with Et₂O. The Et₂O solution was concentrated in vacuo and cooled to -30 °C to obtain green crystals of **8a**. Yield: 65 mg, 80%. Anal. Calcd for C₅₅H₅₉MnP₂Sn₂ (1074.36): C, 61.48; H, 5.53. Found: C, 61.23; H, 5.32. ¹H NMR (THF-*d*₆, 300 MHz, 20 °C; δ): 7.41 (m, 12H, C₆H₅), 7.15 (m, 18H, C₆H₅), 4.34 (s, 5H, C₅H₅), 1.77 (2H, PCH₂), 1.60 (6H, PCH₂CH₃), 1.38 (2H, PCH₂), 1.09 (6H, PCH₂CH₃),

0.68 (6H, PCH_2CH_3), 0.63 (6H, PCH_2CH_3). $^{31}P\{^1H\}$ NMR (THF- d_6 , 121.5 MHz, 20 °C; δ): 109.8 (s). $^{13}C\{^1H\}$ NMR (THF- d_6 , 125 MHz, 20 °C; δ): 267.3 (1C, C_1), 133.2 (1C, C_4), 131.8 (1C, C_2), and 121.6 (1C, C_3), 84.2 (5C, C_5H_5), 26.3 (2C, PCH_2), 25.2 (2C, PCH_2), 23.96 (2C, PCH_2CH_3), 14.9 (1C, $C_5H_4CH_3$), 9.47 (PCH_2CH_3). ^{119}Sn NMR (THF- d_6 , 20 °C; δ): -125.4 (t, $^6J_{P-Sn}$ = 64 Hz). IR (CH_2Cl_2 , 20 °C; cm^{-1}): 1596 $\nu(C=C)$, 1548 $\nu(C=C)$.

[(MeC₅H₄)Mn(depe)=C=C=C(SnPh₃)₂] (8b). A benzene (20 mL) solution of (MeC₅H₅)Mn(depe)=C=C(SnPh₃)C≡C(SnPh₃) (80 mg, 0.073 mmol) was irradiated for 5 h using a 125 W medium-pressure mercury lamp. After the solvent was removed, the residue was extracted with Et₂O. The Et₂O solution was concentrated in vacuo and cooled to -30 °C to obtain green crystals of **8b**. Yield: 63 mg, 80%. Anal. Calcd for C₅₆H₆₁MnP₂Sn₂ (1088.38): C, 61.79; H, 5.64. Found C, 62.00; H, 5.84. 1H NMR (THF- d_6 , 300 MHz, 20 °C; δ): 7.42 (m, 12H, C_6H_5), 7.21 (m, 18H, C_6H_5), 4.51 (2H, C_5H_4), 3.96 (2H, C_5H_4), 1.93 (s, 3H, $C_5H_4CH_3$), 1.77 (2H, PCH_2), 1.60 (6H, PCH_2CH_3), 1.38 (2H, PCH_2), 1.09 (6H, PCH_2CH_3), 0.68 (6H, PCH_2CH_3), 0.63 (6H, PCH_2CH_3). $^{31}P\{^1H\}$ NMR (THF- d_6 , 121.5 MHz, 20 °C; δ): 111.7 (s, 2P). $^{13}C\{^1H\}$ NMR (THF- d_6 , 125 MHz, 20 °C; δ): 267.1 (1C, C_1), 131.9 (1C, C_4), 131.6 (1C, C_2), 121.2 (1C, C_3), 100.4 (C_5H_4 , C_{ipso}), 85.4 (2C, C_5H_4), 80.2 (2C, C_5H_4), 26.3 (2C, PCH_2), 25.2 (2C, PCH_2), 23.96 (2C, PCH_2CH_3), 14.9 (1C, $C_5H_4CH_3$), 9.47 (PCH_2CH_3). ^{119}Sn NMR (THF- d_6 , 20 °C; δ): -122.8 (t, J_{P-Sn} = 63.0 Hz). IR (CH_2Cl_2 , 20 °C; cm^{-1}): 1594 $\nu(C=C)$, 1557 $\nu(C=C)$.

[(C₅H₅)Mn(dmpe)=C=C=C=CH₂] (9a). To a mixture of (C₅H₅)Mn(dmpe)=C=C=C=C(SnPh₃)₂ (20 mg, 0.020 mmol) and TBAF (0.040 mL, 0.040 mmol) was added 0.75 mL of THF- d_6 at -20 °C. The temperature was raised to -5 °C, and the deprotected species **9a** was observed as the only Mn-containing complex present in the solution after 5 min. The compound could be characterized only in solution. 1H NMR (THF- d_6 , 300 MHz, -40 °C; δ): 4.54 (s, 5H, C_5H_5), 2.04 (m, 2H, PCH_2), 1.92 (t, J_{PH} = 2.01 Hz, 2H, = CH_2), 1.84 (m, 2H, PCH_2), 1.28 (m, 6H, PCH_3), 0.57 (m, 6H, PCH_3). $^{31}P\{^1H\}$ NMR (THF- d_6 , 121.5 MHz, -40 °C; δ): 113.2 (s, 2P). $^{13}C\{^1H\}$ NMR (THF- d_6 , 125 MHz, -40 °C; δ): 281.8 (1C, C_1), 44.3 (1C, C_4), 158.6 (1C, C_2), 141.0 (1C, C_3), 84.2 (5C, C_5H_5), 31.0 (2C, m, PCH_2), 22.8 (2C, PCH_3), 20.3 (2C, PCH_3).

[(MeC₅H₄)Mn(dmpe)=C=C=C=CH₂] (9b). To a mixture of (MeC₅H₄)Mn(dmpe)=C=C=C=C(SnPh₃)₂ (20 mg, 0.019 mmol) and TBAF (0.038 mL, 0.038 mmol) was added 0.75 mL of THF- d_6 at -20 °C. The temperature was raised to -5 °C, and the deprotected species **9b** was observed as the only Mn-containing complex present in the solution after 5 min. The compound could be characterized only in solution. 1H NMR (THF- d_6 , 300 MHz, -40 °C; δ): 4.50 (2H, C_5H_4), 3.97 (2H, C_5H_4), 2.07 (m, 2H, PCH_2), 2.03 (s, 3H, $C_5H_4CH_3$), 1.93 (t, J_{PH} = 2.0 Hz, 2H, = CH_2), 1.82 (m, 2H, PCH_2), 1.25 (m, 6H, PCH_3), 0.57 (m, 6H, PCH_3). $^{31}P\{^1H\}$ NMR (THF- d_6 , 121.5 MHz, -40 °C; δ): 94.3 (s, 2P). $^{13}C\{^1H\}$ NMR (THF- d_6 , 125 MHz, -40 °C; δ): 280.8 (1C, C_1), 157.9 (1C, C_2), 140.2 (1C, C_3), 44.3 (1C, C_4), 100.2 (C_5H_4 , C_{ipso}), 85.2 (2C, C_5H_4), 80.0 (2C, C_5H_4), 31.0 (2C, m, PCH_2), 22.8 (2C, PCH_3), 21.4 (1C, $C_5H_4CH_3$), 20.3 (2C, PCH_3).

[(C₅H₅)Mn(depe)=C=C=C=CH₂] (10a). To a mixture of (C₅H₅)Mn(depe)=C=C=C=C(SnPh₃)₂ (20 mg, 0.019 mmol) and TBAF (0.040 mL, 0.040 mmol) was added 0.75 mL of THF- d_6 at -20 °C. The temperature was raised to -5 °C, and the deprotected species **10a** was observed as the only Mn-containing complex present in the solution after 5 min. The compound could be characterized only in solution. 1H NMR (THF- d_6 , 300 MHz, -40 °C; δ): 4.54 (s, 5H, C_5H_5), 2.04 (m, 2H, PCH_2), 1.92 (t, J_{PH} = 2.01 Hz, 2H, = CH_2), 1.77 (2H, PCH_2), 1.60 (6H, PCH_2CH_3), 1.38 (2H, PCH_2), 1.09 (6H, PCH_2CH_3), 0.68 (6H, PCH_2CH_3), 0.63 (6H, PCH_2CH_3). $^{31}P\{^1H\}$ NMR (THF- d_6 , 121.5 MHz, -40 °C; δ): 113.2 (s, 2P). $^{13}C\{^1H\}$ NMR (C₆D₆, 125 MHz, -40 °C; δ): 281.8 (1C, C_1), 44.3 (1C, C_4), 158.6 (1C, C_2) and 141.0

(1C, C_3), 84.2 (5C, C_5H_5), 26.3 (2C, PCH_2), 25.2 (2C, PCH_2), 23.96 (2C, PCH_2CH_3), 9.47 (PCH_2CH_3).

[(MeC₅H₄)Mn(depe)=C=C=C=CH₂] (10b). To a mixture of (MeC₅H₄)Mn(depe)=C=C=C=C(SnPh₃)₂ (20 mg, 0.018 mmol) and TBAF (0.038 mL, 0.038 mmol) was added 0.75 mL of THF- d_6 at -20 °C. The temperature was raised to -5 °C, and the deprotected species **10b** was observed as the only Mn-containing complex present in the solution after 5 min. The compound could be characterized only in solution. 1H NMR (THF- d_6 , 300 MHz, -40 °C; δ): 4.51 (2H, C_5H_4), 3.96 (2H, C_5H_4), 2.05 (s, 3H, $C_5H_4CH_3$), 1.93 (t, J_{PH} = 2.01 Hz, 2H, = CH_2), 1.77 (2H, PCH_2), 1.60 (6H, PCH_2CH_3), 1.38 (2H, PCH_2), 1.09 (6H, PCH_2CH_3), 0.68 (6H, PCH_2CH_3), 0.63 (6H, PCH_2CH_3). $^{31}P\{^1H\}$ NMR (THF- d_6 , 121.5 MHz, -40 °C; δ): 114.8 (s, 2P). $^{13}C\{^1H\}$ NMR (THF- d_6 , 125 MHz, -40 °C; δ): 281.6 (1C, C_1), 158.6 (1C, C_2) and 141.2 (1C, C_3), 44.3 (1C, C_4), 100.4 (C_5H_4 , C_{ipso}), 85.4 (2C, C_5H_4), 80.2 (2C, C_5H_4), 26.3 (2C, PCH_2), 25.2 (2C, PCH_2), 23.96 (2C, PCH_2CH_3), 14.9 (1C, $C_5H_4CH_3$), 9.47 (PCH_2CH_3).

[(C₅H₄CH₃)(dmpe)Mn=C=C(H)=CH₂=C(OCH₃)]₂ (11b). To a toluene solution (10 mL) of **2b** (100 mg, 0.19 mmol) was added an excess of methanol. The solution was stirred at room temperature for 2 h to give a pink solution. The solvent was removed under vacuum and washed with pentane and ether to give a pink solid of **11b**. Yield: 120 mg, 90%. Anal. Calcd for C₃₄H₅₈Mn₂P₄ (700.59): C, 58.28; H, 8.34. Found: C, 58.54; H, 8.68. 1H NMR (toluene- d_6 , 500 MHz, 20 °C; δ): 5.40 (2H, t, $^3J_{P-H}$ = 25 Hz, Mn=C=CH), 4.31 (4H, C_5H_4), 3.92 (2H, Mn=C=CHCH₂), 3.84 (4H, C_5H_4), 3.5 (2H, Mn=C=CHCH₂), 3.34 (6H, Mn=C=CHCH₂C(OCH₃)), 1.95 (6H, $C_5H_4CH_3$), 1.71 (4H, PCH_2), 1.27 (4H, PCH_3), 1.24 (4H, PCH_2), 0.59 (12H, PCH_3). $^{31}P\{^1H\}$ NMR (THF- d_6 , 121.5 MHz, 20 °C; δ): 94.2 (s, 4P). $^{13}C\{^1H\}$ NMR (THF- d_6 , 125 MHz, 20 °C; δ): 339.5 (m, 2C, Mn-C), 117.9 (2C, m, = C_{β}), 162.5 (2C, m, CH₂C(OCH₃)), 98.3 (2C, $C_{ipso}(C_5H_4Me)$), 85.2 (4C, C_5H_4), 80.8 (4C, C_5H_4), 70.4 (2C, m, CH₂C(OCH₃)), 53.4 (2C, m, CH₂C(OCH₃)), 30.6 (4C, PCH_2), 23.3 (4C, PCH_3), 22.4 (2C, $C_5H_4CH_3$), 21.0 (4C, PCH_3). IR (CH_2Cl_2 , 20 °C; cm^{-1}): 1988 $\nu(C\equiv C)$, 1947 $\nu(C\equiv C)$, 1598 $\nu(C=C)$, 1550 $\nu(C=C)$.

Computational Details. These calculations were carried out using the Amsterdam Density Functional program package ADF, release 2003.01,^{80,81} on model systems with C₅H₅ and dHpe ligands on the metal center. Geometries and energies were calculated by using the local exchange-correlation potential of Vosko, Wilk, and Nusair⁸² with the addition of gradient corrections due to Becke⁸³ for the exchange energy and Perdew^{84,85} for the correlation energy. The standard triple- ζ basis sets with one set of polarization functions were employed for all non-hydrogen atoms (ADF database TZP), while the standard double- ζ STO basis was applied for H atoms (ADF database DZP). The frozen-core approximation was applied for the 1s electrons of C atoms, for the 1s-2p electrons of phosphorus and manganese, and for the 1s-4d electrons of tin atoms. The solvation energies based on gas-phase geometries were calculated by the conductor-like screening model (COSMO) suggested by Klamt and Schuurman⁸⁶ and implemented by Pye and Ziegler.⁸⁷ The solvent-accessible surface was chosen and constructed using the following radii (Å): H, 1.16; C, 2.00; P, 1.70; Mn, 2.40. A dielectric constant of 7.58 was used for THF.

(80) ADF2003.01; SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands; <http://www.scm.com>. te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; Van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931-967.

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The linear transit calculation performed to calculate the bending hypersurface of the model complex $Mn(C_5H_5)(dHpe)-[C=C=C=C(SnMe_3)_2]$ (**4-H**) as a function of one terminal bond angle α ($=C-C-Sn$) used the TURBOMOLE program package, version 5.5.^{88–90} Gradient-corrected density functional calculations were carried out, with corrections for exchange and correlation according to Becke⁸³ and Perdew,^{84,85} respectively (BP86). Geometries were optimized within the framework of the RI- J approximation.^{89,91} The geometries were preoptimized using a triple- ζ valence basis plus polarization,

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TZVP,⁹² for Mn and Sn, and a split-valence basis set with one set of polarization functions for the non-H atoms, SV(P),⁹³ for the remaining elements. In the final steps of the geometry optimizations, all elements were treated with the TZVP basis.

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Supporting Information Available: Tables giving Cartesian coordinates of optimized geometries, computed total bonding energies, solvation energies for all compounds and crystal structure data for compound **4b**. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data (excluding structure factors) for the structures given in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 241977. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336033; e-mail, deposit@ccdc.cam.ac.uk).

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