

## $\mu$ -Carbon–Carbon Bonds of Dinuclear Manganese Half-Sandwich Complexes as Electron Reservoirs

Koushik Venkatesan, Olivier Blacque, Thomas Fox, Montserrat Alfonso, Helmut W. Schmalke, Sohrab Kheradmandan, and Heinz Berke\*

Anorganisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

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The mononuclear vinylidene complexes of the type  $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2)(=\text{C}=\text{C}(\text{R}^1)(\text{SnMe}_3))$  were obtained by the reaction of  $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\eta^6\text{-cycloheptatriene})$  ( $\text{R}' = \text{H}$ , **1a**;  $\text{CH}_3$ , **1b**) with 1 equiv of  $\text{R}^1\text{-C}\equiv\text{C-SnMe}_3$  ( $\text{R}^1 = \text{SnMe}_3$ ,  $\text{C}_6\text{H}_5$ ,  $\text{C}_4\text{H}_3\text{S}$ ,  $\text{C}_6\text{H}_4\text{CH}_3$ ) and  $\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2$  ( $\text{R}'' = \text{CH}_3$  (dmppe),  $\text{C}_2\text{H}_5$  (depe)) in toluene at 50 °C for 3 h. The reactions of these tin-substituted complexes with 1 equiv of 1.0 M TBAF yielded the corresponding parent vinylidene species  $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2)(=\text{C}=\text{C}(\text{R}^1)(\text{H}))$ . Treatment of some of these vinylidene species with 1 equiv of  $[\text{Cp}_2\text{Fe}][\text{PF}_6]$  led to the oxidative coupling product  $[(\text{C}_5\text{H}_4\text{R}')(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2)_2\text{Mn}\equiv\text{C-CHR}^1\text{-CHR}^1\text{-C}\equiv\text{Mn}(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2)(\text{C}_5\text{H}_4\text{R}')][\text{PF}_6]_2$  ( $\text{R}' = \text{CH}_3$ ,  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{H}$ ;  $\text{R}' = \text{CH}_3$ ,  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{C}_6\text{H}_5$ ;  $\text{R}' = \text{CH}_3$ ,  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{C}_4\text{H}_3\text{S}$ ;  $\text{R}' = \text{H}$ ,  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{H}$ ;  $\text{R}' = \text{H}$ ,  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{C}_6\text{H}_5$ ;  $\text{R}' = \text{H}$ ,  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{C}_4\text{H}_3\text{S}$ ). In some cases these products of oxidative coupling,  $[(\text{C}_5\text{H}_4\text{R}')(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2)_2\text{Mn}\equiv\text{C-CHR}^1\text{-CHR}^1\text{-C}\equiv\text{Mn}(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2)(\text{C}_5\text{H}_4\text{R}')][\text{PF}_6]_2$ , were accompanied by formation of dinuclear complexes of the type  $[(\text{C}_5\text{H}_4\text{R}')(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2)_2\text{Mn}\equiv\text{C-CR}^1=\text{CR}^1\text{-C}\equiv\text{Mn}(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2)(\text{C}_5\text{H}_4\text{R}')][\text{PF}_6]_2$  and of the cationic carbyne complexes  $[(\text{C}_5\text{H}_4\text{R}')(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2)_2\text{Mn}\equiv\text{C-CH}_2\text{R}^1][\text{PF}_6]$  obtained by proton transfer. Reduction of these dinuclear complexes with  $\text{Cp}_2^*\text{Co}$  yielded back the corresponding mononuclear precursor complexes involving a reductive decoupling process. Both the reductive coupling and the oxidative coupling are fully reversible, which is supported by DFT calculations. The mononuclear and the dinuclear compounds were characterized by NMR, IR, and cyclic voltammetric studies. X-ray diffraction studies have been performed on complexes **3a**, **11**, **13a**, **15a**, and **22b**.

### Introduction

The miniaturization of components for the construction of useful devices and machines is currently pursued.<sup>1–13</sup> Electron reservoirs are one of the basic motifs of a single-electron device, which can store and release electrons in a reversible fashion, thereby forming

crucial components of such devices.<sup>14–32</sup> One could certainly envisage the possibility of utilizing the process of formation and cleavage of chemical bonds for this

\* To whom correspondence should be addressed. E-mail: hberke@aci.unizh.ch.

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purpose.<sup>33–43</sup> Two complementary electron-storage and -releasing units are the fundamental constituents of storage cells.<sup>44–48</sup> Coupling a metal and an independent electron reservoir in the same molecule opens attractive perspectives in the design of molecules devoted to energy storage (molecular batteries). The most common mechanisms by which electrons can be stored and released can be classified into three categories. The most obvious involves the change in the oxidation of the metal, thereby a number of electrons are made available at different potentials. Another originating from organic chemistry perspective involves the use of polyaromatic systems able to accept electrons in the  $\pi^*$  orbitals, although this is limited in its storage capacity.<sup>49,50</sup> A third possibility concerns the formation and cleavage of chemical bonds. The latter mechanism would normally make available electrons in pairs and relatively large in number. Very rarely does the redox chemistry of ligands in complexes have chemical consequences such as the formation or cleavage of bonds, and even more rarely is the event reversible.<sup>51</sup> Many cases are known that operate in at least one direction,<sup>52–56</sup> while very few systems exhibit reactions in both directions. Floriani and co-workers have reported one such system.<sup>33–42</sup> Recently, we have communicated the synthesis of novel half-sandwich manganese(I) vinylidene systems and their tendency to undergo facile oxidative coupling

and reductive decoupling process.<sup>43</sup> We present here a detailed account of the investigations carried out on the electron-rich manganese(I) systems of the type  $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{R}'')_2\text{PCH}_2\text{CH}_2\text{PR}'')$  ( $=\text{C}=\text{CR}^3\text{R}^4$ ) and their tuning. A first conclusion of a previous study was that vinylidene complexes gained considerable stability through the presence of the phosphane ligand (dmpe)<sup>57–59</sup> in comparison with the reported CO-substituted species  $\text{Mn}(\text{Cp})\text{L}^1\text{L}^2(\text{C}=\text{CR}_2)$ , where  $\text{L}^1 = \text{L}^2 = \text{CO}$ , or  $\text{L}^1 = \text{CO}$ ,  $\text{L}^2 = \text{PR}_3$ .<sup>60</sup>

## Results and Discussion

### I. Stannyl-Substituted Vinylidene Complexes. A

common method to obtain vinylidene complexes is making use of the high propensity of terminal acetylene derivatives to rearrange to vinylidene compounds.<sup>61–78</sup> For such a process to be initiated in the realm of half-sandwich  $\text{Mn}^{\text{I}}$  chemistry, we thought the complexes  $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\eta^6\text{-cycloheptatriene})$  ( $\text{R}' = \text{H}$ , **1a**;  $\text{CH}_3$ , **1b**)<sup>79</sup> to be excellent starting materials, since facile cycloheptatriene (CHT) exchange was expected to occur with donating ligands, such as phosphanes or acetylenes.<sup>43,59</sup> Conversions with tin mono- or disubstituted acetylenes were anticipated to finally lead to the desired vinylidene species. Stirring  $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{CHT})$  ( $\text{R}' = \text{H}$ , **1a**;  $\text{CH}_3$ , **1b**) with 1 equiv of  $\text{R}^1\text{-C}\equiv\text{C-SnMe}_3$  ( $\text{R}^1 = \text{SnMe}_3$ ,  $\text{C}_6\text{H}_5$ ,  $\text{C}_4\text{H}_9\text{S}$ ,  $\text{CH}_3$ ,  $\text{C}_6\text{H}_4\text{CH}_3$ ) and  $\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2$  ( $\text{R}'' = \text{CH}_3$  (dmpe),  $\text{C}_2\text{H}_5$  (depe)) in toluene at 50 °C for 3 h gave the corresponding vinylidene complexes of the type  $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2)(=\text{C}=\text{C}(\text{R}^1)(\text{SnMe}_3))$  ( $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{SnMe}_3$ ,  $\text{R}' = \text{H}$  **2a**,  $\text{CH}_3$  **2b**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1$

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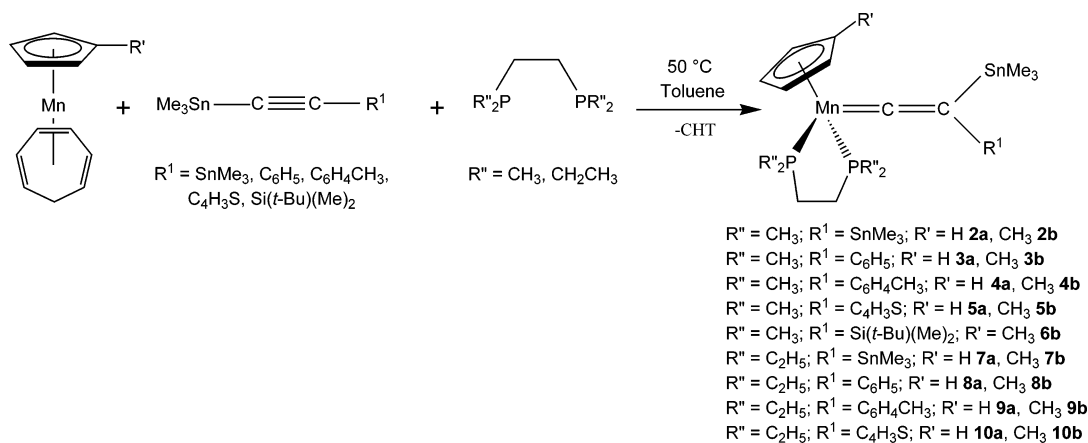
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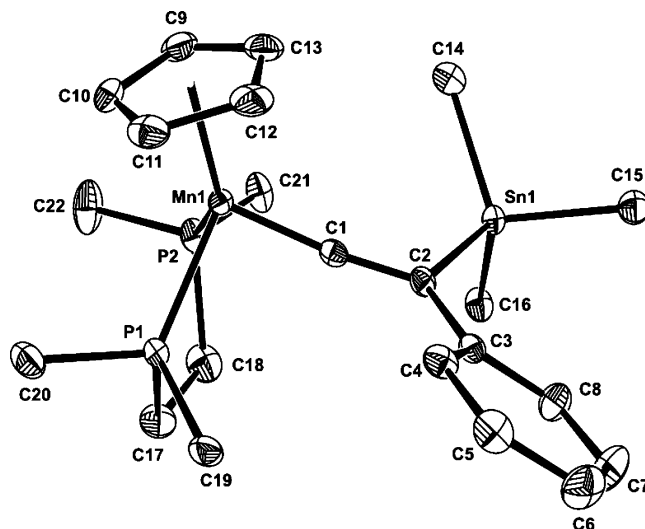
Scheme 1



$= \text{SnMe}_3, R' = \text{H } \mathbf{7a}, \text{CH}_3 \mathbf{7b}; R'' = \text{CH}_3, R^1 = \text{C}_6\text{H}_5, R' = \text{H } \mathbf{3a}, \text{CH}_3 \mathbf{3b}; R'' = \text{C}_2\text{H}_5, R^1 = \text{C}_6\text{H}_5, R' = \text{H } \mathbf{8a}, \text{CH}_3 \mathbf{8b}; R'' = \text{CH}_3, R^1 = \text{C}_6\text{H}_4\text{CH}_3, R' = \text{H } \mathbf{4a}, \text{CH}_3 \mathbf{4b}; R'' = \text{C}_2\text{H}_5, R^1 = \text{C}_6\text{H}_4\text{CH}_3, R' = \text{H } \mathbf{9a}, \text{CH}_3 \mathbf{9b}; R'' = \text{CH}_3, R^1 = \text{C}_4\text{H}_3\text{S}, R' = \text{H } \mathbf{5a}, \text{CH}_3 \mathbf{5b}; R'' = \text{C}_2\text{H}_5, R^1 = \text{C}_4\text{H}_3\text{S}, R' = \text{H } \mathbf{10a}, \text{CH}_3 \mathbf{10b}; R'' = \text{CH}_3, R^1 = \text{Si}(t\text{-Bu})(\text{Me})_2, R' = \text{CH}_3 \mathbf{6b}$  in quantitative yields (Scheme 1).

This reaction seems to require the initial formation of a Mn- $\pi$ -alkyne species.<sup>63</sup> However, NMR studies of the reaction carried out in the range  $-70$  to  $20$  °C did not reveal any intermediate. The  $^{13}\text{C}$  NMR spectra of complexes **2–10** show the  $C_\alpha$  and the  $C_\beta$  resonances at around 321 and 114 ppm, respectively. The  $^{31}\text{P}$  NMR resonances appear between 92 and 93 ppm for complexes **2–6**, which are comparable to those obtained for the related  $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{H}_3\text{C})_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2(=\text{C}=\text{CR}'\text{H})$  complexes.<sup>43,59,63,80–82</sup> However the resonances were shifted further downfield between 110 and 115 ppm for complexes **7–10**. The  $^{119}\text{Sn}$  resonances corresponding to the trimethyl tin groups were observed as a triplet between  $-16$  and  $-20$  ppm. The structure of **3a** was additionally confirmed by an X-ray diffraction analysis (Figure 1). The bond lengths of 1.761(6) and 1.344(8) Å for Mn1–C1 and C1–C2, respectively, confirm the double-bond character of the two bonds.<sup>43,59,80,81</sup>

Reaction of **1a** with 1 equiv of  $\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$  and depe yields a mixture of the corresponding vinylidene complex **8a** and the bis-acetylide  $\text{Mn}^{\text{II}}$  complex  $\text{Mn}(\text{depe})_2(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)_2$ , **11**. The  $^1\text{H}$  NMR spectrum of **11** shows two broad signals in the high-field region at  $-13.7$  and  $-9.8$  ppm corresponding to the depe protons. The resonances for the aromatic protons were observed as broad signals both in the downfield region at 16.9 ppm and in the high-field region at  $-4.9$  and  $-1.1$  ppm. Both the vinylidene complexes **8a** and **11** could be separated and characterized due to their different solubilities. The formation of **11** is believed to pass through a half-sandwich Mn<sup>II</sup> monoacetylide followed by the displacement of the cyclopentadienyl ring with a depe and an acetylide. The axial symmetry of these



**Figure 1.** Molecular structure of **3a** (30% probability displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Mn1–C1 1.761(6), C1–C2 1.344(8), C2–Sn1 2.139(6), Mn1–P1 2.1895(17), Mn1–P2 2.1877(17); Mn1–C1–C2 172.9(5), C1–C2–Sn1 115.2(4), C1–C2–C3 123.8(5), C3–C2–Sn1 120.9(4). All hydrogen atoms have been omitted for clarity.

species was corroborated by an X-ray study (Figure 2). The structure of **11** shows the manganese in a pseudo-octahedral environment with the phenyl alkynyl ligands in *trans* position. The Mn–C11 bond distance of 1.978(2) Å is in the same range as those found for similar symmetric *trans*-bis-alkynyl complexes, while the bond distance of 1.211(3) Å for C11–C12 indicates clearly a triple-bond character of the alkynyl ligand. These values are characteristic for this type of low-spin  $d^5$  complexes.<sup>57,83,84</sup>

**II. Vinylidene Complexes via Removal of the Stannyl Group(s).** It has been observed earlier<sup>43,60</sup> that the substituents on the  $\beta$  carbon of the vinylidene complexes have a great effect on the stability of these complexes and also on the further reactivity. The reaction of the species  $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}''_2)(=\text{C}=\text{C}(\text{R}^1)(\text{SnMe}_3))$  ( $R'' = \text{CH}_3, R^1 = \text{SnMe}_3, R' = \text{H}$

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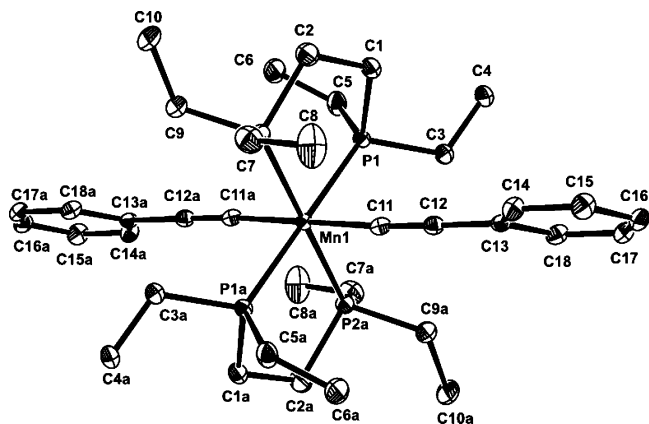
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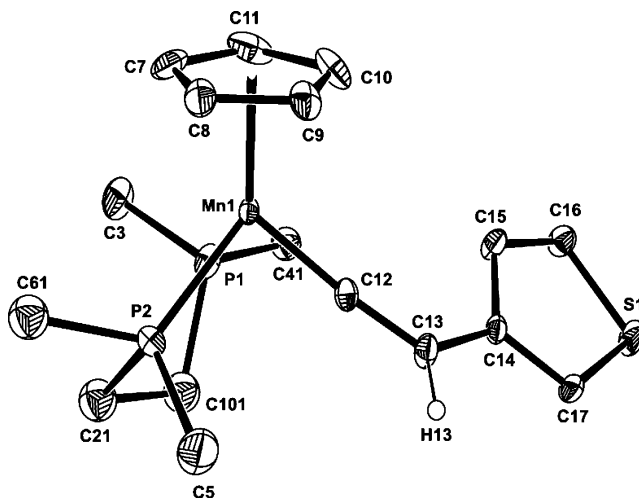




**Figure 2.** Molecular structure of **11** (30% probability displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Mn1–C11 1.978(2), C11–C12 1.211(3), C12–C13 1.439(3); Mn1–C11–C12 171.7(2), C11–C12–C13 176.7(3), C11–Mn1–C11a 180.0. All hydrogen atoms have been omitted for clarity.

**2a**, CH<sub>3</sub> **2b**; R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = SnMe<sub>3</sub>, R' = H **7a**, CH<sub>3</sub> **7b**; R'' = CH<sub>3</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>, R' = H **3a**, CH<sub>3</sub> **3b**; R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>, R' = H **8a**, CH<sub>3</sub> **8b**; R'' = CH<sub>3</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, R' = H **4a**, CH<sub>3</sub> **4b**; R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, R' = H **9a**, CH<sub>3</sub> **9b**; R'' = CH<sub>3</sub>, R<sup>1</sup> = C<sub>4</sub>H<sub>3</sub>S, R' = H **5a**, CH<sub>3</sub> **5b**; R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = C<sub>4</sub>H<sub>3</sub>S, R' = H **10a**, CH<sub>3</sub> **10b**; R'' = CH<sub>3</sub>, R<sup>1</sup> = Si(*t*-Bu)(Me)<sub>2</sub>, R' = CH<sub>3</sub> **6b**) with 1 equiv of NBu<sub>4</sub>F (5% H<sub>2</sub>O) yields the corresponding parent vinylidene species Mn(C<sub>5</sub>H<sub>4</sub>R')(R''<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR''<sub>2</sub>)(=C=C(R<sup>1</sup>)(H)) (R'' = CH<sub>3</sub>, R<sup>1</sup> = H, R' = H **12a**, CH<sub>3</sub> **12b**; R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = H, R' = H **17a**, CH<sub>3</sub> **17b**; R'' = CH<sub>3</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>, R' = H **13a**, CH<sub>3</sub> **13b**; R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>, R' = H **18a**, CH<sub>3</sub> **18b**; R'' = CH<sub>3</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, R' = H **14a**, CH<sub>3</sub> **14b**; R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, R' = H **19a**, CH<sub>3</sub> **19b**; R'' = CH<sub>3</sub>, R<sup>1</sup> = C<sub>4</sub>H<sub>3</sub>S, R' = H **15a**, CH<sub>3</sub> **15b**; R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = C<sub>4</sub>H<sub>3</sub>S, R' = H **20a**, CH<sub>3</sub> **20b**; R'' = CH<sub>3</sub>, R<sup>1</sup> = Si(*t*-Bu)(Me)<sub>2</sub>, R' = CH<sub>3</sub> **16b**) by the nucleophilic substitution of the SnMe<sub>3</sub> groups (Scheme 2). Complexes **12** and **17** constitute the finest examples of thermally stable half-sandwich Mn<sup>I</sup> vinylidene complexes with phosphine ligands and two hydrogen atoms at the C<sub>β</sub> atom.

The structure of **15a** in the solid state was confirmed by an X-ray diffraction study (Figure 3). The Mn1–C12 and C12–C13 bond distances are 1.739(3) and 1.336(4) Å, quite similar to those of the related complexes

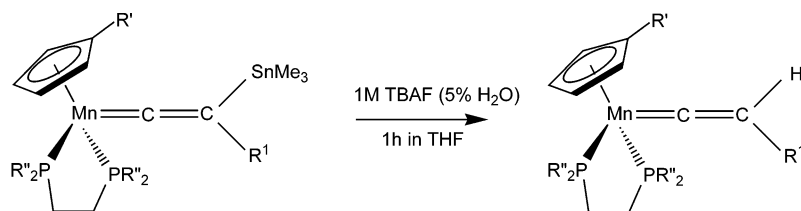


**Figure 3.** Molecular structure of **15a** (30% probability displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Mn1–C12 1.739(3), C12–C13 1.336(4); Mn1–C12–C13 174.5(3), C12–C13–C14 123.9(3). Selected hydrogen atoms and the disordered atoms are omitted for clarity.

already reported.<sup>43,59,80,84</sup> We could also obtain an X-ray diffraction analysis for **13a** (Figure 4). The structure of both independent molecules revealed bond lengths very similar to **15a** and **3a**. However, the Mn–C<sub>α</sub>–C<sub>β</sub> angles of 179.5(3)° and 177.9(3)° show almost linearity of the C<sub>2</sub> chain in comparison to the slightly bent Mn–C<sub>2</sub> chain in **15a** and **3a** at 174.5(3)° and 172.9(5)°, respectively.

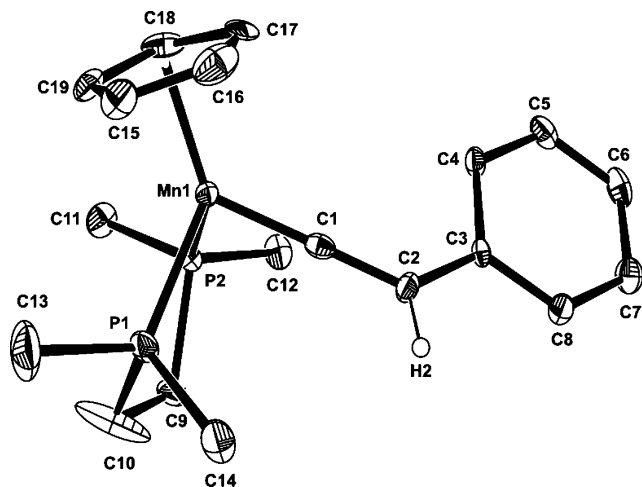
**III. Reversible Oxidative Coupling of Vinylidene Complexes.** A major route to dinuclear manganese systems bearing cumulene bridges utilizes coupling processes of appropriate mononuclear species.<sup>43,80–82,85</sup> Our observations show that the oxidation products of the parent vinylidene complexes depend on the type of substituents on the cyclopentadienyl ring and the C<sub>β</sub> atom. Oxidation of complexes **12b**, **13b**, **15b**, **17a**, **18a**, and **20a** with 1 equiv of [Cp<sub>2</sub>Fe][PF<sub>6</sub>]<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> after 1 h yields the corresponding dinuclear carbyne complexes of the type [(C<sub>5</sub>H<sub>4</sub>R')(R''<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR''<sub>2</sub>)Mn≡C–CHR<sup>1</sup>–CHR<sup>1</sup>–C≡Mn(R''<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR''<sub>2</sub>)(C<sub>5</sub>H<sub>4</sub>R')][PF<sub>6</sub>]<sub>2</sub> (R' = CH<sub>3</sub>, R'' = CH<sub>3</sub>, R<sup>1</sup> = H **21b**; R' = CH<sub>3</sub>, R'' = CH<sub>3</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub> **22b**; R' = CH<sub>3</sub>, R'' = CH<sub>3</sub>, R<sup>1</sup> = C<sub>4</sub>H<sub>3</sub>S **23b**; R' = H, R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = H **24a**; R' = H, R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub> **25a**; R' = H, R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = C<sub>4</sub>H<sub>3</sub>S **26a**), which are the obvious coupling products (Scheme 3). The <sup>1</sup>H

### Scheme 2



R'' = CH<sub>3</sub>, R<sup>1</sup> = SnMe<sub>3</sub>; R' = H **2a**, CH<sub>3</sub> **2b**  
 R'' = CH<sub>3</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>; R' = H **3a**, CH<sub>3</sub> **3b**  
 R'' = CH<sub>3</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>; R' = H **4a**, CH<sub>3</sub> **4b**  
 R'' = CH<sub>3</sub>, R<sup>1</sup> = C<sub>4</sub>H<sub>3</sub>S; R' = H **5a**, CH<sub>3</sub> **5b**  
 R'' = CH<sub>3</sub>, R<sup>1</sup> = Si(*t*-Bu)(Me)<sub>2</sub>; R' = CH<sub>3</sub> **6b**  
 R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = SnMe<sub>3</sub>; R' = H **7a**, CH<sub>3</sub> **7b**  
 R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>; R' = H **8a**, CH<sub>3</sub> **8b**  
 R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>; R' = H **9a**, CH<sub>3</sub> **9b**  
 R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = C<sub>4</sub>H<sub>3</sub>S; R' = H **10a**, CH<sub>3</sub> **10b**

R'' = CH<sub>3</sub>; R<sup>1</sup> = H; R' = H **12a**, CH<sub>3</sub> **12b**  
 R'' = CH<sub>3</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>; R' = H **13a**, CH<sub>3</sub> **13b**  
 R'' = CH<sub>3</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>; R' = H **14a**, CH<sub>3</sub> **14b**  
 R'' = CH<sub>3</sub>, R<sup>1</sup> = C<sub>4</sub>H<sub>3</sub>S; R' = H **15a**, CH<sub>3</sub> **15b**  
 R'' = CH<sub>3</sub>, R<sup>1</sup> = Si(*t*-Bu)(Me)<sub>2</sub>; R' = CH<sub>3</sub> **16b**  
 R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = H; R' = H **17a**, CH<sub>3</sub> **17b**  
 R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>; R' = H **18a**, CH<sub>3</sub> **18b**  
 R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>; R' = H **19a**, CH<sub>3</sub> **19b**  
 R'' = C<sub>2</sub>H<sub>5</sub>, R<sup>1</sup> = C<sub>4</sub>H<sub>3</sub>S; R' = H **20a**, CH<sub>3</sub> **20b**



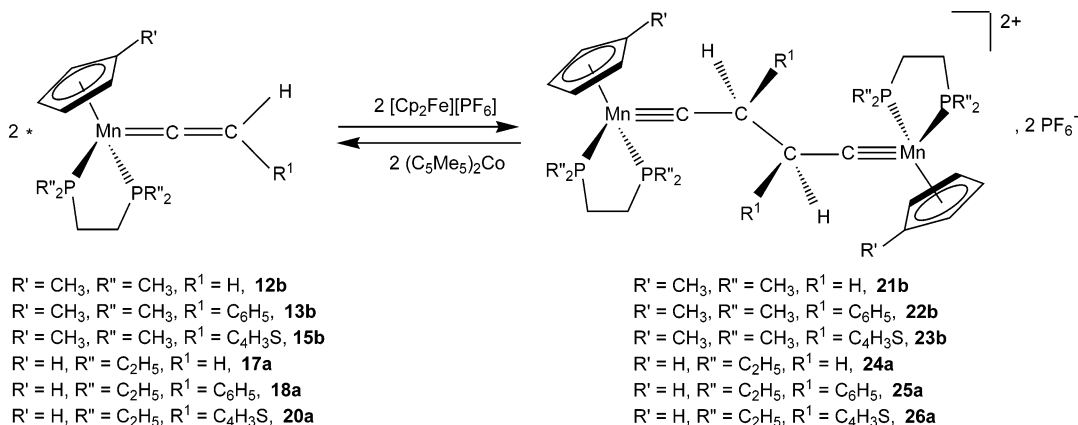
**Figure 4.** Molecular structure of **13a** (only one of the two independent molecules is shown with 30% probability displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Mn1–C1 1.737(4), C1–C2 1.351(6); Mn1–C1–C2 179.5(3), C1–C2–C3 127.1(4) (the following values are the corresponding bond parameters for the second independent molecule: Mn2–C20 1.726(4), C20–C21 1.361(6); Mn2–C20–C21 177.9(3), C20–C21–C22 125.8(4)). Selected hydrogen atoms and the disordered atoms have been omitted for clarity.

NMR spectra show characteristic multiplet signals at around 2.72 ppm for complexes **21b** and **24a** and at 4.39 ppm for complexes **22b**, **23b**, **25a**, and **26a**. The  $^{31}\text{P}$  NMR resonances appear as a broad singlet at 81.1 ppm (**21b**) and 100.1 ppm (**24a**) for the dmpe ligand and the depe ligand, respectively. However, two multiplets were observed between 79 and 80 ppm for complexes **22b** and **23b** and between 100 and 101 ppm for **25a** and **26a**. Further, a septet was observed at  $-145.4$  ppm for the  $[\text{PF}_6]^-$  anion for all complexes **21b**, **22b**, **23b**, and **24a**. Additionally, the  $^{13}\text{C}$  NMR spectrum shows the  $\text{C}_\alpha$  atom between 330 and 340 ppm for all complexes and  $\text{C}_\beta$  between 46 and 50 ppm for **21b** and **24a**, and between 72 and 90 ppm for complexes **22b**, **23b**, **25a**, and **26a**, which is characteristic for these kinds of carbyne complexes. $^{81,82}$  The formation of complexes **21b**, **24a**, **22b**, **23b**, **25a**, and **26a** implies highly selective oxidative C–C coupling processes starting from mononuclear cationic radicals as intermediates. The coupling process is believed to go through a radical cationic species, which consequently undergoes a dimerization to yield the coupling product. However, the oxidation of complexes

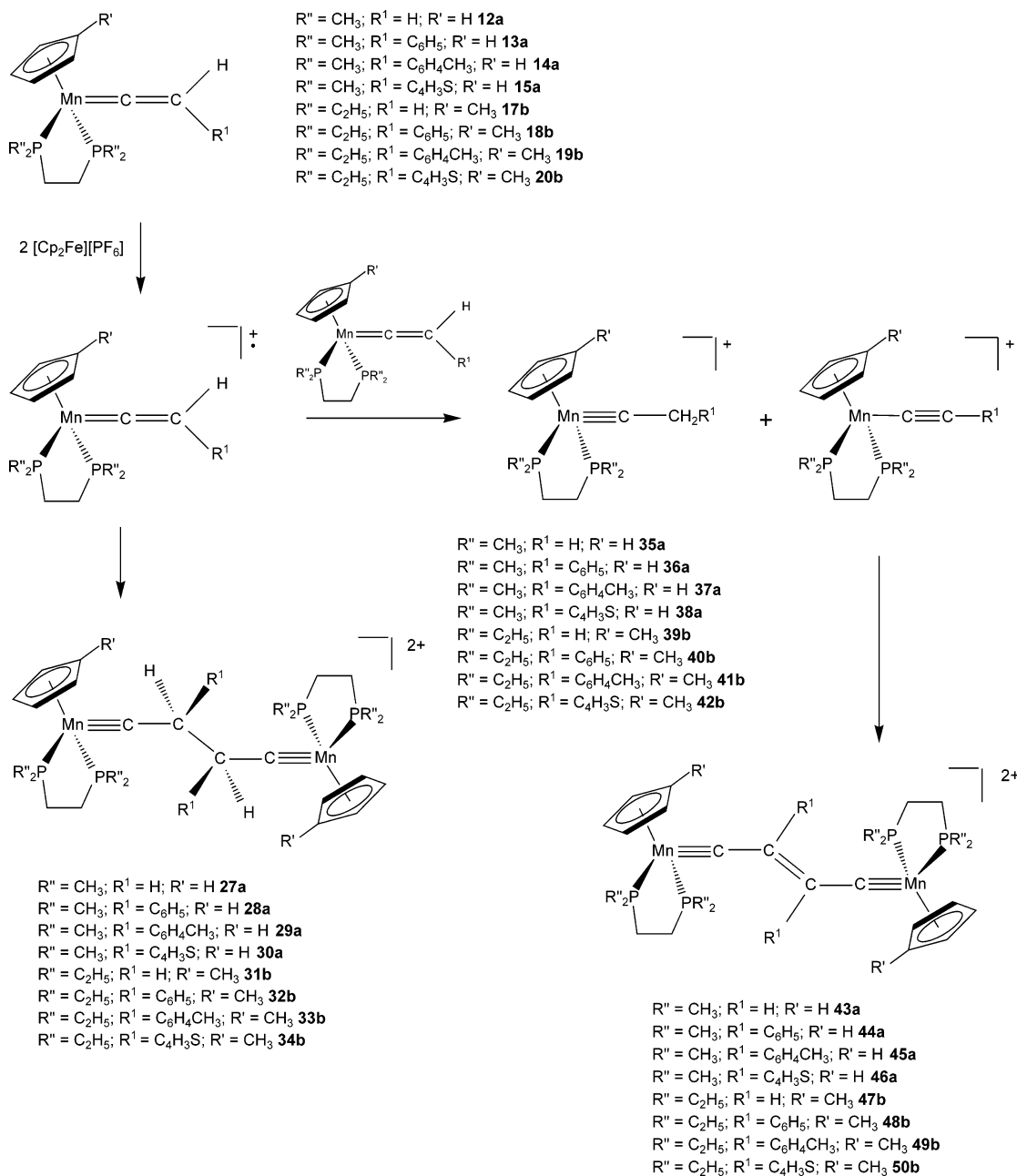
**12a**, **13a**, **14a**, **14b**, **15a**, **16b**, **17b**, **18b**, **19a**, **19b**, and **20b** with 1 equiv of  $[\text{Cp}_2\text{Fe}][\text{PF}_6]$  in  $\text{CH}_2\text{Cl}_2$  was much less selective and after 1 h yielded complicated mixtures, for which the separation could not be accomplished, but NMR spectroscopic characterization was performed.

We describe here the oxidation of the parent vinylidene complexes  $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}'')(\text{C}=\text{C}(\text{R}^1)(\text{H}))$  ( $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{H}$ ,  $\text{R}' = \text{H}$  **12a**;  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{C}_6\text{H}_5$ ,  $\text{R}' = \text{H}$  **13a**;  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{C}_6\text{H}_4\text{CH}_3$ ,  $\text{R}' = \text{H}$  **14a**;  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{C}_4\text{H}_3\text{S}$ ,  $\text{R}' = \text{H}$  **15a**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{H}$ ,  $\text{R}' = \text{CH}_3$  **17b**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{C}_6\text{H}_5$ ,  $\text{R}' = \text{CH}_3$  **18b**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{C}_6\text{H}_4\text{CH}_3$ ,  $\text{R}' = \text{CH}_3$  **19b**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{C}_4\text{H}_3\text{S}$ ,  $\text{R}' = \text{CH}_3$  **20b**) with 1 equiv of  $[\text{Cp}_2\text{Fe}][\text{PF}_6]$ , which yielded in each case a mixture containing the corresponding dinuclear carbyne complex  $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}'')\text{Mn}\equiv\text{C}-\text{CHR}^1-\text{CHR}^1-\text{C}\equiv\text{Mn}(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}'')(\text{C}_5\text{H}_4\text{R}')][\text{PF}_6]_2$  ( $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{H}$ ,  $\text{R}' = \text{H}$  **27a**;  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{C}_6\text{H}_5$ ,  $\text{R}' = \text{H}$  **28a**;  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{C}_6\text{H}_4\text{CH}_3$ ,  $\text{R}' = \text{H}$  **29a**;  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{C}_4\text{H}_3\text{S}$ ,  $\text{R}' = \text{H}$  **30a**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{H}$ ,  $\text{R}' = \text{CH}_3$  **31b**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{C}_6\text{H}_5$ ,  $\text{R}' = \text{CH}_3$  **32b**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{C}_6\text{H}_4\text{CH}_3$ ,  $\text{R}' = \text{CH}_3$  **33b**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{C}_4\text{H}_3\text{S}$ ,  $\text{R}' = \text{CH}_3$  **34b**), the dehydrogenative coupling  $\mu$ -vicinal alkylidene type product  $[(\text{C}_5\text{H}_4\text{R}')(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}'')\text{Mn}\equiv\text{C}-\text{CR}^1=\text{CR}^1-\text{C}\equiv\text{Mn}(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}'')(\text{C}_5\text{H}_4\text{R}')][\text{PF}_6]_2$  ( $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{H}$ ,  $\text{R}' = \text{H}$  **35a**;  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{C}_6\text{H}_5$ ,  $\text{R}' = \text{H}$  **36a**;  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{C}_6\text{H}_4\text{CH}_3$ ,  $\text{R}' = \text{H}$  **37a**;  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{C}_4\text{H}_3\text{S}$ ,  $\text{R}' = \text{H}$  **38a**;  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{Si}(t\text{-Bu})(\text{Me})_2$ ,  $\text{R}' = \text{CH}_3$  **39b**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{H}$ ,  $\text{R}' = \text{CH}_3$  **40b**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{C}_6\text{H}_5$ ,  $\text{R}' = \text{CH}_3$  **41b**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{C}_6\text{H}_4\text{CH}_3$ ,  $\text{R}' = \text{CH}_3$  **42b**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{C}_4\text{H}_3\text{S}$ ,  $\text{R}' = \text{CH}_3$  **43b**), and additionally the protonation product of the vinylidenes producing the mononuclear carbyne species  $[(\text{C}_5\text{H}_4\text{R}')(\text{R}''_2\text{PCH}_2\text{CH}_2\text{PR}'')\text{Mn}\equiv\text{C}-\text{CH}_3][\text{PF}_6]$  ( $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{H}$ ,  $\text{R}' = \text{H}$  **44a**;  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{C}_6\text{H}_5$ ,  $\text{R}' = \text{H}$  **45a**;  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{C}_6\text{H}_4\text{CH}_3$ ,  $\text{R}' = \text{H}$  **46a**;  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{C}_4\text{H}_3\text{S}$ ,  $\text{R}' = \text{H}$  **47a**;  $\text{R}'' = \text{CH}_3$ ,  $\text{R}^1 = \text{Si}(t\text{-Bu})(\text{Me})_2$ ,  $\text{R}' = \text{CH}_3$  **48b**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{H}$ ,  $\text{R}' = \text{CH}_3$  **49b**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{C}_6\text{H}_5$ ,  $\text{R}' = \text{CH}_3$  **50b**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{C}_6\text{H}_4\text{CH}_3$ ,  $\text{R}' = \text{CH}_3$  **51b**;  $\text{R}'' = \text{C}_2\text{H}_5$ ,  $\text{R}^1 = \text{C}_4\text{H}_3\text{S}$ ,  $\text{R}' = \text{CH}_3$  **52b**) (Scheme 4). In an exemplary fashion we describe here the  $^1\text{H}$  NMR spectrum of the mixture obtained from the oxidation of **12a**, which shows a characteristic multiplet at 2.72 ppm for the  $\text{CH}_2$  groups of **27a**, a triplet at 6.33 ppm with  $^4J_{\text{P-H}} = 6.0$  Hz for the vinylidene protons of **28a**, and a multiplet at 2.10 ppm for the terminal  $\text{CH}_3$  group of **29a**. The  $^{31}\text{P}$  NMR spectrum revealed broad resonances at 78.9 (**27a**),

### Scheme 3



Scheme 4



77.8 (**28a**), and 81.5 ppm (**29a**) corresponding to the dmpe ligands. The  $^{13}\text{C}$  spectra showed resonances for  $\text{C}_\alpha$  at 325.0 ppm for **27a**, 317.2 ppm for **28a**, and 300.5 ppm for **29a**, respectively. The reason for the formation of this complex series is due to a too slow oxidation of the starting vinylidene complex by  $[\text{FeCp}_2][\text{PF}_6]$ , which leaves the radical cation of the vinylidene species enough time to undergo proton transfer to the residual vinylidene complex, which can act as base and form the generally quite stable carbyne complexes.<sup>84</sup> The remaining  $(\text{C}_5\text{H}_4\text{R})(\text{R}'')_2\text{PCH}_2\text{CH}_2\text{PR}''_2\text{Mn}-\text{C}\equiv\text{C}-\text{R}^1$  complexes, being radicals as well, undergo self-coupling to the  $\mu$ -vicinal alkylidene type bridged compounds (Scheme 4).

To investigate the role of substituents on the  $\text{C}_\beta$  atom in the coupling process leading to dinuclear manganese systems, we carried out density functional calculations<sup>86–88</sup> on various model compounds: the mononuclear cationic radical systems  $[(\text{C}_5\text{H}_4\text{Me})(\text{H}_2\text{PCH}_2\text{CH}_2-$

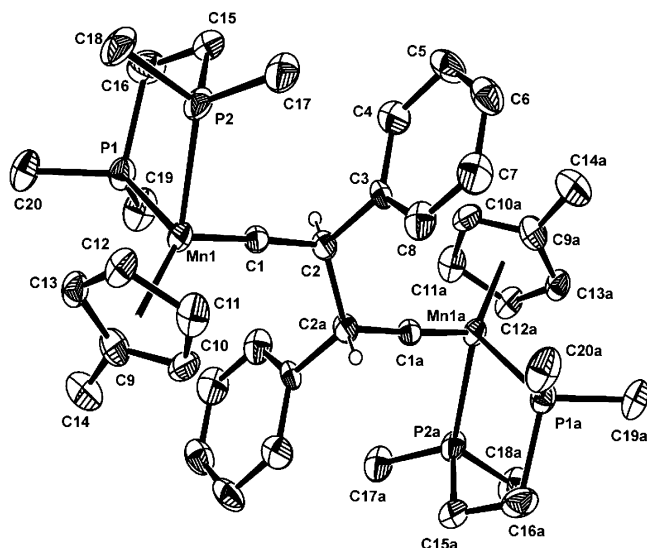
$\text{PH}_2)\text{Mn}=\text{C}=\text{CHR}]^{+\bullet}$  ( $\text{R} = \text{H}$  **12b-H**,  $\text{Me}$ ,  $\text{C}_6\text{H}_5$  **13b-H**,  $\text{C}_6\text{H}_4\text{CH}_3$  **14b-H**,  $\text{Si}(t\text{-Bu})(\text{CH}_3)_2$  **16b-H**) and the corresponding dinuclear products  $[(\text{C}_5\text{H}_4\text{Me})(\text{H}_2\text{PCH}_2\text{CH}_2\text{-PH}_2)\text{Mn}\equiv\text{C}-\text{CHR}-\text{CHR}-\text{C}\equiv\text{Mn}(\text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2)(\text{C}_5\text{H}_4\text{-Me})]^{2+}$  ( $\text{R} = \text{H}$  **21b-H**,  $\text{Me}$ ,  $\text{C}_6\text{H}_5$  **22b-H**,  $\text{C}_6\text{H}_4\text{CH}_3$ ,  $\text{Si}(t\text{-Bu})(\text{CH}_3)_2$ ), for which the dHpe ligands have been used instead of the dmpe ligands. In the selected molecules only the dimer complexes **21b** ( $\text{R} = \text{H}$ ) and **22b** ( $\text{R} = \text{C}_6\text{H}_5$ ) have been formed and experimentally characterized without ambiguity, while the reaction starting from **14b** ( $\text{R} = \text{C}_6\text{H}_4\text{CH}_3$ ) or **16b** ( $\text{R} = \text{Si}(t\text{-Bu})(\text{CH}_3)_2$ ) led to

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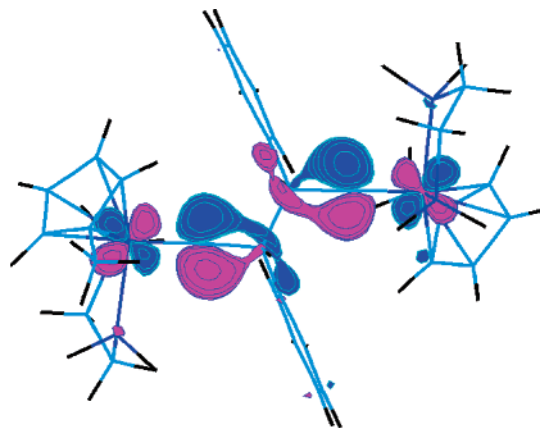
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**Figure 5.** Molecular structure of **22b** (50% probability displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Mn1–C1 1.653(4), C1–C2 1.493(6), C2–C2a 1.503(9); Mn1–C1–C2 176.0(4), C1–C2–C2a 114.6(5), C1–C2–C3 108.2(4). Selected hydrogen atoms and the PF<sub>6</sub><sup>−</sup> anions have been omitted for clarity.

complicated mixtures. The model complex with R = Me has also been chosen, because it is sterically and electronically intermediate between R = H and R = C<sub>6</sub>H<sub>5</sub>. The optimized mononuclear cationic radical systems showed spin densities located at the manganese and the C<sub>β</sub> atoms. The probability of finding the unpaired electron of the system on the terminal carbon atom C<sub>β</sub> decreases following the order R = H (+0.367α) > Me (+0.366α) > C<sub>6</sub>H<sub>5</sub> (+0.358α) > C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> (+0.344α) > Si(*t*-Bu)(CH<sub>3</sub>)<sub>2</sub> (+0.332α). Furthermore, single-point calculations including a model for solvation effects performed on the gas-phase geometries of the mononuclear and dinuclear model complexes led to dimerization energies Δ*E* of −24.2 (R = H), −12.3 (R = Me), −3.9 (R = C<sub>6</sub>H<sub>5</sub>), −2.1 (R = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), and +12.1 kcal/mol (R = Si(*t*-Bu)(CH<sub>3</sub>)<sub>2</sub>), following the same order as the C<sub>β</sub> spin density (Δ*E* = *E*<sub>dimer</sub> − 2*E*<sub>monomer</sub>). These calculations suggest that the dimerization process to generate a C–C-coupled dinuclear product should be easier for [(C<sub>5</sub>H<sub>4</sub>Me)(dHpe)Mn=C=CH<sub>2</sub>]<sup>•+</sup> in comparison to the last one of the series, [(C<sub>5</sub>H<sub>4</sub>Me)(dHpe)Mn=C=CH(Si(*t*-Bu)(CH<sub>3</sub>)<sub>2</sub>)]<sup>•+</sup>, which is in very good agreement with the experimental observations. Nevertheless, for all studied systems the negative dimerization energies indicate that the formation of the dinuclear compounds are more or less thermodynamically favored, and consequently we believe that such reactions can be tuned toward obtaining single products taking into account the oxidation potential of the complexes by using powerful oxidizing agents, and this kind of study is currently being investigated.

It is also noteworthy that the oxidation of complexes **13b**, **15b**, **18a**, and **20a** gives specifically only one diastereomer in each case: the meso (*R, S*) isomer **22b**, **23b**, **25a**, and **26a**. In the case of complex **22b** the (*R, S*) configuration has been characterized spectroscopically as well as crystallographically (Figure 5). DFT calculations performed on the dinuclear products [(C<sub>5</sub>H<sub>4</sub>Me)(dHpe)Mn≡C–CHR–CHR–C≡Mn(dHpe)(C<sub>5</sub>H<sub>4</sub>–



**Figure 6.** Calculated LUMO of the dinuclear model complex **22b-H** showing the π-type antibonding interactions between Mn and C<sub>α</sub> and between C<sub>β</sub> and C<sub>β</sub>'.

Me)]<sup>2+</sup> (R = Me and C<sub>6</sub>H<sub>5</sub>) confirmed the assumption that the selectivity arises from an appropriate sterically enforced structure of the radical cation appearing during the dimerization process. Indeed, full geometry optimizations carried out for both configurations of the complexes studied led to differences of energy between the true minima in favor of the (*R, S*) diastereomer by 4.5 and 19.3 kJ/mol for compounds with R = Me and C<sub>6</sub>H<sub>5</sub>, respectively.

The cyclic voltammetric studies of **12b** and **13b** show quasi-reversible behavior. The first oxidation step is a relatively slow step at −0.246 V, but the dimerization occurs very rapidly and was observed at 0.368 V. Further, the dinuclear complex can be re-reduced, and thus, the whole process turns out to be quasi-reversible. The reduction of the dinuclear carbyne complexes **21b**, **22b**, **23b**, **24a**, **25a**, and **26a** with Cp<sub>2</sub><sup>\*</sup>Co yielded quantitatively the corresponding mononuclear vinylidene complexes **12b**, **13b**, **15b**, **17a**, **18a**, and **20a**, respectively. The reversibility of this process can be explained and is highlighted by the shape of the LUMO of the low-spin dinuclear model complex **22b-H** (Figure 6). The vacant orbital is mainly of π-type antibonding character between Mn and C<sub>α</sub> and σ-antibonding between C<sub>β</sub> and C<sub>β</sub>'. The reduction of the dinuclear compound resulting formally from an addition of two electrons into the LUMO destabilizes the Mn≡C<sub>α</sub> and the C<sub>β</sub>–C<sub>β</sub>' bonds and leads back to the mononuclear vinylidene systems. Single-point calculations on the gas-phase geometries with a model for solvation effects performed on the selected dinuclear model complexes gave the energy level of the corresponding LUMO at −5.26 (R = H), −5.14 (R = Me), −4.85 (R = C<sub>6</sub>H<sub>5</sub>), and −4.75 (R = C<sub>6</sub>H<sub>4</sub>–CH<sub>3</sub>). The energy difference between the HOMO and the LUMO follows the same order with Δ*E*<sub>(HOMO–LUMO)</sub> = 2.16 (R = H), 2.18 (R = Me), 2.29 (R = C<sub>6</sub>H<sub>5</sub>), and 2.33 (R = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) to indicate that the reduction of the dinuclear carbyne complexes should be the easiest in the case of R = H because the LUMO is in this case more accessible to add two electrons to it. The complex [(C<sub>5</sub>H<sub>4</sub>Me)(dHpe)Mn≡C–CH(Si(*t*-Bu)(CH<sub>3</sub>)<sub>2</sub>)CH(Si(*t*-Bu)(CH<sub>3</sub>)<sub>2</sub>)C≡Mn(dHpe)(C<sub>5</sub>H<sub>4</sub>Me)]<sup>2+</sup> should be treated separately from the others because it seems clear that the very positive dimerization energy of Δ*E* = +12.1 kcal/mol is due to the very bulky ligand Si(*t*-Bu)(CH<sub>3</sub>)<sub>2</sub>, which prevents the formation of the dimer. Nevertheless, the



energy difference  $\Delta E_{(\text{HOMO-LUMO})}$  of 2.33 eV (the largest one calculated together with  $R = \text{C}_6\text{H}_4\text{CH}_3$ ) makes this dicationic dinuclear complex the last complex of the series.

The observation of reactions described above is significant in many respects: (i) the C-C bond formation and cleavage are reversible, (ii) the C-C bond cleavage acts as a shuttle of two electrons, and (iii) such an electron transfer can occur intermolecularly. On the whole, these systems would function as a device for storing and releasing two electrons involving the following balance:  $4e_{\pi} \rightarrow 2e_{\sigma} + 2e$ . On a reversible basis one could certainly envisage using these molecules as electron reservoirs.<sup>14-32</sup>

## Conclusion

In conclusion, a series of mononuclear half-sandwich complexes of the type  $\text{Mn}(\text{C}_5\text{H}_4\text{R}')(\text{R}'_2\text{PCH}_2\text{CH}_2\text{PR}'_2)_2$ - $(=\text{C}=\text{C}(\text{R}^1)(\text{H}))$  have been prepared. Coupling and the reverse decoupling processes of these complexes have been investigated. The influence exerted by the substituents of the  $\text{C}_{\beta}$  atom of the vinylidene system on the oxidative coupling and the reductive decoupling processes investigated by DFT calculations corroborates that of the experimental findings. This study highlights the potential of utilizing the ubiquitous C-C bonds in organometallic systems as electron reservoirs, thereby allowing further development of molecular batteries, which could find application as components in nanodevices.

## Experimental Section

**General Procedures.** 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  $\text{P}_2\text{O}_5$ , and then prior to use from  $\text{CaH}_2$ . Literature procedures were used to prepare the following compounds: 1,2-bis(dimethylphosphino)ethane (dmpe),<sup>89</sup> 1,2-bis(diethylphosphino)ethane (depe),<sup>89</sup> ( $\eta^5$ - $\text{C}_5\text{H}_4\text{R}'$ ) $\text{Mn}(\text{CMT})$ ,<sup>79</sup>  $\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{SnMe}_3$ ,<sup>90</sup>  $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{SnMe}_3$ ,<sup>90</sup>  $\text{CH}_3\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{SnMe}_3$ ,<sup>90</sup>  $\text{SC}_4\text{H}_9-\text{C}\equiv\text{C}-\text{SnMe}_3$ , (*t*-Bu)(Me)<sub>2</sub>Si-C≡C-SnMe<sub>3</sub>,<sup>90</sup>  $[\text{Cp}_2\text{Fe}][\text{PF}_6]$ ,<sup>91</sup>  $[\text{Cp}_2^*\text{Co}]$ , *n*-BuLi (1.6 M in hexane), MeLi·LiBr (1.5 M in diethyl ether), Me<sub>3</sub>SnCl, tetrabutylammonium fluoride (1.0 M in tetrahydrofuran),  $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{H}$ ,  $\text{CH}_3\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{H}$ ,  $\text{SC}_4\text{H}_9-\text{C}\equiv\text{C}-\text{H}$ , and (*t*-Bu)(Me)<sub>2</sub>Si-C≡C-H 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 <sup>1</sup>H and 121.5 MHz for <sup>31</sup>P{<sup>1</sup>H} and on a Bruker-DRX-500 spectrometer at 125.8 MHz for <sup>13</sup>C{<sup>1</sup>H} and 186.5 MHz for <sup>119</sup>Sn, respectively. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C are given in ppm relative to the solvent signals. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra were referenced to 98% external H<sub>3</sub>PO<sub>4</sub> and the <sup>119</sup>Sn{<sup>1</sup>H} NMR spectra to SnBu<sub>4</sub>.

**$[(\text{C}_5\text{H}_5)\text{Mn}(\text{dmpe})=\text{C}=\text{C}(\text{SnMe}_3)_2]$ , **2a.**** To a toluene solution (10 mL) of  $(\text{C}_5\text{H}_5)\text{Mn}(\text{CMT})$  (100 mg, 0.48 mmol) was added a toluene solution (10 mL) of dmpe (70 mg, 0.48 mmol) and  $\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{SnMe}_3$  (170 mg, 0.48 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 oil. Then the oil was extracted with pentane and filtered through Celite. The pentane fraction was evaporated to give an orange-red solid. Crystallization from pentane at -35 °C gave single orange-red crystals. Yield: 292 mg, 98%. Anal. Calcd for  $\text{C}_{19}\text{H}_{39}\text{MnP}_2\text{Sn}_2$  (621.81): C, 36.69; H, 6.32. Found: C, 36.76; H, 6.42. <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ , 300 MHz, 20 °C):  $\delta$  4.12 (5H,  $\text{C}_5\text{H}_5$ ), 1.42 (2H,  $\text{PCH}_2$ ), 1.31 (3H,  $\text{P}(\text{CH}_3)_3$ ), 1.16 (2H,  $\text{PCH}_2$ ), 0.87 (3H,  $\text{P}(\text{CH}_3)_3$ ), 0.32 (3H,  $\text{Sn}(\text{CH}_3)_3$ ). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{C}_6\text{D}_6$ , 121.5 MHz, 20 °C):  $\delta$  91.3 (s, 2P). <sup>13</sup>C NMR ( $\text{C}_6\text{D}_6$ , 125 MHz, 20 °C):  $\delta$  321.4 (m, Mn-C<sub>α</sub>), 114.8 (m, =C<sub>β</sub>), 83.8 (Cp), 30.8 ( $\text{PCH}_2$ ), 23.5 ( $\text{P}(\text{CH}_3)_3$ ), 21.3 ( $\text{P}(\text{CH}_3)_3$ ), -8.1 ( $\text{Sn}(\text{CH}_3)_3$ ). <sup>119</sup>Sn NMR ( $\text{C}_6\text{D}_6$ , 186.4 MHz, 20 °C):  $\delta$  -20 (t, 77.0 Hz,  $\text{Sn}(\text{CH}_3)_3$ ). IR ( $\text{CH}_2\text{Cl}_2$ , 20 °C): 1598  $\text{cm}^{-1}$   $\nu(\text{C}=\text{C})$ , 1550  $\text{cm}^{-1}$   $\nu(\text{C}=\text{C})$ .

**$[(\text{MeC}_5\text{H}_4)\text{Mn}(\text{dmpe})=\text{C}=\text{C}(\text{SnMe}_3)_2]$ , **2b.**** The same procedure was adopted as above using **1b** as the starting component. Crystallization from pentane at -35 °C gave single orange-red crystals. Yield: 270 mg, 96%. Anal. Calcd for  $\text{C}_{20}\text{H}_{41}\text{MnP}_2\text{Sn}_2$  (635.84): C, 37.77; H, 6.49. Found: C, 37.65; H, 6.25. <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ , 300 MHz, 20 °C):  $\delta$  4.04 (2H,  $\text{C}_5\text{H}_4\text{Me}$ ), 3.77 (2H,  $\text{C}_5\text{H}_4\text{Me}$ ), 2.06 (3H,  $\text{C}_5\text{H}_4\text{Me}$ ), 1.51 (2H,  $\text{PCH}_2$ ), 1.31 (3H,  $\text{PMe}_3$ ), 1.22 (2H,  $\text{PCH}_2$ ), 0.88 (3H,  $\text{PMe}_3$ ) 0.32 (3H,  $\text{SnMe}_3$ ). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{C}_6\text{D}_6$ , 121.5 MHz, 20 °C):  $\delta$  91.2 (s, 2P). <sup>13</sup>C NMR ( $\text{C}_6\text{D}_6$ , 125 MHz, 20 °C):  $\delta$  321.6 (m, Mn-C<sub>α</sub>), 114.8 (m, =C<sub>β</sub>), 84.2 ( $\text{C}_5\text{H}_4\text{Me}$ ), 77.8 ( $\text{C}_5\text{H}_4\text{Me}$ ), 31.8 ( $\text{PCH}_2$ ), 21.5 ( $\text{PMe}_3$ ), 14.8 ( $\text{PMe}_3$ ), 14.5 (1C,  $\text{C}_5\text{H}_4\text{Me}$ ), -4.9 ( $\text{SnMe}_3$ ). <sup>119</sup>Sn NMR ( $\text{C}_6\text{D}_6$ , 186.4 MHz, 20 °C):  $\delta$  -20 (t, 77.0 Hz,  $\text{Sn}(\text{CH}_3)_3$ ). IR ( $\text{CH}_2\text{Cl}_2$ , 20 °C): 1594  $\text{cm}^{-1}$   $\nu(\text{C}=\text{C})$ , 1552  $\text{cm}^{-1}$   $\nu(\text{C}=\text{C})$ .

**$[(\text{C}_6\text{H}_5)\text{Mn}(\text{dmpe})=\text{C}=\text{C}(\text{Ph})(\text{SnMe}_3)]$ , **3a.**** To a toluene solution (10 mL) of  $(\text{C}_5\text{H}_5)\text{Mn}(\text{CMT})$  (100 mg, 0.48 mmol) was added a toluene solution (10 mL) of dmpe (70 mg, 0.48 mmol) and  $\text{Ph}-\text{C}\equiv\text{C}-\text{SnMe}_3$  (130 mg, 0.48 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 oil. Then the oil was extracted with pentane and filtered through Celite. The pentane fraction was evaporated to give an orange-red solid. Crystallization from pentane at -35 °C gave single orange-red crystals. Yield: 250 mg, 98%. Anal. Calcd for  $\text{C}_{22}\text{H}_{35}\text{MnP}_2\text{Sn}$  (535.10): C, 49.38; H, 6.59. Found: C, 49.43; H, 6.97. <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ , 300 MHz, 20 °C):  $\delta$  7.25 (2H, m,  $\text{C}_6\text{H}_5$ ), 7.16 (2H, m,  $\text{C}_6\text{H}_5$ ), 6.83 (1H, m,  $\text{C}_6\text{H}_5$ ), 4.31 (5H,  $\text{C}_5\text{H}_5$ ), 1.42 (2H,  $\text{PCH}_2$ ), 1.18 (3H,  $\text{P}(\text{CH}_3)_3$ ), 0.96 (2H,  $\text{PCH}_2$ ), 0.87 (3H,  $\text{P}(\text{CH}_3)_3$ ), 0.35 (3H,  $\text{Sn}(\text{CH}_3)_3$ ). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{C}_6\text{D}_6$ , 121.5 MHz, 20 °C):  $\delta$  93.1 (s, 2P). <sup>13</sup>C NMR ( $\text{C}_6\text{D}_6$ , 125 MHz, 20 °C):  $\delta$  329.4 (m, Mn-C<sub>α</sub>), 145.8 (m, =C<sub>β</sub>), 136.7 (s, 1C,  $\text{C}_{\text{ipso}}(\text{C}_6\text{H}_5)$ ), 122.2 (s, 1C,  $\text{C}_6\text{H}_5$ ), 120.5 (s, 2C,  $\text{C}_6\text{H}_5$ ), 120.2 (s, 2C,  $\text{C}_6\text{H}_5$ ), 84.3 (5C,  $\text{C}_5\text{H}_5$ ), 31.1 ( $\text{PCH}_2$ ), 24.1 ( $\text{PCH}_2$ ), 23.2 ( $\text{P}(\text{CH}_3)_3$ ), 21.3 ( $\text{P}(\text{CH}_3)_3$ ), -6.3 ( $\text{Sn}(\text{CH}_3)_3$ ). <sup>119</sup>Sn NMR ( $\text{C}_6\text{D}_6$ , 186.4 MHz, 20 °C):  $\delta$  -16.32 (t, 71.0 Hz,  $\text{Sn}(\text{CH}_3)_3$ ). IR ( $\text{CH}_2\text{Cl}_2$ , 20 °C): 1596  $\text{cm}^{-1}$   $\nu(\text{C}=\text{C})$ , 1549  $\text{cm}^{-1}$   $\nu(\text{C}=\text{C})$ .

**$[(\text{MeC}_5\text{H}_4)\text{Mn}(\text{dmpe})=\text{C}=\text{C}(\text{Ph})(\text{SnMe}_3)]$ , **3b.**** The same procedure was adopted as above using **1b** as the starting component. Crystallization from pentane at -35 °C gave single orange-red crystals. Yield: 240 mg, 98%. Anal. Calcd for  $\text{C}_{23}\text{H}_{37}\text{MnP}_2\text{Sn}$  (549.15): C, 50.30; H, 6.79. Found: C, 49.94; H, 6.75. <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ , 300 MHz, 20 °C):  $\delta$  7.25 (2H, m,  $\text{C}_6\text{H}_5$ ), 7.16 (2H, m,  $\text{C}_6\text{H}_5$ ), 6.83 (1H, m,  $\text{C}_6\text{H}_5$ ), 4.27 (2H,  $\text{C}_5\text{H}_4\text{Me}$ ), 3.91 (2H,  $\text{C}_5\text{H}_4\text{Me}$ ), 2.04 (3H,  $\text{C}_5\text{H}_4\text{CH}_3$ ), 1.40 (2H,  $\text{PCH}_2$ ), 1.11 (3H,  $\text{P}(\text{CH}_3)_3$ ), 0.92 (2H,  $\text{PCH}_2$ ), 0.75 (3H,  $\text{P}(\text{CH}_3)_3$ ) 0.31 (3H,  $\text{Sn}(\text{CH}_3)_3$ ). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{C}_6\text{D}_6$ , 121.5 MHz, 20 °C):  $\delta$  92.8 (s, 2P). <sup>13</sup>C NMR ( $\text{C}_6\text{D}_6$ , 125 MHz, 20 °C):  $\delta$  329.6 (m, Mn-C<sub>α</sub>), 143.8 (m, =C<sub>β</sub>), 137.7 (s, 1C,  $\text{C}_{\text{ipso}}(\text{C}_6\text{H}_5)$ ), 122.6 (s, 1C,  $\text{C}_6\text{H}_5$ ), 121.1 (s, 2C,  $\text{C}_6\text{H}_5$ ), 121.7 (s, 2C,  $\text{C}_6\text{H}_5$ ), 98.4 (s,  $\text{C}_{\text{ipso}}(\text{MeC}_5\text{H}_4)$ ), 81.3 ( $\text{C}_5\text{H}_4\text{Me}$ ), 80.2 ( $\text{C}_5\text{H}_4\text{Me}$ ), 31.8 ( $\text{PCH}_2$ ), 24.1 ( $\text{PCH}_2$ ), 21.5 ( $\text{P}(\text{CH}_3)_3$ ), 14.8 ( $\text{P}(\text{CH}_3)_3$ ), 14.5 (s,  $\text{C}_5\text{H}_4\text{CH}_3$ ), -6.1 ( $\text{Sn}(\text{CH}_3)_3$ ). <sup>119</sup>Sn NMR ( $\text{C}_6\text{D}_6$ , 186.4 MHz, 20 °C):  $\delta$  -17.2 (t, 77.0 Hz,  $\text{Sn}(\text{CH}_3)_3$ ). IR ( $\text{CH}_2\text{Cl}_2$ , 20 °C): 1596  $\text{cm}^{-1}$   $\nu(\text{C}=\text{C})$ , 1548  $\text{cm}^{-1}$   $\nu(\text{C}=\text{C})$ .

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[(C<sub>5</sub>H<sub>5</sub>)Mn(dmpe)=C=C(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)(SnMe<sub>3</sub>)] **4a**. To a toluene solution (10 mL) of (C<sub>5</sub>H<sub>5</sub>)Mn(HT) (100 mg, 0.48 mmol) was added a toluene solution (10 mL) of dmpe (70 mg, 0.48 mmol) and CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-C≡C-SnMe<sub>3</sub> (130 mg, 0.48 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 oil. Then the oil was extracted with pentane and filtered through Celite. The pentane fraction was evaporated to give an orange-red solid. Crystallization from pentane at -35 °C gave single orange-red crystals. Yield: 255 mg, 98%. Anal. Calcd for C<sub>23</sub>H<sub>37</sub>MnP<sub>2</sub>Sn (549.13): C, 50.30; H, 6.79. Found: C, 50.63; H, 6.87. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 20 °C): δ 7.26 (2H, m, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 7.10 (2H, m, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 4.32 (5H, C<sub>5</sub>H<sub>5</sub>), 2.23 (3H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 1.42 (2H, PCH<sub>2</sub>), 1.18 (3H, P(CH<sub>3</sub>)<sub>3</sub>), 0.96 (2H, PCH<sub>2</sub>), 0.79 (3H, P(CH<sub>3</sub>)<sub>3</sub>), 0.37 (9H, Sn(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz, 20 °C): δ 94.5 (s, 2P). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz, 20 °C): δ 343.5 (m, Mn-C<sub>α</sub>), 139.2 (m, =C<sub>β</sub>), 130.8 (s, 1C, C<sub>ipso</sub>(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)), 129.5 (s, 2C, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 123.1 (s, 2C, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 122.7 (s, 1C, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 82.9 (5C, C<sub>5</sub>H<sub>5</sub>), 31.2 (PCH<sub>2</sub>), 23.7 (PCH<sub>2</sub>), 22.1 (P(CH<sub>3</sub>)<sub>3</sub>), 21.7 (P(CH<sub>3</sub>)<sub>3</sub>), 21.3 (1C, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), -6.3 (Sn(CH<sub>3</sub>)<sub>3</sub>). <sup>119</sup>Sn NMR (C<sub>6</sub>D<sub>6</sub>, 186.4 MHz, 20 °C): δ -16.5 (t, 71.0 Hz, Sn(CH<sub>3</sub>)<sub>3</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, 20 °C): 1596 cm<sup>-1</sup> ν(C=C), 1549 cm<sup>-1</sup> ν(C=C).

[(MeC<sub>5</sub>H<sub>4</sub>)Mn(dmpe)=C=C(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)(SnMe<sub>3</sub>)] **4b**. The same procedure was adopted as above using **1b** as the starting component. Crystallization from pentane at -35 °C gave single orange-red crystals. Yield: 235 mg, 93%. Anal. Calcd for C<sub>24</sub>H<sub>39</sub>MnP<sub>2</sub>Sn (563.16): C, 51.18; H, 6.98. Found: C, 51.34; H, 6.82. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 20 °C): δ 7.21 (2H, m, C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>), 7.14 (2H, m, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 4.27 (2H, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 3.91 (2H, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 2.21 (3H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 2.03 (3H, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 1.40 (2H, PCH<sub>2</sub>), 1.11 (3H, P(CH<sub>3</sub>)<sub>3</sub>), 0.92 (2H, PCH<sub>2</sub>), 0.75 (3H, P(CH<sub>3</sub>)<sub>3</sub>) 0.28 (9H, Sn(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz, 20 °C): δ 93.1 (s, 2P). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz, 20 °C): δ 329.6 (m, Mn-C<sub>α</sub>), 143.8 (m, =C<sub>β</sub>), 130.8 (s, 1C, C<sub>ipso</sub>(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)), 129.5 (s, 2C, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 123.1 (s, 2C, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 122.7 (s, 1C, C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>), 98.4 (s, C<sub>ipso</sub>(MeC<sub>5</sub>H<sub>4</sub>)), 81.3 (C<sub>5</sub>H<sub>4</sub>Me), 80.1 (C<sub>5</sub>H<sub>4</sub>Me), 31.4 (PCH<sub>2</sub>), 24.1 (PCH<sub>2</sub>), 21.3 (1C, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 21.2 (P(CH<sub>3</sub>)<sub>3</sub>), 14.6 (P(CH<sub>3</sub>)<sub>3</sub>), 14.5 (s, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), -5.8 (Sn(CH<sub>3</sub>)<sub>3</sub>). <sup>119</sup>Sn NMR (C<sub>6</sub>D<sub>6</sub>, 186.4 MHz, 20 °C): δ -17.2 (t, 71.0 Hz, Sn(CH<sub>3</sub>)<sub>3</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, 20 °C): 1596 cm<sup>-1</sup> ν(C=C), 1548 cm<sup>-1</sup> ν(C=C).

[(C<sub>5</sub>H<sub>5</sub>)Mn(dmpe)=C=C(C<sub>4</sub>H<sub>3</sub>S)(SnMe<sub>3</sub>)] **5a**. To a toluene solution (10 mL) of (C<sub>5</sub>H<sub>5</sub>)Mn(HT) (100 mg, 0.48 mmol) was added a toluene solution (10 mL) of dmpe (70 mg, 0.48 mmol) and SC<sub>4</sub>H<sub>3</sub>-C≡C-SnMe<sub>3</sub> (155 mg, 0.48 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 oil. Then the oil was extracted with pentane and filtered through Celite. The pentane fraction was evaporated to give an orange-red solid. Crystallization from pentane at -35 °C gave single orange-red crystals. Yield: 245 mg, 95%. Anal. Calcd for C<sub>20</sub>H<sub>33</sub>MnP<sub>2</sub>SSn (541.13): C, 44.39; H, 6.14. Found: C, 44.43; H, 6.37. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 20 °C): δ 7.08 (1H, m, C<sub>4</sub>H<sub>3</sub>S), 6.79 (1H, m, C<sub>4</sub>H<sub>3</sub>S), 6.41 (1H, m, C<sub>4</sub>H<sub>3</sub>S), 4.35 (5H, C<sub>5</sub>H<sub>5</sub>), 1.41 (2H, PCH<sub>2</sub>), 1.20 (3H, P(CH<sub>3</sub>)<sub>3</sub>), 0.94 (2H, PCH<sub>2</sub>), 0.82 (3H, P(CH<sub>3</sub>)<sub>3</sub>), 0.05 (3H, Sn(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz, 20 °C): δ 93.1 (s, 2P). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz, 20 °C): δ 329.6 (m, Mn-C<sub>α</sub>), 144.8 (m, =C<sub>β</sub>), 136.7 (s, 1C, C<sub>ipso</sub>(C<sub>6</sub>H<sub>5</sub>)), 125.1 (s, 1C, C<sub>4</sub>H<sub>3</sub>S), 122.3 (s, 1C, C<sub>4</sub>H<sub>3</sub>S), 110.5 (s, 1C, C<sub>4</sub>H<sub>3</sub>S), 84.1 (5C, C<sub>5</sub>H<sub>5</sub>), 31.4 (PCH<sub>2</sub>), 24.5 (PCH<sub>2</sub>), 23.3 (P(CH<sub>3</sub>)<sub>3</sub>), 21.3 (P(CH<sub>3</sub>)<sub>3</sub>), -6.4 (Sn(CH<sub>3</sub>)<sub>3</sub>). <sup>119</sup>Sn NMR (C<sub>6</sub>D<sub>6</sub>, 186.4 MHz, 20 °C): δ -17.1 (t, 74.5 Hz, Sn(CH<sub>3</sub>)<sub>3</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, 20 °C): 1594 cm<sup>-1</sup> ν(C=C), 1543 cm<sup>-1</sup> ν(C=C).

[(MeC<sub>5</sub>H<sub>4</sub>)Mn(dmpe)=C=C(C<sub>4</sub>H<sub>3</sub>S)(SnMe<sub>3</sub>)] **5b**. The same procedure was adopted as above using **1b** as the starting component. Crystallization from pentane at -35 °C gave single orange-red crystals. Yield: 240 mg, 96%. Anal. Calcd for C<sub>21</sub>H<sub>35</sub>MnP<sub>2</sub>SSn (555.16): C, 45.43; H, 6.35. Found: C, 45.67; H, 6.59. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 20 °C): δ 7.08 (1H, m, C<sub>4</sub>H<sub>3</sub>S), 6.79 (1H, m, C<sub>4</sub>H<sub>3</sub>S), 6.41 (1H, m, C<sub>4</sub>H<sub>3</sub>S), 4.31 (2H, C<sub>5</sub>H<sub>4</sub>Me), 4.01 (2H, C<sub>5</sub>H<sub>4</sub>Me), 2.01 (3H, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 1.38 (2H,

PCH<sub>2</sub>), 1.13 (3H, P(CH<sub>3</sub>)<sub>3</sub>), 0.90 (2H, PCH<sub>2</sub>), 0.74 (3H, P(CH<sub>3</sub>)<sub>3</sub>) 0.13 (3H, Sn(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz, 20 °C): δ 95.3 (s, 2P). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz, 20 °C): δ 329.6 (m, Mn-C<sub>α</sub>), 144.8 (m, =C<sub>β</sub>), 136.7 (s, 1C, C<sub>ipso</sub>(C<sub>4</sub>H<sub>3</sub>)), 125.1 (s, 1C, C<sub>4</sub>H<sub>3</sub>S), 122.3 (s, 1C, C<sub>4</sub>H<sub>3</sub>S), 110.5 (s, 1C, C<sub>4</sub>H<sub>3</sub>S), 98.3 (s, C<sub>ipso</sub>(MeC<sub>5</sub>H<sub>4</sub>)), 81.1 (C<sub>5</sub>H<sub>4</sub>Me), 80.5 (C<sub>5</sub>H<sub>4</sub>Me), 31.7 (PCH<sub>2</sub>), 24.1 (PCH<sub>2</sub>), 21.5 (P(CH<sub>3</sub>)<sub>3</sub>), 14.8 (P(CH<sub>3</sub>)<sub>3</sub>), 14.5 (s, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), -6.4 (Sn(CH<sub>3</sub>)<sub>3</sub>). <sup>119</sup>Sn NMR (C<sub>6</sub>D<sub>6</sub>, 186.4 MHz, 20 °C): δ -17.2 (t, 75.0 Hz, Sn(CH<sub>3</sub>)<sub>3</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, 20 °C): 1592 cm<sup>-1</sup> ν(C=C), 1551 cm<sup>-1</sup> ν(C=C).

[(MeC<sub>5</sub>H<sub>4</sub>)Mn(dmpe)=C=C(Si(*t*-Bu)(Me)<sub>2</sub>)(SnMe<sub>3</sub>)] **6b**. To a toluene solution (10 mL) of (MeC<sub>5</sub>H<sub>4</sub>)Mn(HT) (100 mg, 0.45 mmol) was added a toluene solution (10 mL) of dmpe (70 mg, 0.45 mmol) and (*t*-Bu)(Me)<sub>2</sub>Si-C≡C-SnMe<sub>3</sub> (140 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 oil. Then the oil was extracted with Et<sub>2</sub>O and filtered through Celite. The Et<sub>2</sub>O fraction was evaporated to give an orange-red oil. Crystallization from pentane at -35 °C gave single orange-red crystals. Yield: 250 mg, 96%. Anal. Calcd for C<sub>23</sub>H<sub>47</sub>MnP<sub>2</sub>SiSn (587.30): C, 47.03; H, 8.06. Found: C, 47.31; H, 8.39. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 20 °C): δ 4.03 (2H, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 3.78 (2H, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 2.05 (3H, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 1.40 (2H, PCH<sub>2</sub>), 1.11 (3H, P(CH<sub>3</sub>)<sub>3</sub>), 1.03 (9H, Si(*t*-C<sub>4</sub>H<sub>9</sub>)(Me)<sub>2</sub>), 0.92 (2H, PCH<sub>2</sub>), 0.75 (3H, P(CH<sub>3</sub>)<sub>3</sub>) 0.54 (6H, Si(*t*-C<sub>4</sub>H<sub>9</sub>)(CH<sub>3</sub>)<sub>2</sub>), 0.23 (9H, Sn(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz, 20 °C): δ 94.6 (s, 2P). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz, 20 °C): δ 327.7 (m, Mn-C<sub>α</sub>), 142.2 (m, =C<sub>β</sub>), 98.4 (s, C<sub>ipso</sub>(MeC<sub>5</sub>H<sub>4</sub>)), 81.3 (C<sub>5</sub>H<sub>4</sub>-Me), 80.1 (C<sub>5</sub>H<sub>4</sub>Me), 35.2 (3C, Si(*t*-C<sub>4</sub>H<sub>9</sub>)(Me)<sub>2</sub>), 28.3 (3C, Si(*t*-C<sub>4</sub>H<sub>9</sub>)(Me)<sub>2</sub>), 31.4 (PCH<sub>2</sub>), 24.1 (PCH<sub>2</sub>), 21.2 (P(CH<sub>3</sub>)<sub>3</sub>), 14.6 (P(CH<sub>3</sub>)<sub>3</sub>), 14.5 (s, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), -1.2 (2C, Si(*t*-C<sub>4</sub>H<sub>9</sub>)(CH<sub>3</sub>)<sub>2</sub>), -3.6 (3C, Sn(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 99.4 MHz, 20 °C): δ -3.2 (t, 5.0 Hz, Si(*t*-C<sub>4</sub>H<sub>9</sub>)(Me)<sub>2</sub>). <sup>119</sup>Sn NMR (C<sub>6</sub>D<sub>6</sub>, 186.4 MHz, 20 °C): δ -20.8 (t, 84.1 Hz, Sn(CH<sub>3</sub>)<sub>3</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, 20 °C): 1573 cm<sup>-1</sup> ν(C=C), 1553 cm<sup>-1</sup> ν(C=C).

[(MeC<sub>5</sub>H<sub>4</sub>)Mn(depe)=C=C(C<sub>4</sub>H<sub>3</sub>S)(SnMe<sub>3</sub>)] **10b**. The same procedure was adopted as above using **1b** as the starting component. Crystallization from pentane at -35 °C gave single orange-red crystals. Yield: 250 mg, 98%. Anal. Calcd for C<sub>25</sub>H<sub>43</sub>MnP<sub>2</sub>SSn (611.27): C, 49.12; H, 7.09. Found: C, 49.27; H, 7.43. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 20 °C): δ 7.08 (1H, m, C<sub>4</sub>H<sub>3</sub>S), 6.79 (1H, m, C<sub>4</sub>H<sub>3</sub>S), 6.41 (1H, m, C<sub>4</sub>H<sub>3</sub>S), 4.38 (2H, C<sub>5</sub>H<sub>4</sub>Me), 3.86 (2H, C<sub>5</sub>H<sub>4</sub>Me), 2.11 (3H, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 1.71 (m, 2H, PCH<sub>2</sub>), 1.45 (m, 4H, PCH<sub>2</sub>CH<sub>3</sub>), 1.22 (m, 4H, PCH<sub>2</sub>CH<sub>3</sub>), 1.03 (m, 2H, PCH<sub>2</sub>), 0.85 (m, 6H, PCH<sub>2</sub>CH<sub>3</sub>), 0.78 (m, 6H, PCH<sub>2</sub>CH<sub>3</sub>), 0.20 (9H, Sn(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz, 20 °C): δ 116.0 (s, 2P). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz, 20 °C): δ 326.6 (m, Mn-C<sub>α</sub>), 136.7 (s, 1C, C<sub>ipso</sub>(C<sub>4</sub>H<sub>3</sub>)), 125.1 (s, 1C, C<sub>4</sub>H<sub>3</sub>S), 122.3 (s, 1C, C<sub>4</sub>H<sub>3</sub>S), 110.5 (s, 1C, C<sub>4</sub>H<sub>3</sub>S), 98.4 (s, 1C, ipso-C MeC<sub>5</sub>H<sub>4</sub>), 95.4 (m, 1C, =C<sub>β</sub>), 81.1 (2C, C<sub>5</sub>H<sub>4</sub>Me), 80.0 (2C, C<sub>5</sub>H<sub>4</sub>-Me), 31.9 (1C, PCH<sub>2</sub>), 24.3 (PCH<sub>2</sub>CH<sub>3</sub>), 24.1 (2C, PCH<sub>2</sub>CH<sub>3</sub>), 23.6 (1C, PCH<sub>2</sub>), 14.5 (s, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 8.6 (2C, PCH<sub>2</sub>CH<sub>3</sub>), 9.8 (PCH<sub>2</sub>CH<sub>3</sub>), -6.7 (3C, Sn(CH<sub>3</sub>)<sub>3</sub>). <sup>119</sup>Sn NMR (C<sub>6</sub>D<sub>6</sub>, 186.4 MHz, 20 °C): δ -16.2 (t, 74.0 Hz, Sn(CH<sub>3</sub>)<sub>3</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, 20 °C): 1592 cm<sup>-1</sup> ν(C=C), 1548 cm<sup>-1</sup> ν(C=C).

[(Mn(depe)<sub>2</sub>(C≡C-Ph)<sub>2</sub>)] **11**. To a toluene solution (10 mL) of (C<sub>5</sub>H<sub>5</sub>)Mn(HT) (100 mg, 0.48 mmol) was added a toluene solution (10 mL) of depe (100 mg, 0.48 mmol) and Ph-C≡C-SnMe<sub>3</sub> (130 mg, 0.48 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 oil. Then the oil was extracted with pentane and filtered through Celite. The pentane fraction was evaporated to give an orange-red solid. The pentane insoluble was then extracted with ether and filtered through Celite. The Et<sub>2</sub>O was then evaporated to give a red solid. Crystallization from ether at -35 °C gave single orange-red crystals. Yield: 64 mg, 20%. Anal. Calcd for C<sub>36</sub>H<sub>58</sub>MnP<sub>4</sub> (669.69): C, 64.57; H, 8.73. Found: C, 64.92; H, 8.59. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 300 MHz, 20 °C): δ 16.9 (2H, H<sub>meta</sub>, C<sub>6</sub>H<sub>5</sub>), 0.5 (24H, PCH<sub>2</sub>CH<sub>3</sub>), -1.1 (2H, H<sub>para</sub>, C<sub>6</sub>H<sub>5</sub>), -4.9 (1H, H<sub>ortho</sub>,

$(C_6H_5)_2Mn(dmpe)=C=C(H)_2$ , **12a**. To a THF solution (10 mL) of  $(C_5H_5)_2Mn(dmpe)=C=C(SnMe_3)_2$  (**2a**) (100 mg, 0.16 mmol) was added tetrabutylammonium fluoride (0.16 mL, 0.16 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. Then the oil was extracted with pentane and filtered through Celite. The pentane fraction was evaporated to give an orange-red solid. Crystallization from pentane at  $-35^\circ C$  gave single orange-red crystals. Yield: 44 mg, 92%. Anal. Calcd for  $C_{13}H_{23}MnP_2$  (296.20): C, 52.71; H, 7.82. Found: C, 53.10; H, 7.46.  $^1H$  NMR (THF- $d_6$ , 300 MHz,  $20^\circ C$ ):  $\delta$  4.3 (5H,  $C_5H_5$ ), 3.77 (2H, t,  $^4J_{PH} = 9.0$  Hz,  $=CH_2$ ), 1.96 (2H,  $PCH_2$ ), 1.67 (2H,  $PCH_2$ ), 1.31 (3H,  $P(CH_3)_3$ ), 1.26 (3H,  $P(CH_3)_3$ ).  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 121.5 MHz,  $20^\circ C$ ):  $\delta$  95.5 (s, 2P).  $^{13}C$  NMR ( $C_6D_6$ , 125 MHz,  $20^\circ C$ ):  $\delta$  341.9 (m,  $Mn-C_\alpha$ ), 97.3 (m,  $=C_\beta$ ), 83.1 (5C,  $C_5H_5$ ), 31.2 ( $PCH_2$ ), 22.4 ( $PCH_2$ ), 20.6 ( $P(CH_3)_3$ ), 19.7 ( $P(CH_3)_3$ ). IR ( $CH_2Cl_2$ ,  $20^\circ C$ ):  $1594\text{ cm}^{-1}$   $\nu(C=C)$ ,  $1556\text{ cm}^{-1}$   $\nu(C=C)$ .

$[(MeC_5H_4)Mn(dmpe)=C=C(H)_2]$ , **12b**. The same procedure was adopted as above using **2b** as the starting component. Crystallization from pentane at  $-35^\circ C$  gave single orange-red crystals. Yield: 42 mg, 92%. Anal. Calcd for  $C_{14}H_{25}MnP_2$  (310.23): C, 54.20; H, 8.12. Found: C, 54.36; H, 8.24.  $^1H$  NMR ( $C_6D_6$ , 300 MHz,  $20^\circ C$ ):  $\delta$  4.34 (2H, t,  $^4J_{PH} = 9.0$  Hz,  $=CH_2$ ), 4.28 (2H,  $C_5H_4Me$ ), 3.94 (2H,  $C_5H_4Me$ ), 2.13 (3H,  $C_5H_4CH_3$ ), 1.82 (2H,  $PCH_2$ ), 1.28 (2H,  $PCH_2$ ), 1.21 (3H,  $P(CH_3)_3$ ), 0.87 (3H,  $P(CH_3)_3$ ).  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 121.5 MHz,  $20^\circ C$ ):  $\delta$  95.6 (s, 2P).  $^{13}C$  NMR ( $C_6D_6$ , 125 MHz,  $20^\circ C$ ):  $\delta$  341.9 (m,  $Mn-C_\alpha$ ), 97.2 (m,  $=C_\beta$ ), 95.4 (s,  $C_{ipso}(MeC_5H_4)$ ), 84.3 ( $C_5H_4Me$ ), 80.3 ( $C_5H_4Me$ ), 30.8 ( $PCH_2$ ), 22.2 ( $PCH_2$ ), 21.8 ( $P(CH_3)_3$ ), 19.7 ( $P(CH_3)_3$ ), 14.5 (s,  $C_5H_4CH_3$ ). IR ( $CH_2Cl_2$ ,  $20^\circ C$ ):  $1598\text{ cm}^{-1}$   $\nu(C=C)$ ,  $1550\text{ cm}^{-1}$   $\nu(C=C)$ .

$[(C_5H_5)_2Mn(dmpe)=C=C(Ph)(H)]$ , **13a**. To a toluene solution (10 mL) of  $(C_5H_5)_2Mn(dmpe)=C=C(Ph)(SnMe_3)$  (**3a**) (100 mg, 0.19 mmol) was added an excess of MeOH. 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. Then the oil was extracted with pentane and filtered through Celite. The pentane fraction was evaporated to give an orange-red solid. Crystallization from pentane at  $-35^\circ C$  gave single orange-red crystals. Yield: 69 mg, 98%. Anal. Calcd for  $C_{19}H_{27}MnP_2$  (372.30): C, 61.29; H, 7.30. Found: C, 61.65; H, 7.53.  $^1H$  NMR ( $C_6D_6$ , 300 MHz,  $20^\circ C$ ):  $\delta$  7.39 (2H, m,  $C_6H_5$ ), 7.30 (2H, m,  $C_6H_5$ ), 6.95 (1H, m,  $C_6H_5$ ), 6.0 (1H, t,  $^4J_{PH} = 8.7$  Hz,  $=CHC_6H_5$ ), 4.34 (5H,  $C_5H_5$ ), 1.45 (2H,  $PCH_2$ ), 1.12 (3H,  $P(CH_3)_3$ ), 0.80 (2H,  $PCH_2$ ), 0.71 (3H,  $P(CH_3)_3$ ).  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 121.5 MHz,  $20^\circ C$ ):  $\delta$  94.0 (s, 2P).  $^{13}C$  NMR ( $C_6D_6$ , 125 MHz,  $20^\circ C$ ):  $\delta$  342.4 (m,  $Mn-C_\alpha$ ), 141.9 (m,  $=C_\beta$ ), 137.7 (s,  $C_{ipso}(C_6H_5)$ ), 122.6 (s,  $C_6H_5$ ), 121.1 (s,  $C_6H_5$ ), 121.7 (s,  $C_6H_5$ ), 82.3 (5C,  $C_5H_5$ ), 30.9 ( $PCH_2$ ), 23.4 ( $PCH_2$ ), 21.3 ( $PMe_3$ ), 19.4 ( $PMe_3$ ). IR ( $CH_2Cl_2$ ,  $20^\circ C$ ):  $1596\text{ cm}^{-1}$   $\nu(C=C)$ ,  $1553\text{ cm}^{-1}$   $\nu(C=C)$ .

$[(MeC_5H_4)Mn(dmpe)=C=C(Ph)(H)]$ , **13b**. The same procedure was adopted as above using **3b** as the starting component. Crystallization from pentane at  $-35^\circ C$  gave single orange-red crystals. Yield: 68 mg, 98%. Anal. Calcd for  $C_{20}H_{29}MnP_2$  (386.33): C, 61.17; H, 7.56. Found: C, 61.35; H, 7.53.  $^1H$  NMR ( $C_6D_6$ , 300 MHz,  $20^\circ C$ ):  $\delta$  7.25 (2H, m,  $C_6H_5$ ), 7.16 (2H, m,  $C_6H_5$ ), 6.83 (1H, m,  $C_6H_5$ ), 5.82 (1H, t,  $^4J_{PH} = 8.7$  Hz,  $=CHC_6H_5$ ), 4.30 (2H,  $C_5H_4Me$ ), 3.86 (2H,  $C_5H_4Me$ ), 1.94 (3H,  $C_5H_4CH_3$ ), 1.46 (2H,  $PCH_2$ ), 1.14 (3H,  $P(CH_3)_3$ ), 1.10 (2H,  $PCH_2$ ), 0.74 (3H,  $P(CH_3)_3$ ).  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 121.5 MHz,  $20^\circ C$ ):  $\delta$  94.5 (s, 2P).  $^{13}C$  NMR ( $C_6D_6$ , 125 MHz,  $20^\circ C$ ):  $\delta$  342.5 (m,  $Mn-C_\alpha$ ), 142.2 (m,  $=C_\beta$ ), 137.7 (s,  $C_{ipso}(C_6H_5)$ ), 122.6 (s,  $C_6H_5$ ), 121.1 (s,  $C_6H_5$ ), 121.7 (s,  $C_6H_5$ ), 98.4 (s,  $C_{ipso}(MeC_5H_4)$ ), 81.3 ( $C_5H_4Me$ ), 80.2 ( $C_5H_4Me$ ), 30.9 ( $PCH_2$ ), 23.4 ( $PCH_2$ ), 21.3 ( $P(CH_3)_3$ ), 19.4 ( $P(CH_3)_3$ ), 14.5 (s,  $C_5H_4CH_3$ ). IR ( $CH_2Cl_2$ ,  $20^\circ C$ ):  $1597\text{ cm}^{-1}$   $\nu(C=C)$ ,  $1555\text{ cm}^{-1}$   $\nu(C=C)$ .

$[(C_5H_5)_2Mn(dmpe)=C=C(C_6H_4CH_3)(H)]$ , **14a**. To a toluene solution (10 mL) of  $(C_5H_5)_2Mn(dmpe)=C=C(C_6H_4CH_3)(SnMe_3)$  (**4a**) (100 mg, 0.18 mmol) was added 1 equiv of 1.0 M TBAF (0.18 mL, 0.18 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. Then the oil was extracted with pentane and filtered through Celite. The pentane fraction was evaporated to give an orange-red solid. Crystallization from pentane at  $-35^\circ C$  gave single orange-red crystals. Yield: 68 mg, 98%. Anal. Calcd for  $C_{20}H_{29}MnP_2$  (386.32): C, 62.17; H, 7.56. Found: C, 62.03; H, 7.43.  $^1H$  NMR ( $C_6D_6$ , 300 MHz,  $20^\circ C$ ):  $\delta$  7.33 (2H, m,  $C_6H_4CH_3$ ), 7.10 (2H, m,  $C_6H_4CH_3$ ), 5.98 (1H, t,  $^4J_{PH} = 8.7$  Hz,  $=CHC_6H_4CH_3$ ), 4.47 (5H,  $C_5H_5$ ), 2.18 (3H, s,  $C_6H_4CH_3$ ), 1.39 (2H,  $PCH_2$ ), 1.12 (3H,  $P(CH_3)_3$ ), 0.80 (2H,  $PCH_2$ ), 0.71 (3H,  $P(CH_3)_3$ ).  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 121.5 MHz,  $20^\circ C$ ):  $\delta$  94.2 (s, 2P).  $^{13}C$  NMR ( $C_6D_6$ , 125 MHz,  $20^\circ C$ ):  $\delta$  339.4 (m,  $Mn-C_\alpha$ ), 138.9 (m,  $=C_\beta$ ), 130.8 (s, 1C,  $C_{ipso}(C_6H_4CH_3)$ ), 128.7 (s, 2C,  $C_6H_4CH_3$ ), 123.1 (s, 2C,  $C_6H_4CH_3$ ), 121.6 (s, 1C,  $C_6H_4CH_3$ ), 82.3 (5C,  $C_5H_5$ ), 30.9 ( $PCH_2$ ), 23.4 ( $PCH_2$ ), 22.1 (s, 1C,  $C_6H_4CH_3$ ), 21.3 ( $PMe_3$ ), 19.4 ( $PMe_3$ ). IR ( $CH_2Cl_2$ ,  $20^\circ C$ ):  $1583\text{ cm}^{-1}$   $\nu(C=C)$ ,  $1559\text{ cm}^{-1}$   $\nu(C=C)$ .

$[(MeC_5H_4)Mn(dmpe)=C=C(C_6H_4CH_3)(H)]$ , **14b**. The same procedure was adopted as above using **4b** as the starting component. Crystallization from pentane at  $-35^\circ C$  gave single orange-red crystals. Yield: 65 mg, 91%. Anal. Calcd for  $C_{21}H_{31}MnP_2$  (400.35): C, 63.00; H, 7.80. Found: C, 63.25; H, 7.63.  $^1H$  NMR ( $C_6D_6$ , 300 MHz,  $20^\circ C$ ): 7.31 (2H, m,  $C_6H_4CH_3$ ), 7.07 (2H, m,  $C_6H_4CH_3$ ), 5.98 (1H, t,  $^4J_{PH} = 8.7$  Hz,  $=CHC_6H_4CH_3$ ), 4.41 (2H,  $C_5H_4Me$ ), 3.95 (2H,  $C_5H_4Me$ ), 2.21 (3H,  $C_6H_4CH_3$ ), 1.91 (3H,  $C_5H_4CH_3$ ), 1.43 (2H,  $PCH_2$ ), 1.14 (3H,  $P(CH_3)_3$ ), 1.10 (2H,  $PCH_2$ ), 0.74 (3H,  $P(CH_3)_3$ ).  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 121.5 MHz,  $20^\circ C$ ):  $\delta$  94.7 (s, 2P).  $^{13}C$  NMR ( $C_6D_6$ , 125 MHz,  $20^\circ C$ ):  $\delta$  341.5 (m,  $Mn-C_\alpha$ ), 141.9 (m,  $=C_\beta$ ), 130.8 (s, 1C,  $C_{ipso}(C_6H_4CH_3)$ ), 127.9 (s, 2C,  $C_6H_4CH_3$ ), 123.6 (s, 2C,  $C_6H_4CH_3$ ), 121.6 (s, 1C,  $C_6H_4CH_3$ ), 98.4 (s,  $C_{ipso}(MeC_5H_4)$ ), 81.3 ( $C_5H_4Me$ ), 80.2 ( $C_5H_4Me$ ), 30.9 ( $PCH_2$ ), 23.4 ( $PCH_2$ ), 22.7 (s, 1C,  $C_6H_4CH_3$ ), 21.3 ( $P(CH_3)_3$ ), 19.4 ( $P(CH_3)_3$ ), 14.5 (s,  $C_5H_4CH_3$ ). IR ( $CH_2Cl_2$ ,  $20^\circ C$ ):  $1597\text{ cm}^{-1}$   $\nu(C=C)$ ,  $1555\text{ cm}^{-1}$   $\nu(C=C)$ .

$[(C_5H_5)_2Mn(dmpe)=C=C(C_4H_3S)(H)]$ , **15a**. To a toluene solution (10 mL) of  $(C_5H_5)_2Mn(dmpe)=C=C(C_4H_3S)(SnMe_3)$  (**5a**) (100 mg, 0.18 mmol) was added 1 equiv of TBAF (0.18 mL, 0.18 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. Then the oil was extracted with pentane and filtered through Celite. The pentane fraction was evaporated in vacuo to give an orange-red solid. Crystallization from pentane at  $-35^\circ C$  gave single orange-red crystals. Yield: 62 mg, 92%. Anal. Calcd for  $C_{17}H_{25}MnP_2S$  (378.33): C, 53.96; H, 6.66. Found: C, 53.67; H, 6.53.  $^1H$  NMR ( $C_6D_6$ , 300 MHz,  $20^\circ C$ ):  $\delta$  7.06 (1H, m,  $C_4H_3S$ ), 6.77 (1H, m,  $C_4H_3S$ ), 6.38 (1H, m,  $C_4H_3S$ ), 6.10 (1H, t,  $^4J_{PH} = 9$  Hz,  $=CHC_4H_3S$ ), 4.32 (5H,  $C_5H_5$ ), 1.43 (2H,  $PCH_2$ ), 1.14 (3H,  $P(CH_3)_3$ ), 0.85 (2H,  $PCH_2$ ), 0.73 (3H,  $P(CH_3)_3$ ).  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 121.5 MHz,  $20^\circ C$ ):  $\delta$  94.8 (s, 2P).  $^{13}C$  NMR ( $C_6D_6$ , 125 MHz,  $20^\circ C$ ):  $\delta$  342.4 (m,  $Mn-C_\alpha$ ), 141.9 (m,  $=C_\beta$ ), 136.7 (s, 1C,  $C_{ipso}(C_4H_3S)$ ), 125.1 (s, 1C,  $C_4H_3S$ ), 122.3 (s, 1C,  $C_4H_3S$ ), 110.5 (s, 1C,  $C_4H_3S$ ), 82.3 (5C,  $C_5H_5$ ), 30.9 ( $PCH_2$ ), 23.4 ( $PCH_2$ ), 21.3 ( $PMe_3$ ), 19.4 ( $PMe_3$ ). IR ( $CH_2Cl_2$ ,  $20^\circ C$ ):  $1597\text{ cm}^{-1}$   $\nu(C=C)$ ,  $1548\text{ cm}^{-1}$   $\nu(C=C)$ .

$[(MeC_5H_4)Mn(dmpe)=C=C(C_4H_3S)(H)]$ , **15b**. The same procedure was adopted as above using **5b** as the starting component. Crystallization from pentane at  $-35^\circ C$  gave single orange-red crystals. Yield: 68 mg, 97%. Anal. Calcd for  $C_{18}H_{27}MnP_2S$  (392.35): C, 55.10; H, 6.93. Found: C, 55.23; H, 6.67.  $^1H$  NMR ( $C_6D_6$ , 300 MHz,  $20^\circ C$ ):  $\delta$  7.03 (1H, m,  $C_4H_3S$ ), 6.73 (1H, m,  $C_4H_3S$ ), 6.35 (1H, m,  $C_4H_3S$ ), 6.06 (1H, t,  $^4J_{PH} = 9.0$  Hz,  $=CHC_4H_3S$ ), 4.37 (2H,  $C_5H_4Me$ ), 3.94 (2H,  $C_5H_4Me$ ), 2.01 (3H,  $C_5H_4CH_3$ ), 1.43 (2H,  $PCH_2$ ), 1.11 (3H,  $P(CH_3)_3$ ), 1.08 (2H,  $PCH_2$ ), 0.70 (3H,  $P(CH_3)_3$ ).  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 121.5 MHz,  $20^\circ C$ ):  $\delta$  94.8 (s, 2P).  $^{13}C$  NMR ( $C_6D_6$ , 125 MHz,  $20^\circ C$ ):  $\delta$  94.8 (s, 2P).  $^{13}C$  NMR ( $C_6D_6$ , 125 MHz,  $20^\circ C$ ):  $\delta$  94.8 (s, 2P).



342.9 (m, Mn-C $_{\alpha}$ ), 142.8 (m, =C $_{\beta}$ ), 136.5 (s, 1C, C $_{\text{ipso}}$ (C $_4$ H $_3$ S)), 125.3 (s, 1C, C $_4$ H $_3$ S), 122.5 (s, 1C, C $_4$ H $_3$ S), 110.6 (s, 1C, C $_4$ H $_3$ S), 98.4 (s, C $_{\text{ipso}}$ (MeC $_5$ H $_4$ )), 81.1 (C $_5$ H $_4$ Me), 80.3 (C $_5$ H $_4$ Me), 30.7 (PCH $_2$ ), 23.4 (PCH $_2$ ), 21.3 (P(CH $_3$ ) $_3$ ), 19.2 (P(CH $_3$ ) $_3$ ), 14.3 (s, C $_5$ H $_4$ CH $_3$ ). IR (CH $_2$ Cl $_2$ , 20 °C): 1595 cm $^{-1}$   $\nu$ (C=C), 1558 cm $^{-1}$   $\nu$ (C=C).

**[(MeC $_5$ H $_4$ )Mn(dmpe)=C=C(Si(t-Bu)(Me) $_2$ )(H)], 16b.** To a toluene solution (10 mL) of (MeC $_5$ H $_4$ )Mn(dmpe)=C=C(Si(t-Bu)(Me) $_2$ )(SnMe $_3$ ) (**6b**) (100 mg, 0.17 mmol) was added an excess of MeOH. 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. Then the oil was extracted with pentane and filtered through Celite. The pentane fraction was evaporated to give an orange-red solid. Crystallization from pentane at -35 °C gave single orange-red crystals. Yield: 60 mg, 93%. Anal. Calcd for C $_{17}$ H $_{33}$ MnP $_2$ -Si (382.41): C, 53.39; H, 8.69. Found: C, 53.23; H, 8.32.  $^1$ H NMR (C $_6$ D $_6$ , 300 MHz, 20 °C):  $\delta$  4.13 (2H, C $_5$ H $_4$ CH $_3$ ), 4.05 (1H, t,  $^4J_{\text{PH}} = 9.0$  Hz, =CH(Si(t-Bu)(Me) $_2$ )), 3.78 (2H, C $_5$ H $_4$ CH $_3$ ), 2.05 (3H, C $_5$ H $_4$ CH $_3$ ), 1.40 (2H, PCH $_2$ ), 1.11 (3H, P(CH $_3$ ) $_3$ ), 1.03 (9H, Si(t-C $_4$ H $_9$ )(Me) $_2$ ), 0.91 (2H, PCH $_2$ ), 0.73 (3H, P(CH $_3$ ) $_3$ ) 0.48 (6H, Si(t-C $_4$ H $_9$ )(CH $_3$ ) $_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (C $_6$ D $_6$ , 121.5 MHz, 20 °C):  $\delta$  95.9 (s, 2P).  $^{13}\text{C}$  NMR (C $_6$ D $_6$ , 125 MHz, 20 °C):  $\delta$  332.4 (m, Mn-C $_{\alpha}$ ), 142.3 (m, =C $_{\beta}$ ), 98.1 (s, C $_{\text{ipso}}$ (MeC $_5$ H $_4$ )), 81.5 (C $_5$ H $_4$ -Me), 80.1 (C $_5$ H $_4$ Me), 35.2 (3C, Si(t-C $_4$ H $_9$ )(Me) $_2$ ), 28.3 (3C, Si(t-C $_4$ H $_9$ )(Me) $_2$ ), 31.4 (PCH $_2$ ), 24.1 (PCH $_2$ ), 21.2 (P(CH $_3$ ) $_3$ ), 14.6 (P(CH $_3$ ) $_3$ ), 14.5 (s, C $_5$ H $_4$ CH $_3$ ), -1.2 (2C, Si(t-C $_4$ H $_9$ )(CH $_3$ ) $_2$ ).  $^{29}\text{Si}$  NMR (C $_6$ D $_6$ , 99.4 MHz, 20 °C):  $\delta$  -2.1 (t, 9.9 Hz, Si(t-C $_4$ H $_9$ )(Me) $_2$ ). IR (CH $_2$ Cl $_2$ , 20 °C): 1573 cm $^{-1}$   $\nu$ (C=C), 1553 cm $^{-1}$   $\nu$ (C=C).

**[(MeC $_5$ H $_4$ )Mn(dmpe)=C-CHPh] $_2$ [PF $_6$ ] $_2$ , 22b.** To a THF solution (10 mL) of (MeC $_5$ H $_4$ )Mn(dmpe)=C=CPh(H) (100 mg, 0.25 mmol) was added [Cp $_2$ Fe][PF $_6$ ] (82 mg, 0.25 mmol). The solution turned from red to green and back to red during the reaction. The solution was stirred at room temperature for 1 h to give a red precipitate. Then the solvent was evaporated and was washed with Et $_2$ O. The precipitate was extracted with CH $_3$ CN and filtered through Celite. The CH $_3$ CN fraction was evaporated to give an orange-red solid. Crystallization from a mixture of CH $_3$ CN-Et $_2$ O at room temperature gave red crystals. Yield: 120 mg, 91%. Anal. Calcd for C $_{40}$ F $_{12}$ H $_{58}$ Mn $_2$ P $_6$  (1062.59): C, 45.21 H, 5.50. Found: C, 45.34 H, 5.72.  $^1$ H NMR (CD $_3$ CN, 300 MHz, 20 °C):  $\delta$  4.39 (2H, -CHC $_6$ H $_5$ ), 4.32 (2H, C $_5$ H $_4$ Me), 4.19 (2H, C $_5$ H $_4$ Me), 4.12 (2  $\times$  2H, C $_5$ H $_4$ Me), 1.93 (2  $\times$  3H, C $_5$ H $_4$ CH $_3$ ), 1.83 (2  $\times$  2H, PCH $_2$ ), 1.42 (2  $\times$  2H, PCH $_2$ ), 1.35 (2  $\times$  3H, P(CH $_3$ ) $_3$ ), 1.14 (2  $\times$  3H, P(CH $_3$ ) $_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (CD $_3$ CN, 121.47 MHz, 20 °C):  $\delta$  -145.4 (sept.,  $^1J_{\text{PF}} = 719$  Hz, PF $_6^-$ ), 80.4 (m, 2P) 79.2 (m, 2P).  $^{19}\text{F}$  NMR (CD $_3$ CN, 282.32 MHz, 20 °C):  $\delta$  -74.0 (d, 719 Hz, PF $_6^-$ ).  $^{13}\text{C}$  NMR (C $_6$ D $_6$ , 125 MHz, 20 °C):  $\delta$  324.4 (m, Mn-C $_{\alpha}$ ), 103.2 (s, C $_{\text{ipso}}$ (MeC $_5$ H $_4$ )), 137.4 (s, C $_{\text{ipso}}$ (C $_6$ H $_5$ )), 131.2 (s, C $_6$ H $_5$ ), 129.8 (s, C $_6$ H $_5$ ), 92.1 (C $_5$ H $_4$ Me), 90.4 (C $_5$ H $_4$ Me), 87.5 (C $_5$ H $_4$ Me), 86.2 (C $_5$ H $_4$ Me), 72.3 (Mn=C-CHPh), 31.4 (PCH $_2$ ), 30.6 (PCH $_2$ ), 21.8 (P(CH $_3$ ) $_3$ ), 20.3 (P(CH $_3$ ) $_3$ ), 15.9 (s, C $_5$ H $_4$ CH $_3$ ).

**[(MeC $_5$ H $_4$ )Mn(dmpe)=C-CH(C $_4$ H $_3$ S) $_2$ ][PF $_6$ ] $_2$ , 23b.** To a THF solution (10 mL) of (MeC $_5$ H $_4$ )Mn(dmpe)=C=C(C $_4$ H $_3$ S)-(H) (100 mg, 0.25 mmol) was added [Cp $_2$ Fe][PF $_6$ ] (82 mg, 0.25 mmol). The solution turned from red to green and back to red during the reaction. The solution was stirred at room temperature for 1 h to give a red precipitate. Then the solvent was evaporated and was washed with Et $_2$ O. The precipitate was extracted with CH $_3$ CN and filtered through Celite. The CH $_3$ -CN fraction was evaporated to give an orange-red solid. Crystallization from a mixture of CH $_3$ CN-Et $_2$ O at room temperature gave red crystals. Yield: 125 mg, 93%. Anal. Calcd for C $_{36}$ F $_{12}$ H $_{54}$ Mn $_2$ P $_6$ S $_2$  (1074.64): C, 40.23 H, 5.06. Found: C, 40.34; H, 5.43.  $^1$ H NMR (CD $_3$ CN, 300 MHz, 20 °C):  $\delta$  7.79 (1H, m, C $_4$ H $_3$ S), 7.46 (1H, m, C $_4$ H $_3$ S), 7.24 (1H, m, C $_4$ H $_3$ S), 7.12 (1H, m, C $_4$ H $_3$ S), 6.95 (1H, m, C $_4$ H $_3$ S), 6.48 (1H, m, C $_4$ H $_3$ S), 4.43 (2H, -CHC $_4$ H $_3$ S), 4.30 (2H, C $_5$ H $_4$ Me), 4.19 (2H, C $_5$ H $_4$ Me), 4.12 (2  $\times$  2H, C $_5$ H $_4$ Me), 1.91 (2  $\times$  3H, C $_5$ H $_4$ CH $_3$ ), 1.81

(2  $\times$  2H, PCH $_2$ ), 1.41 (2  $\times$  2H, PCH $_2$ ), 1.33 (2  $\times$  3H, P(CH $_3$ ) $_3$ ), 1.08 (2  $\times$  3H, P(CH $_3$ ) $_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (CD $_3$ CN, 121.47 MHz, 20 °C):  $\delta$  -145.4 (sept.,  $^1J_{\text{PF}} = 719$  Hz, PF $_6^-$ ), 80.9 (m, 2P), 78.7 (m, 2P).  $^{19}\text{F}$  NMR (CD $_3$ CN, 282.32 MHz, 20 °C):  $\delta$  -74.0 (d, 719 Hz, PF $_6^-$ ).  $^{13}\text{C}$  NMR (C $_6$ D $_6$ , 125 MHz, 20 °C):  $\delta$  323.1 (m, Mn-C $_{\alpha}$ ), 102.9 (s, C $_{\text{ipso}}$ (MeC $_5$ H $_4$ )), 136.5 (s, 1C, C $_{\text{ipso}}$ (C $_4$ H $_3$ S)), 125.3 (s, 1C, C $_4$ H $_3$ S), 122.5 (s, 1C, C $_4$ H $_3$ S), 110.6 (s, 1C, C $_4$ H $_3$ S), 92.1 (C $_5$ H $_4$ Me), 90.3 (C $_5$ H $_4$ Me), 87.3 (C $_5$ H $_4$ Me), 86.7 (C $_5$ H $_4$ Me), 71.9 (Mn=C-CH(C $_4$ H $_3$ S)), 31.4 (PCH $_2$ ), 30.6 (PCH $_2$ ), 21.8 (P(CH $_3$ ) $_3$ ), 20.3 (P(CH $_3$ ) $_3$ ), 15.9 (s, C $_5$ H $_4$ CH $_3$ ).

**Reduction of 21b.** To a CH $_2$ Cl $_2$  solution (10 mL) of [(MeC $_5$ H $_4$ )Mn(dmpe)=C-CH $_2$ ] $_2$ [PF $_6$ ] $_2$  (100 mg, 0.10 mmol) was added Cp $_2^*$ Co (36 mg, 0.10 mmol). The solution turned from red to green and back to red during the reaction. The solution was stirred at room temperature for 1 h. Then the solvent was evaporated and was extracted with ether and filtered through Celite. The ether fraction was evaporated to give quantitative yield of the pure orange-red solid of **12b**.

**Reduction of 22b.** To a CH $_2$ Cl $_2$  (10 mL) solution of [(MeC $_5$ H $_4$ )Mn(dmpe)=C-CHPh] $_2$  (110 mg, 0.10 mmol) was added Cp $_2^*$ Co (36 mg, 0.10 mmol). The solution turned from red to green and back to red during the reaction. The solution was stirred at room temperature for 1 h. Then the solvent was evaporated and was extracted with ether and filtered through Celite. The ether fraction was evaporated to give quantitative yield of the pure orange red solid of **13b**.

**Reduction of 23b.** To a CH $_2$ Cl $_2$  (10 mL) solution of [(MeC $_5$ H $_4$ )Mn(dmpe)=C-CHC $_4$ H $_3$ S] $_2$  (110 mg, 0.10 mmol) was added Cp $_2^*$ Co (36 mg, 0.10 mmol). The solution turned from red to green and back to red during the reaction. The solution was stirred at room temperature for 1 h. Then the solvent was evaporated and was extracted with ether and filtered through Celite. The ether fraction was evaporated to give quantitative yield of the pure orange red solid of **15b**.

**Oxidation of (C $_5$ H $_5$ )Mn(dmpe)=C=CH $_2$  (12a).** To a THF solution (10 mL) of (MeC $_5$ H $_4$ )Mn(dmpe)=C=CH $_2$  (**12a**) (100 mg, 0.34 mmol) was added [Cp $_2$ Fe][PF $_6$ ] (110 mg, 0.34 mmol). The solution turned from red to green and back to red during the reaction. The solution was stirred at room temperature for 1 h to give a red precipitate. Then the solvent was evaporated and was washed with ether. The precipitate was extracted with acetonitrile and filtered through Celite. The CH $_3$ CN fraction was evaporated to give an orange-red solid, which was composed of three compounds. The NMR data of these compounds have been provided below.

**NMR Data for [(C $_5$ H $_5$ )Mn(dmpe)=C-CH $_2$ ] $_2$ [PF $_6$ ] $_2$ , 27a.**  $^1$ H NMR (CD $_3$ CN, 300 MHz, 20 °C):  $\delta$  4.83 (5H, C $_5$ H $_5$ ), 2.72 (2  $\times$  2H, t,  $^4J_{\text{PH}} = 9.0$  Hz, -CH $_2$ ), 1.75 (2  $\times$  2H, PCH $_2$ ), 1.38 (2  $\times$  2H, PCH $_2$ ), 1.27 (2  $\times$  3H, P(CH $_3$ ) $_3$ ), 1.08 (2  $\times$  3H, P(CH $_3$ ) $_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (CD $_3$ CN, 121.5 MHz, 20 °C):  $\delta$  -145.4 (sept.,  $^1J_{\text{PF}} = 719$  Hz, PF $_6^-$ ), 79.5 (s, 2  $\times$  2P).  $^{19}\text{F}$  NMR (CD $_3$ CN, 282.3 MHz, 20 °C):  $\delta$  -74.0 (d, 719 Hz, PF $_6^-$ ).  $^{13}\text{C}$  NMR (C $_6$ D $_6$ , 125 MHz, 20 °C):  $\delta$  328.3 (m, Mn-C $_{\alpha}$ ), 92.1 (C $_5$ H $_5$ ) 50.3 (Mn=C-CH $_2$ ), 31.4 (PCH $_2$ ), 30.6 (PCH $_2$ ), 21.8 (P(CH $_3$ ) $_3$ ), 20.3 (P(CH $_3$ ) $_3$ ).

**NMR Data for [(C $_5$ H $_5$ )Mn(dmpe)=C-CH $_3$ ][PF $_6$ ] $_2$ , 35a.**  $^1$ H NMR (CD $_3$ CN, 300 MHz, 20 °C):  $\delta$  4.72 (5H, C $_5$ H $_5$ ), 1.40 (2H, PCH $_2$ ), 1.11 (3H, P(CH $_3$ ) $_3$ ), 0.91 (2H, PCH $_2$ ), 0.73 (3H, P(CH $_3$ ) $_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (CD $_3$ CN, 121.5 MHz, 20 °C):  $\delta$  -145.4 (sept.,  $^1J_{\text{PF}} = 719$  Hz, PF $_6^-$ ), 81.3 (s, 2P).  $^{19}\text{F}$  NMR (CD $_3$ CN, 282.3 MHz, 20 °C):  $\delta$  -74.0 (d, 719 Hz, PF $_6^-$ ).  $^{13}\text{C}$  NMR (C $_6$ D $_6$ , 125 MHz, 20 °C):  $\delta$  300.5 (m, Mn-C $_{\alpha}$ ), 87.3 (C $_5$ H $_5$ ), 48.3 (Mn=C-CH $_3$ ), 31.4 (PCH $_2$ ), 30.6 (PCH $_2$ ), 21.8 (P(CH $_3$ ) $_3$ ), 20.3 (P(CH $_3$ ) $_3$ ).

**NMR Data for [(C $_5$ H $_5$ )Mn(dmpe)=C-CH] $_2$ [PF $_6$ ] $_2$ , 43a.**  $^1$ H NMR (CD $_3$ CN, 300 MHz, 20 °C):  $\delta$  6.33 (2H, t,  $^4J_{\text{PH}} = 6.0$  Hz, -C(H)), 4.72 (5H, C $_5$ H $_5$ ), 1.40 (2  $\times$  2H, PCH $_2$ ), 1.11 (2  $\times$  3H, P(CH $_3$ ) $_3$ ), 0.91 (2  $\times$  2H, PCH $_2$ ), 0.73 (2  $\times$  3H, P(CH $_3$ ) $_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (CD $_3$ CN, 121.5 MHz, 20 °C, 85% H $_3$ PO $_4$  ext):  $\delta$  -145.44 (sept.,  $^1J_{\text{PF}} = 719$  Hz, PF $_6^-$ ), 83.7 (s, 2  $\times$  2P).  $^{19}\text{F}$  NMR (CD $_3$ CN, 282.3 MHz, 20 °C):  $\delta$  -74.0 (d, 719 Hz, PF $_6^-$ ).  $^{13}\text{C}$  NMR (CD $_3$ CN, 125 MHz, 20 °C):  $\delta$  321.3 (m, Mn-C $_{\alpha}$ ), 149.7 (Mn=C=CH), 89.7 (C $_5$ H $_5$ ), 31.1 (PCH $_2$ ), 30.6 (PCH $_2$ ), 21.4



Table 1. Crystallographic Details of **3a**, **11**, and **13a**

	<b>3a</b>	<b>11</b>	<b>13a</b>
empirical formula	C <sub>22</sub> H <sub>35</sub> MnP <sub>2</sub> Sn	C <sub>36</sub> H <sub>58</sub> MnP <sub>4</sub>	C <sub>19</sub> H <sub>27</sub> MnP <sub>2</sub>
color	red block	red	red block
$M_r$ [g mol <sup>-1</sup> ]	535.07	669.64	372.29
cryst size [mm]	0.12 × 0.17 × 0.26	0.24 × 0.38 × 0.55	0.12 × 0.17 × 0.26
$T$ [K]	183(2)	183(2)	183(2)
$\lambda$ (Mo K $\alpha$ ) [Å]	0.71073	0.71073	0.71073
cryst syst	orthorhombic	triclinic	monoclinic
space group	<i>Pbca</i>	<i>P1</i>	<i>P2<sub>1</sub>/n</i>
$a$ [Å]	11.8039(6)	9.9971(8)	16.2767(11)
$b$ [Å]	17.3012(8)	10.1842(8)	14.4759(7)
$c$ [Å]	23.6718(14)	19.3926(17)	16.3697(9)
$\alpha$ [deg]	90	96.467(10)	90
$\beta$ [deg]	90	101.506(10)	102.370(7)
$\gamma$ [deg]	90	109.279(9)	90
$V$ [Å <sup>3</sup> ]	4834.3(4)	1791.9(3)	3767.5(4)
$Z$	8	2	8
$\rho_{\text{calcd}}$ [g cm <sup>-3</sup> ]	1.470	1.241	1.313
$\mu$ [mm <sup>-1</sup> ]	1.692	0.570	0.865
$F(000)$	2176	718	1568
transmn range	0.7120–0.8401	0.7388–0.8721	0.8378–0.9118
$2\theta$ range [deg]	6.64 < $2\theta$ < 30.70	4.96 < $2\theta$ < 56.16	4.88 < $2\theta$ < 56.00
no. of measd reflns	34 289	17 364	35 645
no. of unique reflns	6638	7982	9023
$I > 2\sigma(I)$ reflns	2863	4800	3809
no. of params	237	381	405
Gof (for $F^2$ )	0.694	1.030	0.790
$R_1[I > 2\sigma(I)]$ , $R_1$ all data	0.0410, 0.1076	0.0358, 0.0694	0.0480, 0.1254
$wR_2[I > 2\sigma(I)]$ , $wR_2$ all data	0.0895, 0.1058	0.0628, 0.0657	0.0807, 0.0878
$\Delta\rho_{\text{max/min}}$ [e <sup>-</sup> Å <sup>-3</sup> ]	0.765, -1.447	0.566, -0.555	0.918, -1.058

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

(P(CH<sub>3</sub>)<sub>3</sub>)<sub>3</sub>, 20.1 (P(CH<sub>3</sub>)<sub>3</sub>)<sub>3</sub>. IR (CH<sub>2</sub>Cl<sub>2</sub>, 20 °C): 1543 cm<sup>-1</sup>  $\nu$ -(C=C), 848 cm<sup>-1</sup>  $\nu$ (P–F).

**X-ray Crystal Structure Analyses.** The X-ray diffraction data were collected at 183(1) K for compounds **3a**, **11**, **13a**, **15a**, and **22b** using an imaging plate detector system (Stoe IPDS)<sup>92</sup> with graphite-monochromated Mo K $\alpha$  radiation. A total of 200, 200, 167, 300, and 182 images were exposed at constant times of 3.00, 5.00, 3.00, 3.00, and 2.30 min per image for the four structures, respectively. The crystal-to-image distances were set to 50, 60, 60, 50, and 56 mm ( $\theta_{\text{max}}$ : 30.35°, 28.08°, 28.00°, 30.30°, and 28.97°).  $\phi$ -Oscillation (for **3a**, **11**, **13a**, and **15a**) and rotation modes (for **22b**) were used with increments of 1.0°, 1.0°, 1.2°, 0.8°, and 1.1° per exposure in each case. Total exposure times were 24, 30, 20, 36, and 20 h. The intensities were integrated by using a dynamic peak profile analysis, and an estimated mosaic spread (EMS) check was performed to prevent overlapping intensities. For the cell parameter refinements 7998 (**15a**) to 8000 (**3a**, **11**, **13a**, and **22b**) reflections were selected out of the whole limiting spheres with intensities  $I > 6\sigma(I)$  for all structures. A total of 34 289, 17 364, 35 645, 24 322, and 48 650 reflections were collected, of which 6638, 7982, 9023, 5414, and 11 757 were unique after data reduction ( $R_{\text{int}} = 0.1289, 0.0498, 0.1324, 0.0784$ , and 0.1150). For the numerical absorption corrections 12, 7, 14, 14, and 13 indexed crystal faces were used.

All crystals were embedded in polybutene oil within the glovebox. The crystal quality was then examined by using a polarizing microscope. Sometimes, crystals with intrusions (holes or solvent) or with tiny intergrown pieces had to be accepted for the X-ray experiment. In general, the structures were solved with an incomplete data set (50% or less completeness) while the measurement was still being performed, because the correct chemical formula cannot always be predicted when solvent molecules cocrystallize with the complex, or, as in the case of **11** and **13a**, two independent complexes ( $Z' = 2$ ) were found. For structure **11**, two independent complexes with central Mn atoms on centers of inversion were

observed. The corrected formula was then used for the final absorption correction. All these procedures were calculated by using the Stoe IPDS software.<sup>92</sup>

The structures were solved with the merged unique data set after checking for correct space groups. The Patterson method was used to solve the crystal structures by applying the software options of the program SHELXS-97.<sup>93</sup> The structure refinements were performed with the program SHELXL-97.<sup>94</sup> The programs PLATON<sup>95</sup> and PLUTON<sup>96</sup> were used to check the results of the X-ray analyses; they are helpful for the interpretation of the initially determined structural models. Relevant crystallographic data are collected in Tables 1 and 2. All five structures crystallize in centrosymmetric space groups.

## Computational Details

Density functional theory (DFT) calculations were carried out using the Amsterdam Density Functional program package ADF, release 2002.02.<sup>97</sup> We used the Vosko–Wilk–Nusair<sup>98</sup> local density approximation (LDA) and the generalized gradient approximation (GGA) with corrections for exchange and correlation according to Becke<sup>99</sup> and Perdew,<sup>100</sup> respectively (BP86). The valence shells of all non-hydrogen atoms were described by triple- $\zeta$  basis sets augmented by one polarization function (ADF database TZP), while a standard double- $\zeta$  basis set was applied for hydrogen atoms (ADF database DZP). The frozen-core approximation was applied for the 1s electrons of

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**Table 2. Crystallographic Details of 15a and 22b**

	15a	22b
empirical formula	C <sub>17</sub> H <sub>25</sub> MnP <sub>2</sub> S	C <sub>40</sub> H <sub>58</sub> F <sub>12</sub> Mn <sub>2</sub> P <sub>6</sub>
color	red block	red block
<i>M<sub>r</sub></i> [g mol <sup>-1</sup> ]	378.31	1062.56
cryst size [mm]	0.15 × 0.16 × 0.20	0.11 × 0.28 × 0.30
<i>T</i> [K]	183(2)	183(2)
λ(Mo Kα) [Å]	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	<i>C2/c</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> [Å]	25.115(4)	17.0339(14)
<i>b</i> [Å]	8.1122(8)	16.5851(12)
<i>c</i> [Å]	18.432(3)	18.4605(16)
α [deg]	90	90
β [deg]	103.249(17)	116.873(9)
γ [deg]	90	90
<i>V</i> [Å <sup>3</sup> ]	3655.2(8)	4652.1(6)
<i>Z</i>	8	4
ρ <sub>calcd</sub> [g cm <sup>-3</sup> ]	1.375	1.517
μ [mm <sup>-1</sup> ]	1.003	0.827
<i>F</i> (000)	1584	2184
transmn range	0.8299–0.9048	0.7749–0.9093
2θ range [deg]	5.3 < 2θ < 60.60	4.92 < 2θ < 57.94
no. of measd reflns	24 322	48 650
no. of unique reflns	5414	11757
<i>I</i> > 2σ( <i>I</i> ) reflns	4220	4465
no. of params refined	184	568
goodness-of-fit	1.144	0.777
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )], <i>R</i> <sub>1</sub> all data [%] <sup>a</sup>	0.0624, 0.0787	0.0781, 0.1542
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )], <i>wR</i> <sub>2</sub> all data [%]	0.1294, 0.1336	0.1967, 0.2176
Δρ <sub>max/min</sub> [e <sup>-</sup> Å <sup>-3</sup> ]	1.025, -0.696	3.188, -0.859

<sup>a</sup>  $R_1 = \sum(F_o - F_c)/\sum F_o$ ;  $I > 2\sigma(I)$ ;  $wR_2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$ .

carbon atoms, and for the 1s–2p electrons of silicon, phosphorus, and manganese. For the mononuclear cationic radical model systems with an odd electron count, spin-unrestricted

calculations have been performed. The solvation energies based on gas-phase geometries were calculated by the conductor-like screening model (COSMO) suggested by Klamt and Schuurmann<sup>101</sup> and implemented in ADF by Pye and Ziegler.<sup>102</sup> The solvent-accessible surface was chosen and constructed using the following radii: H 1.16, C 2.00, P 1.70, Si 2.20, and Mn 2.40 Å. A dielectric constant of 7.58 was used for THF.

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 244878, 244879, 244880, 244881, and 214889. 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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**Supporting Information Available:** Cartesian coordinates of optimized geometries, computed total bonding energies, and solvation energies are given. Experimental details and details of crystal structure determination for compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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