Organometallics **2005,** *24,* 2834−2847

Articles

Synthesis and Characterization of Redox-Active C_4-Bridged Rigid-Rod Complexes with Acetylide-Substituted Manganese End Groups

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Received September 27, 2004

The symmetric d^5 *trans*-bis(alkynyl) complexes $[Mn(R'_2PCH_2CH_2PR'_2)_2(C{\equiv}CR)_2]$ (R′ = Me, R = $SiEt_3$, **3a**; R′ = Me, R = Si^iPr_3, **3b**; R′ = Me, R = $Si(^tBu)Me_2$, **3c**; R′ = Et, R = $SiEt_3$, **4a**; R′ = Et, R = Si^iPr_3, **4b**; R′ = Et, R = $Si(^tBu)Me_2$, **4c**) can be prepared by the reaction of $[Mn(R'_2PCH_2CH_2PR'_2)_2Br_2]$ (R′ = Me, **1**; R′ = Et, **2**) with 2 equiv of $LiC{\equiv}CR$ (R = $SiEt_3$, Si^iPr_3, $Si(^tBu)Me_2$). The reactions of species **3** and **4** with $[Cp_2Fe][PF_6]$ yield the corresponding d^4 complexes $[Mn(dmpe)_2(C{\equiv}CR)_2][PF_6]$ (R′ = Me, R = $SiEt_3$, **5a**; R′ = Me, R = Si^iPr_3, **5b**; R′ = Me, R = $Si(^tBu)Me_2$, **5c**; R′ = Et, R = $SiEt_3$, **6a**; R′ = Et, R = Si^iPr_3, **6b**; R′ = Et, R = $Si(^tBu)Me_2$, **6c**). The asymmetrically substituted *trans*-bis(alkynyl) complexes $[Mn(dmpe)_2(C{\equiv}CR)(C{\equiv}CH)][PF_6]$ (R′ = Me, R = $SiEt_3$, **10a**; R′ = Me, R = Si^iPr_3, **10b**; R′ = Me, R = $Si(^tBu)Me_2$, **10c**) are prepared by the reaction of the vinylidene compounds $Mn(dmpe)_2(C{\equiv}CR)(C{=}CH_2)$ (R′ = Me, R = $SiEt_3$, **9a**; R′ = Me, R = Si^iPr_3, **9b**; R′ = Me, R = $Si(^tBu)Me_2$, **9c**) with 2 equiv of $[Cp_2Fe][PF_6]$ and 1 equiv of quinuclidine. The mixed-valent complexes $[\{Mn(dmpe)_2(C{\equiv}CR)\}_2(\mu\text{-}C_4)][PF_6]$ $[\mathbf{11}]^+$ are obtained by the reaction of **10** with 1 equiv of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). The neutral dinuclear Mn(II)/Mn(II) compounds $[\{Mn(dmpe)_2(C{\equiv}CR)\}_2(\mu\text{-}C_4)]$ (R = $SiEt_3$, **11a**; R = Si^iPr_3, **11b**; R = $Si(^tBu)Me_2$, **11c**) are synthesized by the reduction of $[\mathbf{11}]^+$ with $Co(C_5Me_5)_2$. Complexes $[\mathbf{11}]^+$ can also be oxidized with $[Cp_2Fe][PF_6]$ to produce the dicationic Mn(III)/Mn(III) species $[\{Mn(dmpe)_2(C{\equiv}CR_3)\}_2(\mu\text{-}C_4)][PF_6]_2$ (R = $SiEt_3$, $[\mathbf{11a}]^{2+}$; R = Si^iPr_3, $[\mathbf{11b}]^{2+}$; R = $Si(^tBu)Me_2$, $[\mathbf{11c}]^{2+}$). Both redox processes are fully reversible. The dinuclear compounds have been characterized by NMR, IR, and Raman spectroscopy, cyclic voltammetry, and elemental analyses. X-ray diffraction studies have also been performed on several complexes.

Introduction

The development of molecular devices requires the preparation of functional materials with suitable properties.[1−6] π-Conjugated conducting polymers and oligomers containing electrochemically active transition-metal end groups, such as $L_mM{-}(C{\equiv}C)_n{-}ML_m$, are of great interest in the area of electronic materials.[7−15] Research into the synthesis and electronic properties of metal ethynyl complexes and polymers continues to develop as a key area of organometallic chemistry.[5,7,16] Owing to its high stability, ease of functionalization, and well-defined electrochemistry, transition-metal units have been widely used as redox-active centers that are linked together with a wide variety of structural units such as saturated and unsaturated carbon bridges, delocalized fused rings, and polymeric and dendritic backbones.[17−19] In particular, their rigid-rod architectures and conjugated backbones have been studied in the field of linear and nonlinear optics, liquid crystallinity, and photovoltaic cells.[1,2,20−25] We anticipated that

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10.1021/om049252p CCC: $30.25
Publication on Web 05/04/2005

electronic properties of electroactive materials could be reasonably satisfied by molecular units with electron-rich phosphine-substituted manganese end groups and a C_4 spacer.[26−29] In addition to the above reasons, the $L_mM{-}C_4{-}ML_m$ systems[30−56] were selected as target molecules because a buildup of Mn di- and oligonuclear species seemed to be synthetically feasible not only by acetylide substitution processes but also by coupling of $Mn{-}C_2$ units, such as Mn−alkynyl and Mn−vinylidene moieties. Such principal possibilities have been corroborated by recent studies of our group.[26−29,57] For instance, we have reported the synthesis of redox-active dinuclear complexes of the type $\{[Mn(dmpe)_2(X)]_2(\mu\text{-}C_4)\}^{n+}$ (X = I, $C{\equiv}CH$, $C{\equiv}CC{\equiv}CSiMe_3$ and $n = 0{-}2$), which were obtained by either the reaction of 2 equiv of $Mn(MeC_5H_4)(dmpe)I$ with $Me_3Sn{-}C_4{-}SnMe_3$ and dmpe[28] and subsequent acetylide substitution[58] or by an in situ C−C coupling of $[Mn^{III}(dmpe)_2(C{\equiv}CH)(C{\equiv}C)]$ units[27] similar to the Eglinton and McCrae oxidative coupling of acetylenic compounds.[59] We had earlier suggested from DFT calculations and experimental evidence that the terminal end group (X) in these kinds of $\{[Mn(dmpe)_2(X)]_2(\mu\text{-}C_4)\}^{n+}$ complexes (X = I, $C{\equiv}CH$, $C{\equiv}CSiMe_3$, $C{\equiv}CC{\equiv}CSiMe_3$, and $n = 0{-}2$),[26−28] have less bearing or influence on the communication between the two metal centers. However, the reactivity of the terminal end groups does matter, considering the fact of further utilizing these molecules for the buildup of longer oligonuclears. The solubility of these dinuclear complexes is very much influenced by the substituents on the phosphorus ligand and also on the terminal end groups. Additionally, the substituents on the phosphorus atom have an effect on the redox properties of these kinds of $[Mn(dmpe)_2(C{\equiv}CSiR_3)X]^+$ molecules. This insight propelled us to gain access to new dinuclear complexes bearing end groups of the type $-C{\equiv}CR$ (R = $SiEt_3$, $Si(^iPr)_3$, $Si(^tBu)(Me)_2$) with the phosphorus atoms bearing both methyl and ethyl groups. Generalization of a principal reaction path and additional insight into the lability of the $C_{sp}{-}Si$ bond was expected to come from further explorations starting from suitable Mn(II) alkynyl complexes of the type $[Mn(R'_2PCH_2CH_2PR'_2)_2(C{\equiv}CSiR_3)X]$ (R′ = Me (dmpe), R′ = Et (depe); X = $C{\equiv}CSiR_3$ (R = $SiEt_3$, $Si(^iPr)_3$, $Si(^tBu)Me_2$)).

Results and Discussion

Synthesis of Symmetric *trans*-Bis(alkynyl) Manganese Derivatives. Paramagnetic d^5 *trans*-bis(alkynyl) manganese compounds $[Mn(R'_2PCH_2CH_2PR'_2)_2(C{\equiv}CR)_2]$ (R′ = Me, R = $SiEt_3$,[27] **3a**; R′ = Me, R = Si^iPr_3, **3b**; R′ = Me, R = $Si(^tBu)Me_2$, **3c**; R′ = Et, R = $SiEt_3$, **4a**; R′ = Et, R = Si^iPr_3, **4b**; R′ = Et, R = $Si(^tBu)Me_2$, **4c**) can be prepared by the reaction of $[Mn(R'_2PCH_2CH_2PR'_2)_2Br_2]$ (R′ = Me, **1**; R′ = Et, **2**) with 2 equiv of $LiC{\equiv}CR$ (R = $SiEt_3$, Si^iPr_3, $Si(^tBu)Me_2$). Similar kinds of complexes were obtained by two other methods: by the reaction of $[MnCp'_2]$ (Cp′ = C_5H_5, C_5H_4Me) with 2 equiv of $EC{\equiv}CSiR_3$ (E = H, $SnMe_3$) in the presence of dmpe[29] or by SiR_3 metathesis.[60] However, the yields were far better using the former method. The synthesis of compound **3a** has been reported earlier.[27] All of these Mn(II) *trans*-bis(alkynyl) species are yellow solids. All of the derivatives **3a**−**c** and **4a**−**c** are soluble in nonpolar solvents such as pentane, Et_2O, etc. The ^1H NMR spectra of **3b**,**c** show two broad signals at −14.3 and −15.19 ppm and at −13.58 and −14.92 ppm, respectively, corresponding to the dmpe protons. However, the resonances for the depe protons in complexes **4a**−**c** appear slightly downfield in comparison with the resonances for the complexes bearing dmpe ligands. These values are characteristic for these types of low-spin d^5

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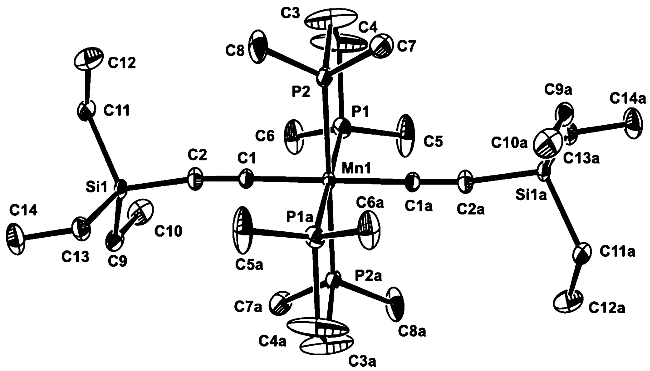

Figure 1. Molecular structure of **3a**. Selected bond lengths (Å) and angles (deg): Mn1−C1 = 1.9652(19), C1−C2 = 1.226(3), Mn1−P1 = 2.2632(6), Mn1−P2 = 2.2590(6), Si1−C2 = 1.814(2); C1−Mn1−C1a = 180.0, C2−C1−Mn1 = 178.8(2), C1−C2−Si1 = 173.3(2), C1−Mn1−P1 = 90.03(7), P2−Mn1−P1 = 83.92(2). The $-CH_2CH_2-$ group of the bis(dmpe) ligand shows a trend of positional disorder. The displacement ellipsoids are at the 30% probability level, and the hydrogen atoms are omitted for clarity.

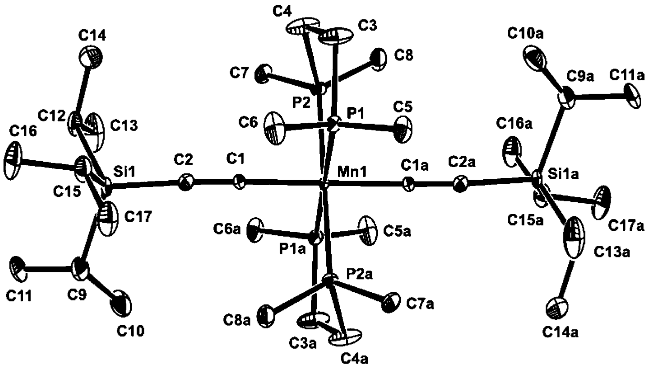

Figure 2. Molecular structure of **3b**. Selected bond lengths (Å) and angles (deg): Mn1−C1 = 1.971(3), C1−C2 = 1.228(4), Mn1−P1 = 2.2714(7), Mn1−P2 = 2.2555(8), Si1−C2 = 1.822(3) Mn2−C19 = 1.970(3), Mn2−C19a = 1.970(3), Si2−C18 = 1.826(3), C18−C19 = 1.225(4), Mn2−P4 = 2.2578(8); C1−Mn1−C1a = 179.999(1), C2−C1−Mn1 = 178.9(2), C1−C2−Si1 = 176.7(2), C1−Mn1−P1 = 90.06(8), P2−Mn1−P1 = 83.65(3), C19−Mn2−C19a = 180.0, C19−C18−Si2 = 177.6(2), C18−C19−Mn2 = 178.6(2). The second independent molecule is not shown. Mn1 and Mn2 occupy different centers of inversion. The ellipsoids are at the 30% probability level, and the hydrogen atoms are omitted for clarity.

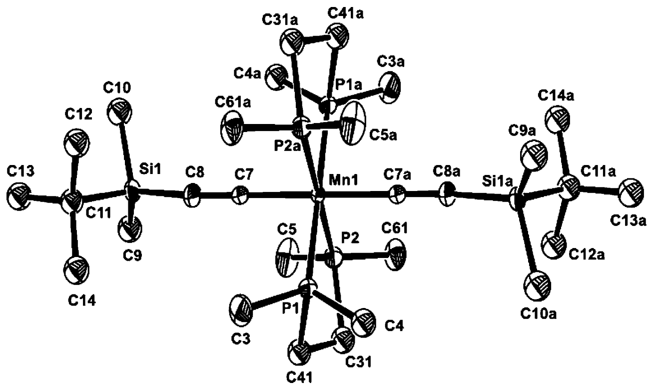

Figure 3. Molecular structure of **3c**. Selected bond lengths (Å) and angles (deg): Mn1−C7 = 1.961(3), C7−C8 = 1.226(5), Mn1−P1 = 2.2621(9), Mn1−P2 = 2.2581(8), Si1−C8 = 1.879(4); C7−Mn1−C7a = 180.0, C8−C7−Mn1 = 179.2(4), C7−C8−Si1 = 161.6(4), C7−Mn1−P1 = 89.87(10), P2−Mn1−P1 = 83.49(3). The ${}^tBu$ groups are positionally disordered, and only one site of occupation is shown. The displacement ellipsoids are at the 30% probability level, and the hydrogen atoms are omitted for clarity.

complexes.[26−29,57,60−62] The Si^iPr_3 groups of **3b** are identified as two broad resonances at 3.52 and 3.16 ppm. The proton resonances for the alkyl groups of the other complexes appear in the region between 3 and 4 ppm.

The structures of complexes **3a**−**c** (Figures 1−3) have been unequivocally established by X-ray diffraction studies. All three complexes show pseudo-octahedral coordination around the metal center. Both acetylide ligands occupy trans positions, and the four P atoms define an equatorial plane. The C≡C bonds of **3a**−**c** are 1.226(3), 1.228(4), and 1.226(5) Å, similar to those found in related complexes.[27,29,60−62] However, a bond angle of 161.6(4)° is found for the C7−C8−Si1 chain of **3c** showing stronger bending in comparison with the bond angles of 178.8(2) and 176.7(2)° for the C1−C2−Si1 chain in **3a**,**b**, respectively. We believe that this significant difference might arise from the bulky *tert*-butyl groups on the silicon atom of complex **3c**.

The Mn(II) species **3** and **4** can easily be oxidized with $[Cp_2Fe][PF_6]$, affording the corresponding d^4 paramagnetic compounds $[Mn(R'_2PCH_2CH_2PR'_2)_2(C{\equiv}CSiR_3)_2]^+$ (R′ = Me, R = $SiEt_3$,[27] **5a**; R′ = Me, R = Si^iPr_3, **5b**; R′ = Me, R = $Si({}^tBu)Me_2$, **5c**; R′ = Et, R = $SiEt_3$, **6a**; R′ = Et, R = Si^iPr_3, **6b**; R′ = Et, R = $Si({}^tBu)Me_2$, **6c**) (Scheme 1). All Mn(III) species were isolated as red PF_6^- salts. They are insoluble in nonpolar solvents such as alkanes but sparingly soluble in THF and very well soluble in CH_2Cl_2. The ^1H NMR spectra of the complexes **5** show characteristic dmpe resonances at high field at around −29 and −39 ppm.[27−29,60,61] However, for complexes **6** the depe resonances were observed further downfield between −27.0 and −33.0 ppm.

The reduction of the Mn(II) species **3a**−**c** with sodium requires forcing conditions of 95 °C over more than 12 h to obtain the corresponding diamagnetic salts $[Mn(R'_2PCH_2CH_2PR'_2)_2(C{\equiv}CR)_2]Na$ (R′ = Me, R = $SiEt_3$,[27] **7a**; R′ = Me, R = Si^iPr_3, **7b**; R′ = Me, R = $Si({}^tBu)Me_2$, **7c**). The compounds were isolated in 80% yield as yellow crystalline solids. Their ^1H, ^{13}C, and ^{31}P NMR spectra are consistent with the indicated *cis*-bis(alkynyl) structures. The cis binding mode is presumably enforced by the alkali-metal chelation found as a general structural motif in bis(alkynyl) pincer complexes. Complexes **7b**,**c** both show two multiplets in the ^{13}C NMR at $\delta \sim 210$ ppm (Mn−C) and in the range of 115−120 ppm (≡C−Si), which are attributed to the alkynyl ligands. The ^{31}P NMR spectra of **7b**,**c** complexes display two broad temperature-independent signals at around 75 and 63 ppm. In contrast to the reductions of **3a**−**c** the reduction of complexes **4** with sodium or lithium led to unidentified decomposition products. We believe that this difference in behavior between complexes **3** and **4** arises from the changes in the redox potential on making slight changes in the substituents on the phosphorus ligands. We thought that we could change the electronic situa-

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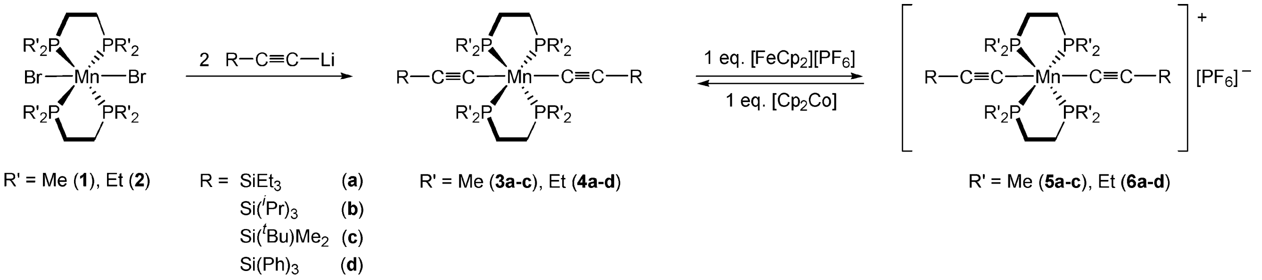
Scheme 1



tion by replacing the alkyl substituents with phenyl groups. We synthesized the corresponding Mn(II) bis(acetylide) complex $[\mathrm{Mn}(\mathrm{R'_2PCH_2CH_2PR'_2})_2(\mathrm{C{\equiv}CR})_2]$ (R′ = Et, R = $\mathrm{SiPh_3}$, **4d**) in a similar fashion as for complexes **4**. An additional single-crystal X-ray diffraction analysis unequivocally confirmed the structure of **4d** (Figure 4). The reduction of **4d** was performed with an excess of Na at 95 °C during 48 h to yield indeed the corresponding diamagnetic salt $[\mathrm{Mn}(\mathrm{R'_2PCH_2CH_2PR'_2})_2(\mathrm{C{\equiv}CR})_2]\mathrm{Na}$ (R′ = Et, R = $\mathrm{SiPh_3}$, **8d**).

Complexes **7** are thermally stable but very reactive.[27,60] In the presence of electrophiles they are quantitatively transformed by C_β attack into d^6 *trans*-alkynyl–vinylidene manganese complexes. The Mn(I) *trans*-alkynyl–vinylidene species $\mathrm{Mn}(\mathrm{R'_2PCH_2CH_2PR'_2})_2(\mathrm{C{\equiv}CR})(\mathrm{C{=}CHR})$ (R′ = Me, R = $\mathrm{SiEt_3}$,[27,60] **8a**; R′ = Me, R = $\mathrm{Si^iPr_3}$, **8b**; R′ = Me, R = $\mathrm{Si(^tBu)Me_2}$, **8c**) could thus be isolated by the reaction of complexes **7** with MeOH. However, the reaction of $[\mathrm{Mn}(\mathrm{R'_2PCH_2CH_2PR'_2})_2(\mathrm{C{\equiv}CR})_2]\mathrm{Na}$ (R′ = Et, R = $\mathrm{SiPh_3}$, **8d**) yielded the alkynyl–vinylidene complex, among other compounds, upon treatment with MeOH. This compound could not be used for further reactions, due to impurities.

An X-ray study on **8b** unequivocally confirmed the proposed structure (Figure 5) with the alkynyl and the vinylidene ligands in trans positions. The vinylidene C=C (1.318(9) Å) and alkynyl C≡C (1.217(9) Å) bond distances compare well to those which were also found for the related compound **8a**.[27,60] There is no significant difference between the Mn–C111 (1.883(8) Å) and the Mn=C112 distances (1.933(9) Å), which might be considered as an artifact due to the statistical disorder of the alkynyl and vinylidene ligands. Nevertheless, the atomic pairs C111/C112 and C211/C212, as well as C311/312 and C411/C412, could be refined as split positions with a refined site occupation ratio of 0.48/0.52.

Subsequent treatment of **8a**–**c** with MeOH/KOH led to $\mathrm{Mn}(\mathrm{R'_2PCH_2CH_2PR'_2})_2(\mathrm{C{\equiv}CR})(\mathrm{C{=}CH_2})$ (R′ = Me, R = $\mathrm{SiEt_3}$,[27] **9a**; R′ = Me, R = $\mathrm{Si^iPr_3}$, **9b**; R′ = Me, R = $\mathrm{Si(^tBu)Me_2}$, **9c**). All of the new complexes **8b**,**c** and **9b**,**c** have been fully characterized.

In the structure of **9a** (Figure 6) the manganese atom is in an octahedral environment with the alkynyl and vinylidene ligands in trans positions. The C1–C2 and Mn–C1 distances are 1.343(7) Å and 1.761(5) Å and compare well to those of the related complex $\mathrm{Mn(dmpe)_2(C{\equiv}CSiMe_3)(C{=}CH_2)}$.[27,60] The C3–C4 bond separation of 1.225(7) Å clearly indicates triple-bond character.

As mentioned earlier, the oxidation state of the manganese center has a great influence on the reactivity

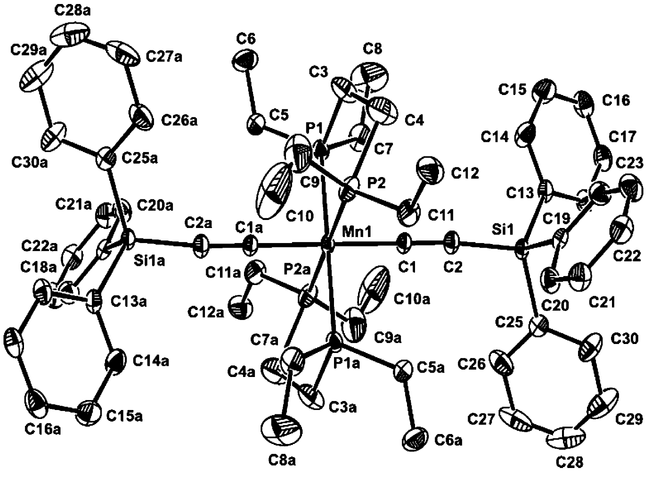


Figure 4. Molecular structure of **4d**. Selected bond lengths (Å) and angles (deg): Mn1–C1 = 1.963(3), C1–C2 = 1.228(4), Mn1–P1 = 2.2996(9), Mn1–P2 = 2.2869(9), Si1–C2 = 1.802(3); C1–Mn1–C1a = 180.0, C2–C1–Mn1 = 177.5(3), C1–C2–Si1 = 172.2(3), C1–Mn1–P1 = 88.88(9), P2–Mn1–P1 = 82.65(3). The displacement ellipsoids are at the 30% probability level, and the hydrogen atoms are omitted for clarity.

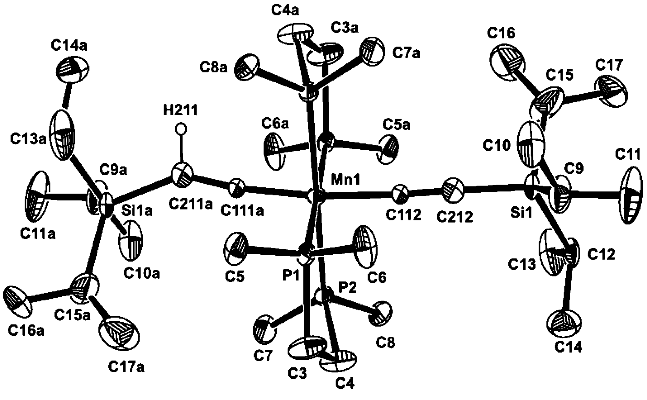


Figure 5. Molecular structure of **8b**. Selected bond lengths (Å) and angles (deg): Mn1–C111a = 1.883(8), C111a–C211a = 1.318(9), Mn1–C112 = 1.933(9), C112–C212 = 1.217(9), Mn1–P1 = 2.2776(7), Mn1–P2 = 2.2451(8), Si1a–C211a = 1.881(7), Si1–C212 = 1.796(8), Mn2–C181 = 1.890(8), Mn2–C182 = 1.925(9), C181–C191 = 1.333(9), Si2–C192 = 1.796(7), C182–C192 = 1.230(9); C111a–Mn1–C112 = 173.7(6), C212–C112–Mn1 = 177.4(9), C211–C111–Mn1 = 173.1(8), C111–C211–Si1 = 148.9(7), C112–C212–Si1 = 178.5(7), P2–Mn1–P1 = 85.41(3), C181–Mn2–C181a = 179.999(2), C181a–Mn2–C182 = 173.7(6), C191–C181–Mn2 = 172.3(8), C181–C191–Si2 = 147.6(7), C182–C192–Si2 = 177.3(7). Only one of the two independent complexes is presented. Mn1 and Mn2 occupy independent centers of inversion. The displacement ellipsoids are at the 30% probability level, and selected hydrogen atoms are omitted for clarity.

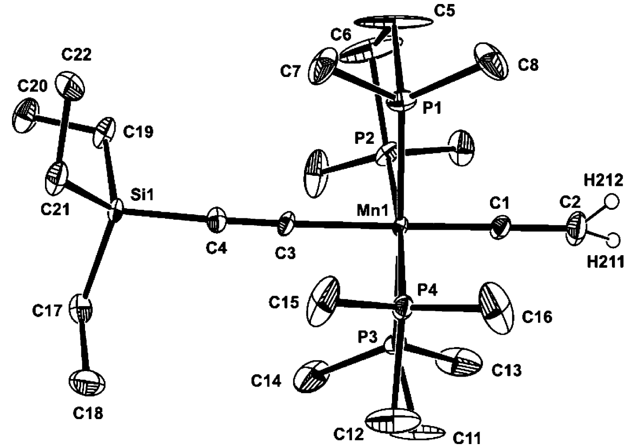


Figure 6. Molecular structure of **9a**. Selected bond lengths (Å) and angles (deg): Mn1−C1 = 1.761(5), Mn1−C3 = 2.011(5), C1−C2 = 1.343(7), C3−C4 = 1.225(7), C4−Si1 = 1.814(5), Mn1−P1 = 2.2354(17), Mn1−P2 = 2.2458(16), Mn2−C23 = 1.774(5), Mn2−C25 = 2.006(5), C25−C26 = 1.239(7), C23−C24 = 1.341(7), C26−Si2 = 1.799(5); C1−Mn1−C3 = 179.4(3), C2−C1−Mn1 = 179.6(5), C4−C3−Si1 = 172.9(5), C4−C3−Mn1 = 178.2(5), C1−Mn1−P1 = 91.9(2), P2−Mn1−P1 = 84.23(6), C23−Mn2−C25 = 178.6(2), C24−C23−Mn2 = 178.7(5), C25−C26−Si2 = 176.0(5). Only one of the two independent complexes is shown. The ellipsoids are at the 30% probability level, and selected hydrogen atoms are omitted for clarity.

of the Si−C$_{\text{acetylene}}$ bond of such *trans*-bis(alkynyl) manganese derivatives. The Mn(II) complexes **3** and **4** do not react with TBAF at room temperature, and upon heating, this mixture yields decomposition products.[27,60] However, similar to previously reported studies the Mn(III) complexes **5** react instantaneously with 1 equiv of TBAF to yield mixed-valent dinuclear complexes of the type $[\{Mn(dmpe)_2(C\equiv CH)\}_2(\mu\text{-}C_4)][PF_6]$ (**12**), for which a detailed mechanism concerning the formation of the mixed-valent complex has been reported earlier.[26,27] However, the reaction of complexes **6** with TBAF yielded a mixture of unidentifiable decomposition products. This again stresses the fact that a slight electronic change on the phosphorus ligands has a dramatic effect on the redox behavior of these manganese acetylide complexes. The spectroscopic properties and the structural properties of complex **7a** have been reported previously.[27]

Synthesis of Asymmetric *trans*-Bis(alkynyl) Manganese Complexes. An already established method to obtain asymmetrically substituted Mn(II)− or Mn(III)−alkynyl complexes is the deprotonation of metal−vinylidene units.[36,63−66] The Mn(I) complexes $[Mn(R'_2PCH_2CH_2PR'_2)_2(C\equiv CR)(C{=}CH_2)]$ (R′ = Me, R = SiEt$_3$,[27] **9a**; R′ = Me, R = Si^{i}Pr$_3$, **9b**; R′ = Me, R = Si(^{t}Bu)Me$_2$, **9c**) indeed react with 1.2 equiv of quinuclidine and 2 equiv of $[Cp_2Fe][PF_6]$ (formal H$^-$ abstraction equivalent) to give the corresponding Mn(III) asymmetric *trans*-bis(alkynyl) species $[Mn(R'_2PCH_2CH_2PR'_2)_2(C\equiv CR)(C\equiv CH)][PF_6]$ (R′ = Me, R = SiEt$_3$,[27] **10a**; R′ = Me, R = Si^{i}Pr$_3$, **10b**; R′ = Me, R = Si(^{t}Bu)Me$_2$, **10c**) (Scheme 2).

Complexes **10** have been isolated as red solids insoluble in nonpolar solvents such as pentane, Et$_2$O, etc. and sparingly soluble in THF. The ^{1}H NMR spectra of the paramagnetic compounds **10b**,**c** in CD$_2$Cl$_2$ at 20 °C exhibit each a pair of two broad signals for the PMe$_2$ protons at −38.31 and −39.64 ppm and at −39.30 and −40.20 ppm, respectively. The appearance of nonequivalent methyl protons of the dmpe ligands confirms the axial asymmetry of this complex. Respective broad resonances at −29.08 ppm of **10b** and at −29.83 ppm of **10c** are due to the ethylene protons. The $C\equiv CH$ proton of **10b**,**c** could be attributed to a broad singlet at 8.74 ppm. The axial asymmetry of one of these species (**10b**) was unequivocally established by an exemplary X-ray study (Figure 7). The cationic moiety of **10b** shows the manganese in a pseudo-octahedral environment with the triisopropylsilyl alkynyl and terminal alkynyl ligands in trans positions. The Mn−C13 and Mn−C24 bond distances are similar (1.943(10) and 1.943(13) Å, respectively) and are in the same range as those Mn−C bond distances found for symmetric *trans*-bis(alkynyl) complexes.[27,29,60−62] The $C\equiv C$ bond distance in the triisopropylsilyl alkynyl ligand (1.209(13) Å) is quite similar to that observed for the terminal alkynyl ligand (1.201(19) Å).

Preparation of [Mn]−C$_4$−[Mn] Rigid-Rod Species. Lapinte and co-workers have previously reported the carbon−carbon coupling of two $[FeCp(dppe)(C\equiv CH)]^+$ molecules to yield a dinuclear vinylidene species, which by subsequent deprotonation with KO^{t}Bu afforded a dinuclear compound containing an Fe−C$_4$−Fe unit.[52] A related carbon−carbon coupling was observed in studies by our group recently.[29,67] Further, we have reported the formation of the dinuclear complexes $[\{Mn(dmpe)_2(C\equiv CR)\}_2(\mu\text{-}C_4)][PF_6]$ involving such a carbon−carbon coupling process.[26,27]

A related coupling process was considered using the starting components $[Mn(dmpe)_2(C\equiv CR)(C\equiv CH)][PF_6]$ (R = SiEt$_3$, **10a**; R = Si^{i}Pr$_3$, **10b**; R = Si(^{t}Bu)Me$_2$, **10c**). Reaction of these complexes with 1.5 equiv of DBU yielded the dinuclear mixed-valent complexes $[\{Mn(dmpe)_2(C\equiv CR)\}_2(\mu\text{-}C_4)][PF_6]$ (R = SiEt$_3$, [**11a**]$^+$; R = Si^{i}Pr$_3$, [**11b**]$^+$; R = Si(^{t}Bu)Me$_2$, [**11c**]$^+$) (Scheme 3). Their formation could be rationalized on the basis of a dimerization of $[Mn(dmpe)_2(C\equiv CR)(C\equiv C)^\bullet]$ species. Intermediates such as $[Mn(dmpe)_2(C\equiv CR)(C\equiv C)^\bullet]$ may possess two principal canonical forms: the singlet form $[Mn(dmpe)_2(C\equiv CR)(C\equiv C|)]$ (**A**), with a formally Mn^{III} center, and the triplet form $[Mn(dmpe)_2(C\equiv CR)(C\equiv C^\bullet)]$ (**B**), with an oxidized C atom and a reduced Mn^{II} center. DFT calculations performed on the hydrogen-substituted model $[Mn(dHpe)_2(C\equiv CH)(C\equiv C)]$ revealed that out of the two possible spin states the triplet state **B** is more stable than the singlet state by ca. 90 kJ mol^{-1} and that the β-alkynyl carbon atom in the triplet state bears a substantial amount of spin density (+0.61α).[26]

The relative triplet stability and the concomitant longevity of the Mn^{II} free radical form then enable the selective C−C coupling process to produce first the neutral dinuclear compounds $[\{Mn(dmpe)_2(C\equiv CR)\}_2(\mu\text{-}C_4)][PF_6]$ (R = SiEt$_3$, **11a**; R = Si^{i}Pr$_3$, **11b**; R = Si(^{t}Bu)Me$_2$, **11c**). The Mn center is thus playing a role similar

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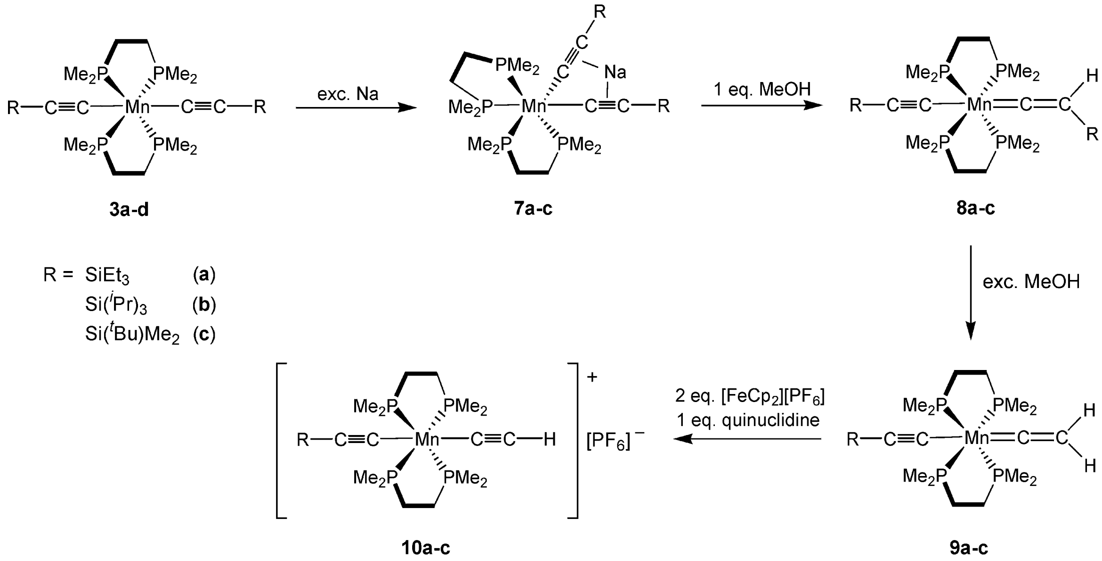
Scheme 2



to that of the Cu^{2+} ion in the Eglinton and McCrae coupling of acetylenic compounds,[59] formally oxidizing the β-carbon atoms of terminally deprotonated species. Once **11a**–**c** are formed, the given mildly oxidizing reaction conditions set by the redox properties of the Mn^{III} complexes $[Mn(dmpe)_2(C{\equiv}CR)(C{\equiv}CH)][PF_6]$ (R = $SiEt_3$, **10a**; R = Si^iPr_3, **10b**; R = $Si(^tBu)Me_2$, **10c**) induce subsequent oxidation of **11a**–**c** to yield [**11a**–**c**]$^+$, respectively. The formed neutral dinuclear complexes $[\{Mn(dmpe)_2(C{\equiv}CR)\}_2(\mu\text{-}C_4)]$ (**11a**–**c**) reduce the corresponding species **10a**–**c** by one electron to yield [**11a**–**c**]$^+$. All these mixed-valent complexes [**11a**–**c**]$^+$ were isolated as violet solids in yields of around 60%. On the basis of the stoichiometry of the relevant reaction steps described above, the yields are almost quantitative.

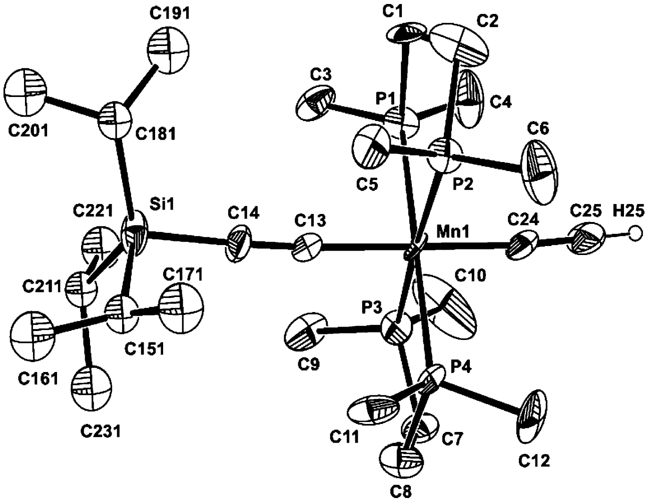
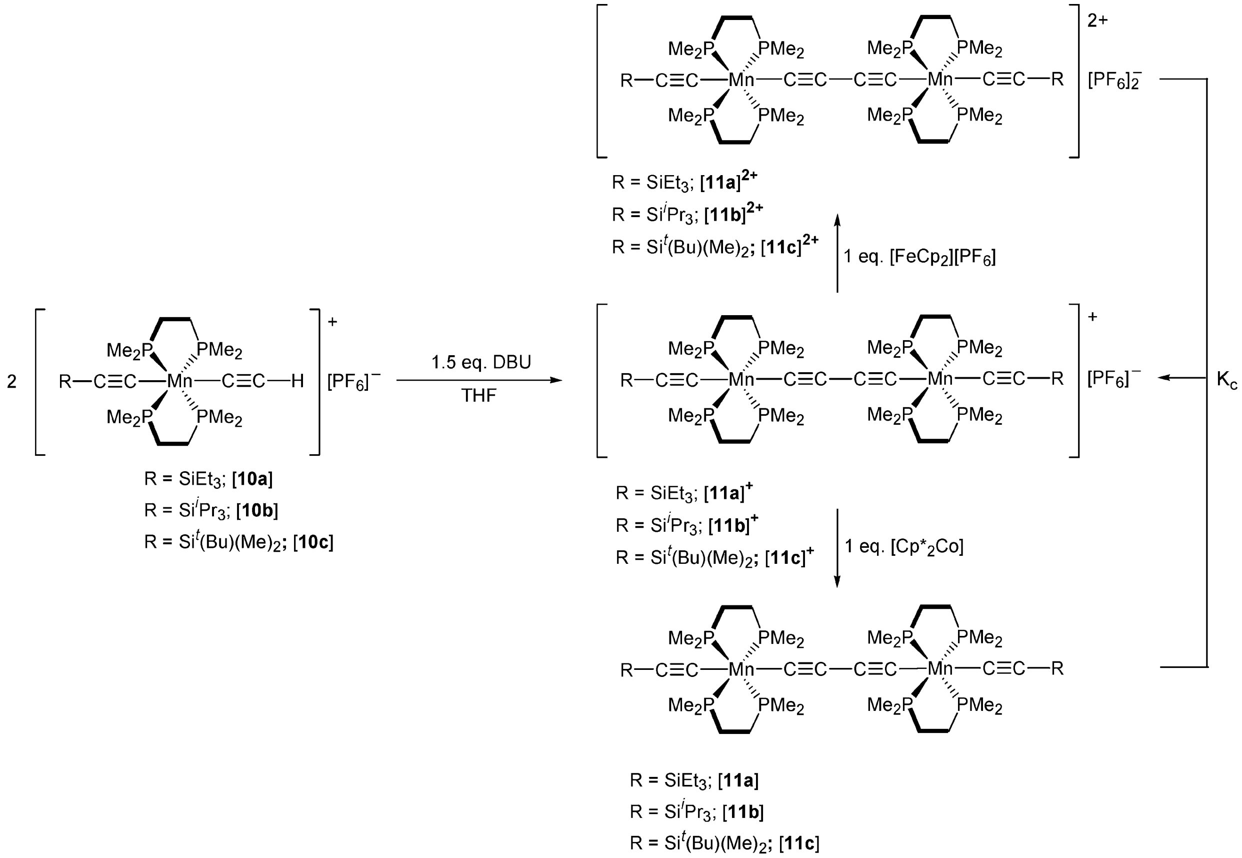


Figure 7. Molecular structure of **10b**. Selected bond lengths (Å) and angles (deg): Mn1−C13 = 1.943(10), Mn1−C24 = 1.943(13), C13−C14 = 1.209(13), C24−C25 = 1.201(9), C14−Si1 = 1.902(11), Mn1−P1 = 2.308(4), Mn1−P2 = 2.327(4); C13−Mn1−C24 = 178.9(6), C14−C13−Mn1 = 176.9(9), C13−C14−Si1 = 165.9(12), C25−C24−Mn1 = 175.2(14), C13−Mn1−P1 = 89.8(3), P1−Mn1−P2 = 83.92(13). Only one positional disordered site of the triisopropyl group is shown. The displacement ellipsoids are at the 30% probability level, and selected hydrogen atoms and the PF_6^- anion are omitted for clarity.

The ^1H NMR spectra of the new species [**11**]$^+$ recorded in CD_2Cl_2 at 20 °C show for each compound four broad signals at −0.27 (br, 8H, PCH_2), −4.47 (br, 24H, PCH_3), −6.30 (br, 24H, PCH_2), and −6.59 ppm (br, 24H, PCH_3) for [**11a**]$^+$, at −0.27 (br, 8H, PCH_2), −4.65 (br, 24H, PCH_3), −6.82 (br, 24H, PCH_2), and −16.11 ppm (br, 24H, PCH_3) for [**11b**]$^+$, and at −0.35 (br, 8H, PCH_2), −4.53 (br, 24H, PCH_3), −6.47 (br, 24H, PCH_2), and −16.43 ppm (br, 24H, PCH_3) for [**11c**]$^+$. They are all assigned to the dmpe protons. Additional resonances for the alkyl groups attached to the silicon atom were observed between 1 and 4 ppm. There is quite a marked difference on comparison of the spectra of complex [**11a**]$^+$ with the other two complexes. One of the resonances corresponding to the methyl protons of the dmpe of compound **11a** appears more downfield than in the other two complexes. The broadening of the resonances of complexes [**11**]$^+$ was caused by their paramagnetism. In a quantitative fashion this was confirmed by the temperature dependence of the chemical shifts following Curie−Weiss behavior (temperature range of −70 to +20 °C). The structure of [**11a**]$^+$ has been established by a single-crystal X-ray diffraction study (Figure 8). This revealed two equivalent manganese centers adopting pseudo-octahedral geometry. The bond distances and angles compare well to those obtained for similar complexes earlier.[26−28] The carbon−carbon bond lengths of 1.311(8) and 1.291(10) Å found for C1−C2 and C2−C2a, respectively, in [**11a**]$^+$ are comparable to those found in closely related compounds of the type $[\{Mn(dmpe)_2(C{\equiv}CR)\}_2(\mu\text{-}C_4)][PF_6]$ (R = $SiMe_3$, H) where carbon−carbon bond distances were found to be 1.309(17) and 1.30(2) Å for $[\{Mn(dmpe)_2(C{\equiv}CR)\}_2(\mu\text{-}C_4)][PF_6]$ (R = $SiMe_3$)[27] and 1.285(6) and 1.307(9) Å for $[\{Mn(dmpe)_2(C{\equiv}CR)\}_2(\mu\text{-}C_4)][PF_6]$ (R = H).[26] These bond lengths reveal a cumulenic type resonance structure of the C_4 chain possessed by these complexes.

The reduction of the mixed-valent complexes [**11a**]$^+$ with $(C_5Me_5)Co$ yields the corresponding neutral paramagnetic dinuclear species $[\{Mn(dmpe)_2(C{\equiv}CR)\}_2(\mu\text{-}C_4)]$ (R = $SiEt_3$, **11a**; R = Si^iPr_3, **11b**; R = $Si(^tBu)Me_2$, **11c**), which were isolated as dark green solids. The reactions

Scheme 3



were fully reversible, and the corresponding mixed-valent species could be recovered by oxidation of the neutral complexes **11** with stoichiometric amounts of [Cp_2Fe][PF_6]. The ^1H NMR spectra of the complexes **11** recorded in C_6D_6 at 20 °C show four signals for each complex between −10 and −21 ppm attributable to the dmpe protons. The proton resonances for the alkyl groups on the silicon atom were observed between 2 and 5 ppm.

The redox-active mixed-valent complexes [**11**]$^+$ can also be oxidized further to the dicationic species [{Mn(dmpe)$_2$(C≡CR)}$_2$(μ-C_4)][PF_6]$_2$ (R = SiEt$_3$, [**11a**]$^{2+}$; R = Si^{i}Pr$_3$, [**11b**]$^{2+}$; R = Si(^{t}Bu)Me$_2$, [**11c**]$^{2+}$), by applying 1 equiv of [Cp_2Fe][PF_6]. Complexes [**11**]$^{2+}$ were isolated quantitatively as brown diamagnetic solids. All three compounds are soluble only in polar solvents such as CH_2Cl_2 and CH_3CN. The ^1H NMR spectra of [**11**]$^{2+}$ in CH_2Cl_2 show resonances of the dmpe ligand in the diamagnetic region between 0 and 5 ppm. The diamagnetism of the Mn^{III}−C$_4$−Mn^{III} species [**11**]$^{2+}$ is in agreement with the magnetic properties described for related iodo-substituted and acetylide-substituted complexes.[26−28]

Due to the local D_{2h} symmetry of the species **11**, [**11**]$^+$, and [**11**]$^{2+}$ with a center of inversion, bands assigned to symmetric vibrations of the C$_4$ chain are expected to be Raman allowed. Symmetric bond stretch vibrations (a$_{1g}$) should appear as strong bands, and indeed the solid-state Raman spectra of these dinuclear complexes exhibit an intense and characteristic band at ν ~1805 cm^{-1}, with a shoulder at ν ~1824 cm^{-1} for the Mn^{II}−C$_4$−Mn^{II} neutral compounds **11**, at ν ~1745 cm^{-1} for the mixed-valent complexes [**11**], and at ν ~2010 cm^{-1} for the diamagnetic species [**11**]$^{2+}$. These emissions indeed correspond to a$_{1g}$ vibrations of the C$_4$ chain.[38,68−77] The observed shifts of the ν(C$_4$) bands indicate significant changes of the electronic configuration of the C$_4$ chain upon oxidation of the metal center(s). This behavior is typical of strongly electronically coupled systems.[28] Other relevant bands in these spectra are ν(C$_3$) vibrations of the C$_4$ chain,[77] which appear at around ν ~1032 cm^{-1}. In addition, an emission at around 335 cm^{-1} is assigned to the Mn−C vibration for all complexes[78] and a band at around 274 cm^{-1} is attributed to a$_{1g}$ Mn−P stretches.[79] The cyclic voltammetric studies show behavior similar to that observed for other related complexes. The comproportionation constant K_c for these complexes **11** were found to be in

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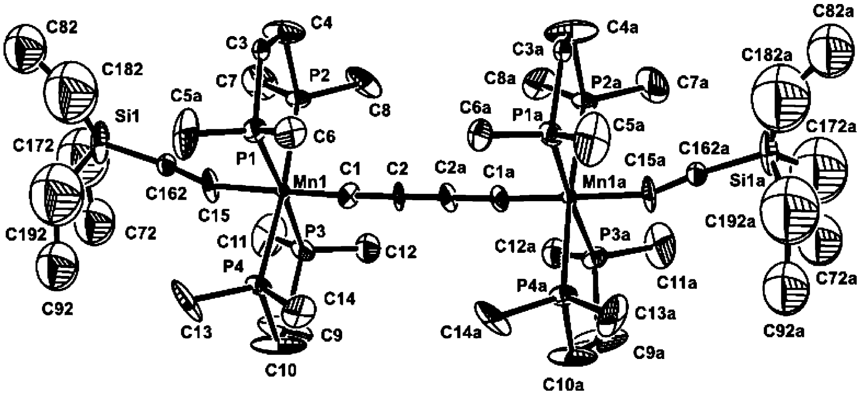

Figure 8. Structure of the cation [**11a**]$^+$. Selected bond lengths (Å) and angles (deg): Mn1−C1 = 1.768(6), C1−C2 = 1.311(8), C2−C2a = 1.291(10), C15−C162 = 1.257(12), Si1−C162 = 1.844(10), Mn1−P1 = 2.285(3), Mn1−P2 = 2.310(2); C1−Mn1−C15 = 179.1(3), C2−C1−Mn1 = 177.8(7), C2a−C2−C1 = 179.3(7), C162−C15−Mn1 = 161.9(9), C15−C161−Si1 = 161.7(11). The displacement ellipsoids are at the 30% probability level. Hydrogen atoms, split positions of the disordered triethylsilyl group, two CH_2Cl_2 solvent molecules, and the PF_6^- anion are omitted for clarity.

Table 1. Cyclic Voltammogram of Complexes 11[a]

redox couple	$E_{1/2}$ (V) first wave	$E_{1/2}$ (V) second wave	K_c
[11a]/[11a]$^+$/[11a]$^{2+}$	−0.843	−0.286	3.5×10^9
[11b]/[11b]$^+$/[11b]$^{2+}$	−0.857	−0.294	4.4×10^9
[11c]/[11c]$^+$/[11c]$^{2+}$	−0.849	−0.289	4.0×10^9

[a] Conditions: 10^{-3} M in THF; ^{n}Bu$_4$PF$_6$/THF as electrolyte; vs Fc/Fc$^+$; gold electrode; 100 mV s^{-1}.

a range quite similar to that for other related complexes (Table 1).[26−28]

Conclusions

A series of Mn(II) and Mn(III) symmetric and asymmetric *trans*-bis(alkynyl) complexes of the type $[Mn(R'_2PCH_2CH_2PR'_2)_2(C{\equiv}CR)_2]^{n+}$ (n = 0, 1; R′ = Me, R = SiEt$_3$; R′ = Me, R = Si^{i}Pr$_3$; R′ = Me, R = Si(^{t}Bu)Me$_2$; R′ = Et, R = SiEt$_3$; R′ = Et, R = Si^{i}Pr$_3$; R′ = Et, R = Si(^{t}Bu)Me$_2$) and $[Mn(dmpe)_2(C{\equiv}CR)(C{\equiv}CH)]^+$ (R = SiEt$_3$, Si^{i}Pr$_3$, Si(^{t}Bu)Me$_2$) have been prepared. The asymmetric *trans*-bis(alkynyl) complexes $[Mn(dmpe)_2(C{\equiv}CR)(C{\equiv}CH)]^+$ (R = SiEt$_3$, Si^{i}Pr$_3$, Si(^{t}Bu)Me$_2$), which are obtained by the reaction of the Mn(I) *trans*-alkynyl−vinylidene species $Mn(dmpe)_2(C{\equiv}CR)(C{=}CH_2)$ with quinuclidine and 2 equiv of $[Cp_2Fe][PF_6]$, yielded on further treatment with 1 equiv of DBU the mixed-valent complexes $[\{Mn(dmpe)_2(C{\equiv}CR)\}_2(\mu\text{-}C_4)][PF_6]$ (R = SiEt$_3$; Si^{i}Pr$_3$; Si(^{t}Bu)Me$_2$) and thus suggest to a certain extent generality for such coupling processes.

The formation of the new dinuclear mixed-valent species recovered from the deprotonation reaction of the corresponding terminal alkynyl manganese complexes are unique examples of radical C−C self-coupling reactions, in which the Mn(III) center may be considered to oxidize C_β of the deprotonated alkynyl species generating a free radical center and subsequently inducing the C−C coupling.

Experimental Section

General Considerations. All operations were performed under an inert atmosphere of N_2 using Schlenk and vacuum-line techniques or in a glovebox (Model MB-150B-G). The following solvents were dried and purified by distillation under nitrogen before use by employing appropriate drying/deoxygenating agents: tetrahydrofuran (sodium/benzophenone), toluene (sodium), hexane (sodium/potassium alloy), and CH_2Cl_2 (P_2O_5, and filtered through active Alox). IR spectra were obtained on a Bio-Rad FTS instrument. Raman spectra were recorded on a Renishaw Ramanscope spectrometer (514 nm). NMR spectra were measured on a Varian Gemini-2000 spectrometer at 300 MHz for ^{1}H and 121.5 MHz for ^{31}P{^{1}H} and on a Bruker-DRX-500 spectrometer at 125.8 MHz for ^{13}C{^{1}H}. Chemical shifts for ^{1}H and ^{13}C are given in ppm relative to the solvent signals, and the ^{31}P{^{1}H} NMR spectra were referenced to 98% external H_3PO_4. The assignment of the ^{1}H NMR signals for paramagnetic compounds is principally based on the investigations of Köhler et al.[85] C and H elemental analyses were performed with a LECO CHN-932 microanalyzer. Cyclic voltammograms were obtained with a BAS 100 B/W instrument (10^{-3} M in 0.1 M THF/[NBu$_4$][PF$_6$], AgO reference electrode). TBAF, TEMPO, DBU, and quinuclidine were obtained from Aldrich. $Mn(dmpe)_2Br_2$[86] and $Mn(depe)_2Br_2$[86] were prepared by literature procedures.

[Mn(dmpe)$_2$(C≡CSiEt$_3$)$_2$] (3a). A THF solution (5 mL) of freshly prepared LiC≡CSiEt$_3$ (0.39 mmol) (which was prepared upon stoichiometric treatment of ^{n}BuLi with HC≡CSiEt$_3$ at −78 °C) was added to a −30 °C THF solution of $Mn(dmpe)_2Br_2$ (100 mg, 0.19 mmol). The temperature was raised to 20 °C, and the mixture was stirred for 10 h. The solvent was removed in vacuo, and the yellow solid of **3a** was extracted with hexane. Yield: 100 mg, 84%. Anal. Calcd for $C_{28}H_{62}MnP_4Si_2$ (633.8): C, 53.06; H, 9.86. Found: C, 52.88; H, 10.17. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C): δ 3.92 (br, 12H, SiEt$_3$), 3.06 (br, 18H, SiEt$_3$), −13.9 (br, 8H, PCH$_2$), −15.17 (br, 24H, PCH$_3$). IR (CH_2Cl_2, 20 °C): 1942 cm^{-1} ν(C≡C).

[Mn(dmpe)$_2$(C≡CSi^{i}Pr$_3$)$_2$] (R = Si^{i}Pr$_3$ (3b), Si(^{t}Bu)Me$_2$ (3c)). A THF solution (10 mL) of freshly prepared LiC≡CR (1.52 mmol) (which was prepared upon stoichiometric treatment of ^{n}BuLi with the corresponding acetylenes HC≡CR (R = Si^{i}Pr$_3$, Si(^{t}Bu)Me$_2$ at −78 °C) was added to a −30 °C THF solution of $Mn(dmpe)_2Br_2$ (400 mg, 0.76 mmol). The temperature was raised to 20 °C, and the mixture was stirred for 10 h. The solvent was removed in vacuo, and the yellow solids were extracted with pentane. Crystallizing in pentane gave large yellow crystals. **3b**: yield 510 mg, 90%. Anal. Calcd for

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$C_{30}H_{66}MnP_4Si_2$ (661.84): C, 54.44; H, 10.05. Found: C, 54.81; H, 10.17. ^1H NMR (C_6D_6, 300 MHz, 20 °C): δ 3.52 (br, 6H, $Si(^iPr)_3$), 3.16 (br, 36H, $Si(^iPr)_3$), −14.3 (br, 8H, PCH_2), −15.19 (br, 24H, PCH_3). IR (CH_2Cl_2, 20 °C): 1946 cm^{-1} ν(C≡C). **3c**: yield 430 mg, 91%. Anal. Calcd for $C_{28}H_{62}P_4Si_2Mn$ (585.75): C, 49.21; H, 10.66. Found: C, 49.05; H, 10.47. ^1H NMR (CD_2Cl_2, 300 MHz, 20 °C): δ 4.80 (br, 12H, Si^tBuMe_2), 3.14 (br, 18H, Si^tBuMe_2), −13.58 (br, 8H, PCH_2), −14.92 (br, 24H, PCH_3). IR (CH_2Cl_2, 20 °C): 1944 cm^{-1} ν(C≡C).

[Mn(depe)$_2$(C≡CR)$_2$] (R = SiEt$_3$ (4a), Si^{i}Pr$_3$ (4b), Si(^{t}Bu)Me$_2$ (4c), SiPh$_3$ (4d)). A THF solution (10 mL) of freshly prepared LiC≡CR (1.27 mmol) (which was prepared upon stoichiometric treatment of ^{n}BuLi with the corresponding acetylenes HC≡CR (R = $SiEt_3$, Si^iPr_3, $Si(^tBu)Me_2$, $SiPh_3$ at −78 °C) was added to a −30 °C THF solution of $Mn(depe)_2Br_2$ (400 mg, 0.63 mmol). The temperature was raised to 20 °C, and the mixture was stirred for 10 h. The solvent was removed in vacuo. After extraction with hexane and removal of the solvent yellow solids were obtained. **4a**: yield 375 mg, 80%. Anal. Calcd for $C_{36}H_{78}MnP_4Si_2$ (746.08): C, 57.95; H, 10.53. Found: C, 57.63; H, 10.88. ^1H NMR (C_6D_6, 300 MHz, 20 °C): δ 4.06 (br, 18H, $Si(CH_2C\mathit{H_3})_3$), 3.23 (br, 12H, $Si(C\mathit{H_2}CH_3)_3$), 0.41 (br, 16H, $PC\mathit{H_2}CH_3$), −9.82 (br, 24H, $PCH_2C\mathit{H_3}$), −13.93 (br, 8H, $PC\mathit{H_2}C\mathit{H_2}P$). IR ($CD_2Cl_2$, 20 °C): 2006 cm^{-1} (s), 1980 cm^{-1} (s) ν(C≡C), 1027 cm^{-1} (s) ν(P−C). **4b**: yield 420 mg, 80%. Anal. Calcd for $C_{42}H_{90}MnP_4Si_2$ (830.16): C, 60.76; H, 10.92. Found: C, 60.43; H, 10.88. ^1H NMR (C_6D_6, 300 MHz, 20 °C): δ 3.25 (br, 36H, $Si(CH(C\mathit{H_3})_2)_3$), 2.71 (br, 6H, $Si(C\mathit{H}(CH_3)_2)$, 0.91 (br, 24H, $PC\mathit{H_2}CH_3$), −2.81 (br, 24H, $PCH_2C\mathit{H_3}$), −4.23 (br, 8H, $PC\mathit{H_2}C\mathit{H_2}P$). IR ($CD_2Cl_2$, 20 °C): 2006 cm^{-1} (s), 1976 cm^{-1} (s) ν(C≡C), 1027 cm^{-1} (s) ν(P−C). **4c**: yield 370 mg, 80%. Anal. Calcd for $C_{36}H_{72}MnP_4Si_2$ (739.96): C, 58.43; H, 9.80. Found: C, 58.38; H, 9.98. ^1H NMR (CD_2Cl_2, 300 MHz, 20 °C): δ 5.04 (br, 12H, Sit-Bu($C\mathit{H_3}$)$_2$), 2.08 (br, 18H, $Si^tBu(CH_3)_2$) 0.80 (br, 16H, $PC\mathit{H_2}CH_3$), −9.87 (br, 8H, $PC\mathit{H_2}C\mathit{H_2}P$), −14.21 (br, 24H, $PCH_2C\mathit{H_3}$). IR (CD_2Cl_2, 20 °C): 2006 cm^{-1} (s), 1979 cm^{-1} (s) ν(C≡C), 1027 cm^{-1} (s) ν(P−C). **4d**: yield 490 mg, 80%. Anal. Calcd for $C_{56}H_{70}MnP_4Si_2$ (978.51): C, 68.76; H, 7.21. Found: C, 68.42; H, 6.78. ^1H NMR (C_6D_6, 300 MHz, 20 °C): δ 9.34 (br, 12H, C_6H_5), 8.32 (s, 12H, C_6H_5), 7.28 (s, 6H, C_6H_5), −9.81 and −14.28 (br, 32H, depe). IR (CD_2Cl_2, 20 °C): 2006 cm^{-1} (s), 1976 cm^{-1} (s) ν(C≡C), 1025 cm^{-1} (s) ν(P−C).

[Mn(dmpe)$_2$(C≡CSiEt$_3$)$_2$][PF$_6$] (5a). A CH_2Cl_2 solution of **3a** (100 mg, 0.17 mmol) was added to a CH_2Cl_2 suspension of $[Cp_2Fe][PF_6]$ (60 mg, 0.18 mmol). The reaction mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a red-orange solid. Then the solid was washed with Et_2O until the solvent was colorless. The solid was then dissolved in dichloromethane and filtered over Celite. The CH_2Cl_2 was then evaporated to give the compound **5a**. Yield: 100 mg, 80%. Anal. Calcd for $C_{28}H_{62}F_6MnP_5Si_2$ (778.8): C, 43.18; H, 8.02. Found: C, 42.91; H, 7.89. ^1H NMR (CD_2Cl_2, 300 MHz, 20 °C): δ 3.70 (br, 12H, $SiEt_3$), 2.96 (br, 18H, $SiEt_3$), −29.33 (br, 8H, $PC\mathit{H_2}$), −39.36 (br, 24H, $PC\mathit{H_3}$), ^{31}P NMR (CD_2Cl_2, 121.5 MHz, 20 °C): δ − 145.5 (spt, 718 Hz, 1P, PF_6). ^{19}F NMR (CD_2Cl_2, 282.32 MHz, 20 °C): δ −75.4 (d, 718 Hz, 6F, PF_6). IR (CD_2Cl_2, 20 °C): 2108 cm^{-1} (w), 1978 cm^{-1} (s) ν(C≡C), 948 cm^{-1} (s), 933 cm^{-1} (s) ν(P−C), 834 cm^{-1} (vs) (P−F).

[Mn(dmpe)$_2$(C≡CSi^{i}Pr$_3$)$_2$][PF$_6$] (5b). A CH_2Cl_2 solution (10 mL) of **3b** (110 mg, 0.16 mmol) was added to a CH_2Cl_2 suspension of $[Cp_2Fe][PF_6]$ (54 mg, 0.16 mmol), and the reaction mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a red-orange solid. Then the solid was washed with Et_2O until the solvent was colorless. The solid was then dissolved in CH_2Cl_2 and filtered over Celite. Further, the CH_2Cl_2 was evaporated in vacuo to give an orange-red powder. Yield: 116 mg, 90%. Anal. Calcd for $C_{30}H_{66}F_6MnP_5Si_2$ (806.81): C, 44.65; H, 8.24. Found: C, 44.91; H, 8.69. ^1H NMR (C_6D_6, 300 MHz, 20 °C): δ 4.52 (br, 6H, $Si(^iPr)_3$), 4.17 (br, 36H, $Si(^iPr)_3$), −19.31 (br, 8H, PCH_2), −29.13 (br, 24H, PCH_3). ^{31}P NMR (CD_2Cl_2, 121.5 MHz, 20 °C): δ −145.5 (spt, 718 Hz, 1P, PF_6). ^{19}F NMR (CD_2Cl_2, 282.3 MHz, 20 °C): δ −75.4 (d, 718 Hz, 6F, PF_6). IR (CD_2Cl_2, cm^{-1}): 2108 (w), 1978 (s) ν(C≡C), 948 (s), 933 (s) ν(P−C), 834 (vs) (P−F).

[Mn(dmpe)$_2$(C≡CSi(^{t}Bu)Me$_2$][PF$_6$] (5c). A CH_2Cl_2 solution (10 mL) of **3c** (110 mg, 0.17 mmol) was added to a CH_2Cl_2 suspension of $[Cp_2Fe][PF_6]$ (57 mg, 0.17 mmol), and the reaction mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a red-orange solid. Then the solid was washed with Et_2O until the solvent was colorless. The solid was then dissolved in CH_2Cl_2 and filtered over Celite. Further, the CH_2Cl_2 was evaporated in vacuo to give an orange-red powder. Yield: 116 mg, 90%. Anal. Calcd for $C_{28}H_{62}F_6MnP_5Si_2$ (778.70): C, 43.18; H, 8.02. Found: C, 43.52; H, 8.31. ^1H NMR (C_6D_6, 300 MHz, 20 °C): δ 4.53 (br, 12H, Si^tBuMe_2), 3.32 (br, 18H, Si^tBuMe_2), −20.56 (br, 8H, PCH_2), −29.87 (br, 24H, PCH_3). ^{31}P NMR (CD_2Cl_2, 121.5 MHz, 20 °C): δ −145.5 (spt, 718 Hz, 1P, PF_6). ^{19}F NMR (CD_2Cl_2, 282.3 MHz, 20 °C): δ −75.4 (d, 718 Hz, 6F, PF_6). IR (CD_2Cl_2, cm^{-1}): 2115 (w), 1968 (s) ν(C≡C), 945 (s), 931 (s) ν(P−C), 834 (vs) (P−F).

[Mn(depe)$_2$(C≡CR)$_2$][PF$_6$] (R = SiEt$_3$ (6a), Si^{i}Pr$_3$ (6b), Si(^{t}Bu)Me$_2$ (6c), SiPh$_3$ (6d)). To a CH_2Cl_2 solution (10 mL) of **4** (100 mg, 0.13 mmol) was added a dichloromethane solution of $[Cp_2Fe][PF_6]$ (44 mg, 0.13 mmol for **6a**,**c**,**d**; 39 mg, 0.12 mmol for **6b**), and the reaction mixture was stirred for 1 h at room temperature. The solvent was evaporated to give red-orange solids. Then the solids were washed with Et_2O until the solvent was colorless. The solids were then dissolved in CH_2Cl_2 and filtered over Celite. The dichloromethane was then evaporated to give the corresponding compounds **6a**−**d**. **6a**: yield 100 mg, 90%. Anal. Calcd for $C_{36}H_{78}F_6MnP_5Si_2$ (890.97): C, 48.52; H, 8.82. Found: C, 48.42; H, 8.45. ^1H NMR (CD_2Cl_2, 300 MHz, 20 °C): δ 4.06 (br, 18H, $Si(CH_2C\mathit{H_3})_3$), 2.84 (br, 12H, $Si(C\mathit{H_2}CH_3)_3$), −15.0 (br, 8H, $PC\mathit{H_2}C\mathit{H_2}P$), −28.3 (br, 16H, $PC\mathit{H_2}CH_3$), −32.4 (br, 24H, $PCH_2C\mathit{H_3}$). ^{31}P {^1H} NMR (CD_2Cl_2, 121.5 MHz, 20 °C): δ −144.2 (sept, $^1J_{P-F}$ = 718 Hz, PF_6^-). ^{19}F NMR (CD_2Cl_2, 282.3 MHz, 20 °C): δ −74.5 (d, $^1J_{P-F}$ = 721 Hz, PF_6^-). IR (CD_2Cl_2, 20 °C): ν 2042 cm^{-1} (s), 1986 cm^{-1} (s) (C≡C), 1033 cm^{-1} (s) (P−C), 841 cm^{-1} (vs) (P−F); **6b**: yield 105 mg, 90%. Anal. Calcd for $C_{42}H_{90}F_6MnP_5Si_2$ (975.13): C, 51.73; H, 9.30. Found: C, 51.49; H, 9.43. ^1H NMR (CD_2Cl_2, 300 MHz, 20 °C): δ 4.12 (br, 36H, $Si(CH(C\mathit{H_3})_2)_3$, 3.23 (br, 6H, $Si(C\mathit{H}(CH_3)_2)_3$), −12.51 (br, 8H, $PC\mathit{H_2}C\mathit{H_2}P$), −28.74 (br, 16H, $PC\mathit{H_2}CH_3$), −33.10 (br, 24H, $PCH_2C\mathit{H_3}$). ^{31}P{^1H} NMR (CD_2Cl_2, 121.5 MHz, 20 °C): δ −144.2 (sept, $^1J_{P-F}$ = 718 Hz, PF_6^-). ^{19}F NMR (CD_2Cl_2, 282.3 MHz, 20 °C): δ −74.5 (d, $^1J_{P-F}$ = 721 Hz, PF_6^-). IR (CD_2Cl_2, 20 °C): 2042 cm^{-1} (s), 1984 cm^{-1} (s) ν(C≡C), 1031 cm^{-1} (s) ν(P−C), 845 cm^{-1} (vs) ν(P−F); **6c**: yield 115 mg, 90%. Anal. Calcd for $C_{36}H_{72}F_6MnP_6Si_2$ (884.92): C, 48.86; H, 8.20. Found: C, 48.55; H, 8.05. ^1H NMR (CD_2Cl_2, 300 MHz, 20 °C): δ 3.98 (br, 12H, $Si^tBu(C\mathit{H_3})_2$), 3.61 (br, 18H, $Si^t\mathit{Bu}(CH_3)_2$), −12.66 (br, 16H, $PC\mathit{H_2}CH_3$), −28.10 (br, 8H, $PC\mathit{H_2}C\mathit{H_2}P$), −32.67 (br, 24H, $PCH_2C\mathit{H_3}$). ^{31}P{^1H} NMR (CD_2Cl_2, 121.5 MHz, 20 °C): δ −144.2 (sept, $^1J_{P-F}$ = 718 Hz, PF_6^-). ^{19}F NMR (CD_2Cl_2, 282.3 MHz, 20 °C): δ −74.5 (d, $^1J_{P-F}$ = 721 Hz, PF_6^-). IR (CD_2Cl_2, 20 °C): 2042 cm^{-1} (s), 1984 cm^{-1} (s) ν(C≡C), 1037 cm^{-1} (s) ν(P−C), 844 cm^{-1} (vs) ν(P−F); **6d**: yield 130 mg, 90%. Anal. Calcd for $C_{56}H_{70}F_6MnP_5Si_2$ (1123.12): C, 59.88; H, 6.28. Found: C, 59.42; H, 6.63. ^1H NMR (CD_2Cl_2, 300 MHz, 20 °C): δ 8.95 (br, 12H, C_6H_5), 8.94 (s, 18H, C_6H_5), 6.85 (s, 6H, C_6H_5), −12.21 (br, 16H, $PC\mathit{H_2}CH_3$), −28.72 (br, 8H, $PC\mathit{H_2}C\mathit{H_2}P$), −33.03 (br, 24H, $PCH_2C\mathit{H_3}$). ^{31}P{^1H} NMR (CD_2Cl_2, 121.5 MHz, 20 °C): δ −144.2 (sept, $^1J_{P-F}$ = 718 Hz, PF_6^-). ^{19}F NMR (CD_2Cl_2, 282.32 MHz, 20 °C): δ −74.5 (d, $^1J_{P-F}$ = 721 Hz, PF_6^-). IR (CD_2Cl_2, 20 °C): 2042 cm^{-1} (s), 1983 cm^{-1} (s) ν(C≡C), 1036 cm^{-1} (s) ν(P−C), 843 cm^{-1} (vs) ν(P−F).

[Mn(dmpe)$_2$(C≡CR)$_2$]Na (R = SiEt$_3$ (7a), Si^{i}Pr$_3$ (7b), Si(^{t}Bu)Me$_2$ (7c)). A toluene solution (15 mL) of **3** (420 mg, 0.74 mmol for **3a**,**c**; 300 mg, 0.41 mmol for **3b**) was added to a large excess of Na placed in a high-vacuum Young tap Schlenk flask. The mixtures were stirred at 95 °C for 12 h to give dark red solutions. The solutions were concentrated in vacuo to 5 mL and chilled to −30 °C for 12 h to afford yellow crystals. **7a**: yield 360 mg, 80%. Anal. Calcd for $\mathrm{C_{28}H_{62}MnNaP_4Si_2}$ (656.8): C, 51.20; H, 9.51. Found: C, 51.40; H, 9.52. ^{1}H NMR (toluene-d_8, 300 MHz, 20 °C): δ 1.53 (s, 6H, $\mathrm{PMe_2}$) 1.43 (m, 4H, $\mathrm{PCH_2}$), 1.36 (s, 6H, $\mathrm{PMe_2}$), 1.23 (s, 6H, $\mathrm{PMe_2}$), 1.10 (m, 4H, $\mathrm{PCH_2}$), 1.06 (t, 18H, $\mathrm{SiCH_2CH_3}$), 0.91 (s, 6H, $\mathrm{PMe_2}$), 0.51 (q, 12H, $\mathrm{SiCH_2CH_3}$). ^{31}P{^{1}H} NMR (toluene-d_8, 121.5 MHz, 20 °C): δ 76.65 (br, 2P). ^{13}C NMR (toluene-d_8, 125 MHz, 20 °C): δ 211.2 (Mn−C), 110.8 (C−Si), 34.7 (m, 2C, $\mathrm{PCH_2}$), 30.2 (m, 2C, $\mathrm{PCH_2}$), 22.9 (m, 2C, $\mathrm{PCH_3}$), 20.9 (m, 2C, $\mathrm{PCH_3}$), 20.5 (m, 2C, $\mathrm{P}\mathit{CH_3}$), 14.5 (m, 2C, $\mathrm{P}\mathit{CH_3}$), 8.5 (s, 6C, $\mathrm{Si}\mathit{CH_2}\mathrm{CH_3}$), 6.5 (s, 6C, $\mathrm{SiCH_2}\mathit{CH_3}$). ^{29}Si NMR (toluene-$d_8$, 99.3 MHz, 20 °C): δ −26.6 (t, Si). IR ($\mathrm{CH_2Cl_2}$, 20 °C): 1987 cm^{-1} ν(C≡C), 1944 cm^{-1} ν(C≡C); **7b**: yield 295 mg, 95%. Anal. Calcd for $\mathrm{C_{34}H_{74}MnNaP_4Si_2}$ (740.95): C, 55.11; H, 10.06. Found: C, 55.32; H, 10.14. ^{1}H NMR (toluene-d_8, 300 MHz, 20 °C): δ 1.53 (s, 6H, $\mathrm{PMe_2}$) 1.43 (m, 4H, $\mathrm{PCH_2}$), 1.36 (s, 6H, $\mathrm{PMe_2}$), 1.23 (s, 6H, $\mathrm{PMe_2}$), 1.10 (m, 4H, $\mathrm{PCH_2}$), 1.14 (d, 6H, $\mathrm{SiC}\mathit{H}\mathrm{(CH_3)_2}$), 1.04 (d, 36H, $\mathrm{SiCH(C}\mathit{H_3}\mathrm{)_2}$), 0.91 (s, 6H, $\mathrm{PMe_2}$). ^{31}P{^{1}H} NMR (toluene-d_8,121.5 MHz, 20 °C): δ 77.66 (br, 2P), 64.76 (br, 2P). ^{13}C{^{1}H} NMR (toluene-d_8, 125 MHz, 20 °C): δ 208.9 (m, 2C, Mn*C*≡C), 108.4 (br, 2C, MnC≡*C*), 34.7 (m, 2C, $\mathrm{P}\mathit{C}\mathrm{H_2}$), 30.2 (m, 2C, $\mathrm{P}\mathit{C}\mathrm{H_2}$), 22.9 (m, 2C, $\mathrm{P}\mathit{C}\mathrm{H_3}$), 20.9 (m, 2C, $\mathrm{P}\mathit{C}\mathrm{H_3}$), 20.5 (m, 2C, $\mathrm{P}\mathit{CH_3}$), 14.5 (m, 2C, $\mathrm{P}\mathit{CH_3}$), 10.9 (s, 12C, $\mathrm{SiCH(}\mathit{C}\mathrm{H_3)_2}$), 8.5 (s, 6C, $\mathrm{Si}\mathit{C}\mathrm{H(CH_3)_2}$). ^{29}Si NMR (toluene-$d_8$, 99.3 MHz, 20 °C): δ −21.2 (t, $J_{\mathrm{P-Si}}$ = 2 Hz, $\mathit{Si}\mathrm{CH(CH_3)_2}$). IR ($\mathrm{CH_2Cl_2}$, 20 °C): 1985 cm^{-1} ν(C≡C), 1949 cm^{-1} ν(C≡C). **7c**: yield 360 mg, 80%. Anal. Calcd for $\mathrm{C_{28}H_{62}MnNaP_4Si_2}$ (656.8): C, 51.20; H, 9.51. Found: C, 51.40; H, 9.52. ^{1}H NMR (toluene-d_8, 300 MHz, 20 °C): δ 1.53 (m, 6H, $\mathrm{P(C}\mathit{H_3}\mathrm{)_2}$), 1.43 (m, 4H, $\mathrm{PC}\mathit{H_2}$), 1.36 (m, 6H, $\mathrm{P(C}\mathit{H_3}\mathrm{)_2}$), 1.23 (m, 6H, $\mathrm{P(C}\mathit{H_3}\mathrm{)_2}$), 1.10 (m, 4H, $\mathrm{PC}\mathit{H_2}$), 1.06 (s, 18H, $\mathrm{Si(}^t\mathit{Bu}\mathrm{(CH_3)_2)}$), 0.91 (s, 6H, $\mathrm{P(C}\mathit{H_3}\mathrm{)_2}$), 0.21 (d, 12H, $\mathrm{Si(}^t\mathrm{Bu(C}\mathit{H_3}\mathrm{)_2)}$. ^{31}P{^{1}H} NMR (toluene-d_8, 121.5 MHz, 20 °C): δ 77.44 (br, 2P), 64.33 (br, 2P). ^{13}C NMR (toluene-d_8, 125 MHz, 20 °C): δ 211.6 (Mn−*C*), 111.9 (*C*−Si), 34.9 (s, 2C, $\mathrm{Si(}^t\mathit{Bu}\mathrm{(CH_3)_2)}$), 34.7 (m, 2C, $\mathrm{P}\mathit{C}\mathrm{H_2}$), 30.2 (m, 2C, $\mathrm{P}\mathit{C}\mathrm{H_2}$), 27.8 (s, 6C, $\mathrm{Si(}^t\mathit{Bu}\mathrm{(CH_3)_2)}$), 23.3 (m, 2C, $\mathrm{P}\mathit{C}\mathrm{H_3}$), 20.9 (m, 2C, $\mathrm{P}\mathit{C}\mathrm{H_3}$), 20.5 (m, 2C, $\mathrm{P}\mathit{C}\mathrm{H_3}$), 14.5 (m, 2C, $\mathrm{P}\mathit{C}\mathrm{H_3}$), −1.2 (s, 4C, $\mathrm{Si(}^t\mathrm{Bu(}\mathit{C}\mathrm{H_3)_2)}$). ^{29}Si NMR (toluene-$d_8$, 99.3 MHz, 20 °C): δ −27.3 (t, $^4J_{\mathrm{Si-P}}$ = 2 Hz, $\mathit{Si}\mathrm{(}^t\mathrm{Bu(CH_3)_2)}$). IR ($\mathrm{CH_2Cl_2}$, 20 °C): 1989 cm^{-1} ν(C≡C), 1947 cm^{-1} ν(C≡C).

[Mn(dmpe)$_2$(C≡CSiEt$_3$)(=C=C(H)(SiEt$_3$)] (8a). MeOH (0.019 mL) was added to a toluene solution (15 mL) of **7a** (390 mg, 0.60 mmol). The mixture was stirred for 1.5 h at room temperature to yield a yellow solution. The solvent was removed in vacuo, and the product was extracted with pentane and was concentrated to give yellow crystals of **8a**. Yield: 330 mg, 90%. Anal. Calcd for $\mathrm{C_{28}H_{63}MnP_4Si_2}$ (634.8): C, 52.97; H, 10.00. Found: C, 52.72; H, 9.91. ^{1}H NMR ($\mathrm{C_6D_6}$, 300 MHz, 20 °C): δ 3.05 (quint, J_{PH} =11.7 Hz, 1H, =CH), 1.50 (br, 4H, $\mathrm{PCH_2}$), 1.43 (s, 12H, $\mathrm{PCH_3}$), 1.36 (s, 12H, $\mathrm{PCH_3}$), 1.30 (s, 4H, $\mathrm{PCH_2}$), 1.17 (t, 9H, $\mathrm{SiCH_2CH_3}$), 1.09 (t, 9H, $\mathrm{SiCH_2CH_3}$), 0.63 (q, 6H, $\mathrm{SiCH_2CH_3}$), 0.48 (q, 6H, $\mathrm{SiCH_2CH_3}$). ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 121.5 MHz, 20 °C): δ 68.5. ^{13}C NMR ($\mathrm{C_6D_6}$, 125 MHz, 20 °C): δ 335.5 (quint, $^2J_{\mathrm{PC}}$ = 25 Hz, Mn=*C*), 170.2 (quint, $^2J_{\mathrm{PC}}$ = 27 Hz, Mn−*C*), 125.8 (*C*−Si), 88.5 (=*C*H), 31.8 (m, $\mathrm{PCH_2}$), 17.9 (m, $\mathrm{PCH_3}$), 8.9 ($\mathrm{-CH_2}\mathit{CH_3}\mathrm{Si}$), 8.5 ($\mathrm{-CH_2}\mathit{CH_3}\mathrm{Si}$), 6.7 ($-\mathit{CH_2}\mathrm{CH_3Si}$), 6.5 ($-\mathit{CH_2}\mathrm{CH_3Si}$). IR ($\mathrm{CH_2Cl_2}$, 20 °C): 1988 cm^{-1} ν(C≡C), 1947 cm^{-1} ν(C≡C), 1598 cm^{-1} ν(C=C), 1550 cm^{-1} ν(C=C).

[Mn(dmpe)$_2$(C≡CSi^{i}Pr$_3$)(=C=C(H)(Si^{i}Pr$_3$)] (8b). MeOH (0.021 mL) was added to a toluene solution (15 mL) of **7b** [Mn(dmpe)$_2$(C≡CSi^{i}Pr$_3$)$_2$]Na (400 mg, 0.54 mmol). The mixture was stirred for 1.5 h at room temperature to yield a yellow solution. The solvent was removed in vacuo, and the product was extracted with pentane and was concentrated to give yellow crystals of **8b**. Yield: 270 mg, 72%. Anal. Calcd for $\mathrm{C_{34}H_{75}MnP_4Si_2}$ (718.96): C, 56.79; H, 10.51. Found: C, 56.54; H, 10.18. ^{1}H NMR ($\mathrm{C_6D_6}$, 300 MHz, 20 °C): δ 2.85 (quint, J_{PH} = 11.7 Hz, 1H, =CH), 1.50 (br, 4H, $\mathrm{PCH_2}$), 1.43 (s, 12H, $\mathrm{PCH_3}$), 1.36 (s, 12H, $\mathrm{PCH_3}$), 1.30 (s, 4H, $\mathrm{PCH_2}$), 1.28 (s, 3H, $\mathrm{SiC}\mathit{H}\mathrm{(CH_3)_2}$), 1.26 (s, 18H, $\mathrm{SiCH(C}\mathit{H_3}\mathrm{)_2}$), 1.18 (s, 3H, $\mathrm{SiC}\mathit{H}\mathrm{(CH_3)_2}$), 1.16 (s, 3H, $\mathrm{SiC}\mathit{H}\mathrm{(CH_3)_2}$). ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 121.5 MHz, 20 °C): δ 69.11. ^{13}C NMR ($\mathrm{C_6D_6}$, 125 MHz, 20 °C): δ 334.9 (quint, $^2J_{\mathrm{PC}}$ = 25.4 Hz, Mn=*C*), 170.3 (quint, $^2J_{\mathrm{PC}}$ = 26.6 Hz, Mn−*C*), 120.8 (quint, $^2J_{\mathrm{PC}}$ = 0.9 Hz, *C*−Si), 86.2 (quint, $^2J_{\mathrm{PC}}$ = 26.6 Hz, =*C*H), 31.8 (m, $\mathrm{PCH_2}$), 20.2 (s, 3C, $\mathrm{Si}\mathit{C}\mathrm{H(CH_3)_2}$), 20.0 (s, 3C, $\mathrm{Si}\mathit{C}\mathrm{H(CH_3)_2}$), 17.9 (m, $\mathrm{PCH_3}$), 10.6 (s, 6C, $\mathrm{-SiCH(}\mathit{C}\mathrm{H_3)_2}$), 10.4 (s, 6C, $\mathrm{-SiCH(}\mathit{C}\mathrm{H_3)_2}$). ^{29}Si NMR ($\mathrm{C_6D_6}$, 99.38 MHz, 20 °C): δ −2.1 (s, −C≡C($\mathit{Si}\mathrm{(}^i\mathrm{Pr)_3)_2}$), −18.2 (s, =C=C($\mathit{Si}\mathrm{(}^i\mathrm{Pr)_3)_2}$(H)). IR ($\mathrm{CH_2Cl_2}$, 20 °C): 1988 cm^{-1} ν(C≡C), 1946 cm^{-1} ν(C≡C), 1594 cm^{-1} ν(C=C), 1548 cm^{-1} ν(C=C).

[Mn(dmpe)$_2$(C≡CSi(^{t}Bu)Me$_2$)(=C=C(H)(Si(^{t}Bu)Me$_2$))] (8c). MeOH (0.010 mL) was added to a toluene solution (15 mL) of [Mn(dmpe)$_2$(C≡CSi(^{t}Bu)Me$_2$]Na (**7c**; 210 mg, 0.33 mmol). The mixture was stirred for 1.5 h at room temperature to yield a yellow solution. The solvent was removed in vacuo, and the product was extracted with pentane and was concentrated to give yellow crystals of **8c**. Yield: 160 mg, 76%. Anal. Calcd for $\mathrm{C_{28}H_{63}MnP_4Si_2}$ (634.80): C, 52.97; H, 10.00. Found: C, 52.59; H, 10.18. ^{1}H NMR ($\mathrm{C_6D_6}$, 300 MHz, 20 °C): δ 2.95 (quint, J_{PH} = 11.8 Hz, 1H, =CH), 1.50 (br, 4H, $\mathrm{PCH_2}$), 1.43 (s, 12H, $\mathrm{PCH_3}$), 1.36 (s, 12H, $\mathrm{PCH_3}$), 1.30 (s, 4H, $\mathrm{PCH_2}$), 1.06 (s, 18H, $\mathrm{Si(}^t\mathit{Bu}\mathrm{(CH_3)_2)}$, 0.91 (s, 6H, $\mathrm{P(C}\mathit{H_3}\mathrm{)_2}$), 0.21 (d, 12H, $\mathrm{Si(}^t\mathrm{Bu(C}\mathit{H_3}\mathrm{)_2)}$. ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 121.5 MHz, 20 °C): δ 68.61. ^{13}C NMR ($\mathrm{C_6D_6}$, 125 MHz, 20 °C): δ 335.8 (quint, $^2J_{\mathrm{PC}}$ = 25.4 Hz, Mn=*C*), 170.4 (quint, $^2J_{\mathrm{PC}}$ = 26.6 Hz, Mn−*C*), 121.8 (quint, $^2J_{\mathrm{PC}}$ = 0.9 Hz, *C*−Si), 87.3 (quint, $^2J_{\mathrm{PC}}$ = 26.6 Hz, =*C*H), 64.5 (s, 2C, $\mathrm{Si}^t\mathit{Bu}\mathrm{(CH_3)_2}$), 31.8 (m, $\mathrm{PCH_2}$), 26.7 (s, 3C, $\mathrm{Si}^t\mathit{Bu}\mathrm{(CH_3)_2}$), 26.4 (s, 3C, $\mathrm{Si}^t\mathit{Bu}\mathrm{(CH_3)_2}$), 17.9 (m, $\mathrm{PCH_3}$), −2.3 (s, 2C, $\mathrm{Si}^t\mathrm{Bu(C}\mathit{H_3}\mathrm{)_2}$), −2.8 (s, 2C, $\mathrm{Si}^t\mathrm{Bu(C}\mathit{H_3}\mathrm{)_2}$). ^{29}Si NMR ($\mathrm{C_6D_6}$, 99.38 MHz, 20 °C): δ −5.3 (s, −C≡C($\mathit{Si}^t\mathrm{Bu(CH_3)_2}$)), −21.6 (s, =C=C($\mathit{Si}^t\mathrm{Bu(CH_3)_2}$(H))). IR ($\mathrm{CH_2Cl_2}$, 20 °C): 1987 cm^{-1} ν(C≡C), 1945 cm^{-1} ν(C≡C), 1598 cm^{-1} ν(C=C), 1548 cm^{-1} ν(C=C).

[Mn(dmpe)$_2$(C≡CSiEt$_3$)(=C=CH$_2$)] (9a). A MeOH solution of KOH (1 mL) was added to a toluene solution (15 mL) of **8a** (330 mg, 0.52 mmol). The mixture was stirred for 1 h at room temperature, turning light yellow. The solvent was removed in vacuo, and the product was extracted with pentane and was concentrated to give light green crystals of **9a**. Yield: 220 mg, 80%. Anal. Calcd for $\mathrm{C_{22}H_{49}MnP_4Si}$ (520.5): C, 50.76; H, 9.48. Found: C, 50.49; H, 9.26. ^{1}H NMR ($\mathrm{C_6D_6}$, 300 MHz, 20 °C): δ 3.55 (q, $^4J_{\mathrm{PH}}$ = 11.5 Hz) 1.48 (br, 4H, $\mathrm{PCH_2}$), 1.42 (s, 12H, $\mathrm{PCH_3}$), 1.34 (s, 12H, $\mathrm{PCH_3}$), 1.28 (s, 4H, $\mathrm{PCH_2}$), 1.17 (t, 18H, $\mathrm{SiCH_2CH_3}$), 0.71 (q, 12H, $\mathrm{SiCH_2CH_3}$). ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 121.5 MHz, 20 °C): δ 68.96. ^{13}C NMR ($\mathrm{C_6D_6}$, 125 MHz, 20 °C): δ 343.5 (quint, $^2J_{\mathrm{PC}}$ = 28.5 Hz, Mn=*C*), 169.8 (quint, $^2J_{\mathrm{PC}}$ = 26 Hz, Mn−*C*), 124.4 (*C*−Si), 89.5 (quint, $^3J_{\mathrm{PC}}$ = 4.1 Hz, =$\mathit{C}\mathrm{H_2}$), 31.8 (m, $\mathrm{PCH_2}$), 17.9 (m, $\mathrm{PCH_3}$), 8.9 ($\mathrm{-CH_2}\mathit{CH_3}\mathrm{Si}$), 6.5 ($-\mathit{CH_2}\mathrm{CH_3Si}$). ^{29}Si NMR ($\mathrm{C_6D_6}$, 99.38 MHz, 20 °C): δ −21.2 (q, $^4J_{\mathrm{PSi}}$ = 2.5 Hz). IR ($\mathrm{CH_2Cl_2}$, 20 °C): 1988 cm^{-1} ν(C≡C), 1946 cm^{-1} ν(C≡C), 1594 cm^{-1} ν(C=C), 1542 cm^{-1} ν(C=C).

[Mn(dmpe)$_2$(C≡CSi^{i}Pr$_3$)(=C=CH$_2$)] (9b). Tetrabutylammonium fluoride (1.0 M; 0.52 mL, 0.52 mmol) was added to a THF solution of (15 mL) of **8b** (370 mg, 0.52 mmol). The mixture was stirred for 1 h at room temperature, turning green. The solvent was removed in vacuo, and the product was extracted with pentane and was concentrated to give light green crystals of **9b**. Yield: 230 mg, 80%. Anal. Calcd for $\mathrm{C_{25}H_{55}MnP_4Si}$ (562.62): C, 53.36; H, 9.85. Found: C, 53.24; H, 9.68. ^{1}H NMR ($\mathrm{C_6D_6}$, 300 MHz, 20 °C): δ 3.58 (quint., $^4J_{\mathrm{PH}}$ = 11.5 Hz), 1.48 (br, 4H, $\mathrm{PCH_2}$), 1.42 (s, 12H, $\mathrm{PCH_3}$), 1.29 (sept, 3H, $\mathrm{SiC}\mathit{H}\mathrm{(CH_3)_2}$), 1.27 (s, 18H, $\mathrm{SiCH(C}\mathit{H_3}\mathrm{)_2}$), 1.22 (s, 12H, $\mathrm{PCH_3}$), 1.17 (s, 4H, $\mathrm{PCH_2}$). ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 121.5 MHz, 20 °C): δ 69.1. ^{13}C NMR ($\mathrm{C_6D_6}$, 125 MHz, 20 °C): δ 342.9 (quint, $^2J_{\mathrm{PC}}$ = 28.5 Hz, Mn=*C*), 169.5 (quint, $^2J_{\mathrm{PC}}$ = 26 Hz, Mn−*C*), 122.2 (*C*−i), 89.8 (quint, $^3J_{\mathrm{PC}}$ = 4.1 Hz, =$\mathit{C}\mathrm{H_2}$), 31.8 (m, $\mathrm{P}\mathit{C}\mathrm{H_2}$), 17.9 (m, $\mathrm{P}\mathit{C}\mathrm{H_3}$), 19.9 (s, 6C, $\mathrm{-SiCH(}\mathit{C}\mathrm{H_3)_2}$), 19.1 (s, 3C, $\mathrm{Si}\mathit{C}\mathrm{H(CH_3)_2}$). ^{29}Si NMR ($\mathrm{C_6D_6}$, 99.38 MHz, 20 °C): δ

-15.2 (q, $^4J_{Psi}$ = 2.5 Hz, *Si*CH(CH$_3$)$_2$). IR (CH$_2$Cl$_2$, 20 °C): 1988 cm^{-1} ν(C≡C), 1943 cm^{-1} ν(C≡C), 1595 cm^{-1} ν(C=C), 1541 cm^{-1} ν(C=C).

[Mn(dmpe)$_2$(C≡CSi(^{t}Bu)Me$_2$)(=C=CH$_2$)] (9c). Tetrabutylammonium fluoride (1.0 M; 0.55 mL, 0.55 mmol) was added to a THF solution (15 mL) of **8c** (350 mg, 0.55 mmol). The mixture was stirred for 1 h at room temperature, turning green. The solvent was removed in vacuo, and the product was extracted with pentane and was concentrated to give light green crystals of **9c**. Yield: 230 mg, 83%. Anal. Calcd for $C_{25}H_{49}MnP_4Si$ (520.43): C, 50.76; H, 9.48. Found: C, 51.03; H, 9.72. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 20 °C): δ 3.55 (q, 2H, $^4J_{PH}$ = 11.5 Hz), 1.53 (br, 4H, PCH$_2$), 1.38 (s, 12H, PCH$_3$), 1.27 (s, 12H, PCH$_3$), 1.14 (s, 4H, PCH$_2$), 0.92 (s, 9H, Si(^{t}C$_4$*H*$_9$)Me$_2$), 0.12 (s, 6H, Si(^{t}C$_4$H$_9$)(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.5 MHz, 20 °C): δ 68.6. ^{13}C NMR (C$_6$D$_6$, 125 MHz, 20 °C): δ 341.4 (quint, $^2J_{PC}$ = 28.5 Hz, Mn=*C*), 166.8 (quint, $^2J_{PC}$ = 26 Hz, Mn−*C*), 121.4 (*C*−Si), 89.6 (quint, $^3J_{PC}$ = 4.1 Hz, =*C*H$_2$), 31.4 (m, P*C*H$_2$), 16.8 (m, P*C*H$_3$), 19.3 (s, 2C, −Si(^{t}C$_4$H$_9$)(*C*H$_3$)$_2$), 17.4 (s, 1C, −Si(^{t}*C*$_4$H$_9$)(**C**H$_3$)$_2$). ^{29}Si NMR (C$_6$D$_6$, 99.4 MHz, 20 °C): δ -15.8 (q, $^4J_{PSi}$ = 2.5 Hz, *Si*(^{t}C$_4$H$_9$)(CH$_3$)$_2$). IR (CH$_2$Cl$_2$, 20 °C): 1984 cm^{-1} ν(C≡C), 1939 cm^{-1} ν(C≡C), 1592 cm^{-1} ν(C=C), 1537 cm^{-1} ν(C=C).

[Mn(dmpe)$_2$(C≡CSiEt$_3$)(C≡CH)][PF$_6$] (10a). To a THF solution of **9a** (100 mg, 0.19 mmol) was added quinuclidine (25 mg, 0.23 mmol; the mixture was stirred for 5 min before adding [Cp$_2$Fe][PF$_6$] (140 mg, 0.38 mmol). The dark red solution that formed was stirred at room temperature. After 1 h the solvent was removed in vacuo and the residue washed with Et$_2$O to yield a red solid. Extraction with CH$_2$Cl$_2$ and evaporation in vacuo led to a red solid. Recrystallization of this material from THF yielded **10a** as orange-red crystals. Yield: 100 mg, 79%. Anal. Calcd for $C_{22}H_{48}F_6MnP_5Si$ (664.34): C, 39.76; H, 7.28. Found: C, 39.56, H, 7.18. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 20 °C): δ 6.69 (br, 1H, C≡CH), 3.37 (br, 9H, SiCH$_2$C*H*$_3$), 1.93 (br, 6H, SiCH$_2$CH$_3$), -29.53 (br, 8H, PCH$_2$), -39.34 (br, 12H, PCH$_3$), -39.80 (br, 12H, PCH$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.5 MHz, 20 °C): δ -145.5 (stp, 718 Hz, 1P, PF$_6$). ^{19}F NMR (CD$_2$Cl$_2$, 282.32 MHz, 20 °C): δ -75.4 (d, 718 Hz, 6F, PF$_6$). IR (CH$_2$Cl$_2$, 20 °C): 2020, 1919 cm^{-1} ν(C≡C), 834 cm^{-1} (vs) ν(P−F).

[Mn(dmpe)$_2$(C≡CSi^{i}Pr$_3$)(C≡CH)][PF$_6$] (10b). To a THF solution of **9b** (100 mg, 0.16 mmol) was added quinuclidine (20 mg, 0.19 mmol); the mixture was stirred for 5 min before adding [Cp$_2$Fe][PF$_6$] (100 mg, 0.32 mmol). The dark red solution that formed was stirred at room temperature. After 1 h the solvent was removed in vacuo and the residue washed with Et$_2$O. Extraction with CH$_2$Cl$_2$ and evaporation in vacuo led to a red solid. Recrystallization of this material from THF yielded **10b** as orange-red crystals. Yield: 100 mg, 84%. Anal. Calcd for $C_{25}H_{54}MnP_5Si$ (734.66): C, 40.87; H, 7.40. Found: C, 40.56, H, 7.18. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 20 °C): δ 8.74 (br, 1H, C≡CH), 3.52 (br, 18H, SiCH(C*H*$_3$)$_2$), 1.88 (br, 6H, SiC*H*(CH$_3$)$_2$), -29.08 (br, 8H, PCH$_2$), -38.31 (br, 12H, PCH$_3$), -39.64 (br, 12H, PCH$_3$), ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.5 MHz, 20 °C): δ -145.5 (stp, 718 Hz, 1P, PF$_6$). ^{19}F NMR (20 °C, CD$_2$Cl$_2$, 282.32 MHz): δ -75.4 (d, 718 Hz, 6F, PF$_6$), IR (CH$_2$Cl$_2$, 20 °C): 2018, 1921 cm^{-1} ν(C≡C), 834 cm^{-1} (vs) ν(P−F).

[Mn(dmpe)$_2$(C≡CSi(^{t}Bu)Me$_2$)(C≡CH)][PF$_6$] (10c). To a THF solution of **9c** (100 mg, 0.19 mmol) was added quinuclidine (23 mg, 0.23 mmol); the mixture was stirred for 5 min before adding [Cp$_2$Fe][PF$_6$] (125 mg, 0.38 mmol). The dark red solution that formed was stirred at room temperature. After 1 h the solvent was removed in vacuo and the residue washed with Et$_2$O to yield a red solid. Extraction with CH$_2$Cl$_2$ and evaporation in vacuo led to a red solid. Recrystallization of this material from THF yielded **10c** as orange-red crystals. Yield: 115 mg, 92%. Anal. Calcd for $C_{22}H_{48}F_6MnP_5Si$ (664.49): C, 39.76; H, 7.28. Found: C, 39.49, H, 7.43. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 20 °C): δ 8.74 (br, 1H, C≡CH), 3.87 (br, 9H, Si(^{t}C$_4$*H*$_9$)(CH$_3$)$_2$), 3.10 (br, 6H, Si(^{t}C$_4$H$_9$)(C*H*$_3$)$_2$), -29.83 (br, 8H, PCH$_2$), -39.30 (br, 12H, PCH$_3$), -40.20 (br, 12H, PCH$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.5 MHz, 20 °C): δ − 145.5 (stp, 718 Hz, 1P, PF$_6$). ^{19}F NMR (20 °C, CD$_2$Cl$_2$, 282.3 MHz): δ -75.4 (d, 718 Hz, 6F, PF$_6$), IR (CH$_2$Cl$_2$, 20 °C): 2012, 1915 cm^{-1} ν(C≡C), 829 cm^{-1} (vs) ν(P−F).

[{Mn(dmpe)$_2$(C≡CSiEt$_3$)}$_2$(μ-C$_4$)][PF$_6$] ([11a]$^+$). To a THF solution (10 mL) of the species **9a** (140 mg, 0.18 mmol) was added DBU (0.040 mL, 0.22 mmol). A fast color change was observed, from red to dark green. The solution was stirred for 1.5 h. The solvent was then removed in vacuo, and the residue was washed with hexane. Recrystallization from Et$_2$O yielded violet crystals of [**11a**]$^+$. Yield: 150 mg, 60%. Anal. Calcd for $C_{44}H_{94}F_6Mn_2P_9Si_2$ (1097.8): C, 44.70; H, 8.01. Found: C, 44.06; H, 8.12. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 20 °C): δ 1.01 (q, 18 H, SiEt$_3$), 0.72 (t, 12 H, SiEt$_3$), -0.27 (br, 8 H, PCH$_2$), -4.47 (br, 24H, PCH$_3$), -6.30 (br, 8H, PCH$_2$), -6.59 (br, 24H, PCH$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.5 MHz, 20 °C): δ -145.12 (sept, $^1J_{PF}$ = 717.9 Hz, PF$_6^-$). ^{19}F NMR (CD$_2$Cl$_2$, 282.3 MHz, 20 °C): δ -74.72 (d, 717.9 Hz, PF$_6^-$). IR (CH$_2$Cl$_2$, 20 °C): 1990 cm^{-1} ν(C≡C), 2016 cm^{-1} (w), 1879 cm^{-1} (w) ν(C$_4$). Raman: 1828 cm^{-1} ν(C≡C), 1745 cm^{-1} ν(C≡C), 1046 cm^{-1} ν(C−C−C), 340 cm^{-1} ν(Mn−C).

[{Mn(dmpe)$_2$(C≡CSiEt$_3$)}$_2$(μ-C$_4$)] ([11a]). To a THF solution (10 mL) of the species [**11a**]$^+$ (100 mg, 0.09 mmol) was added (C$_5$Me$_5$)$_2$Co (29 mg, 0.09 mmol). The mixture was stirred for 1 h, and the solvent was removed in vacuo. The product was extracted with pentane to yield a green solid of [**11a**]. Yield: 72 mg, 78%. Anal. Calcd for $C_{44}H_{94}Mn_2P_8Si_2$ (1037.05): C, 50.95; H, 9.13. Found: C, 50.70; H, 9.46. ^{1}H NMR (300 MHz, 20 °C, C$_6$D$_6$): δ 1.31 (q, 18 H, SiEt$_3$), 0.42 (t, 12 H, SiEt$_3$), -10.42 (br, 8 H, PCH$_2$), -15.83 (br, 8H, PCH$_2$), -16.43 (br, 24H, PCH$_3$), -20.35 (br, 24H, PCH$_3$). IR (CH$_2$Cl$_2$, 20 °C): 1995 cm^{-1} ν(C≡C), 2026 cm^{-1}(s), 1881 cm^{-1} (s) ν(C$_4$). Raman: 2004 cm^{-1} ν(C≡C), 1036 cm^{-1} ν(C−C−C), 410 cm^{-1} ν(Mn−C).

[{Mn(dmpe)$_2$(C≡CSiEt$_3$)}$_2$(μ-C$_4$)][PF$_6$]$_2$ ([11a]$^{2+}$). To a CH$_2$Cl$_2$ solution (10 mL) of the species [**11a**]$^+$ (100 mg, 0.09 mmol) was added [Cp$_2$Fe][PF$_6$] (30 mg, 0.09 mmol). An immediate color change from dark red to brown occurred. The mixture was stirred for 1 h, and the solvent was concentrated in vacuo to 2 mL. The product was precipitated with Et$_2$O to yield a red-brown solid of [**11a**]$^{2+}$. Yield: 105 mg, 89%. Anal. Calcd for $C_{44}H_{94}F_{12}Mn_2P_{10}Si_2$ (1326.92): C, 39.82; H, 7.13 Found: C, 39.53; H, 7.38. ^{1}H NMR (300 MHz, 20 °C, CD$_2$Cl$_2$): δ 1.92 (br, 16 H, PC*H*$_2$), 1.40 (br, 24H, PC*H*$_3$), 1.32 (br, 24H, PC*H*$_3$), 1.24 (q, 18H, SiCH$_2$C*H*$_3$), 0.21 (t, 12H, SiC*H*$_2$CH$_3$). ^{31}P NMR (CD$_2$Cl$_2$, 121.5 MHz, 20 °C): δ -141.6 (sept., $^1J_{PF}$ = 720 Hz, PF$_6^-$). ^{19}F NMR (CD$_2$Cl$_2$, 282.3 MHz, 20 °C): δ -73.3 (d, 720 Hz, PF$_6^-$). IR (CH$_2$Cl$_2$, 20 °C): 2010 cm^{-1} (w), 1650 cm^{-1} (br). Raman: 2146 cm^{-1} ν(C≡C), 1943 cm^{-1} ν(C≡C), 1760 cm^{-1} ν(C≡C), 1021 cm^{-1} ν(C−C−C), 430 cm^{-1} ν(Mn−C), 267 cm^{-1} ν(Mn−C).

[{Mn(dmpe)$_2$(C≡CSi^{i}Pr$_3$)}$_2$(μ-C$_4$)][PF$_6$] ([11b]$^+$). To a THF solution (10 mL) of the species **10b** (130 mg, 0.18 mmol) were added of DBU (0.040 mL, 0.22 mmol). A fast color change was observed, from red to dark green. The solution was stirred for 1.5 h. The solvent was then removed in vacuo, and the residue was washed with hexane. Recrystallization from Et$_2$O yielded violet crystals of [**11b**]$^+$. Yield: 125 mg, 56%. Anal. Calcd for $C_{50}H_{106}F_6Mn_2P_9Si_2$ (1266.17): C, 47.42; H, 8.43 Found: C, 47.26; H, 8.35. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 20 °C): δ 2.24 (m, 36H, SiCH(C*H*$_3$)$_2$), 1.56 (m, 6H, SiC*H*(CH$_3$)$_2$), -0.27 (br, 8H, PCH$_2$), − 4.65 (br, 24H, PCH$_3$), -6.82 (br, 8H, PCH$_2$), -16.11 (br, 24H, PCH$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.5 MHz, 20 °C): δ -145.1 (sept, $^1J_{PF}$ = 717.9 Hz, PF$_6^-$). ^{19}F NMR (CD$_2$Cl$_2$, 282.3 MHz, 20 °C): δ -74.7 (d, 717.9 Hz, PF$_6^-$). IR (CH$_2$Cl$_2$, 20 °C): 1990 cm^{-1} ν(C≡C), 2016 cm^{-1} (w), 1879 cm^{-1} (w) ν(C$_4$). Raman: 1832 cm^{-1} ν(C≡C), 1746 cm^{-1} ν(C≡C), 1043 cm^{-1} ν(C−C−C), 345 cm^{-1} ν(Mn−C).

[{Mn(dmpe)$_2$(C≡CSi^{i}Pr$_3$)}$_2$(μ-C$_4$)] ([11b]). To a THF solution (10 mL) of the species [**11b**]$^+$ (110 mg, 0.09 mmol) was added (C$_5$Me$_5$)$_2$Co (0.029 g, 0.09 mmol). The mixture was

Table 2. Crystallographic Data and Structure Refinement Details of 3a−c and 4d

	3a	**3b**	**3c**	**4d**
empirical formula	$C_{28}H_{62}MnP_4Si_2$	$C_{34}H_{74}MnP_4Si_2$	$C_{28}H_{62}MnP_4Si_2$	$C_{60}H_{78}MnP_4Si_2$
color	yellow	yellow	yellow	yellow
M_r	633.78	717.93	633.78	1034.22
cryst size (mm)	0.15 × 0.23 × 0.38	0.06 × 0.15 × 0.17	0.09 × 0.17 × 0.24	0.18 × 0.21 × 0.38
T (K)	183(2)	153(2)	183(2)	183(2)
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	9.2055(8)	9.1314(7)	10.6944(8)	10.3222(10)
b (Å)	9.6007(8)	15.5814(11)	11.4568(7)	10.9492(9)
c (Å)	10.5978(10)	16.0887(11)	16.2848(12)	14.0153(12)
α (deg)	101.262(11)	113.338(8)	90	72.255(10)
β (deg)	93.235(11)	91.176(9)	108.276(8)	73.343(10)
γ (deg)	90.261(11)	90.726(9)	90	75.992(10)
V (Å^3)	917.01(14)	2100.8(3)	1894.6(2)	1424.4(2)
Z	1	2	2	1
ρ(calcd) (g cm^{-3})	1.148	1.135	1.111	1.206
μ (mm^{-1})	0.615	0.544	0.595	0.423
F(000)	343	782	686	551
transmissn range	0.8204−0.9189	0.8912−0.9637	0.8786−0.9438	0.8863−0.9410
2θ range (deg)	$6.10 < 2\theta < 60.90$	$5.32 < 2\theta < 60.68$	$5.40 < 2\theta < 60.70$	$5.64 < 2\theta < 60.72$
no. of measd rflns	17518	37591	24974	25467
no. of unique rflns	5043	11479	5658	7799
no. of rflns with $I > 2\sigma(I)$	3584	5966	2591	4252
no. of params	167	393	143	306
GOF (for F^2)	1.015	1.004	0.810	1.019
R1: $I > 2\sigma(I)$, all data[a]	0.0437, 0.0621	0.0488, 0.1030	0.0562, 0.1335	0.0662, 0.1060
wR2: $I > 2\sigma(I)$, all data[a]	0.1117, 0.1182	0.0809, 0.0866	0.1267, 0.1484	0.1492, 0.1610
max, min $\Delta\rho$ (e Å^{-3})	0.764, −0.776	0.946, −0.908	0.736, −0.532	1.567, −0.735

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

stirred for 1 h, and the solvent was removed in vacuo. The product was extracted with pentane to yield a green solid of [**11b**]. Yield: 72 mg, 78%. Anal. Calcd for $C_{50}H_{106}Mn_2P_8Si_2$ (1121.13): C, 53.56; H, 9.52. Found: C, 53.70; H, 9.46. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C): 2.13 (m, 6H, $SiCH(CH_3)_2$), 1.86 (m, 36H, $SiCH(CH_3)_2$), −10.39 (br, 8 H, PCH_2), −15.43 (br, 8H, PCH_2), −16.56 (br, 24H, PCH_3), −20.35 (br, 24H, PCH_3). IR (CH_2Cl_2, 20 °C): 1995 cm^{-1} ν(C≡C), 2026 cm^{-1} (s), 1881 cm^{-1} (s) $\nu(C_4)$. Raman: 1996 cm^{-1} ν(C≡C), 1036 cm^{-1} ν(C−C−C), 410 cm^{-1} ν(Mn−C).

[{Mn(dmpe)$_2$(C≡CSi^{i}Pr$_3$)}$_2$(μ-C$_4$)][PF$_6$]$_2$ ([11b]$^{2+}$). To a CH_2Cl_2 solution (10 mL) of the species [**11b**]$^+$ (100 mg, 0.08 mmol) was added [Cp_2Fe][PF_6] (26 mg, 0.08 mmol). An immediate color change from green to dark red occurred. The mixture was stirred for 1 h, and the solvent was concentrated in vacuo to 2 mL. The product was precipitated with Et_2O to yield a red-brown solid of [**11b**]$^{2+}$. Yield: 105 mg, 93%. Anal. Calcd for $C_{50}H_{106}F_{12}Mn_2P_{10}Si_2$ (1411.14): C, 42.55; H, 7.57. Found: C, 42.83; H, 7.87. ^{1}H NMR (300 MHz, 20 °C, CD_2Cl_2): δ 2.24 (m, 6H, $Si(CH(CH_3)_2)_3$), 1.96 (br, 16 H, PCH_2), 1.67 (m, 36H, $Si(CH(CH_3)_2)_3$), 1.38 (br, 24H, PCH_3), 1.32 (br, 24H, PCH_3), 0.21 (t, 12H, $SiCH_2CH_3$). ^{31}P NMR (CD_2Cl_2, 121.5 MHz, 20 °C): δ −141.6 (sept., $^1J_{PF}$ = 720 Hz, PF_6^-). ^{19}F NMR (CD_2Cl_2, 282.3 MHz, 20 °C): δ −73.3 (d, 720 Hz, PF_6^-). IR (CH_2Cl_2, 20 °C): 2018 cm^{-1} (w), 1643 cm^{-1} (br). Raman: 2152 cm^{-1} ν(C≡C), 1938 cm^{-1} ν(C≡C), 1752 cm^{-1} ν(C≡C), 1028 cm^{-1} ν(C−C−C), 413 cm^{-1} ν(Mn−C), 269 cm^{-1} ν(Mn−C).

[{Mn(dmpe)$_2$(C≡CSi(^{t}Bu)Me$_2$)}$_2$(μ-C$_4$)][PF$_6$] ([11c]$^+$). To a THF solution (10 mL) of the species **10c** (150 mg, 0.22 mmol) was added DBU (0.050 mL, 0.26 mmol). A fast color change was observed, from red to dark green. The solution was stirred for 1.5 h. The solvent was then removed in vacuo, and the residue was washed with hexane. Recrystallization from Et_2O yielded violet crystals of [**11c**]$^+$. Yield: 150 mg, 58%. Anal. Calcd for $C_{44}H_{94}F_6Mn_2P_9Si_2$ (1182.01): C, 44.70; H, 8.01 Found: C, 44.39; H, 8.27. ^{1}H NMR (CD_2Cl_2, 300 MHz, 20 °C): δ 3.67 (br, 18H, $Si(t\text{-}C_4H_9)(CH_3)_2$), 3.23 (br, 12H, $Si(t\text{-}C_4H_9)(CH_3)_2$), −0.35 (br, 8H, PCH_2), −4.53 (br, 24H, PCH_3), −6.47 (br, 8H, PCH_2), −16.43 (br, 24H, PCH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz, 20 °C): δ −145.1 (sept, $^1J_{PF}$ = 718 Hz, PF_6^-). ^{19}F NMR (CD_2Cl_2, 282.3 MHz, 20 °C): δ −74.7 (d, 717.9 Hz, PF_6^-). IR (CH_2Cl_2, 20 °C): 1986 cm^{-1} ν(C≡C), 2013 cm^{-1} (w), 1872 cm^{-1} (w) $\nu(C_4)$. Raman: 1826 cm^{-1} ν(C≡C), 1756 cm^{-1} ν(C≡C), 1041 cm^{-1} ν(C−C−C), 337 cm^{-1} ν(Mn−C).

[{Mn(dmpe)$_2$(C≡CSi(^{t}Bu)Me$_2$}$_2$(μ-C$_4$)] ([11c]). To a THF solution (10 mL) of the species [**11c**]$^+$ (110 mg, 0.09 mmol) was added $(C_5Me_5)_2Co$ (0.030 g, 0.09 mmol). The mixture was stirred for 1 h, and the solvent was removed in vacuo. The product was extracted with pentane to yield a green solid of [**11c**]. Yield: 72 mg, 78%. Anal. Calcd for $C_{44}H_{94}Mn_2P_8Si_2$ (1037.05): C, 50.95; H, 9.13 Found: C, 50.83; H, 8.92. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C): 3.87 (m, 18H, $Si(t\text{-}C_4H_9)(CH_3)_2$), 3.34 (m, 12H, $Si(t\text{-}C_4H_9)(CH_3)_2$), −10.78 (br, 8H, PCH_2), −15.31 (br, 8H, PCH_2), −16.70 (br, 24H, PCH_3), −20.73 (br, 24H, PCH_3). IR (CH_2Cl_2, 20 °C): 1992 cm^{-1} ν(C≡C), 2035 cm^{-1} (s), 1872 cm^{-1} (s) $\nu(C_4)$. Raman: 2002 cm^{-1} ν(C≡C), 1048 cm^{-1} ν(C−C−C), 403 cm^{-1} ν(Mn−C).

[{Mn(dmpe)$_2$(C≡CSi(^{t}Bu)Me$_2$)}$_2$(μ-C$_4$)][PF$_6$]$_2$ ([11c]$^{2+}$). To a CH_2Cl_2 solution (10 mL) of the species [**11c**]$^+$ (100 mg, 0.10 mmol) was added [Cp_2Fe][PF_6] (35 mg, 0.10 mmol). An immediate color change from green to dark red occurred. The mixture was stirred for 1 h, and the solvent was concentrated in vacuo to 2 mL. The product was precipitated with Et_2O to yield a red-brown solid of [**11c**]$^{2+}$. Yield: 124 mg, 94%. Anal. Calcd for $C_{50}H_{106}F_{12}Mn_2P_{10}Si_2$ (1326.98): C, 39.82; H, 7.13. Found: C, 39.63; H, 7.47. ^{1}H NMR (300 MHz, 20 °C, CD_2Cl_2): δ 3.92 (m, 18H, $Si(t\text{-}C_4H_9)(CH_3)_2$), 3.63 (m, 12H, $Si(t\text{-}C_4H_9)(CH_3)_2$), 1.78 (br, 16 H, PCH_2), 1.38 (br, 24H, PCH_3), 1.14 (br, 24H, PCH_3). ^{31}P NMR (CD_2Cl_2, 121.5 MHz, 20 °C): δ −141.6 (sept, $^1J_{PF}$ = 720 Hz, PF_6^-). ^{19}F NMR (CD_2Cl_2, 282.3 MHz, 20 °C): δ −73.3 (d, 720 Hz, PF_6^-). IR (CH_2Cl_2, 20 °C): 2018 cm^{-1} (w), 1643 cm^{-1} (br). Raman: 2157 cm^{-1} ν(C≡C), 1935 cm^{-1} ν(C≡C), 1745 cm^{-1} ν(C≡C), 1032 cm^{-1} ν(C−C−C), 408 cm^{-1} ν(Mn−C), 264 cm^{-1} ν(Mn−C).

X-ray Structure Determinations of 3a−c, 4d, 8b, 9a, 10b, and [11a]$^+$. Crystallographic data for compounds **3a**−**c**, **4d**, **8b**, **9a**, **10b**, and [**11a**]$^+$ are collected in Tables 2 and 3. The crystals were embedded in polybutene oil and mounted on glass fibers; they were fixed by a cold N_2-gas stream of an Oxford Cryogenic System at the diffractometer. Measurement

Table 3. Crystallographic Data and Structure Refinement Details of 8b, 9a, 10b, and [11a]$^+$

	8b	**9a**	**10b**	**[11a]$^+$**
empirical formula	$C_{34}H_{75}MnP_4Si_2$	$C_{22}H_{49}MnP_4Si$	$C_{25}H_{54}F_6MnP_5Si$	$C_{46}H_{98}Cl_4F_{12}Mn_2P_{10}Si_2$
color	yellow	yellow-green	red-orange	orange-green
M_r	718.94	520.52	706.56	1496.80
cryst size (mm)	0.09× 0.16 × 0.21	0.17× 0.19 × 0.30	0.03× 0.06 × 0.39	0.20× 0.31 × 0.31
T (K)	183(2)	153(2)	183(2)	183(2)
λ(Mo Kα) (Å)	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/m$
a (Å)	9.2840(7)	9.3921(7)	9.1806(13)	10.2829(6)
b (Å)	15.5617(12)	18.1971(15)	11.852(2)	34.8853(13)
c (Å)	16.1187(11)	18.5720(15)	16.909(3)	10.2861(6)
α (deg)	66.846(8)	72.585(9)	92.27(2)	90
β (deg)	88.773(9)	89.315(9)	105.689(19)	98.593(7)
γ (deg)	89.648(9)	75.095	89.844(19)	90
V (Å^3)	2140.7(3)	2919.4(4)	1769.7(5)	3648.4(3)
Z	2	4	2	2
ρ(calcd) (g cm^{-3})	1.115	1.184	1.326	1.363
μ (mm^{-1})	0.534	0.720	0.679	0.805
F(000)	784	1120	744	1556
transmissn range	0.8954−0.9511	0.8566−0.9329	0.9379−0.9786	0.7536−0.8526
2θ range (deg)	$5.22 < 2\theta < 60.98$	$5.68 < 2\theta < 60.56$	$4.18 < 2\theta < 56.22$	$4.0 < 2\theta < 49.66$
no. of measd rflns	35 645	37 931	31 131	23 754
no. of unique rflns	11 693	15 903	7918	6352
no. of rflns with $I > 2\sigma(I)$	4165	8862	3279	3728
no. of params	385	532	321	243
GOF (for F^2)	0.624	1.050	1.576	1.408
R1: $I > 2\sigma(I)$, all data[a]	0.0458, 0.1295	0.0831, 0.1369	0.1655, 0.2535	0.0880, 0.1276
wR2: $I > 2\sigma(I)$, all data[a]	0.0861, 0.0952	0.2163, 0.2333	0.3714, 0.3883	0.2279, 0.2468
max, min $\Delta\rho$ (e Å^{-3})	0.597, −0.459	1.500, −0.948	1.007, −0.945	1.205, −0.935

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

temperatures of 183(2) K for compounds **3a**,**c**, **4d**, **8b**, **10b**, [**11a**]$^+$ and 153(2) K for **3b** and **9a** were used. An imaging plate detector system (Stoe IPDS) with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ A) was used for the exposure of 200, 250, 200, 231, 233, 200, 300, and 222 images at constant times of 1.8, 4.0, 3.0, 1.6, 3.0, 3.0, 6.0, and 3.0 min per image.[80] The crystal-to-image distances were set to 50 mm for structures **3a**−**c**, **4d**, **8b**, and **9a**, to 60 mm for **10b**, and to 76 mm for [**11a**]$^+$ (θ_{max} range between 30.49 and 24.83°). ϕ-rotation (for **3a** and **4d**) and ϕ-oscillation modes (for the six structures **3b**,**c, 8b**, **9a**, **10b**, and [**11a**]$^+$) were necessary for the increments of 1.6 and 1.3° or of 1.2, 1.2, 1.2, 1.1, 1.2, and 0.9° per exposure in each case. For the cell parameter refinements, 8000 reflections[80] for the eight compounds were selected out of the whole limiting spheres with intensities $I > 6\sigma(I)$. A total of 17 518, 37 591, 24 974, 25 467, 35 645, 37 931, 31 131, and 23 754 reflections were collected, of which 5043, 11 479, 5658, 7799, 11 693, 15 903, 7918, and 6352 were unique after performing absorption correction and data reduction (R_{int} = 5.08, 8.30, 6.48, 8.91, 9.70, 8.13, 15.16, and 5.45%). A total of 11, 11, 10, 14, 10, 10, 6, and 10 indexed crystal faces were used for the numerical absorption corrections.[81]

A common feature of the eight complexes is that their surfaces consist of hydrogen atoms; thus, only H- - -H contacts of van der Waals type are realized in these structures, which could explain the relatively poor crystallinity and sensitivity to stress during the crystal preparation. Disorder observed for some of these complexes may also arise from this fact.

The Mn atom of the structure of compound **3a** lies on a center of inversion; thus, only half of the ligands had to be refined. The anisotropic displacement parameters of the ethyl group (C3, C4) were relatively large. A split atomic disorder refinement with distance restraints did not improve the result; thus, a conventional anisotropic refinement was finally preferred. For structure **3b** two independent Mn complexes with Mn atoms on centers of inversion were found. The Mn atom in structure **3c** also occupies an inversion center; however, 16 distance restraints were necessary to refine the disordered ethyl group and the Si(^{t}Bu)Me$_2$ group properly. The compound **4d** shows the same symmetry property (Mn on center of inversion) as structures **3a**,**c**, whereas compound **8b** has two independent complexes, as does compound **3b**. The Si^{i}Pr$_3$−alkyl and the Si^{i}Pr$_3$−vinylidene moieties in **8b** are statistically distributed over the independent centers of inversion. Thus, eight distance restraints were used altogether to refine the positional disorder of the C≡C triple bonds and C=C double bonds of the structure.

The crystal structure of compound **9a** showed a superstructure with two independent complexes in the asymmetric unit of the cell in space group $P\bar{1}$. A check for higher symmetry with PLATON[82] indicated a monoclinic I lattice with one independent molecule, in the monoclinic space group $I2/a$; however, the refinement resulted in heavy disorder of the SiEt$_3$ group and very bad R values. Thus, we decided to refine the independent complexes in the triclinic space group $P\bar{1}$. The relatively bad R values may result from the bad quality of the crystal, which had to be cut from an intergrown aggregate with tiny intrusions.

The tiny needlelike crystal of compound **10b** had poor quality comparable to that of **9a**. Furthermore, heavy disorder of the Si^{i}Pr$_3$ group was found. A total of 23 distance restraints was necessary to stabilize the refinement, using EADP and PART instructions of SHELXL-97.[83] There was only one example of a crystal worth using for the X-ray experiment. In the final refinement it was necessary to fix the y coordinates of the disordered atoms C152 and C172 to achieve convergence.

Compound [**11a**]$^+$ crystallized in the monoclinic space group $P2_1/m$; a center of inversion was found in the middle of the interconnecting C4 group, and therefore only half of the complex had to be refined. Unfortunately, the structure not only is merohedrically twinned but also shows heavy disorder of the PF$_6$ counterion and of the SiEt$_3$ moiety. The twin matrix (001, 010, 100) was applied (the twin ratio was finally about 1:1). Two dichloromethane solvent molecules cocrystallized with the structure. A total of 36 distance restraints was used for the PF$_6$ group. Many difference electron density calculations were necessary to localize the SiEt$_3$ carbon atoms. A total of 12 distance restraints was used for PART 1 of these disordered atoms, and for PART 2 the SAME instruction of SHELXL-97[83] was applied to stabilize the refinement. Many FREE instructions were necessary to calculate the positions of H atoms of the disordered ethyl groups. A total of 64 distance restraints were finally used in the refinement.

All structures were solved with the Patterson method of SHELXS-97[84] and refined with SHELXL-97. The program PLATON[82] was used to complete the structures and check for possible higher symmetry.

Acknowledgment. Funding from the Swiss National Science Foundation (SNSF) and from the University of Zürich is gratefully acknowledged.

Supporting Information Available: Crystallographic data for the structures given in this paper are given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) have also been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC 251110, 251111, 251112, 251113, 251114, 251115, 251116, and 251117. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336033; e-mail, deposit@ccdc.cam.ac.uk).

OM049252P