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Carbon−Carbon Bonds of Manganese Half-Sandwich Complexes for Electron Reservoir Functions

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Summary: Vinylidene species of the type $Mn(C_5H_4CH_3)[(H_3C)_2PCH_2CH_2P(CH_3)_2]({=}C{=}CR^1R^2)$ ($R^1 = R^2 = H$; $R^1 = H$, $R^2 = Ph$) *can be fully reversibly coupled to yield the dinuclear complexes* $[(C_5H_4CH_3)(dmpe)Mn{\equiv}CC(R^1)(R^2)C(R^1)(R^2)C{\equiv}Mn(dmpe)(C_5H_4CH_3)][PF_6]_2$ (R^1, $R^2 = H$; $R^1 = H$, $R^2 = Ph$) *by an oxidation/reduction cycle involving formation and cleavage of a C−C σ bond.*

Two complementary electron-storing and -releasing units are the fundamental constituents of storage cells.[1] Coupling a metal and an independent electron reservoir in the same molecule opens attractive perspectives in the design of molecules devoted to energy (molecular batteries) or for a functioning mode in charge storage different from that in photosystem II.[2] One could certainly envisage the possibility of utilizing the process of formation and cleavage of chemical bonds for this purpose. This would allow one to make electrons available 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. The reductive or the oxidative coupling and their reverse, which are well-known classes of reactions in organometallic chemistry, can be used for the formation and cleavage of bonds. It is very evident that we must pass through a mechanism which involves reductive or oxidative coupling and the reverse decoupling.[3] Many cases are known which operate in at least one direction,[4] while very few systems exhibit reactions in both directions; one such system was reported by Floriani and coworkers.[5] Herein, we report novel half-sandwich manganese(I) systems which undergo facile oxidative coupling and the reverse reductive decoupling, which might be utilized in electron storage devices.

We have recently reported the chemistry and reactivity of Mn^{II} and Mn^{III} half-sandwich $Me_2PCH_2CH_2PMe_2$ (dmpe) alkynyl complexes and their conversion to Mn^I vinylidene species.[6a−c] The first conclusion of this study was that vinylidene complexes gained considerably in stability through the presence of the bis(dimethylphosphino)ethane ligand (dmpe) in comparison with the reported CO-substituted species $Mn(Cp)L^1L^2(C{=}CR_2)$, where $L^1 = L^2 =$ CO, PR_3 or $L^1 =$ CO, $L^2 = PR_3$.[6d] A common method to obtain vinylidene complexes makes use of the high propensity of terminal acetylide derivatives to rearrange to vinylidene compounds.[6e,f,7] For such a process to be initiated in half-sandwich Mn^I chemistry,

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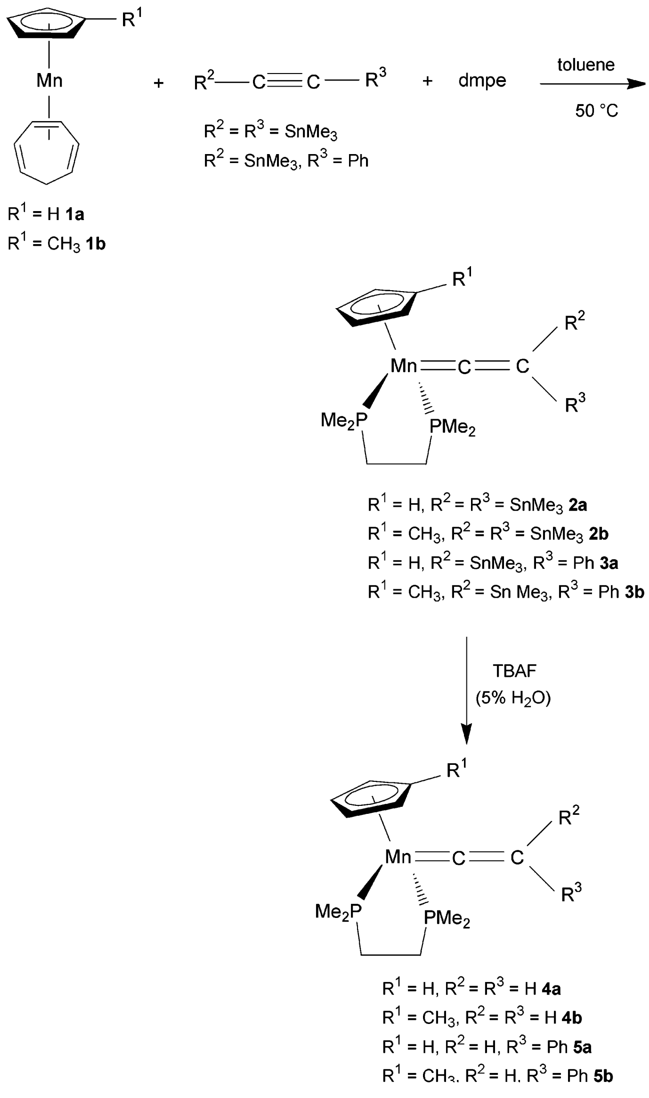
Scheme 1



we believed the complexes $\mathrm{Mn(C_5H_4R^1)}$(η^6-cycloheptatriene) ($\mathrm{R^1}$ = H (**1a**), $\mathrm{CH_3}$ (**1b**))[8a] to be excellent starting materials, since facile cycloheptatriene exchange was expected to occur with electron donor ligands, such as phosphines or acetylenes.[8b] Reactions with mono- or disubstituted tin acetylides were anticipated to then lead to the desired vinylidene species. Indeed, the reaction of $\mathrm{Mn(C_5H_4R^1)}$(η^6-cycloheptatriene) ($\mathrm{R^1}$ = H (**1a**), $\mathrm{CH_3}$ (**1b**)) with $\mathrm{R^2C{\equiv}CR^3}$ ($\mathrm{R^2 = R^3 = SnMe_3}$; $\mathrm{R^2 = SnMe_3}$, $\mathrm{R^3}$ = Ph) and dmpe at 50 °C for 3 h gave corresponding vinylidene complexes of the type $\mathrm{Mn(C_5H_4R^1)((H_3C)_2PCH_2CH_2P(CH_3)_2)({=}C{=}CR^2R^3)}$ ($\mathrm{R^1}$ = H, $\mathrm{R^2 = R^3 = SnMe_3}$, **2a**; $\mathrm{R^1 = CH_3}$, $\mathrm{R^2 = R^3 = SnMe_3}$, **2b**; $\mathrm{R^1}$ = H, $\mathrm{R^2 = SnMe_3}$, $\mathrm{R^3}$ = Ph, **3a**; $\mathrm{R^1 = CH_3}$, $\mathrm{R^2 = SnMe_3}$, $\mathrm{R^3}$ = Ph, **3b**) in quantitative yield (Scheme 1).

This reaction appears to require the initial formation of a Mn−alkyne species.[7a] However, NMR studies of the reaction carried out in the range of −70 to 20 °C did not reveal any intermediate. The ^{13}C NMR spectra of complexes **2** and **3** show the $\mathrm{C_\alpha}$ and the $\mathrm{C_\beta}$ resonances at around 321 and 114 ppm, respectively. The ^{31}P NMR resonances appear between 92 and 93 ppm and are thus comparable to those which were observed for the related $\mathrm{Mn(C_5H_4R^1)((H_3C)_2PCH_2CH_2P(CH_3)_2)({=}C{=}CRH)}$ complexes.[6c,7a,8c,d] The resonances corresponding to the trimethyltin groups were observed at high field as a triplet between −16 and −20 ppm in the ^{119}Sn NMR spectra. Complexes **2a** and **2b** constitute the first examples of half-sandwich manganese(I) vinylidene complexes with terminal $\mathrm{SnMe_3}$ groups. The X-ray structure analysis of **2a** (Figure 1) confirms the double-bond character of the two bonds (Mn2−C3 = 1.790(6) Å and C3−C4 = 1.310(8) Å).[6c]

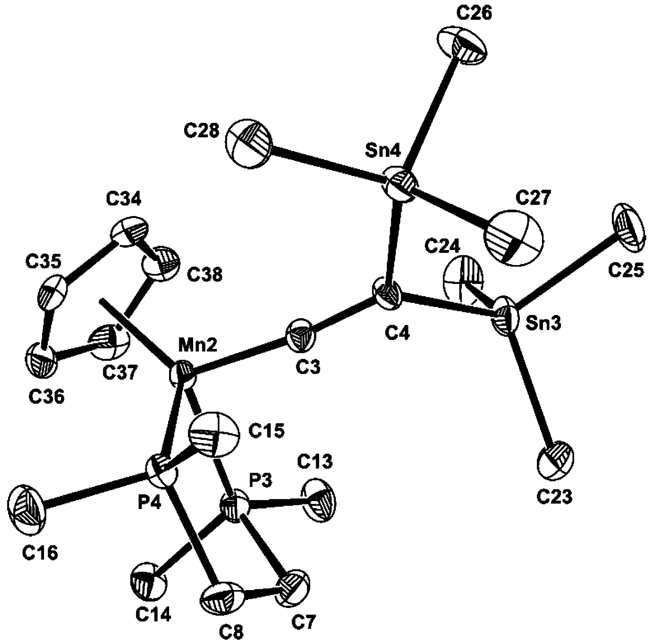


Figure 1. Molecular structure of **2a** (30% probability displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Mn2−C3 = 1.790(6), C3−C4 = 1.310(8), C4−Sn2 = 2.126(6), Mn2−P4 = 2.183(18); C4−C3−Mn2 = 172.5(5), C3−C4−Sn1 = 120.2(4), Sn1−C4−Sn2 = 120.7(3). Hydrogen atoms are omitted for clarity.

It has been observed earlier[6d] that the substituents on the β-carbon of the vinylidene complexes have a great effect on the stability of these complexes and also on the further reactivity. The reactions of the species $\mathrm{Mn(C_5H_4R^1)((H_3C)_2PCH_2CH_2P(CH_3)_2)({=}C{=}CR^2R^3)}$ ($\mathrm{R^1}$ = H, $\mathrm{R^2 = R^3 = SnMe_3}$, **2a**; $\mathrm{R^1 = CH_3}$, $\mathrm{R^2 = R^3 = SnMe_3}$, **2b**; $\mathrm{R^1}$ = H, $\mathrm{R^2 = SnMe_3}$, $\mathrm{R^3}$ = Ph, **3a**; $\mathrm{R^1 = CH_3}$, $\mathrm{R^2 = SnMe_3}$, $\mathrm{R^3}$ = Ph, **3b**) with 1 equiv of $\mathrm{[Bu_4N]F}$ (containing 5% $\mathrm{H_2O}$) yielded the deprotected species $\mathrm{Mn(C_5H_4R^1)((H_3C)_2PCH_2CH_2P(CH_3)_2)({=}C{=}CR^2R^3)}$ ($\mathrm{R^1}$ = H, $\mathrm{R^2 = R^3}$ = H, **4a**; $\mathrm{R^1 = CH_3}$, $\mathrm{R^2 = R^3}$ = H, **4b**; $\mathrm{R^1}$ = H, $\mathrm{R^2}$ = H, $\mathrm{R^3}$ = Ph, **5a**; $\mathrm{R^1 = CH_3}$, $\mathrm{R^2}$ = H, $\mathrm{R^3}$ = Ph, **5b**) by the nucleophilic substitution of the $\mathrm{SnMe_3}$ groups (Scheme 1). Complexes **4a** and **4b** constitute the finest examples of thermally stable half-sandwich Mn(I) vinylidene complexes with phosphine ligands and two H atoms on the $\mathrm{C_\beta}$ atom. The structure of **4a** was confirmed by X-ray diffraction analysis (Figure 2).

The Mn1−C1 and C1−C2 bond distances are 1.755(3) and 1.316(4) Å, similar to those of **2a**. A major route to dinuclear manganese systems bearing cumu-

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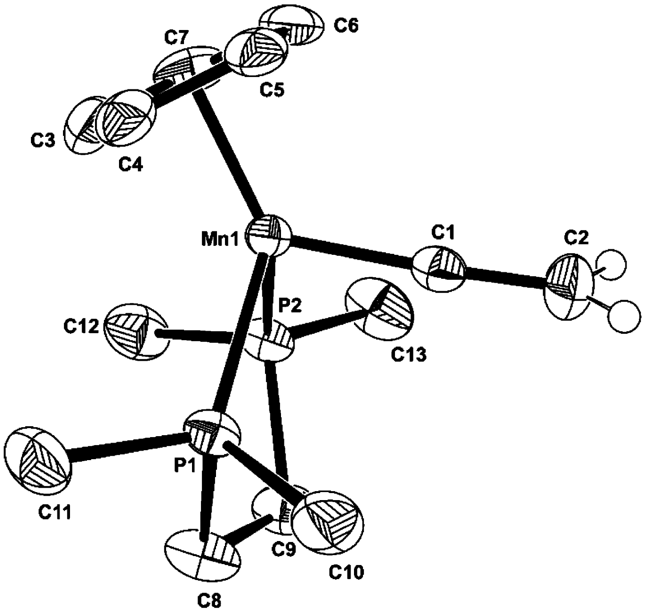
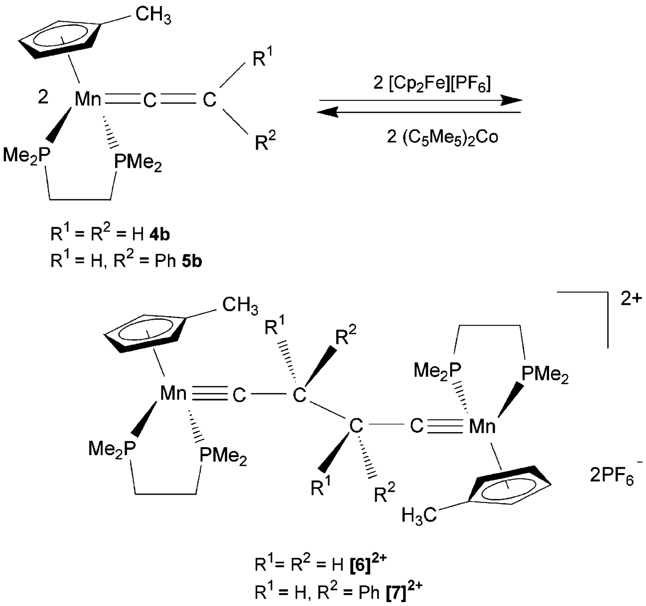


Figure 2. Molecular structure of **4a** (30% probability displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Mn1−C1 = 1.755(3), C1−C2 = 1.316(4); C2−C1−Mn1 = 176.6(3). Selective hydrogen atoms are omitted for clarity.

Scheme 2



lene bridges utilizes coupling processes of appropriate mononuclear species.[6b,c,8c,d,9] Oxidation of complexes **4b** and **5b** with 1 equiv of $[Cp_2Fe][PF_6]$ in CH_2Cl_2 after 1 h yielded the corresponding dinuclear carbyne complex $[(C_5H_4CH_3)(dmpe)Mn{\equiv}CC(R^1)(R^2)C(R^1)(R^2)C{\equiv}Mn(dmpe)(C_5H_4CH_3)][PF_6]_2$ (R^1, R^2 = H, $[\mathbf{6}]^{2+}$; R^1 = H, R^2 = Ph, $[\mathbf{7}]^{2+}$), which is the obvious coupling product (Scheme 2). The oxidation of **5b** to $[\mathbf{7}]^{2+}$ gives specifically a meso (*R,S*) diastereomer, which has been characterized spectroscopically and crystallographically. This selectivity might arise from an appropriate sterically enforced transition state. The ^1H NMR spectrum shows a characteristic multiplet signal at 2.72 ppm ($[\mathbf{6}]^{2+}$) and 4.39 ppm ($[\mathbf{7}]^{2+}$). The ^{31}P NMR resonances appear at 81.1 ppm for the dmpe ligand and at −145.4 ppm for the $[PF_6]$ anion. Additionally, the ^{13}C NMR shows C_α around 330.0 ppm and C_β at 46.4 ppm, which is characteristic for these kinds of carbyne complexes.[8c,d] The formation of complexes $[\mathbf{6}]^{2+}$ and $[\mathbf{7}]^{2+}$ implies highly selective oxidative C−C coupling processes starting from mononuclear cationic radicals as intermediates. Oxidation of complexes **4a** and **5a** with 1 equiv of $[Cp_2Fe][PF_6]$ in CH_2Cl_2 was much less selective and yielded after 1 h complicated mixtures containing the corresponding dinuclear carbyne complex $[(C_5H_5)(dmpe)Mn{\equiv}CC(R^1)(R^2)C(R^1)(R^2)C{\equiv}Mn(dmpe)(C_5H_5)][PF_6]_2$ (R^1, R^2 = H; R^1 = H, R^2 = Ph). However, their separation could not be accomplished. DFT calculations[10] on the model compound $[\mathbf{4b}\text{-H}]^{\bullet+}$ simulating a mononuclear cationic radical system with the dHpe ligand instead of dmpe showed spin densities of +0.98α and +0.37α located at the manganese and the C_β atoms, respectively. The high probability of finding the unpaired electron of the system on the terminal carbon atom corroborates with the fact of generating a C−C-coupled dinuclear product. Furthermore, single-point calculations including a model for solvation effects performed on the gas-phase geometries led to a dimerization energy ΔE of −24.2 kcal/mol ($\Delta E = 2E_{\text{monomer}} - E_{\text{dimer}}$). The detailed analysis shows that a major part of the driving force for this process consists not only of the energy for the formation of the new σ bond but also of the great solvation energy for the dinuclear dicationic model system, calculated to be −240.9 vs 2 × −57.9 kJ/mol of the mononuclear system. Major counteracting energetic contributions stem from the loss of the vinylidene double bonds. The structures of $[\mathbf{6}]^{2+}$ (Figure 3) and $[\mathbf{7}]^{2+}$ were confirmed by X-ray diffraction analyses.

It is worth mentioning that the C1−C2 distances of both compounds are on the short side of a C−C single bond, presumably reflecting a residual double-bond character, while the newly formed C−C bond would correspond to a “real” single bond. The cyclic voltammetry studies of **4b** and **5b** 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 oxidized, and thus, the whole process turns out to be quasi-reversible.

The reduction of the dinuclear carbyne complexes $[\mathbf{6}]^{2+}$ and $[\mathbf{7}]^{2+}$ with Cp^*_2Co yielded the corresponding mononuclear vinylidene complexes **4b** and **5b** in quantitative yield. The reversibility of this process can be

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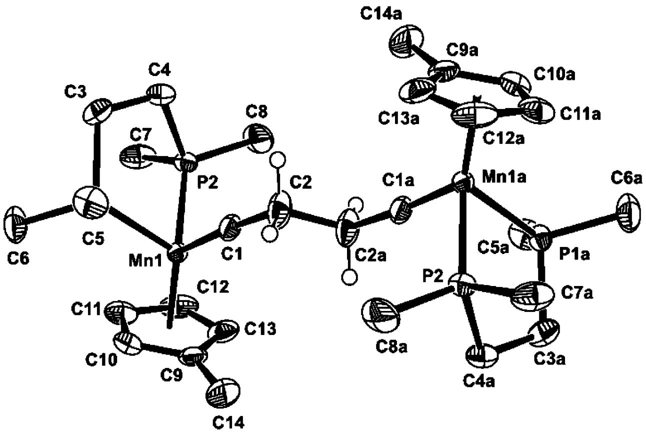

Figure 3. Molecular structure of [**6**]$^{2+}$ (50% probability displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Mn1−C1 = 1.655(3), C1−C2 = 1.463(4), C(2)−C(2a) = 1.509(6); C(2)−C(1)−Mn(1) = 114.4(3), C(1)−C(2)−C(2a) = 127.1(4). Selected hydrogen atoms and the PF_6^- anions are omitted for clarity.

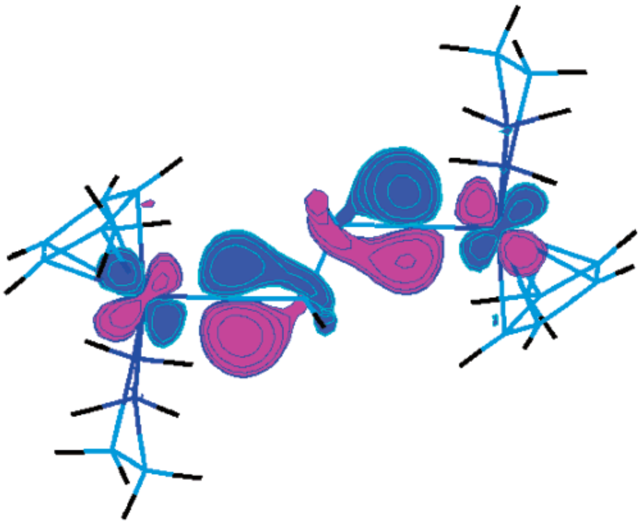

Figure 4. Calculated LUMO of the dinuclear model complex [**6**-H]$^{2+}$, showing the π-type antibonding interactions between Mn and C_α and between C_β and $C_{\beta'}$.

explained and is highlighted by the shape of the LUMO of the low-spin dinuclear model complex [**6**-H]$^{2+}$ (Figure 4).

The vacant orbital is mainly of π-type antibonding character between Mn and C_α and σ-antibonding between C_β and $C_{\beta'}$. The reduction of the dinuclear compound resulting formally from an addition of two electrons into the LUMO destabilizes the $Mn{\equiv}C_\alpha$ and the $C_\beta{-}C_{\beta'}$ bonds and leads back to the mononuclear vinylidene systems. The oxidation−reduction process for the vinylidene complexes of the type $Mn(C_5H_4R^1)(Me_2PCH_2CH_2PMe_2)({=}C{=}CR^2R^3)$ ($R^1 = CH_3$, $R^2 = R^3 = H$, **4b**; $R^1 = CH_3$, $R^2 = Ph$, $R^3 = H$, **5b**) can be summarized as processes involving reversible C−C σ-bond formation (Scheme 2).

Occurrence of such a reaction 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.

In conclusion, this study highlights the potential of utilizing the ubiquitous C−C bonds in organometallic systems as electron reservoirs,[11] thereby allowing further development of molecular batteries which could find application as components in nanodevices.

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Supporting Information Available: Text, figures, and tables giving experimental details, computational details, and crystallographic data of [**7**]$^{2+}$; crystallographic data are also given in a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Crystal structure data are as follows. **2a**: $C_{19}H_{39}MnP_2Sn_2$, $M_r = 621.76$, red, triclinic, space group $P\bar{1}$, $a = 9.6423(7)$ Å, $b = 13.8440(10)$ Å, $c = 21.3211(16)$ Å, $\alpha = 101.095(9)°$, $\beta = 93.364(8)°$, $\gamma = 108.495(8)°$, $V = 2626.7(3)$ Å^3, $T = 223(2)$ K, $Z = 4$, $d = 1.572$ g cm^{-3}, 14 248 independent reflections (Mo Kα; $2\theta_{max} = 60.84°$), $R_{int} = 0.1492$, R1 = 0.0499, wR2 = 0.1239 (7936 reflections, $I > 2\sigma(I)$) and R1 = 0.0886, wR2 = 0.1436 (all data), GOF(F^2) = 0.745. **4a**: $C_{13}H_{23}MnP_2$, $M_r = 296.19$, red, orthorhombic, space group *Pcab* (No. 61), $a = 12.2933(6)$ Å, $b = 13.3410(7)$ Å, $c = 18.5494(7)$ Å, $\alpha = \beta = \gamma = 90.0°$, $V = 3042.2(2)$ Å^3, $T = 183(2)$ K, $Z = 8$, $d = 1.293$ g cm^{-3}, 3680 independent reflections (Mo Kα; $2\theta_{max} = 56.14°$), $R_{int} = 0.0762$, R1 = 0.0358, wR2 = 0.0797 (2294 reflections, $I > 2\sigma(I)$) and R1 = 0.0604, wR2 = 0.0843 (all data), GOF(F^2) = 0.888. [**6**]$^{2+}$: $C_{28}H_{50}F_{12}Mn_2P_6$, $M_r = 910.38$, red, orthorhombic, space group *Pbca* (No. 61), $a = 14.4052(7)$ Å, $b = 17.1481(9)$ Å, $c = 15.9240(9)$ Å, $\alpha = \beta = \gamma = 90.0°$, $V = 3933.6(4)$ Å^3, $T = 183(2)$ K, $Z = 4$, $d = 1.537$ g cm^{-3}, 2879 independent reflections (Mo Kα; $2\theta_{max} = 60.68°$), $R_{int} = 0.0578$, R1 = 0.0386, wR2 = 0.0838 (3041 reflections, $I > 2\sigma(I)$) and R1 = 0.0823, wR2 = 0.0898 (all data), GOF(F^2) = 0.750. Data were collected on a Stoe IPDS diffractometer[13a] and structure solutions performed by using SHELXS-97.[13b] Refinement calculations were done with SHELXL-97.[13c]

(13) (a) STOE-IPDS Software package, Version 2.87 5/1998; STOE & Cie, GmbH, Darmstadt, Germany, 1998. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1996**, *46*, 467. (c) Sheldrick, G. M. SHELXL-97, Program for Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany. 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 212245, 212246, and 212247. 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).