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# Utilization of Redox and Acid/Base Chemistry for the Deprotection of a Mn(dmpe)$_2$(C≡CSiMe$_3$)$_2$ Complex

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The reaction of the low-spin d$^5$ complex Mn(dmpe)$_2$(C≡CSiMe$_3$)$_2$ (**1**) (dmpe = 1,2-bis(dimethylphosphino)ethane) with [NBu$_4$][Ph$_3$F$_2$M] (M = Si or Sn) yields the SiMe$_3$ metathesis products Mn(dmpe)$_2$(C≡CMPh$_3$)$_2$ (M = Si **2a**, Sn **2b**). When the Mn(II) species **1** was dissolved in MeOH in the presence of NaBF$_4$, disproportionation occurred with formation of the Mn(I) products Mn(dmpe)$_2$(C≡CSiMe$_3$)(C=CH$_2$) (**3a**) and [Mn(dmpe)$_2$(C≡CSiMe$_3$)(≡C−CH$_3$)][BF$_4$] (**5a**) and the cationic Mn(III) complex [Mn(dmpe)$_2$(C≡CSiMe$_3$)$_2$][BF$_6$] (**4a**). In a similar way **1** was transformed into [Mn(dmpe)$_2$(C≡CSiMe$_3$)$_2$][H$_2$F$_3$] (**4b**) and [Mn(dmpe)$_2$(C≡CSiMe$_3$)(≡C−CH$_3$)][H$_2$F$_3$] (**5b**) by its reaction with excess of HF·pyridine. The reaction of **1** with Li or Na in toluene at 100 °C gave the new d$^6$ *cis*-bisalkynyl complexes [Mn(dmpe)$_2$(C≡CSiMe$_3$)$_2$][M] (M = Li **6a**, Na **6b**). The *trans*-alkynylvinylidene derivatives Mn(dmpe)$_2$(C≡CSiMe$_3$)(C=C(E)SiMe$_3$) (E = H **3b**, SnMe$_3$ **3c**) were obtained by the reaction of species **6** with stoichiometric MeOH or ClSnMe$_3$. In MeOH/KOH solutions complex **3b** or **3c** was converted into the *trans*-alkynylvinylidene species **3a**. The reaction of complex **3a** with HBF$_4$ or HF·pyridine produced the carbyne complexes [Mn(dmpe)$_2$(C≡CSiMe$_3$)(≡C−CH$_3$)][A] (A = BF$_4$ **5a**, H$_2$F$_3$ **5b**). These new compounds have been characterized by NMR and IR spectroscopy and elemental analyses, and for **2a**, **2b**, **3a**, **4b**, and **6b** X-ray diffraction studies have been performed.

## Introduction

Transition metal complexes with two *trans* $\sigma$-alkynyl ligands may serve as building blocks in the controlled buildup of linear rodlike metal $\mu$-acetylide oligomers.[1] Such macromolecules have been prepared with precise lengths and topologies by stepwise approaches utilizing acetylenic C−C coupling methodologies.[2] Several *trans*-bisalkynyl complexes with metals of groups 8[3] and 10[4] are known, all of which form diamagnetic compounds. The use of group 7 metals such as manganese in +II or +III oxidation state is expected to lead in octahedral environment to paramagnetic *trans*-bisalkynyl complexes. These paramagnetic species exhibit electronic open shell configurations and should therefore be more polarizable, a fundamental requirement for electron-delocalized materials[5] and nonlinear optical materials.[6]

The first d$^5$ complexes of manganese, such as Mn(dmpe)$_2$X$_2$ (X= Br, Me), were reported by Wilkinson in 1983.[7] We have prepared Mn(dmpe)$_2$(C≡CR)$_2$ (R = SiMe$_3$, Ph) complexes making use of the reaction of (dmpe)$_2$MnBr$_2$ with 2 equiv of LiC≡CR[8] or alternatively by the reaction of (C$_5$H$_4$R)$_2$Mn (R = H or Me) with 2 equiv of terminal- or trimethyltin-substituted alkynes R′C≡CR (R′ = H, SnMe$_3$; R = SiMe$_3$, Ph) and 2 equiv of dmpe.[9] These *trans*-bisalkynyl Mn(II) complexes are

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[1] (a) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602. (b) Altmann, M.; Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 569. (c) Diederich, F.; Rubin, Y. *Angew. Chem., Int, Ed. Engl.* **1992**, *31*, 1101.

[2] Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178−180*, 431.

[3] (a) Albertin, G.; Antoniutti, S.; Bordignon, E.; Granzotto, M. *J. Organomet. Chem.* **1999**, *585*, 83. (b) Younus, M.; Long, N. J.; Raithby, P. R.; Lewis, J.; Page, N. A.; White, A. J. P.; Willians, D. J.; Colbert, M. C. B.; Hodge, A. J.; Khan, M. S.; Parker, D. G. *J. Organomet. Chem.* **1999**, *578*, 198. (c) Touchard, D.; Haquette, P.; Daridor, A.; Romero, A.; Dixneuf, P. H. *Organometallics* **1998**, *17*, 3844. (d) Lebreton, C.; Touchard, D.; Le Pichon, L.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *Inorg. Chim. Acta* **1998**, *272*, 188. (e) Touchard, D.; Haquette, P.; Guesmi, S.; Le Pichon, L.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 3640. (f) Jones, N. D.; Wolf, M. O.; Giaquinta, D. M. *Organometallics* **1997**, *16*, 1352. (g) McDonagh, A. M.; Cifuentes, M. P.; Whittal, I. R.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B.; Hockless, D. C. R. *J. Organomet. Chem.* **1996**, *526*, 99. (h) Field, L. D.; George, A. V.; Purches, G. R.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1996**, *9*, 2011. (i) Albertin, G.; Antoniutti, S.; Bordignon, E.; Cazzaro, F.; Ianelli, S.; Pelizzi, G. *Organometallics* **1995**, *14*, 4114. (j) Khan, M. S.; Kakkar, A. K.; Ingham, S. L.; Raithby, P. R.; Lewis, J.; Spencer, B.; Wittmann, F.; Friend, R. H. *J. Organomet. Chem.* **1994**, *472*, 247. (k) Atherton, Z.; Faulkner, C. W.; Ingham, S. L.; Kakkar, A. K.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1993**, *462*, 265. (l) Lewis, J.; Khan, M. S.; Kakkar, A. K.; Raithby, P. R.; Fuhrmann, K.; Friend, R. H. *J. Organomet. Chem.* **1992**, *433*, 135. (m) Touchard, D.; Haquette, P.; Pirio, N.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1993**, *12*, 3132. (n) Sun, Y.; Taylor, N. J.; Carty, A. J. *Organometallics* **1992**, *11*, 4293. (o) Field, L. D.; George, A. V.; Malouf, E. Y.; Slip, I. H. M.; Hambley, T. W. *Organometallics* **1991**, *10*, 3842.

[4] (a) Hissler, M.; Connick, W. B.; Geiger, D. K.; McGarrach, J. E.; Lipa, D.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2000**, *39*, 447. (b) Ara, I.; Falvello, L. R.; Fernández, S.; Forniés, J.; Lalinde, E.; Martín, A.; Moreno, M. T. *Organometallics* **1997**, *16*, 5923. (c) James, S. L.; Younus, M.; Raithby, P. R.; Lewis, J. *J. Organomet. Chem.* **1997**, *543*, 233. (d) Russo, M. V.; Furlani, A.; Altamura, P.; Fratoddi, I.; Polzonetti, G. *Polymer* **1997**, *38*, 3677. (e) Khan, M. S.; Davies, S. J.; Kakkar, A. K.; Schwartz, D.; Lin, B.; Jonhson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1992**, *424*, 87. (f) Lewis, J.; Khan, M. S.; Kakkar, A. K.; Johnson, B. F. G.; Marder, T. B.; Fyfe, H. B.; Wittmann, F.; Friend, R. H.; Dray, A. E. *J. Organomet. Chem.* **1992**, *425*, 165. (g) Kotani, S.; Shiina, K.; Sonogashira, K. *Appl. Organomet. Chem.* **1991**, *5*, 417.

[5] (a) Ward, M. D. *Chem. Soc. Rev.* **1995**, *24*, 121. (b) Astruc, D. *Acc. Chem. Res.* **1997**, *30*, 383. (c) McCleverty, J. A.; Ward, M. D. *Acc. Chem. Res.* **1998**, *31*, 842.

[6] Marder, S. R.; Gorman, C. B.; Meyers, F.; Perry, J. W.; Bourhill, G.; Brédas, J.-L.; Pierce, B. M. *Science* **1994**, *265*, 632.

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easily oxidized by ferrocenium hexafluorophosphate or tetrafluoroboric acid etherate, yielding the corresponding cationic Mn(III) species.[8] The mentioned *trans*-bisalkyl Mn(III) were also prepared by reaction of $Mn(acac)_3$ with $AlMe_3$ and dmpe.[10] A related binuclear species $[\{Mn(dmpe)_2I\}_2(\mu\text{-}C_4)]$ was obtained by the reaction of MnCp(dmpe)I with 0.5 equiv of $Me_3Sn{-}C{\equiv}C{-}C{\equiv}C{-}SnMe_3$ in the presence of dmpe. This Mn(II)/Mn(II) complex not only is strongly electron delocalized but also allows facile adjustment of its delocalized electrons through its redox properties. It can selectively and reversibly be oxidized to the corresponding Mn(II)/Mn(III) and Mn(III)/Mn(III) derivatives.[11]

To be able to go beyond dinuclear derivatives and to prepare oligomeric metal acetylide strands in a controlled way, it seemed necessary to have a synthetic methodology available, which would allow deprotection of silylalkynyl ligands in such complexes. Thus, a prototypical $Mn(dmpe)_2(C{\equiv}CSiMe_3)_2$[8] system (**1**) was selected to probe appropriate transformations affording $Mn(dmpe)_2(C{\equiv}CR)_2$ (R = H or $SnR_3$) or $Mn(dmpe)_2(C{\equiv}CSiMe_3)(C{=}CHR)$ (R = H or $SiMe_3$) with more reactive and readily exchangeable terminal groups. These species would indeed open up the possibilities for a step by step buildup of the described oligonuclear units via Mn−C bond formations as they were achieved in our group[9,11] or by oxidative carbon−carbon coupling processes.[12]

## Results and Discussion

**Direct Desilylation of Complex 1.** One of the most common reagents used for the deprotection of trimethylsilylalkynylmetal complexes is $NBu_4F$ (TBAF).[13] $^1H$ NMR studies of the reaction of **1** with commercially available TBAF revealed that there is no reaction at room temperature and that at 60 °C complete decomposition occurred within 5 min. These unsuccessful attempts made us aware of the fact that in some related cases TBAF was not capable of removing the $SiMe_3$ groups from organometallic acetylenic moieties.[14] One of the possible reasons for this behavior could be that TBAF always contains water,[15] which might hamper the initial attack of $F^-$ on the Si atom in certain less reactive systems. For this reason we looked first for completely aprotic desilylation alternatives.

$[NBu_4][Ph_3F_2M]$, where M = Si[16a] or Sn,[16b] have indeed been proposed as versatile anhydrous $F^-$ ion sources. When the reaction of **1** with an excess of $[NBu_4][Ph_3F_2Si]$ was carried out in THF, no reaction was observed at room temperature, but under more forcing conditions, heating at 90 °C for 7 days, it was possible to obtain the corresponding metathesis product $Mn(dmpe)_2(C{\equiv}CSiPh_3)_2$ (**2a**) in 80% yield. When the related transformation using $[NBu_4][Ph_3F_2Sn]$ was attempted, a dark solid was produced after 14 days at 90 °C. The reaction mixture did not show remaining complex **1**. The expected compound $Mn(dmpe)_2(C{\equiv}CSnPh_3)_2$ (**2b**) could be extracted, however in only low yields of 30%. Both complexes **2** were isolated as yellow crystalline compounds. The $^1H$ NMR spectra of **2** at room temperature exhibit in either case two broad resonances for the dmpe methyl and methylene protons at around $\delta$ −15 and −14 ppm, characteristic for $Mn(dmpe)_2(C{\equiv}CR)_2$ species,[8] and three broad signals for the $C_6H_5$ protons. $^{31}P$ NMR resonances were not observable, presumably because of the line broadening induced by the too close proximity of the phosphorus nuclei to the paramagnetic Mn(II) center.[8]

Even though the reaction to **2a** proceeded quite satisfactory, **2a** itself seemed to be of limited value, since as a silyl derivative comparable to **1** it was expected to have similar disadvantages in the above-mentioned oligomer buildup strategy. Principally **2b** appeared to be much more useful for this purpose. However, the low yield obtained for it and the long reaction time for its formation were considered of too great a disadvantage to further pursue the optimization of its preparation.

Therefore the protic reagent KF/MeOH has been additionally considered, which was expected to lead to reactive terminal acetylene derivatives.[17] When the reaction of **1** with KF was performed in dry MeOH, the diamagnetic Mn(I) *trans*-alkynylvinylidene complex $Mn(dmpe)_2(C{\equiv}CSiMe_3)(C{=}CH_2)$ (**3a)** was isolated as a yellow crystalline solid in 38% yield together with an intractable insoluble solid. Compound **3a** is the first example of a manganese complex stable at room temperature bearing the parent vinylidene unit. The only other literature-reported Mn compound with an unsubstituted vinylidene ligand is $CpMn(CO)_2({=}C{=}CH_2)$, which was quite unstable and could be observed in solution at −50 °C.[18]

As it finally turned out, the presence of the $F^-$ ion is apparently not essential and the same results were obtained using MeOH/KOH. However, when the reaction of **1** was carried out with MeOH alone, first established by an NMR pursuit in $CD_3OD$, this transformation revealed that not only **3a** is formed but also

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(7) (a) Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 6752. (b) Howard, C. G.; Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 2631. (c) Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 1339.

(8) Krivykh, V. V.; Eremenko, I. L.; Veghini, D.; Petrunenko, I. A.; Pountney, D. L.; Unseld, D.; Berke, H. *J. Organomet. Chem.* **1996**, *511*, 111.

(9) Unseld, D.; Krivykh, V. V.; Heinze, K.; Wild, F.; Artus, G.; Schmalle; H.; Berke, H. *Organometallics* **1999**, *18*, 1525.

(10) Komiya, S.; Kimura, T.; Kaneda, M. *Organometallics* **1991**, *10*, 1311.

(11) Kheradmandan, S.; Heinze, K.; Schmalle, H.; Berke, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 2270.

(12) (a) Eglinton, G.; McCrae, W. *Adv. Org. Chem.* **1963**, *4*, 225. (b) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 2632.

(13) (a) Wong, A.; Kang, P. C. W.; Tagge, C. D.; Leon, D. R. *Organometallics* **1990**, *9*, 1992. (b) Lavastre, O.; Even, M.; Dixneuf, P. H.; Pacreau, A.; Vairon, J.-P. *Organometallics* **1996**, *15*, 1530. (c) Dembinski, R.; Lis, T.; Szafert, S.; Mayne, C. L.; Bartik, T.; Gladysz, J. A. *J. Organomet. Chem.* **1999**, *578*, 229.

(14) Garcia-Yebra, C.; Lopez-Mardomingo, C.; Fajardo, M.; Antiñolo, A.; Otero, A.; Rodriguez, A.; Vallat, A.; Lucas, D.; Mugnier, Y.; Carbó, J. J.; Lledós, A.; Bo, C. *Organometallics* **2000**, *19*, 1749.

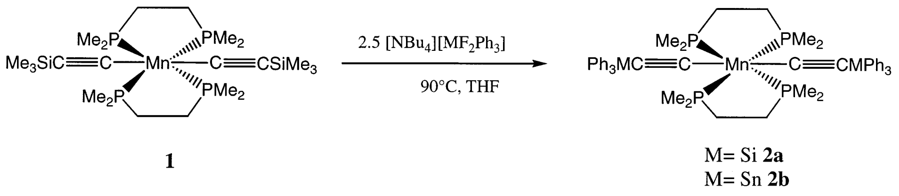
(15) (a) Clark, J. H. *J. Chem. Soc., Chem. Commun.* **1978**, 789. (b) Sharma, R. K.; Fry, J. L. *J. Org. Chem.* **1983**, *48*, 2112 (c) Cox, D. P.; Terpinski, J.; Lawrynowicz, W. *J. Org. Chem.* **1984**, *49*, 3216.

(16) (a) Pilcher, A. S.; Ammon, H. L.; DeShong, P. *J. Am. Chem. Soc.* **1995**, *117*, 5166. (b) Gingras, M. *Tetrahedron Lett.* **1991**, *32*, 7381.

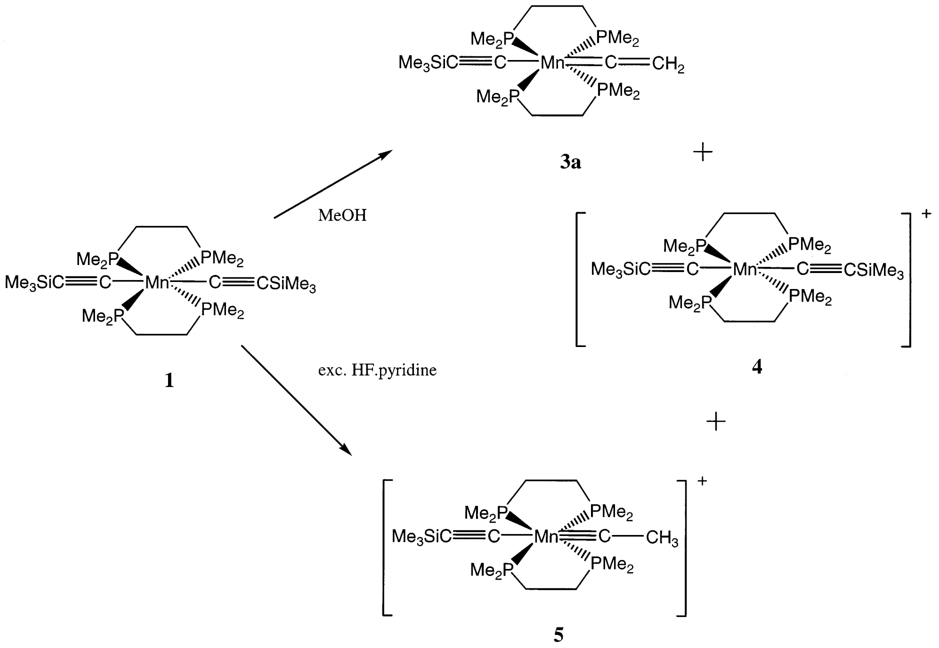
(17) (a) Hartbaum, C.; Fischer, H. *Chem. Ber.-Rec.* **1997**, *130*, 1063. (b) Cambridge, J.; Choudhary, A.; Friend, J.; Garg, R.; Hill, G.; Hussain, Z. I.; Lovett, S. M.; Whiteley, M. W. *J. Organomet. Chem.* **1999**, *577*, 249. (c) Bruce, M. I.; Hall, B. C.; Kelly, B. D.; Low, P. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1999**, *21*, 3719.

(18) Terry, M. R.; Mercando, L. A.; Kelley, C.; Geoffroy, G. L.; Nombel, P.; Lugan, N.; Mathieu, R.; Ostrander, R. L.; Owens-Waltermire, B. E.; Rheingold, A. L. *Organometallics* **1994**, *13*, 843.

**Scheme 1**



**Scheme 2**



the cationic species $[Mn(dmpe)_2(C{\equiv}CSiMe_3)_2]^+$ (**4**) and a carbyne complex $[Mn(dmpe)_2(C{\equiv}CSiMe_3)({\equiv}C{-}Me)]^+$ (**5**). These latter two compounds were isolated as $BF_4^-$ salts in 35% (**4a**) and 10% (**5a**) yield by adding $NaBF_4$ to the MeOH solution of **1**. Protic conditions apparently change the course of the reaction, inducing disproportionation of the Mn(II) starting material.

Protic conditions with enforced acidity are provided by the HF·pyridine reagent.[19] The reaction of **1** with excess of HF·pyridine proceeded smoothly and gave a mixture of two complexes, in which the Mn(III) complex $[Mn(dmpe)_2(C{\equiv}CSiMe_3)_2][H_2F_3]$ (**4b**) was identified together with the cationic carbyne complex $[Mn(dmpe)_2(C{\equiv}CSiMe_3)({\equiv}C\text{-}Me)][H_2F_3]$ (**5b**) in about 50% NMR yields each. The $^1H$ NMR spectrum of the cationic moiety in **4b** is similar to that reported for complex **4a**.[8] For the $[H_2F_3]^-$ anion a broad resonance was observed at $\delta$ 13.8 ppm.[20] The structure proposed for **4b** was confirmed by spectroscopic means and by an X-ray diffraction study.

The HF·pyridine reaction again demonstrates disproportionation of the Mn(II) species **1**. This behavior is also reflected in the CV derived comproportionation equilibrium in acetonitrile (vide infra). On the basis of the equilibrium constant we can predict that only low but chemically relevant equilibrium amounts of **4** and **6** are present together with the Mn(II) species **1**. It can be anticipated that disproportionation may also occur in other polar solvents than the CV applied acetonitrile. It would be reasonable to assume that in the presence of electrophiles the most nucleophilic disproportionation product, the Mn(I) derivative **6**, could be attacked by a proton and thus be withdrawn from the equilibrium (Scheme 3). As we will see later, **6** can be prepared independently and indeed reacts with stoichiometric MeOH to afford the Mn(I) complex $Mn(dmpe)_2(C{\equiv}CSiMe_3)(C{=}C(SiMe_3)H)$ (**3b**). In an excess of MeOH further desilylation to **3a** is observed. The ultimate formation of the carbyne complex **5b** can then be explained through further protonation of species **3a** occurring in more acidic media. The cationic Mn(III) component **4** remains in the reaction mixture, and both complexes **4b** and **5b** were isolated as the $H_2F_3^-$ salts in the presence of an excess of HF·pyridine. In basic medium species **4** is not stable and is converted into an insoluble residue.[21]

The $\beta$-carbon atom of complex **3a** can also be directly reacted with $HBF_4$ or HF·pyridine to yield quantitatively the corresponding cationic carbyne complexes $[Mn(dmpe)_2(C{\equiv}CSiMe_3)({\equiv}C{-}CH_3)][A]$ ($A^- = BF_4^-$ **5a**, $H_2F_3^-$ **5b**). The anion has a great influence on the solubility of these species. **5b** is generally more soluble than **5a**. The latter can be dissolved only in polar or ionizing solvents such as $CH_2Cl_2$. Complexes **5** are diamagnetic, as could be expected for $d^6$ Mn(I) compounds. Characteristic NMR data are the $^{13}C$ carbyne resonance, which appears at $\delta$ 314 ppm, and the $C_\alpha$, $C_\beta$ signals of the alkynyl ligand, which are observed at $\delta$

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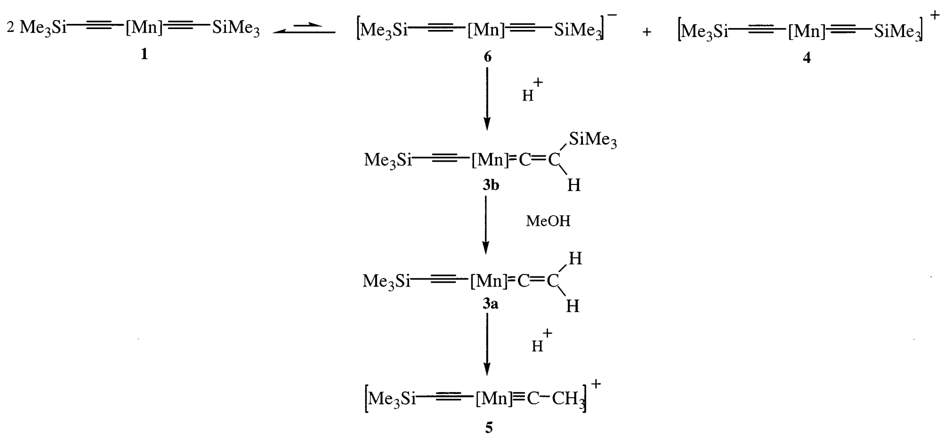
[19] Eddarir, S.; Mestdagh, H.; Rolando, C. *Tetrahedron Lett.* **1991**, *32*, 69.

[20] Cousseau, J.; Albert, P. *Bull. Soc. Chim. Fr.* **1986**, 910.

[21] Fernández, F. J.; Berke, H. Unpublished results.

**Scheme 3**



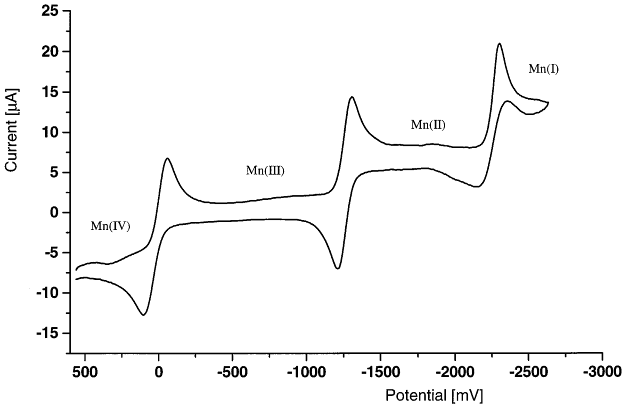


**Figure 1.** Cyclic voltammogram of **6a** ($10^{-3}$ M in MeCN, n-Bu$_4$NPF$_6$/MeCN; vs Fc/Fc$^+$; 0.5 V s$^{-1}$).

145.8 and 126.7 ppm, respectively. The $^{31}$P NMR spectrum of both species **5** displays a signal at 58.6 ppm. It should furthermore be noted that they are stable at room temperature for short periods of time. This stability is in marked contrast to that observed for the CO-substituted cationic carbyne complexes [Mn(Cp)(CO)$_2$(≡C−CH$_2$R)]$^+$ reported by (R = H) Fischer [22] and (R = Me, Ph) Geoffroy,[18] which were stable only at low temperature.

**Cyclic Voltammetry (CV) Studies of [Mn(dmpe)$_2$-(C≡CSiMe$_3$)$_2$][BF$_4$] (4a).** Inspired by the above disproportionation behavior of **1** to yield the Mn(III) complex [Mn(dmpe)$_2$(C≡CSiMe$_3$)$_2$]$^+$ (**4**) and the Mn(I) species [Mn(dmpe)$_2$(C≡CSiMe$_3$)$_2$]$^-$ (**6**), we envisaged studying the quantitative redox properties of **4a** applying CV (Figure 1).

Two fully reversible redox couples were found at $E_{1/2} = +0.22$ and $-1.26$ V vs Fc/Fc$^+$ ($\Delta E_p = 0.070$ V and $i_{pa}/i_{pc} \approx 1$ for scan rates of 0.100−0.500 V s$^{-1}$) in acetonitrile at 25 °C corresponding to Mn(IV)/Mn(III) and Mn(III)/Mn(II) reduction pairs.[8] A somewhat irreversible redox couple was identified at $E_{1/2} = -2.30$ V attributed to a Mn(II)/Mn(I) reduction. The irreversibility is presumably caused by protonation of the quite basic Mn(I) species by acetonitrile.

The comproportionation constant ($K_c = 10^{\Delta E/0.059\text{V}}$)[23] for the equilibrium Mn(I) + Mn(III) $\rightleftharpoons$ 2Mn(II) amounts to $4 \times 10^{17}$. This means that when starting from a single Mn(II) component, the ratio between the concentrations of Mn(II) and Mn(I) or Mn(III) is in the range of $7 \times 10^8$. Despite these, in absolute terms, quite low equilibrium concentrations of the Mn(III) and Mn(I) derivatives, they are still high enough to allow appropriate reactivity.

**Synthesis of Manganese(I) Species.** While the cationic bisalkynyl Mn(III) compounds were prepared earlier in good yields by the oxidation of the corresponding Mn(II) derivatives Mn(dmpe)$_2$(C≡CR)$_2$,[8] preparative access to the corresponding bisalkynyl Mn(I) anions has yet not been attempted. In this context it should be mentioned that several related half-sandwich monoalkynyl Mn(I) complexes of the type [MnCpL$_2$C≡CR]$^-$ (L = CO,[24] L = PPh$_3$[25]) have been reported.

The new d$^6$ *cis*-bisalkynyl manganese derivatives [Mn(dmpe)$_2$(C≡CSiMe$_3$)$_2$][M] (M = Li **6a**, Na **6b**) were prepared by reduction of **1** using Li or Na in toluene at 100 °C. These compounds were isolated in 80% yield as yellow crystalline solids. Complexes **6a** and **6b** are the first examples of anionic bisalkynyl Mn(I) species. Their $^1$H, $^{13}$C, and $^{31}$P NMR spectra are consistent with the indicated *cis*-alkynyl structures. The *cis* binding mode is presumably enforced by the alkali metal chelation found as a general structural motif in pincer complexes.[26] Both complexes **6** show two multiplets in the $^{13}$C NMR at $\delta \approx 210$ ppm (Mn−C) and in the range $\delta = 115-120$ ppm (≡C−Si), which are attributed to the alkynyl ligands. The $^{31}$P NMR spectrum of **6a** and **6b** complexes displays two broad temperature-independent signals at around 75 and 63 ppm. The $^7$Li NMR spectrum of **6a** in C$_6$D$_6$ exhibits a singlet at $\delta = 0.9$ ppm.

Species **6** are thermally stable, but very reactive. In the presence of electrophiles they are quantitatively transformed by C$_\beta$ attack into d$^6$ *trans*-alkynylvinylidene manganese complexes. The compounds Mn(dmpe)$_2$(C≡CSiMe$_3$)(C=C(E)SiMe$_3$) (E = H **3b**, SnMe$_3$

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[22] Fischer, E. O.; Clough, R. L.; Best, G.; Kreissl, F. R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 543.

[23] Kaim, W.; Klein, A.; Glöckle, M. *Acc. Chem. Res.* **2000**, *33*, 755.

[24] (a) Berke, H. *Z. Naturforsch.* **1980**, *35b*, 86. (b) Berke, H.; Huttner, G.; Von Seyerl, J. *J. Organomet, Chem.* **1981**, *218*, 193.

[25] (a) Lugan, N.; Kelley, C.; Terry, M. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1990**, *112*, 3220. (b) Kelley, C.; Lugan, N.; Terry, M. R.; Geoffroy, G. L.; Haggerty, B. S.; Rheingold, A. *J. Am. Chem. Soc.* **1992**, *114*, 6735. (c) Terry, M. R.; Kelley, C.; Lugan; N.; Geoffroy, G. L. *Organometallics* **1993**, *12*, 3607.

[26] (a) Hiller, J.; Varga, V.; Thewalt, U.; Mach, K. *Collect. Czech. Chem. Commun.* **1997**, *62*, 1446. (b) Back, S.; Gossage, R. A.; Lutz, M.; del Rio, I.; Spek, A. L.; Lang, H.; van Koten, G. *Organometallics* **2000**, *19*, 3926.

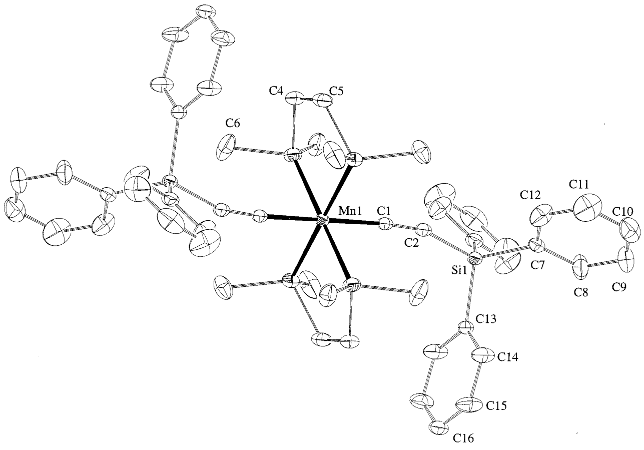


**Figure 2.** ORTEP plot of the structure of **2a**. The thermal ellipsoids are drawn at 30% probability. Disorder of the ethylene moieties and hydrogen atoms have been omitted for clarity.

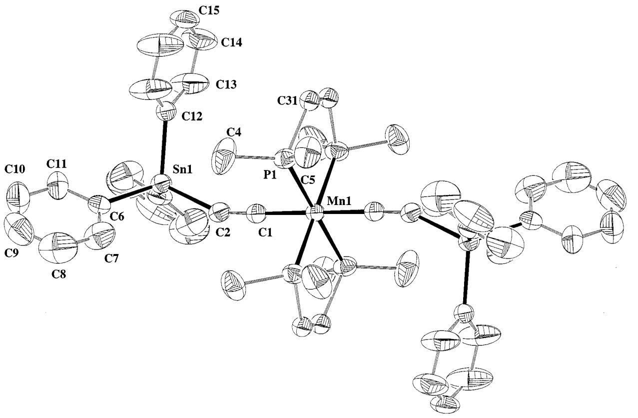
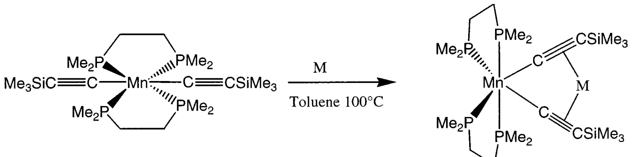


**Figure 3.** ORTEP plot of the structure of **2b**. The thermal ellipsoids are drawn at 50% probability, and hydrogen atoms have been omitted for clarity.

**Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 2a, 2b, and 4b**

| | 2a | 2b | 4b |
|---|---|---|---|
| Mn−P1 | 2.2682(6) | 2.256(6) | 2.3082(12) |
| Mn−P2 | 2.2682(6) | 2.281(6) | 2.3211(12) |
| C1−C2 | 1.227(4) | 1.236(8) | 1.237(8) |
| Mn−C1 | 1.971(3) | 1.962(6) | 1.958(4) |
| Mn−C1−C2 | 175.2(2) | 176.2(17) | 177.2(4) |
| C1−C2−Si | 162.8(2) | | 177.9(4) |
| C1−C2−Sn | | 157.5(6) | |

**Scheme 4**



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M = Li, **6a**
M = Na, **6b**

**3c**) could thus be isolated by the reaction of **6** with 1 equiv of dry MeOH or $ClSnMe_3$, respectively. Quite remarkable and yet unexplained is that no reaction of **6** occurred with $ClSiMe_3$. Compounds **3** were characterized as crystalline solids, yellow **3b** and green-yellow **3c**. In further conversions these complexes were reacted with a large excess of MeOH in the presence of KOH, to afford the yellow crystalline *trans*-alkynylvinylidene derivative $Mn(dmpe)_2(C{\equiv}CSiMe_3)(C{=}CH_2)$ (**3a**) in 80% yield.

The $^1H$, $^{13}C$, and $^{31}P$ NMR spectra of the alkynylvinylidene complexes **3** are consistent with the indicated pseudo-octahedral *trans* $C_2$ ligand structure. Examples of *trans*-alkynylvinylidene species have been reported for group 8[3i,27] and 9[28] metals, but complexes **3** are the first examples of *trans*-alkynylvinylidene group 7 compounds. The $^1H$ NMR spectra of **3** revealed characteristic signals, which are due to the $H_\beta$ of the vinylidene ligand. They appear at $\delta$ 3.55 ppm (**3a**) and $\delta$ 3.15 ppm (**3b**), as quintets with $^4J_{PH} = 11.8$ Hz. These resonances are shifted to higher field with respect to the value of $\delta = 4.10$ ppm found for $H_\beta$ in $Mn(C_5H_4Me)(dmpe)({=}C{=}CH(SiMe_3))$.[9] The $^{13}C$ NMR spectra for these new *trans*-alkynylvinylidene complexes show resonances for the vinylidene $C_\alpha$ between $\delta = 320-345$ ppm. These values are in the same range as found for the $C_\alpha$ of the abovementioned $Mn(C_5H_4Me)(dmpe)({=}C{=}CH(SiMe_3))$ at $\delta = 339$ ppm, but quite different from that found for the complex $Mn(C_5H_4Me)(CO)_2({=}C{=}CHPh)$[29] at $\delta = 380$ ppm. The vinylidene $C_\beta$ signals of **3** are observed in the range $\delta = 90-92$ ppm, clearly shifted to high field with respect to the $\delta$ 137 and 122 ppm found for the $C_\beta$ atoms in the related half-sandwich compounds. The signals of the $C_\alpha$ and $C_\beta$ atoms of the alkynyl ligand in complexes **3** appear at $\delta \approx 170$ ppm ($C_\alpha$) and in the range $\delta = 125-128$ ppm ($C_\beta$). The closest analogy was thought to be the anionic alkynyl complex $[Mn(Cp)(CO)(PPh_3)(C{\equiv}CMe)]^-$. However, this species displays $C_\alpha$, $C_\beta$ resonances at much higher field at $\delta$ 83.8 and 112.7 ppm.[25a] In the $^{31}P$ NMR spectrum of these *trans*-alkynylvinylidene compounds resonances appear in the range of $\delta = 67-69$ ppm shifted to high field compared to the values of $\delta \approx 93$ ppm observed for the related monocyclopentadienyl derivatives.[9]

**X-ray Diffraction Studies of 2a, 2b, 3a, 4b, and 6b.** The structures of **2a** (Figure 2) and **2b** (Figure 3) were determined by single-crystal X-ray diffraction analyses. Both complexes show pseudo-octahedral coordination around the metal center. The two acetylide ligands occupy *trans* positions, and the four P atoms define an equatorial plane. Bond lengths and angles are given in Table 1. The participation of a vinylidene type resonance form[30] **B** (Scheme 6) is indicated by the values for the $C{\equiv}C{-}X$ angles of 162.8° and 157.5° ($X = SiPh_3$ **2a**, $SnPh_3$ **2b**). There is a pronounced bending, in particular in comparison with the corresponding complexes with $X = CR_3$, in which this angle is around 179°.[31] The $C{\equiv}C$ bonds of **2a** and **2b** are slightly longer, 1.227 and 1.236 Å, than in the Ph-substituted molecule (1.216 Å). The Mn−C and Mn−P bond distances are similar to those found for X = Ph.[8]

The spectroscopically derived molecular structure of **3a** shown in Figure 4 was additionally confirmed by an

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(27) Albertin, G.; Antoniutti, S.; Bordignon, E.; del Ministro, E.; Ianelli, S.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* **1995**, 1783.

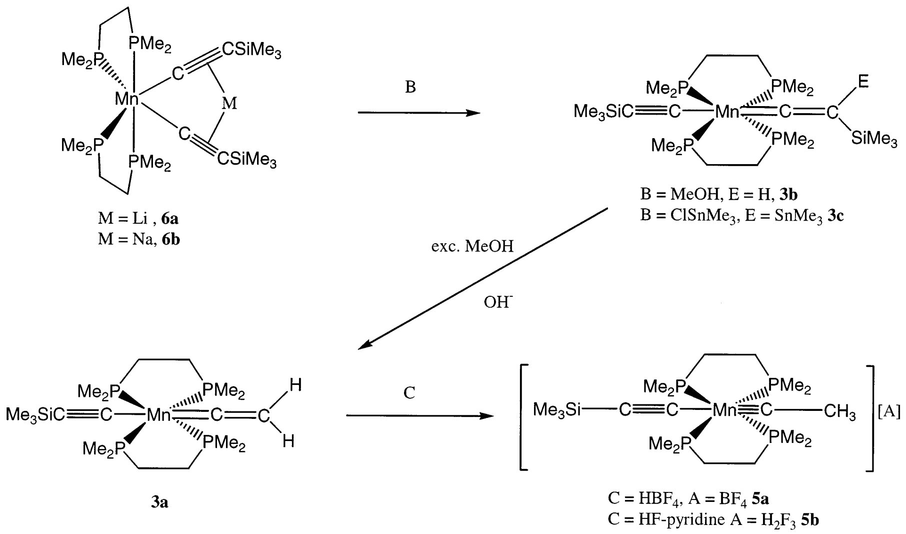
(28) (a) Werner, H.; Wiedemann, R.; Mahr, N.; Steinert, P.; Wolf, J. *Chem. Eur. J.* **1996**, *2*, 561. (b) Schafer, M.; Wolf, J.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1991**, *19*, 1341.

(29) Adams, H.; Broughton, S. G.; Walters, S. J.; Winter, M. J. *Chem. Commun.* **1999**, 1231.

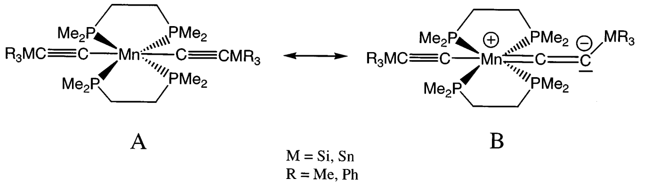
(30) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

(31) Unseld, D. PhD Thesis, University of Zürich, 1999.

**Scheme 5**



**Scheme 6**



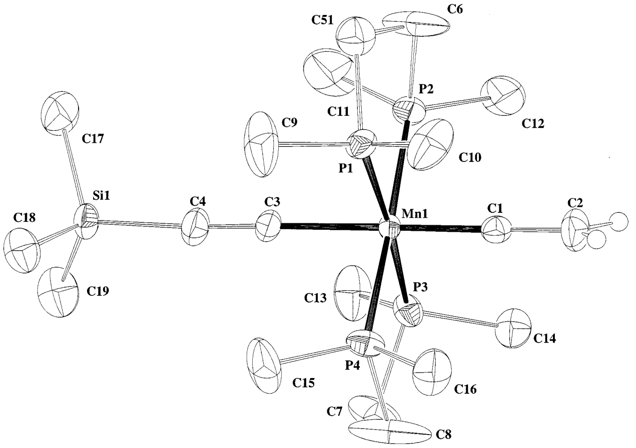


**Figure 4.** ORTEP plot of the structure of **3a**. The thermal ellipsoids are drawn at 50% probability. Disorder of the ethylene moieties and hydrogen atoms have been omitted for clarity.

X-ray diffraction study. Selected bond lengths and angles are given in Table 2. In this molecule the manganese center possesses octahedral coordination with the alkynyl and vinylidene ligands in a *trans* position and the four P atoms in an equatorial arrangement displaying Mn−P distances of 2.24 Å. The Mn=C and C=C bond distances are 1.782 and 1.317 Å. The latter one is somewhat shorter with respect to that found for Cp(CO)$_2$Mn=C=CMe$_2$[24b] (1.33 Å). The Mn=C=C moiety is practically linear. The Mn−C$_{\text{acetylide}}$ distance of 2.018 Å is somewhat longer than the 1.97 Å value found for the Mn−C distance in *trans*-bisalkynyl complexes,[8] presumably as a consequence of the *trans* influence of the tightly bound vinylidene unit. The C≡C distance is expectedly on the short side of the metal−acetylide range of 1.213 Å and the C≡C−Si angle of 175.8° shows almost no bending, which indicates only very little or no participation of the vinylidene type resonance structure **B** (Scheme 6).

**Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 3a and 6b**

| | 3a | 6b |
|---|---|---|
| Mn−P1 | 2.2463(12) | 2.2295(10) |
| Mn−P2 | 2.2423(13) | 2.2563(12) |
| Mn−P3 | 2.2458(13) | |
| Mn−P4 | 2.2466(13) | |
| C1−C2 | 1.317(6) | 1.244(6) |
| C3−C4 | 1.213(5) | |
| Mn−C1 | 1.782(4) | 1.938(4) |
| Mn−C3 | 2.018(4) | |
| Na−C1 | | 2.478(4) |
| Na−C2 | | 2.577(4) |
| Mn−C1−C2 | 179.2(4) | 178.0(13) |
| Mn−C3−C4 | 178.4(4) | |
| C−C−Si | 175.8(4) | 168.8(4) |
| P1−Mn−P3 | 175.91(5) | |
| P4−Mn−P2 | 178.14(5) | |
| P1−Mn−P1a | | 100.05(5) |
| C1−Na−C1a | | 69.39(18) |
| C2−Na−C2a | | 126.20(19) |
| C1−Mn−C1a | | 93.4(2) |

From the reaction of **1** with HF·pyridine a mixture of **4b** and **5b** was isolated, from which single crystals of **4b** were obtained. The molecular structure of **4b** was confirmed by an X-ray diffraction study. The structure is shown in Figure 5. Selected bond distances and angles are given in Table 1. Compound **4b** crystallizes as an ionic compound. In the cationic moiety the Mn shows octahedral coordination, in which the two acetylide ligands occupy *trans* sites and the four P atoms are arranged in an equatorial plane. There is no deviation from linearity of the C≡C−Mn−C≡C moiety, and even the C≡C−SiMe$_3$ angle is 180°. The C≡C bond is slightly longer (1.237 Å) than that found for Mn(dmpe)$_2$(C≡CPh)$_2$,[8] but it is the same as found for **2a** and **2b**.

The molecular structure of complex **6b** (Figure 6) was also confirmed by X-ray diffraction. Selected bond distances and angles are given in Table 2. The coordination geometry can be described as pseudo-octahedral with the two acetylide ligands in *cis* disposition. The Mn−P distances *trans* to the acetylide ligands are slightly longer (2.256 Å) than the *trans* Mn−P distances

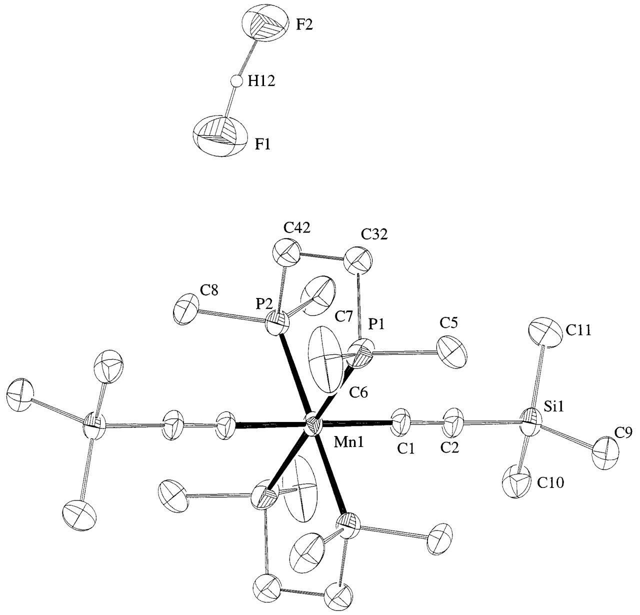


**Figure 5.** ORTEP plot of the structure of **4b**. The thermal ellipsoids are drawn at 30% probability. Disorder of the ethylene moieties and hydrogen atoms have been omitted for clarity.

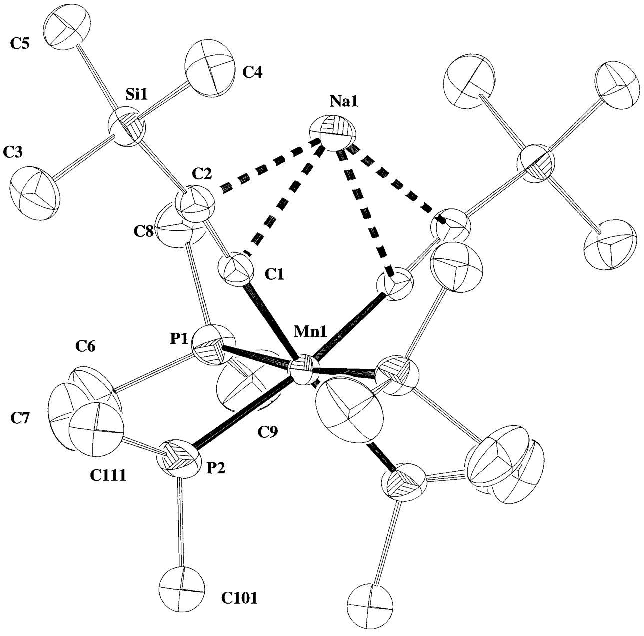


**Figure 6.** ORTEP plot of the structure of **6b**. The thermal ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

(2.229 Å). The sodium ion of **6b** is located in the plane bisecting the acetylide ligands at 2.478 and 2.577 Å from the α- and β-carbon atoms. These distances to these acetylide atoms are expectedly significantly shorter than the Na−C$_\alpha$ (2.533, 2.577 Å), −C$_\beta$ (2.848, 2.820 Å) distances found in the nonoctahedral [Cp*$_2$Ti(C≡CSiMe$_2$)$_2$]Na.[26a] The Mn−C≡C−Si moiety shows also differences with respect to the Mn(dmpe)$_2$(C≡CPh)$_2$ compound.[8] For instance, the Mn−C distance (1.938 Å) of **6b** appears shorter and the C≡C distance (1.244 Å) longer. Furthermore, the C≡C−Si angle of **6b** amounts to 168.8°. These data together with the unusual chemical shifts of the $^{13}$C NMR resonances for the C$_\alpha$ and C$_\beta$ suggest for the electronic description of **6** major contributions of the vinylidene type resonance form **B** (Scheme 6).

## Conclusions

This work has explored the deprotection chemistry of acetylide groups in Mn(dmpe)$_2$(C≡CSiMe$_3$)$_2$ (**1**) and revealed that the Me$_3$Si units are relatively strongly bound to the alkynyl ligands. It appears even that they are kinetically or thermodynamically stabilized with respect to comparable organic alkynes, presumably due to accumulation of extra charge on C$_\beta$ via a vinylidene type resonance structure. Thus starting from **1**, the nonprotic deprotection on the Mn(II) stage required drastic conditions yielding the Me$_3$Si metathesis complexes **2a** and **2b**.

Under protic conditions using MeOH milder conditions turned out to be applicable. However, then the reaction takes a different course, with disproportionation of **1** and formation of a Mn(I) compound **6**. This reduced and basic species enables after protolysis reactions generations of a vinylidene Mn=C=CH$_2$ species **3a** as the Mn(I) component. Consequently the stable Mn(III) species **4** was additionally obtained. On the basis of the presumed existence of a Mn(I) species, the preparation of the anionic acetylide complex [Mn(dmpe)$_2$(C≡CSiMe$_3$)$_2$]$^-$ (**6**) has then been approached and verified by reduction of **1** with lithium or sodium. The species **6** could subsequently be transformed into vinylidene compounds by protonation (**3b**) or stannylation (**3c**). The replacement of non-hydrogen substituents of the vinylidene complexes was instantaneously achieved with methanol in basic medium to yield **3a**. Under more acidic conditions (excess MeOH or HF·pyridine) **3a** was further protonated to the carbyne complex **5**.

These investigations thus established that silyl deprotection of pseudo-octahedral Mn(dmpe)$_2$(C≡CSiMe$_3$)$_2$ species is accomplished best at the Mn(I) stage, where conversions to appropriate types of vinylidene products proceed smoothly and in high yields.

## Experimental Section

**General Comments.** All operations were carried out under an inert atmosphere of N$_2$ using Schlenk and vacuum-line techniques or a MBraun glovebox Model MB-150B-G. The following solvents were dried and purified by distillation under argon before use employing the appropriate drying/deoxygenating agents: tetrahydrofuran (sodium/benzophenone), toluene (sodium), pentane (sodium), and CH$_2$Cl$_2$ (P$_2$O$_5$). Compounds **1**, **4a**,[8] and [NBu$_4$][Ph$_3$F$_2$M] (M = Si, Sn)[16] were prepared according to literature procedures.

IR spectra were obtained on a BIO-Rad FTS-45 instrument. NMR spectra were recorded on Unity-300 or Varian Gemini-200 spectrometers at 300 or 200 MHz for $^1$H, 75.4 or 50.3 for $^{13}$C{$^1$H}, 121.5 MHz for $^{31}$P{$^1$H}, and 111.9 MHz for $^{119}$Sn{$^1$H} spectra, respectively. The assignment of the $^1$H NMR signals for paramagnetic compounds is principally based on the reports of Köhler et al.[32,33] Chemical shifts for $^1$H and $^{13}$C{$^1$H} NMR are reported in ppm units with respect to the signals of residual solvents. $^{31}$P{$^1$H} and $^{119}$Sn{$^1$H} NMR spectra were

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(32) (a) Hebendanz, N.; Köhler, F. H.; Müller, G.; Riede, J. *J. Am. Chem. Soc.* **1986**, *108*, 3281. (b) Köhler, F. H.; Schlesinger, B. *Inorg. Chem.* **1992**, *31*, 2853.

(33) Köhler, F. H.; Hebendanz, N.; Müller, G.; Thewalt, U.; Kanellakopulos, B.; Klenze, R. *Organometallics* **1987**, *6*, 115.

referenced to 85% external $H_3PO_4$ and external $Me_4Sn$, respectively. Elemental C and H analyses were performed with a LECO CHN-932 microanalyzer. Cyclic voltammograms were obtained with a BAS 100B/W instrument ($10^{-3}$ M in 0.1 M MeCN/[NBu$_4$][PF$_6$]).

**Mn(dmpe)$_2$(C≡CSiPh$_3$)$_2$ (2a).** THF (30 mL) was added to a mixture of **1** (0.5 g, 0.91 mmol) and [NBu$_4$][Ph$_3$SiF$_2$] (0.98 g, 1.82 mmol) placed in a high-vacuum Young tap Schlenk. The mixture was heated to 90 °C and stirred for 7 days to afford a dark red solution. The solvent was removed in vacuo, and the product was extracted with toluene and washed with pentane to give a yellow solid that has been analyzed as complex **2a**. Yield: 0.67 g (80%). Anal. Calcd for $C_{52}H_{62}MnP_4Si_2$: C, 67.74; H, 6.78. Found: C, 67.59; H, 6.68. $^1$H NMR ($C_6D_6$, 300 MHz, 20 °C): $\delta$ 9.14 (br, 12H, $C_6H_5$), 8.33 (s, 12H, $C_6H_5$), 7.22 (s, 6H, $C_6H_5$), −13.8 and −14.9 (br, 32H, dmpe). IR ($CH_2Cl_2$, 20 °C): 1927 cm$^{-1}$ $\nu$(C≡C).

**Mn(dmpe)$_2$(C≡CSnPh$_3$)$_2$ (2b).** To a mixture of **1** (0.5 g, 0.91 mmol) and [NBu$_4$][Ph$_3$SnF$_2$] (1.15 g, 1.82 mmol), in a high-vacuum Young tap Schlenk, was added 30 mL of THF. The mixture was heated to 90 °C and stirred for 14 days to give a dark solution. The solvent was removed in vacuo, and the residue was washed with pentane and extracted with 50 mL of toluene . The toluene solution was concentrated to 10 mL and cooled to −30 °C for 12 h. A yellow precipitate of compound **2b** was formed. Yield: 0.33 g (30%). Anal. Calcd for $C_{52}H_{62}MnP_4Sn_2$: C, 56.61; H, 5.66. Found: C, 56.90; H, 5.97. $^1$H NMR ($C_6D_6$, 300 MHz, 20 °C): $\delta$ 9.28 (br, 12H, $C_6H_5$), 8.17 (s, 12H, $C_6H_5$), 7.45 (s, 6H, $C_6H_5$), −14.00 and −15.10 (br, 32H, dmpe). IR ($CH_2Cl_2$, 20 °C): 1914 cm$^{-1}$ $\nu$(C≡C).

**Reaction of 1 with MeOH.** Dry MeOH (10 mL) was added to **1** (0.2 g, 0.36 mmol) and $NaBF_4$ (0.36 mmol). The mixture was stirred for 4 h. The orange solution formed was filtered, and the solvent was removed in vacuo. The resulting solid was extracted with toluene to afford the yellow complex **3a** and an insoluble residue from which the mixture of complexes **4a** and **5a** was extracted with $CH_2Cl_2$. Yield: **3a** 38%, **4a** 35%, and **5a** 10% (the yield of **4a** and **5a** was determined by NMR integration).

**Reaction of 1 with Excess HF·Pyridine.** HF·pyridine (0.15 mL, 70%) was added to a THF solution (10 mL) of **1** (0.2 g, 0.36 mmol), prepared in a polyethylene flask. The reaction mixture was stirred at room temperature for 12 h to give a dark red solution. The solvent was removed, and the residue was extracted with toluene. The toluene solution was removed in vacuo to give a red solid, which was washed with pentane and dried. This red solid was characterized by $^1$H NMR as an inseparable 50/50 mixture of the complexes **4b** and **5b**. Data for **4b**: $^1$H NMR ($CD_2Cl_2$, 300 MHz, 20 °C): $\delta$ 13.8 (2H, br, $H_2F_3$), 7.81 (br, 18H, SiMe$_3$), −29.01 (br, 8H, PCH$_2$), −39.27 (br, 24H, PCH$_3$). $^{19}$F NMR ($CD_2Cl_2$ 20 °C): $\delta$ −172.24 (br, 3F, $H_2F_3$).

**Mn(dmpe)$_2$(C≡CSiMe$_3$)(=C=CH$_2$) (3a).** A MeOH solution of KOH (15 mL, 0.50 mmol) was added to 0.36 mmol of complex **3b** (or **3c**). The mixture was stirred for 5 h at room temperature to give an orange suspension. The solution was filtered, and the solvent was removed in vacuo to give a orange oil. The product was extracted with toluene. A yellow solid of complex **3a** was left behind. Yield: 0.14 g, (80%). Anal. Calcd for $C_{19}H_{43}MnP_4Si$: C, 47.70; H, 9.06. Found: C, 47.81; H, 9.19. $^1$H NMR ($C_6D_6$, 300 MHz, 20 °C): $\delta$ 3.55 (q, $^4J_{PH}$ = 11.8 Hz, 2H, =CH$_2$), 1.52 (br, 4H, PCH$_2$), 1.40 (br, 4H, PCH$_2$), 1.34 (s, 12H, PCH$_3$), 1.18 (s, 12H, PCH$_3$), 0.23 (s, 9H, SiMe$_3$). $^{31}$P NMR ($C_6D_6$, 300 MHz, 20 °C): $\delta$ 68.87. $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta$ 345.1 (m, Mn=C), 170.4 (m, Mn−C), 128.30 (C−Si), 90.21 (=CH-), 31.26 (m, PCH$_2$), 17.30 (m, PCH$_3$), 2.07 (SiMe$_3$). IR ($CH_2Cl_2$, 20 °C): 1988 cm$^{-1}$ $\nu$(C≡C), 1948 cm$^{-1}$ $\nu$(C≡C), 1595 cm$^{-1}$ $\nu$(C=C), 1542 cm$^{-1}$ $\nu$(C=C).

**Mn(dmpe)$_2$(C≡CSiMe$_3$)(=C=C(H)SiMe$_3$) (3b).** MeOH (0.014 mL) was added to a toluene solution (15 mL) of **6** (0.35 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 to give a yellow solid of complex **3b**. Yield: 0.17 g, (90%). Anal. Calcd for $C_{22}H_{51}MnP_4Si_2$: C, 47.99; H, 9.34. Found: C, 48.10; H, 9.43. $^1$H NMR ($C_6D_6$, 300 MHz, 20 °C): $\delta$ 3.15 (quint, $J_{PH}$ =11.7 Hz, 1H, =CH), 1.50 (br, 4H, PCH$_2$), 1.41 (s, 12H, PCH$_3$), 1.34 (s, 12H, PCH$_3$), 1.30 (s, 4H, PCH$_2$), 0.26 (s, 9H, SiMe$_3$), 0.19 (s, 9H, SiMe$_3$). $^{31}$P NMR ($C_6D_6$, MHz, 20 °C): $\delta$ 67.54. $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta$ 337.0 (quint, $^2J_{PC}$ = 25 Hz, Mn=C), 170.2 (quint, $^2J_{PC}$ = 27 Hz, Mn−C), 125.9 (C−Si), 91.94 (=CH−), 32.0 (m, PCH$_2$), 17.2 (m, PCH$_3$), 2.4 (−CSi*Me*$_3$), 1.7 (=CHSi*Me*$_3$). IR ($CH_2Cl_2$, 20 °C): 1988 cm$^{-1}$ $\nu$(C≡C), 1947 cm$^{-1}$ $\nu$(C≡C), 1598 cm$^{-1}$ $\nu$(C=C), 1550 cm$^{-1}$ $\nu$(C=C).

**Mn(dmpe)$_2$(C≡CSiMe$_3$)(=C=C(SnMe$_3$)(SiMe$_3$)) (3c).** ClSnMe$_3$ (0.09 g) was added to a toluene solution (15 mL) of **6** (0.35 mmol). The mixture was stirred for 1.5 h at room temperature to give an orange solution. The solvent was removed and the product was extracted with pentane to afford a yellow-green solid of complex **3c**. Yield: 0.22 g (90%). Anal. Calcd for $C_{25}H_{59}P_4MnSi_2Sn$: C, 42.09; H, 8.34. Found: C, 42.40; H, 8.37. $^1$H NMR ($C_6D_6$, 300 MHz, 20 °C): $\delta$ 1.62 (br, 4H, PCH$_2$), 1.46 (s, 12H, PCH$_3$), 1.40 (s, 12H, PCH$_3$), 1.38 (s, 4H, PCH$_2$), 0.34 (t, 9H, $^2J_{SnH}$ = 24 Hz, SnMe$_3$), 0.25 (s, 9H, SiMe$_3$), 0.23 (s, 9H, SiMe$_3$). $^{31}$P NMR ($C_6D_6$, MHz, 20 °C): $\delta$ 67.27. $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta$ 319.0 (m, Mn=C), 170.5 (quint, $^2J_{PC}$ = 28 Hz, Mn−C), 125.5 (−C−Si), 91,5 (=CH−), 32.1 (m, PCH$_2$), 18.6 (m, PCH$_3$), 5.1 (−CSn*Me*$_3$), 1.8 (−CSi*Me*$_3$), −1.3 (=CHSi*Me*$_3$). $^{119}$Sn NMR ($C_6D_6$, 20 °C): −22.2 (quint, $^4J_{SnP}$ = 108 Hz). IR ($CH_2Cl_2$, 20 °C): 1981 cm$^{-1}$ $\nu$(C≡C), 1946 cm$^{-1}$ $\nu$(C≡C), 1596 cm$^{-1}$ $\nu$(C=C), 1550 cm$^{-1}$ $\nu$(C=C).

**[Mn(dmpe)$_2$(C≡CSiMe$_3$)(≡C−CH$_3$)][A] (A = BF$_4$ 5a; H$_2$F$_3$ 5b). Synthesis of 5a.** A 54 wt % solution of $HBF_4$ in 0.06 mL of diethyl ether was added to a toluene (10 mL) solution of **3a** (0.2 g, 0.4 mmol). The solution was stirred for 3 h, and a yellow precipitate was formed. The remaining solution was removed by filtration and the solid was washed with toluene to afford a yellow solid, **5a**. Yield: 0.20 g (90%). Anal. Calcd for $C_{19}H_{44}BF_4MnP_4Si$: C, 40.30; H, 7.83. Found: C, 40.65; H, 7.95. $^1$H NMR ($CD_2Cl_2$, 300 MHz, 20 °C): $\delta$ 2.00 (m, 3H, C−CH$_3$), 1.96 (m, 4H, PCH$_2$), 1.79 (m, 4H, PCH$_2$), 1.60 (s, 12H, PMe$_2$), 1.56 (s, 12H, PMe$_2$), −0.11 (s, 9H, SiMe$_3$). $^{31}$P NMR ($CD_2Cl_2$, 300 MHz, 20 °C): $\delta$ 58.56 (s, 4P). $^{19}$F NMR ($CD_2Cl_2$, 20 °C): $\delta$ −91.13 (s, 4F). IR ($CH_2Cl_2$, 20 °C): 1971.7 cm$^{-1}$ $\nu$(C≡C).

**Synthesis of 5b.** An excess of HF·pyridine (70%, 0.06 mL) was added to a THF (10 mL) solution of **3a** (0.2 g, 0.4 mmol), prepared in a 25 mL polyethylene flask. The solution was stirred for 12 h at room temperature, and a red solution was formed. The solvent was removed in vacuo, and the residue was extracted with toluene to yield a yellow solution, from which the solvent was removed and **5b** was obtained as a yellow solid. Yield: 0.175 g (80%). Anal. Calcd for $C_{19}H_{46}F_3MnP_4SiMn$: C, 42.38; H, 8.61. Found: C, 42.55; H, 8.67. $^1$H NMR ($CD_2Cl_2$, 300 MHz, 20 °C): $\delta$ 13.80 (br, 2H, $H_2F_3$) 2.00 (m, 3H, C−CH$_3$), 1.96 (m, 4H, PCH$_2$), 1.79 (m, 4H, PCH$_2$), 1.60 (s, 12H, PMe$_2$), 1.56 (s, 12H, PMe$_2$), −0.11 (s, 9H, SiMe$_3$). $^1$H NMR (300 MHz, $C_6D_6$, 20 °C): $\delta$ 14.70 (br, 2H, $H_2F_3$) 2.37 (m, 3H, C-Me), 1.61 (m, 4H, PCH$_2$), 1.42 (m, 12H, PCH$_3$), 1.37 (m, 4H, PCH$_2$), 1.09 (m, 12H, PCH$_3$), −0.06 (s, 9H, SiMe$_3$). $^{31}$P NMR ($CD_2Cl_2$, 300 MHz, 20 °C): $\delta$ 58.42 (s, 4P). $^{19}$F NMR ($CD_2Cl_2$, 20 °C): $\delta$ −172.24 (br, 3F). $^{19}$F NMR ($C_6D_6$, 20 °C): $\delta$ −165.70 (br, 3F). $^{13}$C NMR ($CD_2Cl_2$, 125 MHz): $\delta$ 314.3 (Mn≡C), 145.8 (Mn−C), 126.7 (C−Si), 38.8 (C−*C*H$_3$), 30.5 (m, PCH$_2$), 19.3 (m, PCH$_3$), 16.4 (m, PCH$_3$), 0.51 (−Si*Me*$_3$). IR ($CH_2Cl_2$, 20 °C): 1969 cm$^{-1}$ $\nu$(C≡C), 1792 cm$^{-1}$ $\nu$($H_2F_3$).

**[Mn(dmpe)$_2$(C≡CSiMe$_3$)$_2$]Li (6a).** A toluene solution of **1** (15 mL, 0.20 g, 0.36 mmol) was added to large excess of Li placed in a high-vacuum Young tap Schlenk. The mixture was stirred at 105 °C during 12 h to give a dark red solution. The solution was concentrated in vacuo to 5 mL and chilled to −30 °C for 12 h to afford a yellow crystalline solid of complex **6a**.

**Table 3. Crystal Data for Compounds 2a, 2b, and 3a**

| | **2a** | **2b** | **3a** |
|---|---|---|---|
| formula | $C_{52}H_{62}MnP_4Si_2$ | $C_{52}H_{62}MnP_4Sn_2$ | $C_{19}H_{43}MnP_4Si$ |
| fw | 922.02 | 1103.22 | 478.44 |
| cryst syst | tetragonal | tetragonal | monoclinic |
| space group | $P4_2/mbc$ (no. 135) | $P4_2/mbc$ (no. 135) | $P2_1/c$ (no. 14) |
| $a$, Å | 16.4383(6) | 16.8227(8) | 16.7916(7) |
| $b$, Å | 16. 4383(6) | 16.8227(8) | 9.3665(4) |
| $c$, Å | 18.0198(7) | 18.142(1) | 18.3896(4) |
| $\beta$, deg | | | 112.738(5) |
| volume, Å$^3$ | 4869.3(3) | 5134.3(5) | 2667.5(2) |
| $Z$ | 4 | 4 | 4 |
| $\rho_{calc}$, g/cm$^3$ | 1.258 | 1.427 | 1.191 |
| cryst size, mm | 0.50 × 0.48 × 0.47 | 0.28 × 0.23 × 0.17 | 0.16 × 0.14 × 0.11 |
| cryst habit | yellow block | yellow block | yellow block |
| $\theta$ range, deg | 2.72 to 28 | 2.42 to 27.99 | 2.25 to 27.97 |
| index ranges | $0 < h < 21$, $0 < k < 21$, $-23 < l < 0$ | $0 < h < 15$, $0 < k < 22$, $-23 < l < 23$ | $-22 < h < 20$, $0 < k < 12$, $-0 < l < 24$ |
| no. of reflns collected/unique | 69649/3025 | 42135/3193 | 25939/6411 |
| $R$(int) | 0.0522 | 0.0717 | 0.1091 |
| $\mu$, mm$^{-1}$ | 0.486 | 1.365 | 0.782 |
| max. and min. transmn | 0.8038 and 0.7931 | 0.8011 and 0.7012 | 0.9189 and 0.8851 |
| no. of params | 149 | 144 | 244 |
| GooF | 1.048 | 1.019 | 0.754 |
| $R^a$ | 0.0415 | 0.0451 | 0.0395 |
| $R_w{}^b$ | 0.1151 | 0.0847 | 0.0797 |
| largest diff peak and hole, e·Å$^3$ | 0.401 and −0.324 | 1.136 and −0.809 | 0.751 and −0.752 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum[w(F_o{}^2 - F_c{}^2)^2/\sum[w(F_o{}^2)^2]\}^{1/2}$.

Yield: 0.160 g (80%). Anal. Calcd for $C_{22}H_{50}LiMnP_4Si_2$: C, 47.48; H, 9.05. Found: C, 47.53; H, 9.06. $^1$H NMR ($C_6D_6$, 300 MHz, 20 °C): $\delta$ 1.58 (m, 6H, $PMe_2$), 1.45 (m, 4H, $PCH_2$), 1.39 (s, 6H, $PMe_2$), 1.20 (s, 6H, $PMe_2$), 0.90 (m, 4H, $PCH_2$), 0.88 (s, 6H, $PMe_2$), 0.21 (s, 18H, $SiMe_3$). $^{31}$P NMR ($C_6D_6$, 20 °C): $\delta$ 74.50 (br, 2P), 63.66 (br, 2P). $^{13}$C NMR ($C_7D_8$, 125 MHz, 20 °C): $\delta$ 208.5 (Mn−C), 119.8 (C−Si), 34.4 (m, 2C, $PCH_2$), 31.2 (m, 2C, $PCH_2$), 29.7 (m, 2C, $PCH_3$), 22.3 (m, 2C, $PCH_3$), 17.5 (m, 2C, $PCH_3$), 13.4 (m, 2C, $PCH_3$), 2.8 (s, 6C, $SiMe_3$). $^7$Li NMR ($C_6D_6$, 20 C): $\delta$ 0.90 (s, 1Li). IR (toluene, 20 °C): 1890 cm$^{-1}$ $\nu$(C≡C), 1848 cm$^{-1}$ $\nu$(C≡C).

**[Mn(dmpe)$_2$(C≡CSiMe$_3$)$_2$]Na (6b).** A toluene solution of **1** (15 mL, 0.20 g, 0.36 mmol) was added to a large excess of Na placed in a high-vacuum Young tap Schlenk. The mixture was stirred at 100 °C during 12 h to give a dark red solution. The solution was concentrated in vacuo to 5 mL and chilled to −30 °C for 12 h to afford yellow crystals of complex **6b**. Yield: 0.164 g (80%). Anal. Calcd for $C_{22}H_{50}MnNaP_4Si_2$: C, 46.15; H, 8.80. Found: C, 46.38; H, 8.50. $^1$H NMR ($C_6D_6$, 300 MHz, 20 °C): $\delta$ 1.65 (m, 4H, $PCH_2$), 1.47 (s, 6H, $PMe_2$), 1.39 (s, 6H, $PMe_2$), 1.23 (s, 6H, $PMe_2$), 1.10 (m, 4H, $PCH_2$), 0.90 (s, 6H, $PCH_3$), 0.19 (s, 18H, $SiMe_3$). $^{31}$P NMR ($C_6D_6$, 20 °C): $\delta$ 75.50 (br, 2P), 62.5 (br, 2P). $^{13}$C NMR ($C_6D_6$, 125 MHz, 20 °C): $\delta$ 211.4 (Mn−C), 114.8 (C−Si), 34.7 (m, 2C, $PCH_2$), 29.8 (m, 2C, $PCH_2$), 22.9 (m, 2C, $PCH_3$), 20.9 (m, 2C, $PCH_3$), 20.5 (m, 2C, $PCH_3$), 14.5 (m, 2C, $PCH_3$), 3.5 (s, 6C, $SiMe_3$). IR ($CH_2Cl_2$, 20 °C): 1987 cm$^{-1}$ $\nu$(C≡C), 1944 cm$^{-1}$ $\nu$(C≡C).

**Crystallographic Studies of Compounds 2a, 2b, 3a, 4b, and 6b.** Crystallographic data of complexes **2a**, **2b**, **3a**, **4b**, and **6b** are summarized in Tables3 and 4.

**Table 4. Crystal Data for Compounds 4b and 6b**

| | **4b** | **6b** |
|---|---|---|
| formula | $C_{22}H_{50}MnP_4Si_2{\cdot}H_2F_3$ | $C_{22}H_{50}MnNaP_4Si_2$ |
| fw | 608.64 | 572.61 |
| crystal system | monoclinic | monoclinic |
| space group | $C2/c$ (no. 15) | $I2/a$ (no. 15) |
| $a$, Å | 19.577(2) | 10.0819(6) |
| $b$, Å | 11.6670(9) | 17.328(1) |
| $c$, Å | 16.224(1) | 18.347(1) |
| $\beta$, deg | 113.850(8) | 97.052(7) |
| volume, Å$^3$ | 3389.2(5) | 3180.9(4) |
| $Z$ | 4 | 4 |
| $\rho_{calc}$, g/cm$^3$ | 1.193 | 1.196 |
| cryst size, mm | 0.36 × 0.19 × 0.05 | 0.35 × 0.27 × 0.19 |
| cryst habit | pink plate | yellow prism |
| $\theta$ range, deg | 2.15 to 27.95 | 2.35 to 27.86 |
| index ranges | $-25 < h < 25$,<br>$0 < k < 15$,<br>$-21 < l < 21$ | $-13 < h < 12$,<br>$0 < k < 22$,<br>$-23 < l < 24$ |
| no. of reflns collected/ unique | 14 625/3799 | 12 855/3757 |
| $R$(int) | 0.1485 | 0.0830 |
| $\mu$, mm$^{-1}$ | 0.675 | 0.714 |
| max. and min. transmn | 0.9670 and 0.7931 | 0.8762 and 0.7881 |
| no. of params | 148 | 140 |
| GooF | 0.658 | 0.911 |
| $R^a$ | 0.0520 | 0.0615 |
| $R_w{}^b$ | 0.1355 | 0.1733 |
| largest diff peak and hole, e·Å$^3$ | 0.393 and −0.339 | 1.706 and −1.106 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum[w(F_o{}^2 - F_c{}^2)^2/\sum[w(F_o{}^2)^2]\}^{1/2}$.

**Data Collection.** X-ray-quality crystals of **2a**, **2b**, **3a**, **4b**, and **6b** were selected and mounted on the top of a glass fiber covered with a small amount of viscous oil on a STOE image plate diffractometer equipped with a one-circle $\varphi$ goniometer and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection was performed at −90 °C with the programm EXPOSE.[34] 8000 reflections distributed over the whole limiting sphere were selected by SELECT.[34] The unit cell parameters were refined with the programms DISPLAY, INDEX, and CELL.[34] All measured reflections were integrated after checking for reflections overlap with PROFILE[34] and EMS;[34] 50−200 standard reflections with $I > 6\sigma(I)$ were chosen by INTEGRATE[34] to check for crystal deterioration and misalignment. The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on measured and indexed crystal faces was applied for all the compounds with the programs FACEitVIDEO and XRED.[34]

**Structure Solution.** The structures of **2a**, **2b**, **3a**, **4b**, and **6b** were solved by direct methods using the program SHELXS-97[35] and completed by subsequent difference Fourier synthesis with SHELXL-97.[36]

**Structure Refinement.** Full-matrix least-squares refinements based on $F^2$ were performed using the SHELXL-97 program,[36] the function minimized was $\sum w(F_o{}^2 - F_c{}^2)^2$. All non-

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(34) STOE-IPDS Software package; Version 2.87 5/1998; STOE & Cie, GmbH: Darmstadt, Germany, 1998.

hydrogen atoms, except the disordered ones (see below), were refined anisotropically. Hydrogen atoms were incorporated in calculated positions and refined with isotropic thermal parameters using riding models.

**Special Features of the Refinements. 2b.** The C3 atom was found to be disordered, modeled in terms of two orientation C31 and C32 with refined occupancies of 0.5/0.5 and kept isotropic.

**3a.** The C5 atom was found to be disordered, modeled in terms of two orientations C51 and C52 with refined occupancies of 0.72/0.28 and kept isotropic.

**4b.** The ethane bridge between the two P atoms appeared to be disordered and had to be refined as split positions using soft restraints for the distances P−C and C−C and PART instructions of the program SHELXL-97.[36] The $H_2F_3^-$ unit showed disorder over the 2-axis of symmetry, and the occupation factor of F2 was set to 1/2. H12 was found in the difference electron density map but could not be refined; therefore its positional and isotropic displacement parameters were fixed in the final refinement stage. All other H atomic positions were calculated after each refinement cycle (riding model). About 66% of the unique reflections are not observed by the criterion $I < 2\sigma(I)$.

**6b.** Inspection of the thermal displacement parameters indicated disorder of two carbon atoms, C10 and C11, which were placed on two sites, C101 and C102; C111 and C112, and refined isotropically with 0.4/0.6 occupancies.

Neutral atom scattering factors and anomalous dispersion terms were taken from usual sources.[36] Crystal drawings were generated by PLATON 97.[37]

Final atomic coordinates of all atoms and structure factors are available as Supporting Information.

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**Supporting Information Available:** Tables of crystal data and structure refinement parameters, atomic coordinates, bond length, bond angles, anisotropic displacement parameters, and hydrogen coordinates of **2a**, **2b**, **3a**, **4b**, and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) Sheldrick, G. M. SHELXS-97: *Acta Crystallogr. A* **1996**, *46*, 467.

(36) Sheldrick, G. M. SHELXL-97, Program for refinement of the Crystal Structures; University of Göttingen: Germany, 1997.

(37) Spek, A. L. PLATON-97, A computer program for the graphical representation of crystallographic models; University of Utrecht, The Netherlands, 1997.