# A facile and new type of route to the redox-active rigid-rod complex [{Mn(dmpe)$_2$(C≡CH)}$_2$(μ-C$_4$)][PF$_6$] *via* Mn–C$_2$· radical coupling†

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The binuclear rigid-rod complex [{Mn(dmpe)$_2$(C≡CH)}$_2$(μ-C$_4$)][PF$_6$] was spontaneously obtained from the reaction of [Mn(dmpe)$_2$(C≡CSiMe$_3$)$_2$][PF$_6$] with one equivalent of TBAF.

Di- and oligo-nuclear organometallic complexes, in which two neighboring metal centers are connected by a C$_x$ chain, have recently attracted great interest due to their potential in NLO applications[1] and the possibility to use them as precursors for molecular wires.[2] During the last decade several organometallic research groups therefore focused on the development of facile synthetic routes to ML$_n$–C$_x$–ML$_n$ rigid-rod transition metal complexes.[3–7] Studies of the electrochemical properties of these species have demonstrated that for $x = 4$ there is strong metal–metal interaction across the carbon chain. This confers great stability to the corresponding mixed-valent species, as indicated by the value of the comproportionation constant ($K_c$) which lies in the range of $10^8$–$10^{12}$. This metal–metal interaction decreases with the length of the chain (C$_x$) and is very small for complexes with values of $x \geqslant 20$.[6a] With regard to the design of new molecular wires particularly great interest arose in new synthetic accesses to short-chain bridged species and polarizable end groups.

We have recently reported the syntheses and characterization of [{Mn(dmpe)$_2$I}$_2$(μ-C$_4$)]$^{n+}$ ($n = 0, 1, 2$) complexes by the reaction of (MeCp)(dmpe)MnI with 0.5 Me$_3$Sn–C$_4$–SnMe$_3$ and dmpe.[7] In order to extend the scope of available versatile routes we initiated reactivity studies on [Mn(dmpe)$_2$(C≡CSiMe$_3$)$_2$]$^n$ ($n = -1, 0, +1$) complexes.[8] As silyl protected acetylide derivatives they were expected to allow deprotection and recovery of the quite reactive parent acetylide species.

Indeed, the reaction of [Mn(dmpe)$_2$(C≡CSiMe$_3$)$_2$]$^+$ **1$^+$** with one equivalent of NBu$_4$F (TBAF) containing 5% H$_2$O[9] led to the deprotected species [Mn(dmpe)$_2$(C≡CH)$_2$]$^+$ **2a$^+$** and subsequent deprotonation of this species produced under the reaction conditions a [(HC≡C)Mn(dmpe)$_2$(C≡C)] intermediate **2b** (Scheme 1).‡ Spontaneous dimerization of **2b** generated [{Mn(dmpe)$_2$(C≡CH)}$_2$(μ-C$_4$)] **3** and subsequently the mixed-valent compound [{Mn(dmpe)$_2$(C≡CH)}$_2$(μ-C$_4$)]$^+$ **3$^+$**. DFT



**Scheme 1** [Mn] = Mn(dmpe)$_2$.

calculations[10]† performed on the hydrogen substituted model Mn(dHpe)$_2$(C≡CH)(C≡C) simulating **2b** revealed that, of the two possible states, triplet and singlet, the triplet state of **2b(A)** with two unpaired electrons is more stable than the singlet state **2b(B)** by *ca.* 90 kJ mol$^{-1}$. Furthermore, the computed spin densities of +1.45$\alpha$ and +0.61$\alpha$, at the manganese atom and at the terminal carbon atom, respectively, clearly indicate that the electronic structure of **2b** is well described by the resonance formula **2b(A)**. The relative stability and therefore longevity of the Mn$^{II}$ free radical apparently supports the C–C coupling process to produce the neutral dinuclear Mn$^{II}$–Mn$^{II}$ species **3**. Under the given redox conditions, *i.e.* in the presence of the mildly oxidizing **2a$^+$**, **3** is converted to **3$^+$** with additional formation of the corresponding Mn(dmpe)$_2$(C≡CH)$_2$ **2a** which is not stable and decomposes.[8] Indeed, the THF soluble fraction of the reaction contains a mixture of **3** and other not specifically identified Mn$^{II}$ and Mn$^{I}$ complexes.[8]

Based on **1$^+$**, the new dinuclear mixed-valent complex **3$^+$** was obtained in about 65% yield, which is almost the ideal yield based on the stoichiometry of Scheme 1. This reaction involving acid–base chemistry in conjunction with the versatile redox properties of the Mn center thus furnishes a new and a facile method to obtain M–C$_4$–M complexes starting from easily accessible M–C$_2$SiR$_3$ units. Mechanistically it appears that there is some relationship of these conversions to the coupling of terminal acetylides with Cu$^{II}$ reagents.[6] However, the intramolecular fashion, along which the redox chemistry of Scheme 1 proceeds, is quite unique. In addition, species **3$^+$** possesses two reactive terminal acetylenic moieties, which might be utilized in further organometallic substitution processes of the H terminus. Compound **3$^+$** has been characterized as a violet solid, soluble only in polar and ionizing solvents such as CH$_2$Cl$_2$. The $^1$H NMR spectrum of **3$^+$** (20 °C, CD$_2$Cl$_2$) shows four broad signals for the dmpe protons at $\delta$ −0.28, −4.58, −6.49 and −6.65, and a resonance at $\delta$ −46.40 due to the C≡CH proton. The paramagnetism is indicated by the broadness of the resonances and more quantitatively confirmed by the contact shift induced Curie–Weiss behavior of **3$^+$** in the temperature range from −80 to 20 °C. The fact that only one set of resonances was observed for the protons of the dmpe ligands is taken as a strong hint for electron delocalization with both manganese ends equivalent on the NMR time scale ($10^{-6}$ s). In the solid state, **3$^+$** has a magnetic moment of 2.53 $\mu_B$ at 290 K that drops to 1.95 $\mu_B$ at 100 K demonstrating strong intramolecular antiferromagnetic interaction comparable to that observed for [{Mn(dmpe)$_2$I}$_2$(μ-C$_4$)][BF$_4$].[7]

Cyclic voltammetry (CV) of complex **3$^+$** in acetonitrile solution displays two fully reversible waves ($\Delta E_p = 0.070$ V and $i_{pa}/i_{pc} \approx 1$ for scan rates of 0.100–0.500 V s$^{-1}$ at 20 °C, *vs.* Fc/Fc$^+$) at $E_{1/2} = -0.89$ V and $E_{1/2} = -1.46$ V corresponding to the Mn$^{III}$–Mn$^{III}$ (**3$^{2+}$**)/Mn$^{III}$–Mn$^{II}$ (**3$^+$**) and Mn$^{III}$–Mn$^{II}$ (**3$^+$**)/Mn$^{II}$–Mn$^{II}$ (**3**) redox couples. The difference of these values of $\Delta E_{1/2}$ ( = 0.576 V) establishes a comproportionation constant of $7.5 \times 10^9$ [$K_c = \exp(F \Delta E_{1/2}/RT)$].[11] Another somewhat irreversible redox couple was identified at $E_{1/2} = -2.29$ V attributed to the Mn$^{II}$–Mn$^{II}$/Mn$^{II}$–Mn$^{I}$ reduction. In accord with this CV behavior the monocation **3$^+$** could
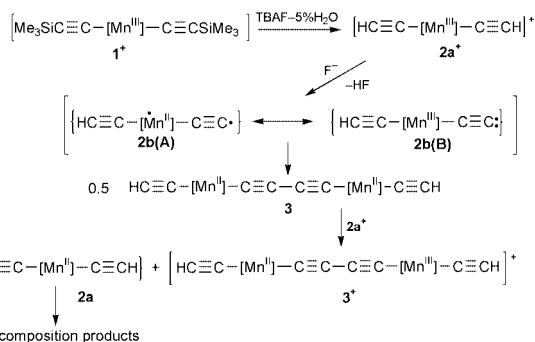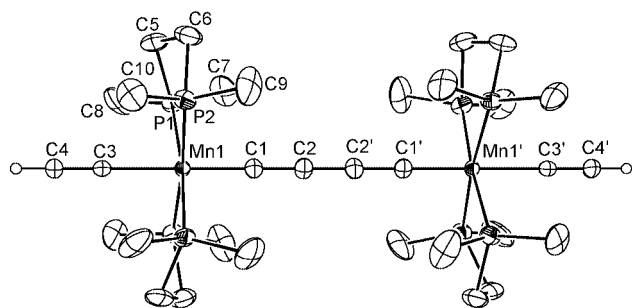
**Fig. 1** Molecular structure of $3^+[PF_6]^-$. Selected bond lengths (Å) and angles (°): Mn1–C1 1.818(4), Mn1–C3 2.026(5), C1–C2 1.285(6), C2–C2′ 1.307(9), C3–C4 1.189(6); Mn1–C1–C2 180.0(4); the $[PF_6]^-$ anion is omitted.

chemically be reduced to the dark-green paramagnetic complex **3** using Cp(C$_6$Me$_6$)Fe and oxidized with $[Cp_2Fe][PF_6]$ to give the dark-brown diamagnetic $[\{Mn(dmpe)_2(C\equiv CH)\}_2(\mu\text{-}C_4)]^{2+}$ species $3^{2+}$. Both processes can be fully reversed with $[Cp_2Fe]^+$ and Cp$_2$Co, respectively [eqn. (1)]. Complexes **3** and $3^{2+}$ were isolated and fully characterized.

$$3 \underset{Cp(C_6Me_6)Fe}{\overset{[Cp_2Fe]^+}{\rightleftharpoons}} 3^+ \underset{Cp_2Co}{\overset{[Cp_2Fe]^+}{\rightleftharpoons}} 3^{2+} \quad (1)$$
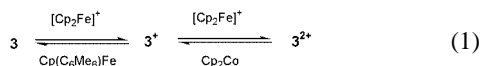
The highly symmetric structure of $3^+$ was determined by single-crystal X-ray diffraction (Fig. 1),§ which indeed revealed two equivalent manganese centers adopting pseudo-octahedral geometry. The C1–C2 and C2–C2′ bond lengths show only little alteration and compare very well to those obtained for the related species $[\{Mn(dmpe)_2I\}_2(\mu\text{-}C_4)]^n$ [$n = 0$, 1.26(2)–1.33(3) Å; $n = 1$, 1.275(3)–1.313(5) Å and $n = 2$, 1.289(5)–1.295(5) Å].[7] The C$_4$ linear chain is thus best described by a cumulenic resonance structure.

## Notes and references

‡ All operations were performed using standard Schlenck or Glove-box techniches. $^1$H NMR data for $2a^+$ prepared *in situ* (CD$_2$Cl$_2$, 300 MHz, −10 °C), $\delta$ −33.0 (br, 8H, PCH$_2$), −44.0 (br, 24H, PCH$_3$).

*Synthesis* of $3^+[PF_6]^-$: A 1 M solution of TBAF (0.15 mL) was added to a CH$_2$Cl$_2$ solution (15 mL) of $1^+$ (0.1 g, 0.15 mmol). After 1.5 h the dark-green solution was concentrated *in vacuo* to 3 mL. Addition of Et$_2$O precipitated $3^+[PF_6]^-$, which was dried *in vacuo*. Yield 0.046 g, (65%). Anal. Calc. for C$_{32}$H$_{66}$F$_6$Mn$_2$P$_9$: C, 40.31; H, 6.98. Found: C, 40.01; H, 6.80. $^1$H NMR (CD$_2$Cl$_2$, 300 MHz, 20 °C): $\delta$ −0.29 (br, 8H, PCH$_2$), −4.60 (br, 24H, PCH$_3$), −6.55 (br, 24H, PCH$_2$), −6.71 (br, 24H, PCH$_3$), −46.39 (br, 2H, ≡CH). $^{31}$P NMR (121.471 MHz, CD$_2$Cl$_2$, 20 °C, 85% H$_3$PO$_4$ ext.): $\delta$ −145.62 (sept, $^1J_{PF}$ 717.9 Hz, PF$_6^-$).$^{19}$F NMR (CD$_2$Cl$_2$, 282.324 MHz, 20 °C, C$_6$H$_5$CF$_3$ ext.): $\delta$ −75.09 (d, 717.9 Hz, PF$_6^-$). IR (CH$_2$Cl$_2$, 20 °C): 2140s 1819w (C$_4$ unit), 1960m cm$^{-1}$ [$\nu$(C≡CH)].

*Synthesis* of $3^{2+}[PF_6]^-_2$: $[Cp_2Fe][PF_6]$ (0.017 g, 0.052 mmol) was added to a CH$_2$Cl$_2$ solution (10 mL) of $3^+$ (0.050 g, 0.052 mmol). After 3 h the solution was concentrated *in vacuo* to 3 mL. Addition of Et$_2$O precipitated $3^{2+}[PF_6]^-_2$, which was dried *in vacuo*. Yield 0.051 g, (90%). Anal. Calc. for C$_{32}$H$_{66}$F$_{12}$Mn$_2$P$_{10}$: C, 34.99; H, 6.06. Found: C, 34.86; H, 6.06. $^1$H NMR (CD$_2$Cl$_2$, 300 MHz, 20 °C): $\delta$ 1.93 (br, 8H, PCH$_2$), 1.83 (br, 24H, PCH$_2$), 1.38 (br, 24H, PCH$_3$), 1.27 (br, 24H, PCH$_3$), −2.30 (br, 2H, ≡CH). $^{31}$P NMR (121.471 MHz, CD$_2$Cl$_2$, 20 °C, 85% H$_3$PO$_4$ ext.): $\delta$ −145.44 (sept, $^1J_{PF}$ 719 Hz, PF$_6^-$). $^{19}$F NMR (CD$_2$Cl$_2$, 282.324 MHz, 20 °C, C$_6$H$_5$CF$_3$ ext.): $\delta$ −74.02 (d, 719 Hz, PF$_6^-$). IR (KBr, 20 °C): 1929 cm$^{-1}$ [$\nu$(C≡C)], 2025, 1915, 1920 cm$^{-1}$ [$\nu$(C≡C)$_2$].

*Synthesis* of **3**: Cp(C$_6$Me$_6$)Fe (0.017 g, 0.053 mmol) dissolved in toluene (5 mL) was added to a THF suspension (5 mL of $3^+[PF_6]^-$ (0.050 g, 0.052 mmol). After 2 h the solution was filtered and the solvent removed to give **3**. Yield 0.038 g, (90%). Anal. Calc. for C$_{32}$H$_{66}$Mn$_2$P$_8$: C, 47.54; H, 8.23. Found: C, 47.62; H, 8.53. $^1$H NMR (C$_6$D$_6$, 300 MHz, 40 °C): $\delta$ −9.47 (br, 8H, PCH$_2$), −14.89 (br, 32H, PMe$_3$ + PCH$_2$), −18.78 (br, 24H, PCH$_3$), −149.44 (br, 2H, ≡CH). IR: no $\nu$(C≡C) are observed.

§ *Crystal data* for $3^+[PF_6]^-$: C$_{32}$H$_{66}$F$_6$Mn$_2$P$_9$, $M = 953.46$, dark red block, $0.30 \times 0.24 \times 0.15$ mm, tetragonal, space group $I\bar{4}c2$, $a = b = 16.1403(9)$, $c = 18.141(1)$ Å, $V = 4725.9(5)$ Å$^3$, $Z = 4$, $D_c = 1.340$ Mg m$^{-3}$, $\mu = 0.884$ mm$^{-1}$. Data were collected on a STOE IPDS diffractometer [graphite monochromatised Mo-K$\alpha$, $\lambda = 0.71073$ Å, $T = 183(2)$ K]. 22664 reflections collected, 2924 unique ($R_{int} = 0.0202$). Refinement converged to $R_1 = 0.0303$, $wR_2 = 0.0732$ [$I > 2\sigma(I)$] and $R_1 = 0.0529$, $wR_2 = 0.0777$ (all data). CCDC reference number 161685. See http://www.rsc.org/suppdata/cc/b1/b102396a/ for crystallographic data in CIF or other electronic format.

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