

Stable paramagnetic bis(alkynyl) manganese complexes

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Abstract

Stable paramagnetic Mn(II) and Mn(III) bis(alkynyl) complexes of the type $[trans(RC\equiv C)_2Mn(dmpe)_2]^{n+}$ ($R = Ph, SiMe_3$, $n = 0, 1$) have been prepared and characterized by spectroscopic, electrochemical, magnetic measurements and X-ray single crystal diffraction studies.

Keywords: Manganese; Alkynyl ligands; X-ray structure, EPR spectroscopy

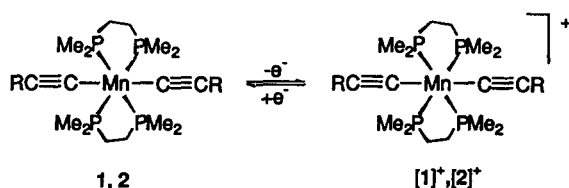
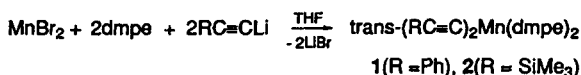
There is growing interest in complexes with two *trans* σ -alkynyl ligands due to their potential application as building blocks in the synthesis of new rigid rod materials. These compounds are expected to display nonlinear optical, conducting or liquid crystal properties [1,2]. Previously, the search for such bisacetylide complexes has been restricted to transition metals of Groups VIII–X [2a–d,3] all of which form diamagnetic compounds. Paramagnetic analogues of such species exhibit electronic open shell configurations and are therefore expected to be more polarizable (open shell molecules normally have small HOMO/SOMO or SOMO/LUMO gaps)—a fundamental requirement for nonlinear optical materials [4]. For such reasons we were therefore challenged to investigate the preparation of paramagnetic bis(alkynyl) Mn(II) and Mn(III) derivatives.

In the presence of bis(dimethylphosphino)ethane (dmpe) the reaction of anhydrous $MnBr_2$ with lithium alkynyls in THF results in the formation of the thermally stable complexes **1** and **2** (Scheme 1) [5]. These compounds are easily oxidized in air, by ferricenium hexafluorophosphate or tetrafluoroboric acid etherate, yielding the cationic species $[1]^+$ and $[2]^+$ with PF_6^- and BF_4^- counterions [7] respectively. Complexes **1** and

2 and $[1]^+$ and $[2]^+$ represent unique bis(alkynyl) derivatives, since only a few examples of stable paramagnetic mono σ -alkynyl metal complexes have been reported previously [8]. It is interesting to note that the reactions of **1** and **2** with HBF_4 did not afford cationic vinylidene complexes with protonation of the β -carbons of the acetylide moieties. These centers are apparently not nucleophilic in contrast to diamagnetic alkynyl derivatives, which can be attacked by electrophiles at this position [9]. Air oxidation of **1** produces the $[1]^+OH^-$ system. The comparable reaction of **2** also leads to an Mn(III) species, however, its exact nature cannot yet be elucidated.

$[1]^+$ and $[2]^+$ turned out to be air-stable in the solid state and in solution, and it was possible to convert them back to **1** and **2** by reducing agents such as sodium amalgam or sodium trimethoxyborohydride (Scheme 1). These transformations were carried out; reaction of $[1]^+$ and $[2]^+$ with trimethoxyborohydride did not lead to products of a nucleophilic attack of H^- on the acetylide ligand, the acetylenic chain of $[1]^+$ and $[2]^+$ could be attributed a nonelectrophilic character. Therefore we assume that these molecules represent electronically highly delocalized systems. This is supported further by the fact that, unlike $17e^-$ transition metal monoalkynyls [10] generated from the oxidation of $18e^-$ precursors, none of the compounds **1** and **2** or $[1]^+$ and $[2]^+$

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Scheme 1.

undergo coupling reactions to form binuclear complexes spaced by 1,3-butadiene-1,4-diylidene ligands.

1 and 2 and [1]⁺ and [2]⁺ were characterized by IR, EPR and ¹H NMR spectroscopy, magnetic susceptibility, and mass spectrometry [5,7]. Their structures are readily derived from these data. In the mass spectra of all compounds (EI, FAB) the parent ions are observed. The IR spectra display ν(C≡C) absorptions and the frozen solution EPR spectra of 1 and 2 show complex isotropic features near g = 2, consistent with low-spin Mn(II) (S = 1/2) in an axial ligand field. A hyperfine structure is observable due to coupling to ⁵⁵Mn (I = 5/2), and four equivalent ³¹P (I = 1/2) of the equatorial dmpe ligands with a slightly larger A value (⁵⁵Mn) for 1 (Fig. 1). The corresponding Mn(III) derivatives [1]⁺ and [2]⁺ were EPR silent.

Magnetic susceptibility data for 1 and 2 [5] and [1]⁺ and [2]⁺ [7] obtained by the Faraday technique confirm paramagnetism in all cases. The magnetic moments of these complexes are near the spin only values for 1 and 2 unpaired electrons for the neutral and the cationic species respectively. They show no temperature depen-

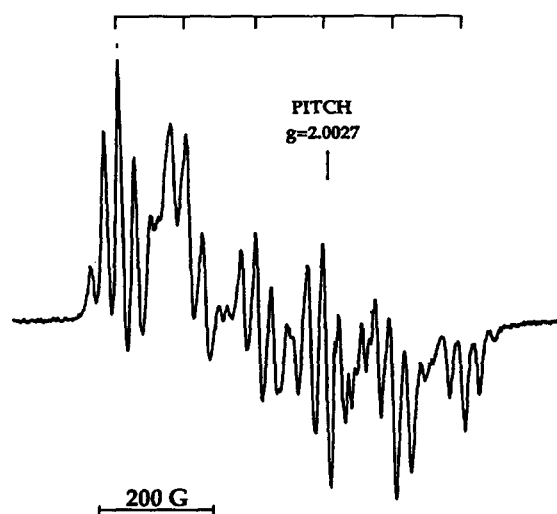


Fig. 1. EPR spectrum of 1 in a toluene glass.

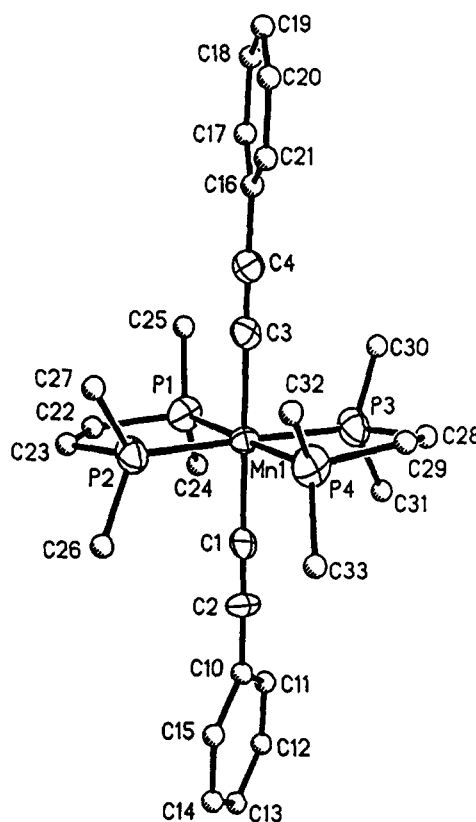


Fig. 2. X-ray structure of complex 1. Selected bond lengths (Å): Mn(1)–P, 2.267.3 (av.); Mn(1)–C(1), 1.953(11), Mn(1)–C(3), 1.970(11); C(1)–C(2), 1.217(16); C(3)–C(4), 1.215(16). Selected bond angles (°): C(1)–Mn(1)–C(3), 179.2(3); Mn(1)–C(1)–C(2), 178.4(9); Mn(1)–C(3)–C(4), 178.1(8); C(1)–C(2)–C(10), 175.0(10); C(3)–C(4)–C(16), 178.8(11).

dence between 79 and 293 K. These values suggest low-spin octahedral d⁵ (1,2) and d⁴ ([1]⁺, [2]⁺) electronic configurations. Low-spin electronic states were also found in the Me₂Mn(dmpe)₂ [11] and [Me₂Mn(dmpe)₂]⁺ [12] derivatives.

¹H NMR spectroscopy provides useful structural information on 1 and 2 and [1]⁺ and [2]⁺ despite the fact that these complexes are paramagnetic species. The spectra exhibit two broad signals of the dmpe methyl and methylene protons (δ (ppm) around –15.5 and –14 (1,2), –38 and –28 ([1]⁺, [2]⁺) respectively). The phosphorus ligand signals of 1 and 2 are close to those of the low-spin Mn(II) complex Me₂Mn(dmpe)₂ and are very different from those of the high-spin complexes, X₂Mn(dmpe)₂ (X = Br, I) [11]. The ¹H NMR resonances of all compounds are temperature dependent, which sharpen and shift low-field [5,7] upon heating. These results reveal that ¹H NMR spectra of such Mn complexes are quite indicative of the respective spin-state of the Mn center and can be used as a sensitive tool for the distinction of their different electronic states. ³¹P NMR resonances were not observable, presumably because of the line broadening induced by the

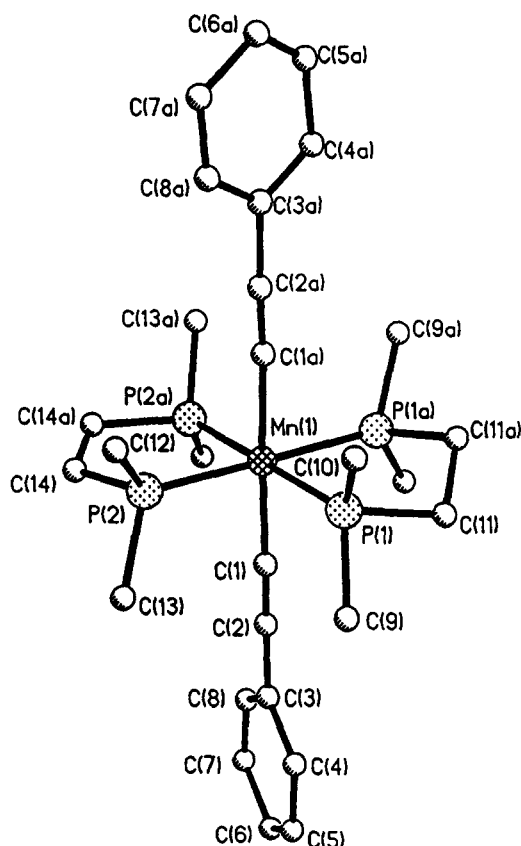


Fig. 3. X-ray structure of the cationic unit of $[1]^+ \text{OH}^- \cdot \text{H}_2\text{O}$. Selected bond lengths (Å): Mn(1)–P, 2.323(5)(av.); Mn(1)–C(1), 1.961(6); C(1)–C(2), 1.216(8). Selected bond angles (°): C(1)–Mn(1)–C(1a), 177.2(12); Mn(1)–C(1)–C(2), 173.7(14); C(1)–C(2)–C(3), 173.7(19).

close proximity of the phosphorus nuclei to the paramagnetic centers.

The crystal structures of **1** [13] (Fig. 2) and $[1]^+$ [14] (Fig. 3) were determined by X-ray diffraction studies [15]. **1** and $[1]^+$ have octahedral coordination, in which the two phenylacetylide ligands occupy *trans* sites and the four P atoms are located in an “equatorial” plane. The manganese atom in $[1]^+$ lies on a crystallographic center of symmetry. There is little distortion from linearity of the $\text{C}\equiv\text{C}-\text{Mn}-\text{C}\equiv\text{C}$ chain in both compounds. It is interesting to note that the Mn–C and $\text{C}\equiv\text{C}$ bond lengths are apparently insensitive to the oxidation state change and are almost identical in **1** and $[1]^+$ (1.96 and 1.22 Å respectively). The Mn–C bonds in **1** and $[1]^+$ are slightly shorter than the Mn–C bond in $\text{PhC}\equiv\text{CMn}(\text{CO})_3[\text{P}(\text{OPh})_3]_2$ (2.002(6) Å) [16]. In contrast to the Mn–C and $\text{C}\equiv\text{C}$ separations, the Mn–P bond distances in **1** and $[1]^+$ differ.

The average Mn–P bond length (2.27 Å) in **1** is significantly shorter than that in the Mn(III) analog $[1]^+$ (2.32 Å). The same bond distance behavior was found for $\text{Me}_2\text{Mn}(\text{dmpe})_2$ [11b] (2.24–2.25 Å) and $[\text{Me}_2\text{Mn}(\text{dmpe})_2]^+ \text{BPh}_4^-$ [12] (2.32 Å).

The cyclic voltammograms of **1**, **2**, $[1]^+$ and $[2]^+$ were recorded for 3×10^{-3} M solutions in 0.1 M tetraethylammonium perchlorate/acetonitrile (scan rate 100 mV s⁻¹). Two chemically reversible one-electron oxidations occur at very close potentials for both series of derivatives: –0.685 V ($\Delta E_p = 90$ mV), +0.58 V ($\Delta E_p = 80$ mV) for **1** and $[1]^+$ and –0.70 V ($\Delta E_p = 80$ mV), +0.57 V ($\Delta E_p = 100$ mV) for **2** and $[2]^+$. These close values also suggest that the redox processes occur at the Mn centers and are therefore only marginally influenced by the rather distant acetylide substituents [4]. The first redox step is attributed to an Mn(II)/Mn(III) transfer and the second can be assigned to the Mn(III)/Mn(IV) couple. These values resemble those for *trans*- Cl_2MnL_2 (L = *o*-phenylenebisdimethylphosphine) (approximately –0.6 V for Mn(II)/Mn(III) and +0.78 V for Mn(III)/Mn(IV)) [17]. The isolation and characterization of the Mn(IV) derivatives is in progress.

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- [5] In a typical reaction 0.43 g (2 mmol) of anhydrous MnBr_2 was refluxed for 1 h in 50 ml of THF under N_2 . The solution was cooled to -80°C , and 0.6 g (4 mmol, 0.7 ml) of dmpe was added. $\text{RC}\equiv\text{CLi}$ (from 4.4 mmol $\text{RC}\equiv\text{CH}$ in 2 ml THF and 2.5 ml 1.6 M BuLi in hexane) was added over a period of 5 min, producing a red brown solution. This solution was then allowed to warm to room temperature, stirred for an additional 3 h, filtered through celite, and evaporated to dryness. The yellow product was extracted with benzene (1) or pentane (2) and crystallized from benzene–heptane (1) or pentane (2) at -30°C , yield 0.45 g (40%) (1), 0.51 g (46%) (2). Anal. Found: C, 60.63; H, 7.46; Mn, 9.85. $\text{C}_{28}\text{H}_{42}\text{MnP}_4$ (1). Calc.: C, 60.33; H, 7.59; Mn, 9.85. Anal. Found: C, 47.86; H, 8.91; Mn, 10.00. $\text{C}_{22}\text{H}_{50}\text{MnP}_4\text{Si}_2$ (2). Calc.: C, 48.07; H, 9.17; Mn, 10.00. All manipulations were carried out under nitrogen. Selected spectroscopic data are as follows. 1: IR (KBr) ν 1975s, 2008s cm^{-1} ($\text{C}\equiv\text{C}$); EPR (toluene), 9.06 GHz, -190°C $A(^{55}\text{Mn}) = 129$ G, $A(^{31}\text{P}) = 28$ G; ^1H NMR (C_6D_6 , 200 MHz, 22°C): -16.3 (24H, 378 Hz [6], CH_3), -14.5 (8H, CH_2), -7.3 (4H, H_o), -3.5 (2H, H_p), 17.9 (93 Hz, H_m). (75°C): -12.5 (24H, 169 Hz, CH_3), -11.3 (8H, CH_2), -3.6 (4H, 63 Hz, H_o), -0.8 (2H, 31 Hz, H_p), 15.6 (4H, 41 Hz, H_m); MS (EI) m/z 557 (M^+); $\mu_{\text{eff}} = 1.79$ μB . 2: IR (KBr) ν 1942s cm^{-1} ($\text{C}\equiv\text{C}$); EPR (toluene), 9.06 GHz, -190°C $A(^{55}\text{Mn}) = 123$ G, $A(^{31}\text{P}) = 28$ G; ^1H NMR (CDCl_3 , 22°C): -14.7 (24H, 276 Hz, CH_3), -13.6 (8H, CH_2), 4.8 (18H, 34 Hz, SiCH_3); MS (EI) m/z 549; $\mu_{\text{eff}} = 1.82$ μB .
- [6] Line-width at half-height.
- [7] $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (0.4 mmol) in 3 ml of diethyl ether was slowly added to a cooled (-60°C) solution of 0.11 g (0.2 mmol) 1,2 in diethyl ether (25 ml). This mixture was allowed to warm to room temperature and stirred for an additional 1 h. The product precipitated from solution which was collected by filtration. Yield 0.10 g (85%) $[1]^+\text{BF}_4^-$. Anal. Found: C, 52.12; H, 6.47; Mn 8.29. $\text{C}_{25}\text{H}_{42}\text{BF}_4\text{MnP}_4$. Calc.: C, 51.80, H, 6.52; Mn, 8.46, 0.11 g (87%) $[2]^+\text{BF}_4^-$. Anal. Found: Mn, 8.92. $\text{C}_{25}\text{H}_{50}\text{BF}_4\text{MnP}_4\text{Si}_2$. Calc. Spectroscopic data. $[1]^+$: IR (KBr) ν 2040m ($\text{C}\equiv\text{C}$), 1080vs cm^{-1} (BF); ^1H NMR (CDCl_3 , 22°C) -57.1 (4H, 276 Hz, H_o), -52.9 (2H, 210 Hz, H_p), -37.8 (24H, 578 Hz, CH_3), -28.5 (8H, 592 Hz, CH_2), 36.5 (4H, 181 Hz, H_m). (55°C) -51.1 (4H, 168 Hz, H_o), -47.3 (2H, 126 Hz, H_p), -34.0 (24H, 427 Hz, CH_3), -25.7 (8H, 380 Hz, CH_2), 33.8 (4H, 158 Hz, H_m); MS (FAB) m/z 557 (M^+); $\mu_{\text{eff}} = 2.60$ μB . $[2]^+$: IR (KBr) ν 1988, 2024w cm^{-1} ($\text{C}\equiv\text{C}$), 1080vs (BF); ^1H NMR (CDCl_3 , 22°C) -38.1 (24H, 413 Hz, CH_3), -28.5 (8H, 403 Hz, CH_2), 7.6 (18H, 92 Hz, SiCH_3). MS (FAB) m/z 549; $\mu_{\text{eff}} = 2.82$ μB .
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- [13] Crystal data and data collection and refinement details for 1: $\text{C}_{28}\text{H}_{42}\text{MnP}_4$, monoclinic, $P2_1/n$, $a = 12.753(4)$ Å, $b = 13.833(3)$ Å, $c = 17.483(5)$ Å, $\beta = 104.26(2)^\circ$, $V = 2989.0(14)$ Å³, $d_{\text{calc}} = 1.239$ g cm^{-3} , $T = 223$ K, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $4.0 \leq 2\theta \leq 60.0^\circ$, direct methods (SHELXTL-PLUS). Of 8747 independent reflections (Siemens R3m/V) 1993 ($F > 6.0\sigma(F)$) were used in the least-squares refinement of 298 parameters ($R = 0.0566$, $R_w = 0.0674$).
- [14] Crystal data, data collection, and refinement details for $[1]^+\text{OH}^-\cdot\text{H}_2\text{O}$: $\text{C}_{28}\text{H}_{45}\text{MnO}_2\text{P}_4$, orthorhombic, $Fdd2$, $a = 11.857(3)$ Å, $b = 22.229(7)$ Å, $c = 24.855(5)$ Å, $V = 6551(3)$ Å³, $d_{\text{calc}} = 1.195$ g cm^{-3} , $T = 223$ K, $Z = 8$, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $3.0 \leq 2\theta \leq 52.0^\circ$, direct methods (SHELXTL-PLUS). Of 1771 independent reflections (Siemens R3m/V) 1157 ($F > 4.0\sigma(F)$) were used in the least-squares refinement of 163 parameters ($R = 0.0627$, $R_w = 0.0863$).
- [15] Further details of the X-ray structure determinations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. Requests should contain the deposition number CSD 59047, names of authors and citation of this article.
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