Bifunctional Cp ∩ N Complexes—Unusual Structural Features and Electronic Coupling in Highly Preorganized Bimetallic Systems**

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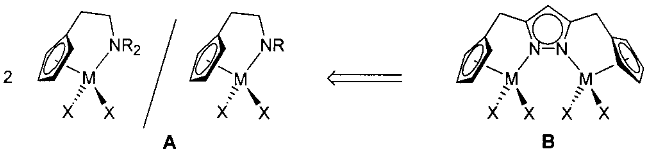
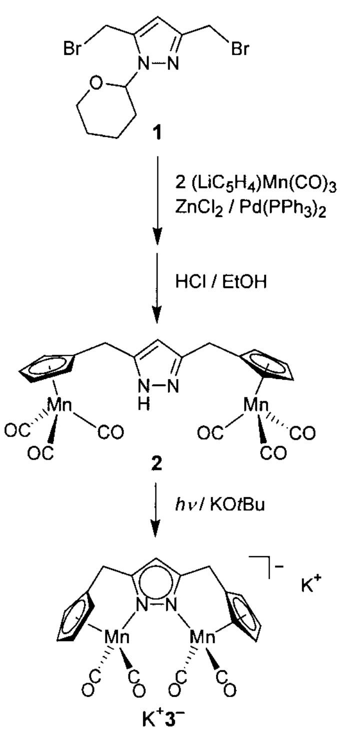
Dedicated to Professor Lutz F. Tietze
on the occasion of his 60th birthday

Complexes of cyclopentadienyl (Cp) ligands with functional amino or amido side chains are currently receiving enormous attention in organometallic chemistry.[1, 2] While the donor substituent tethered to the Cp moiety usually serves a hemilabile chelate function in generic type **A** complexes, we recently put forward a novel approach in which a pyrazolate group in complexes of type **B** links two Cp units and acts both as an intramolecular N donor and as a bridging group spanning two metal ions .[3] Such a strategy, that is the formal coupling of two N-containing ligand compartments through a functionalized pyrazolate bridge to constitute a preorganized dinuclear scaffold, has successfully been employed for mimicking cooperative effects in biomimetic coordination compounds.[4] Accordingly, type **B** systems are now expected to give rise to novel organometallic chemistry in which two adjacent metal ions might work in concert. Here we report the first transition metal complex of type **B**, its unusual structural features in the solid state, and characteristics of the metal–metal interaction in the mixed-valent form.



It proved difficult to introduce the parent Cp into the side arms of functionalized pyrazole derivatives such as **1**,[5] and thus we employed a "protected" form of Cp: attachment of [CpMn(CO)$_3$] to the pyrazole nucleus was achieved in a [Pd(PPh$_3$)$_2$]/ZnCl$_2$-catalyzed cross-coupling reaction[6] yielding **2** (Scheme 1).

A single-crystal structure analysis[7] showed that **2** contains a protonated (noncoordinating) 1*H*-pyrazole heterocycle suitably arranged to potentially interact with the pendant metal carbonyl fragments. Photolytic decarbonylation of **2** and deprotonation using KO*t*Bu gave $K^+\mathbf{3}^-$, the first bimetallic complex of type **B**. Its formation can be monitored by IR spectroscopy through the characteristic changes of the CO stretching frequencies (2015/1927 cm^{-1} for **2** versus 1919(1896)/1848(1816) cm^{-1} for $\mathbf{3}^-$).[8]



Scheme 1. Synthesis of the complex $K^+\mathbf{3}^-$.

Single crystals of $K^+\mathbf{3}^-\cdot 0.9\,THF$ obtained from THF/light petroleum were analyzed by X-ray crystallography.[9] The asymmetric unit contains four (very similar) dimanganese(I) units of the anticipated constitution—one of which is depicted in Figure 1. The N-Mn-$C_{C\equiv O}$ angles in $\mathbf{3}^-$ are rather large (mean value 101.9°) compared to those in other [CpMn(CO)$_2$L] complexes (L = N-donor ligand; 92.6–98.1° according to a CSD search), indicating a somewhat strained situation in the chelate complex $\mathbf{3}^-$.

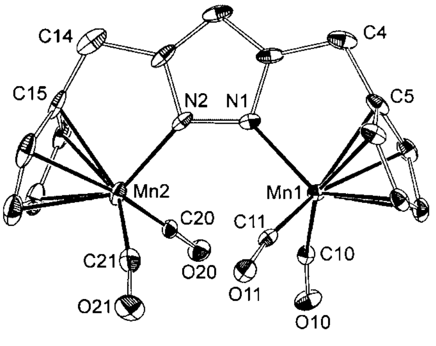


Figure 1. Molecular structure of $\mathbf{3}^-$ (30% probability ellipsoids). Selected interatomic distances [Å] and range of selected bond angles and dihedral angles [°]; values for the other three independent molecules in square brackets: Mn1-N1 2.034(4) [2.032(4), 2.066(3), 2.047(4)], Mn2-N2 2.053(4) [2.060(4), 2.053(4), 2.033(4)]; $C_{C\equiv O}$-Mn-N 98.6(2)-102.9(2) [100.0(2)-103.8(2), 102.3(2)-104.7(2), 96.3(2)-102.8(2)], Mn1-N1-N2-Mn2 27.9(1) [22.3(1), 10.3(1), 34.3(1)].

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The bimetallic entities are connected through potassium ions to form a three-dimensional coordination polymer in the solid state. All K^+ ions are involved in unusual η^5 π interactions with the pyrazolate heterocycle (Figure 2; d(K–N) 2.83–3.07, d(K–C) 3.14–3.52 Å).[10] Such η^5 coordination to a pyrazolate group is very rare and has only recently been reported in a few cases,[11] while to the best of our knowledge the η^1:η^1:η^5 pyrazolate binding mode observed in **3** is unprecedented.[12]

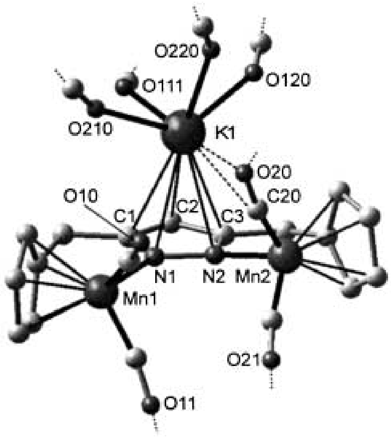

Figure 2. Part of the solid-state structure of ($K^+\mathbf{3}^-$) · 0.9 THF.

The coordination sphere of two of the four crystallographically distinct K^+ ions is completed by three O atoms of CpMn-bound CO groups and by one THF solvent molecule, while the other two K^+ ions are coordinated to four neighboring carbonyl-O atoms. These latter K^+ ions display a further open coordination site and exhibit a remarkably short additional side-on π contact with one CO ligand that is already end-on-bound to a second K^+ ion (see Figure 2: d(K1 ··· C20/O20) 3.07/3.14, d(K2 ··· C310/O310) 3.02/2.95 Å). According to a CSD search these are among the shortest side-on $K^+ \cdots$ CO contacts detected thus far.[13]

The Mn^IMn^I compound $\mathbf{3}^-$ is easily oxidized, for example, by air. The cyclic voltamogram of $\mathbf{3}^-$ in THF reveals two well-separated reversible redox waves at $E_{1/2} = -0.37$ and $E_{1/2} = +0.14$ V (Figure 3),[14] corresponding to the formation of the Mn^IMn^{II} (d^5/d^6) and the oxidized $Mn^{II}Mn^{II}$ (d^5/d^5) species. The rather large separation of these single-electron processes ($\Delta E_{1/2} = 509$ mV) suggests strong electronic coupling and significant stabilization of the mixed-valent compound **3** ($K_{comp} = 3.8 \times 10^8$). A related Mn^IZn^{II} complex with only one redox-active Mn ion gave a single wave at $E_{1/2} = -0.20$ V in CH_2Cl_2.[6c]

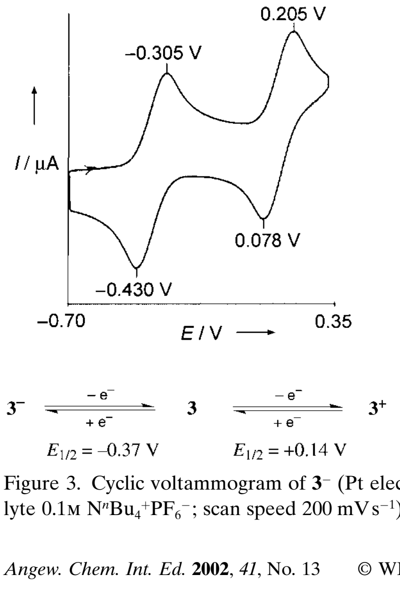

Figure 3. Cyclic voltammogram of $\mathbf{3}^-$ (Pt electrode, solvent THF, electrolyte 0.1 M $N^nBu_4^+PF_6^-$; scan speed 200 mV s^{-1}).[14]

Complex **3** can be prepared on a preparative scale by stoichiometric oxidation of $\mathbf{3}^-$ with $AgBF_4$ and was isolated as a red powder. It should be noted that **3** is a rare example of a neutral d^5/d^6 mixed-valent complex, which is of particular interest because the absence of charge trapping in nonpolar solvents is expected to favour a high degree of delocalization. The EPR spectrum of **3** in 2-methyltetrahydrofuran at 293 K shows an 11-line pattern ($g_{iso} = 2.028$; $a(^{55}Mn)_{iso} = 28.3 \times 10^{-4}$ cm^{-1}; Figure 4), confirming the equivalence of the two metal centers on the EPR time scale. A spectrum in frozen solution (123 K), however, indicates localized valency with electron coupling to only one ^{55}Mn nucleus. Variable-temperature EPR spectra were measured to locate the coalescence temperature, that is the transition between EPR-localized and -delocalized states (Figure 4). Transition between the isotropic 11-line pattern and a 6-line profile occurs around 185 K, where the solution (2-methyltetrahydrofuran/3-methylcyclopentane 1:4) still retains its fluidity. If one assumes sufficiently slow intramolecular electron transfer at low temperature as the reason, a rough estimate of the activation energy $E_{th}^{\ddagger}$ and the thermal electron transfer rate k_{th} can be derived from Gagné's approximation [Eq. (1)]:[15] $E_{th}^{\ddagger} = 13.6$ kJ mol^{-1} and $k_{th} = 2.5 \times 10^{10}$ s^{-1} at 298 K.

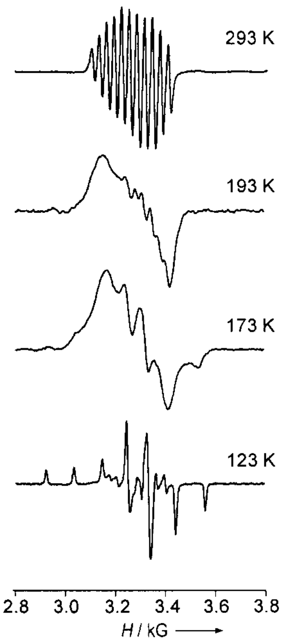

Figure 4. EPR spectra of the mixed-valent complex **3** in 2-methyltetrahyrofuran/3-methylcyclopentane (1:4) at selected temperatures.

$$k_{th} = (kT/h)\exp(-E_{th}^{\ddagger}/RT) \qquad (1)$$

Based on these initial results, a Robin–Day class II assignment may be proposed for **3**. Accordingly, four CO absorptions are observed for the neutral mixed-valent Mn^IMn^{II} compound **3** (2027, 1952, 1899, and 1827 cm^{-1}), confirming that **3** is a valence-trapped species on the short vibrational time scale (ca. 10^{-12} s).

While the kinetically inert $CpMn(CO)_2$ fragment has frequently been used for the stabilization of unusual molecules[16] and for the construction of d^5/d^6 mixed-valent systems,[17] the notorious lability of $[CpMn(CO)_2(L)]$ complexes has generally hampered the isolation and detailed characterization of systems with "inorganic" ligands L, in particular in the oxidized Mn^{II} forms. In **3**, the rigid chelate arrangement now precludes dissociation, and the π plane of the bridging pyrazolate roughly coincides with the mirror plane of the $Mn^{II}(CO)_2$ fragment, which is a favorable situation for stabilizing electronic π interactions. A more detailed study of the electronic properties of $\mathbf{3}^{-/0/+}$ will be reported in due course.

Experimental Section

2: $[CpMn(CO)_3]$ was dissolved in THF and deprotonated with *n*BuLi at −78 °C. The solution was sequentially treated with $ZnCl_2$, $[Pd(PPh_3)_2]$ (prepared by the reduction of $[PdCl_2(PPh_3)_2]$ with diisobutylaluminum hydride (DIBAH)) and **1**, and stirred for 1 h at −78 °C and at room temperature under exclusion of light for a further 72 h. Following hydrolysis with brine, the tetrahydropyran(THP)-protected product was purified by column chromatography (diethyl ether/light petroleum 1:1, $R_f = 0.33$, yield 44%). The THP protecting group was cleaved with ethanolic HCl, and the product **2** obtained as yellowish crystals from CH_2Cl_2/light petroleum (yield 66% for the second step). Details of the synthetic procedures and full characterization of the compounds will be reported elsewhere.[7]

$K^+\mathbf{3}^-$: A solution of **2** (0.29 g, 0.58 mmol) in THF (200 mL) was irradiated with a high-pressure mercury lamp in a quartz apparatus for 15 min at −40 °C, which caused the reaction mixture to turn deep red. The progress of the reaction was monitored by IR spectroscopy in the CO stretching region (2015, 1927 before irradiation; 1916, 1843 after irradiation). After the mixture had been warmed to room temperature, KO*t*Bu (0.65 g, 0.58 mmol) was added and the reaction mixture was left to stir for 1 h. All volatile material was then removed under vacuum and the red residue washed with light petroleum and dissolved in a small amount of THF. Slow diffusion of light petroleum into the solution deposited red crystals of $K^+\mathbf{3}^- \cdot 0.9\,THF$ (yield: 0.18 g, 0.37 mmol, 64%). IR (KBr): $\tilde{\nu} = 1911$ vs, 1885 m, 1844 vs, 1804 m cm^{-1}; IR (THF): $\tilde{\nu} = 1919$ vs, 1896 m, 1848 vs, 1816 m cm^{-1}; UV/Vis (THF): $\lambda_{max}(\varepsilon) =$ 400 nm (460 $m^{-1}cm^{-1}$); MS (FAB): *m/z* (%): 482 (10) $[M^+]$, 443 (20) $[M^+ - K]$, 387 (45) $[M^+ - K - 2CO]$; elemental analysis: calcd (%) for $C_{19}H_{13}KMn_2N_2O_4$ (482.29): C 49.82, H 3.81, N 5.05; found: C 49.24, H 3.81, N 5.04.

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[9] Crystal structure of $(K^+\mathbf{3}^-)_4 \cdot 3.6\,THF$ ($C_{76}H_{52}K_4Mn_8N_8O_{16} \cdot 3.6\,THF$, $M_r = 2188.8$): monoclinic, $P2_1/c$, $a = 23.071(5)$, $b = 25.404(5)$, $c = 15.501(3)$ Å, $\beta = 91.14(3)$, $V = 9083(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.601$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.33$ mm^{-1}, $2\theta_{max} = 54.9°$, 20751 independent reflections ($R_{int} = 0.093$), 12009 observed $[I > 2\sigma(I)]$, 1192 parameters; final $R1[I > 2\sigma(I)] = 0.076$, $wR2 = 0.127$, goodness of fit on $F^2 = 1.020$, largest difference peak $+0.73/-0.48$ eÅ^{-3}. Data were collected on a Nonius Kappa CCD diffractometer at 200 K using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods with the SHELXS-97 and refined with the SHELXL-97 programs. Non-hydrogen atoms were refined in anisotropic models. Hydrogen atoms were placed at calculated positions and allowed to ride on the atoms they are attached to. CCDC 162374 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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