Synthesis and molecular structure of the first vinylidene complex $[Cp(CO)_2MnCu(\mu\text{-}C{=}CHPh)(\mu\text{-}Cl)]_2$ with the Mn—Cu bond

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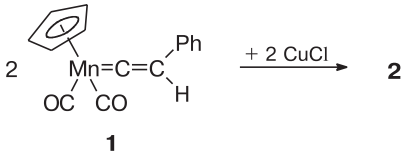
Copper-containing μ-vinylidene complexes are very rare. The CuOs complex[1] and three CuRh complexes[2] with the μ-C=CHR (R = H, Me, Ph) ligands have earlier been reported. However, their structures were not reliably determined. A CuTi μ-vinylidene complex without metal—metal bond is known.[3]

In this work we report the synthesis, structure, and some properties of the new compound $[Cp(CO)_2MnCu(\mu\text{-}C{=}CHPh)(\mu\text{-}Cl)]_2$ (**2**), which is the first μ-vinylidene complex with the transition metal—copper bond established by X-ray diffraction analysis.

The reaction of $Cp(CO)_2Mn{=}C{=}CHPh$ (**1**) with CuCl (THF, 20 °C, 30 min) affords the dark-green complex **2** (Scheme 1, Fig. 1) in ~100% yield.

Scheme 1



Compound **2** is moderately stable in the solid state but its solutions in polar organic solvents rapidly decompose. Single crystals of complex **2** appropriate for X-ray diffraction analysis* were prepared from a CH_2Cl_2—hexane (1 : 1) mixture.

Complex **2** is a dimer, whose two binuclear fragments are linked to each other by asymmetrical chloride bridges (Cu(1)—Cl(1) 2.256(2), Cu(1)—Cl(1A) 2.278(2) Å). The center of inversion lies in the intersection point of the Cl(1)—Cl(1A) and Cu(1)—Cu(1A) vectors.

The central part of each binuclear fragment represents the MnCuC(1) triangle with the bond lengths Mn—Cu 2.438(1), Cu—C(1) 1.924(5), and Mn—C(1) 1.874(5) Å. The Mn—C(1) bond in complex **2** is much shorter than those in the known[4,5] manganese μ-vinylidene derivatives (1.93—1.98 Å). The C(1)=C(2) bond length (1.322(7) Å) in complex **2** is also somewhat shorter than the typical value (1.35 Å). The vector of this bond is noticeably inclined toward the Cu atom (bond angles Mn(1)—C(1)—C(2) 157.2(4)° and Cu(1)—C(1)—C(2) 122.7(4)°).

Both CO groups at the Mn atom are terminal (bond angles Mn—C—O 174.7(4) and 177.4(5)°). In the IR spectrum of a solution of compound **2** in CH_2Cl_2, two ν(CO) bands at 2005 and 1953 cm^{-1} correspond to stretching vibrations of these groups. Their position is almost the same as that of the bands in the initial complex **1** (2008 and 1948 cm^{-1}).

The ^{13}C NMR spectrum of complex **2** (in $CDCl_3$) contains a singlet signal at 88.37 ppm corresponding to the C_5H_5 ligand, and the signal from C(2) was detected at 136.26 ppm. The signal from the vinylidene C(1) atom in the cycle lies in a rather weak field at 317.05 ppm. This is unusual for μ-vinylidene complexes, which are characterized by signals from μ-C at 240—270 ppm.[4,6] The signal from the vinylidene proton ($=C(2)\underline{H}Ph$) is observed in the ^1H NMR spectrum at 7.69 ppm. The singlet signal at 5.27 ppm corresponds to resonance of the protons in C_5H_5.

The structural and spectral parameters of the complex point to a weak binding of the Cu atom with the Mn=C(1)=C(2) system. This is confirmed by our preliminary data on the chemical behavior of complex **2**. The treatment of complex **2** with PPh_3 affords the initial complex **1**. The reactions of complex **2** with $Fe_2(CO)_9$

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* The complete X-ray diffraction data were deposited in the Cambridge Structural Data Bank.

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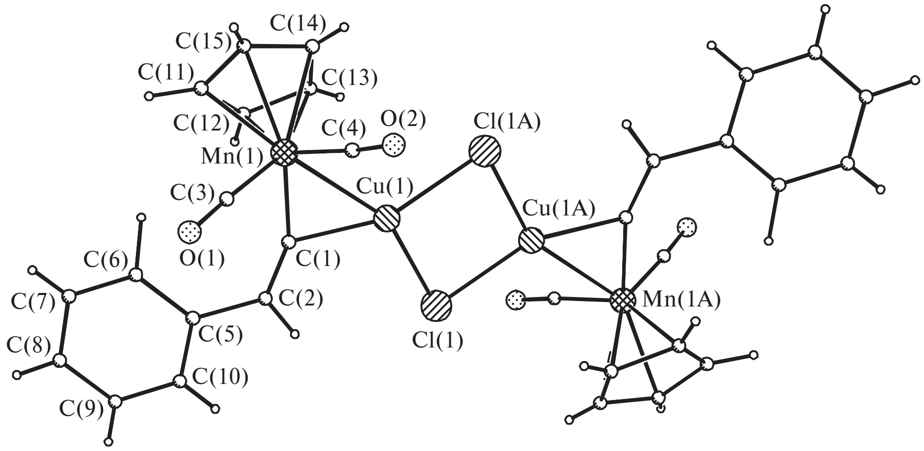

Fig. 1. Crystal structure of complex **2**.

and with $Pt(PPh_3)_4$ produce the transmetallation products, *viz.*, known[6] binuclear compounds with the Mn—Fe and Mn—Pt bonds, respectively.

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