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Preliminary communication

NOVEL COMPLEXES OF MANGANESE WITH PHENYLVINYLIDENE AS A LIGAND

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Summary

Three novel stable complexes of manganese were prepared by interaction of $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(THF)]$ with phenylacetylene. X-ray structure analysis of two of the complexes established the presence of a phenylvinylidene ligand. In $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(C{=}CHPh)]$ this ligand forms an unusual double Mn=C bond and in $[(\eta^5\text{-}C_5H_5)_2Mn_2(CO)_4(C{=}CHPh)]$ it acts as a bridge strengthening the Mn—Mn bond.

It was reported [1] that a photochemical reaction of $[(\eta^5\text{-}C_5H_5)Mn(CO)_3]$ with phenylacetylene led to a very unstable π-acetylenic complex I. We carried out [2] the reaction of phenylacetylene with $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(THF)]$ and by chromatography with Al_2O_3 of a reaction mixture, isolated three stable complexes, viz. II (yield 7%), III (2%) and IV (12%). According to the composition of the complexes this reaction can be represented by Scheme 1.

Compound II is dark-red crystalline, m.p. 64°C. It is characterized by higher CO stretching frequencies in the infrared spectrum (ν(CO) 2008, 1954 cm^{-1}, in cyclohexane) compared with those of the isomeric π-acetylene complex I (1981, 1921 cm^{-1}) and a series of other complexes of the type $[(\eta^5\text{-}C_5H_5)Mn(CO)_2L]$ with L = Ph_3P, $(PhO)_3P$, π-ethylene, π-acetylene [1, 3]. This indicates a considerable π-accepting ability of the C_8H_6 ligand.

The binuclear complex III crystallizes in violet prisms with m.p. 144°C. Its infrared spectrum in cyclohexane contains ν(CO) bands at 2006, 1981, 1952 and 1928 cm^{-1}.

In the mass spectra of II and III molecular ions were found with *m/e* 278 and 454, respectively. C_8H_6 ligands in II and III are more strongly bound to the metal than the CO-groups.

To elucidate the structures of II and III unequivocally we undertook their X-ray study. The corresponding investigation of IV is now in progress.

$$(\eta^5\text{-}C_5H_5)Mn(CO)_2(THF) + PhC{\equiv}CH \rightarrow \underset{(I)}{(\eta^5\text{-}C_5H_5)Mn(CO)_2(PhC{\equiv}CH)} \rightarrow$$

$$\rightarrow \underset{(II)}{(\eta^5\text{-}C_5H_5)Mn(CO)_2(C_8H_6)} + \underset{(III)}{(\eta^5\text{-}C_5H_5)_2Mn_2(CO)_4(C_8H_6)} + \underset{(IV)}{(\eta^5\text{-}C_5H_5)_2Mn_2(CO)_4(C_{16}H_{10})}$$

SCHEME 1

Crystal structure data. Crystals of II are orthorhombic, $a = 10.492(2)$, $b = 33.038(6)$, $c = 7.475(2)$ Å, $D_m = 1.42$, $D_c = 1.433$ g cm^{-3} for $Z = 8$, space group *Pccn*. Crystals of III are also orthorhombic, $a = 15.336(3)$, $b = 15.391(3)$, $c = 7.998(1)$ Å, $D_m = 1.58$, $D_c = 1.606$ g cm^{-3} for $Z = 4$, space group $P2_12_12_1$. Intensities were measured with an automatic four-circle Hilger & Watts diffractometer (copper radiation, graphite monochromator). The structures were solved by the heavy atom method on the basis of 600 (II) and 1200 (III) reflections with $F^2 \geqslant 3\sigma$ and refined by an anisotropic block-diagonal least-squares procedure, $R = 0.093$ (II) and 0.071 (III). Relatively small numbers of reflections and only moderate accuracy of results are due to rapid radiation damage of crystals during an X-ray exposure.

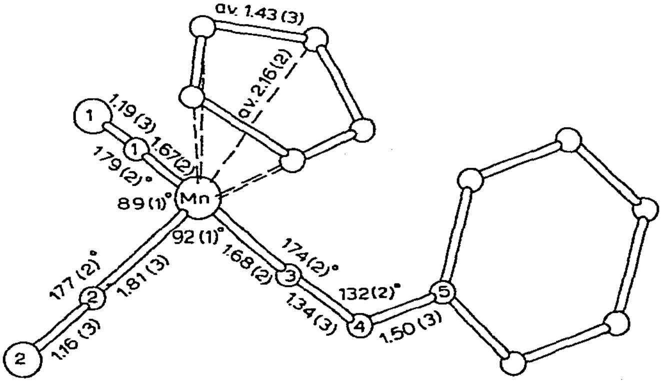

Fig. 1. The molecular structure of $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(C{=}CHPh)]$ with main bond lengths and angles.

The molecular structure of II is shown in Fig. 1. This complex has an unusual monodentate phenylvinylidene ligand which arises due to a hydrogen migration to the neighbouring carbon atom in the π-coordinated PhC≡CH. Thus II is (η^5-cyclopentadienyl)(phenylvinylidene)manganese dicarbonyl. The MnC(3)C(4) fragment represents an almost strictly linear metalallene system. The angle at C(3) is equal to 174(2)°, the angle at C(4) is increased to 132(2)° due to steric repulsion C(3)· · ·C(6) (the corresponding distance is only 3.13(3) Å). The C(3)=C(4) distance of 1.34(3) Å corresponds to the double bond. The Mn=C(3) bond (1.68(2) Å) could also be considered a double bond since it is shorter than a Mn—Alk σ-bond (2.16 Å) [4] and even shorter than the Mn—C(carbene) bond (1.88 Å) in $[(\eta^5\text{-}C_5H_5)Mn(CO)_2\{C(Ph)COPh\}]$ [5]. Taking into account the difference in Mn and Mo covalent radii, which is equal [4] to ca. 0.20 Å, this Mn=C double bond is close in length to the double Mo=C bond (1.83 Å) in $[MoCl(\eta^5\text{-}C_5H_5)\}C{=}C(CN)_2\}\{P(OMe)_3\}_2]$ with the dicyanovinylidene ligand [6]. The metalallene system is almost coplanar with the phenyl ring (the torsional angle around the C(4)—C(5) bond is equal to 10°).

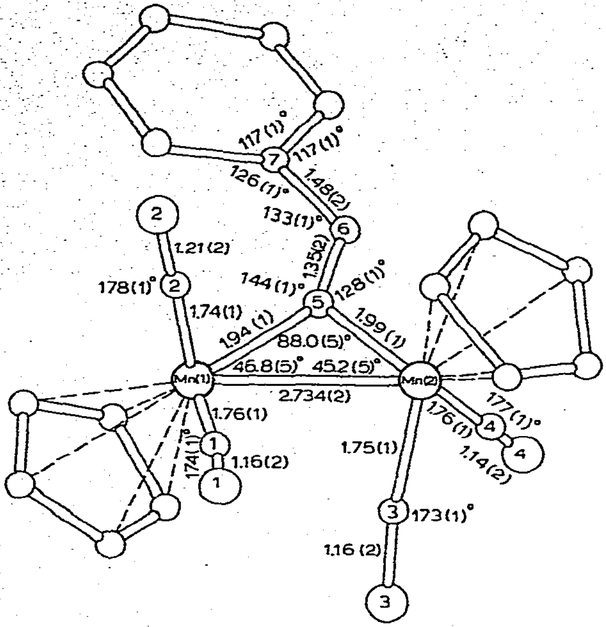

Fig. 2. The molecular structure of [(μ-C=CHPh){Mn(CO)$_2$(η^5-C$_5$H$_5$)}$_2$] with main bond lengths and angles.

In the binuclear complex III (Fig. 2), μ-phenylvinylidene-bis(η^5-cyclopentadienylmanganese dicarbonyl), two (η^5-C$_5$H$_5$)Mn(CO)$_2$ fragments are connected by the Mn—Mn bond of 2.734(2) Å and the bridging phenylvinylidene ligand. Its geometry (Mn—C 1.94(1) and 1.99(1) Å, angle Mn—C—Mn 88.0(5)°) is close to that of the dicyanovinylidene bridge in [*cis*-Fe$_2$(CO)$_2$(η^5-C$_5$H$_5$)$_2$(μ-CO){μ-C=C(CN)$_2$}] [7] (Fe—C 1.96 and 1.97 Å, angle Fe—C—Fe 84°). This similarity is explained by the closeness of Mn and Fe covalent radii [4].

The torsional angles around C(5)—C(6) and C(6)—C(7) bonds are equal to 7 and 11° respectively. Thus just as in II there is a pronounced tendency to conserving of planarity despite a steric repulsion between the Ph ring and the Mn(1)-(CO)$_2$ fragment causing bond angle distortions at C(5), C(6) and C(7). Relative to the Mn—Mn bond, CO-groups have different orientations : the angles Mn(2)—Mn(1)—C(1) 77(1)° and Mn(1)—Mn(2)—C(3) 79(1)° are considerably smaller than Mn(2)—Mn(1)—C(2) 100(1)° and Mn(1)—Mn(2)—C(4) 104(1)°. The Mn(CO)$_2$(η^5-C$_5$H$_5$) fragments are in *trans*-position in respect to the metal—metal bond and the planar cyclopentadienyl ligands are practically parallel to each other (dihedral angle is 9°).

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