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Vinylidene carbonylation at a manganese–iron complex: A density functional study of mechanism

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ABSTRACT

Treating the phenylvinyldene manganese complex $Cp(CO)_2Mn{=}C^1{=}C^2HPh$, **1**, with $[Fe(CO)_4]$ yields the binuclear μ-vinylidene complex $Cp(CO)_2MnFe(\mu\text{-}C^1{=}C^2HPh)(CO)_4$, **2**, that further isomerizes to the carbonylated product $\eta^4\text{-}[Cp(CO)_2MnC^1(CO)C^2HPh]Fe(CO)_3$, **3**. In a computational study of the mechanism using a hybrid density functional method, we considered two stereoisomers for species **2** and **3** where the phenyl group at center C^2 is oriented in *cis* (**E** form) or *trans* (**Z** form) fashion to the $Cp(CO)_2Mn$ unit. Isomers **2E** and **2Z** were calculated to be degenerate whereas the experimentally detected species **3E** is 8 kcal/mol more stable than its isomer **3Z**. The two-step pathway **1** → **2Z** → **3E** was calculated to be the lowest-energy route with the highest activation barrier at 12 kcal/mol. The activation energy of the alternative single-step pathway **1** → **3E** is 19 kcal/mol. We rationalized the stabilization of the ground state of **3E** and the transition states leading to or starting from isomer **2Z** as conjugation effect between the Mn–C=C metallaallene fragment and the co-planar phenyl ring.

1. Introduction

Carbonylation reactions of vinylidene are quite rare. In contrast, carbonylation of a carbene or a carbyne ligand, resulting in the formation of free ketenes as well as η^2-ketene, η^1- or η^2-ketenyl ligands are well known and have intensively been studied [1]. Organometallic compounds participating in similar reactions are considered as models of likely intermediates in a Fischer-Tropsch process [2]. The first example of a vinylidene carbonylation was reported for the reaction of $Cp(CO)_2Mn{=}C^1{=}C^2HPh$, **1**, with $Fe_2(CO)_9$ (Fig. 1) when instead of the expected μ–vinylidene complex $Cp(CO)_2MnFe(\mu\text{-}C^1{=}C^2HPh)(CO)_4$, **2**, the carbonylated product $\eta^4\text{-}[Cp(CO)_2MnC^1(CO)C^2HPh]Fe(CO)_3$, **3**, was isolated [3,4]. Later on two further examples of vinylidene carbonylation at a metal center were discovered, for the di-iron complex $[Fe(CO)_3(Et_3P)]_2(\mu\text{-}C{=}CH_2)$ [5] and the diplatinum complex $Pt_2(\mu\text{-}C{=}CHPh)(PPh_3)_2(CO)(C_6F_5)_2$ [6].

In all these cases a CO ligand migrates from a metal center to the α-carbon atom (center C^1) of vinylidene; simultaneously a vinylideneketene ligand $O{=}C{=}C^1{=}C^2HR$ (R = H, Ph) forms. These vinylideneketene ligands which do not exist as free molecules are bound to one of the metal centers in η^3-allylic fashion, featuring one σ-bond to the second metal center. This η^3-allylic ligand together with a metal-containing fragment – $Cp(CO)_2Mn$ or $(Et_3P)(CO)_3Fe$ – represents a heterometallic analog of the trimethylenemethane (TMM) ligand $C^1(CH_2)_3$ [7]. The ligand $PhC^2H{=}C^1{=}C^3{=}O$ of the diplatinum complex $(C_6F_5)_2(PPh_3)Pt[(\eta^3\text{-}PhC^2HC^1C^3O)Pt(PPh_3)_2]$ is of π-allylic type [6]. The C_4 fragment of the TMM ligand exhibits an almost planar structure with three delocalized C–C π-bonds at the C^1 center. “Heterotrimethylenemethane” systems are (formally) created by replacing each of the three CH_2 moieties in isolobal fashion, the first one by C=O, the second one by C^2HR (R = H, Ph), and the third one by the metal fragment. The structures of the heterometallic moieties are almost planar similar to that of their purely organic analog TMM.

Using methods based on density functional theory (DFT), the present computational study explored the reaction of the vinylidene complex **1** with $[Fe(CO)_4]$ to obtain complex **2** and the subsequent carbonylation reaction that occurs at the MnFe core (Fig. 1). To the best of our knowledge this is the first computational study of the structure, the properties, and the reactivity of binuclear vinylidene complexes with two different transition metal centers. Previous quantum chemistry studies of vinylidene polynuclear complexes addressed only homoatomic species. The Ru–Ru vinylidene species

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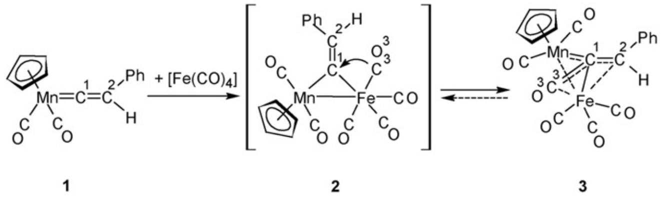

Fig. 1. Formation of the Mn–Fe phenylvinylidene complex, **2**, and its isomerization to the benzylideneketene complex **3**.

$[(C_5H_5)Ru]_2(\mu\text{-}C{=}CH_2)H(\mu\text{-}\eta^1{:}\eta^2{-}CH{=}CH_2)(\eta^2{-}C_2H_4)$ and $[(C_5H_5)Ru]_2(\mu\text{-}C{=}CH_2)(\mu{-}CH{-}CH_3)(\eta^2{-}C_2H_4)$ were explored as the products of C–H bond cleavage in a vinyl $CH{=}CH_2$ ligand [8]. Another theoretical study considered Re–Re species [9]. Yet, mononuclear vinylidene complexes of Mn, Fe, Ru, Os, Rh, Ir, W, and Nb were very extensively examined, mainly with regard to their ability to foster the transformation of acetylene to vinylidene at the metal center; see the detailed review of Wakatsuki [10] and references therein. All these studies predicted the vinylidene form of the metal complex to be more stable than its acetylene congener. Among the three variants of this transformation the one via 1,2-hydrogen shift is least energy-demanding. Arguing from the structure of the highest occupied molecular orbital (HOMO), the vinylidene complex $Cp(CO)_2Mn{=}C{=}CH_2$ was suggested to undergo addition of a nucleophile [11].

The present work aims at unraveling the mechanism for forming binuclear Mn–Fe species as well as factors that affect their stability. We studied reaction pathways that connect the two experimentally detected complexes **1** and **3**. Thereby we compared the two-step mechanism **1** → **2** → **3** via the intermediate complex **2** and the single-step mechanism **1** → **3** where species **3** forms directly from the reactants. The first mechanism seems reasonable as recent IR and NMR measurements showed that both μ-vinylidene **2** and the TMM isomeric form **3** co-exist in solution [12]. As more than one form of μ-vinylidene may occur, we modeled several isomers of the binuclear complexes **2** and **3**.

2. Computational details

All calculations were carried out using the hybrid density functional method B3LYP [13] as implemented in the program package TURBOMOLE [14]. We used contracted all-electron basis sets of triple-zeta quality with polarization functions (TZVP) [15]: (17s11p6d) → [6s4p3d] for Fe and Mn, (11s6p1d) → [5s3p1d] for C and O, and (5s1p) → [3s1p] for H. Structures were optimized without any symmetry restrictions. All systems studied have a closed-shell electronic structure, except $[Fe(CO)_4]$ which is more stable as a triplet.

Approximate geometries for transition states (TSs) were obtained with the program Dimer [16], based on first-order energy derivatives only. Subsequently, these structures were refined using the Newton–Raphson algorithm available in Turbomole. The nature of all saddle points was confirmed via a normal mode analysis; all TS structures exhibited one mode with a negative force constant. Second-order energy derivatives were approximated as finite differences of analytically calculated first-order derivatives. To render comparison with measured values straightforward, we scaled the calculated harmonic vibrational frequencies by the factor 0.9659 which, in part, also accounts for anharmonicity [17]. NMR shielding constants were estimated using the GIAO algorithm [18]; values are given relative to those calculated for tetramethylsilane (TMS).

We are discussing the energetics using Gibbs free reaction and activation energies ΔG. These quantities were estimated from zero-point energies as well as thermal motion and entropy contributions at standard conditions (temperature 298.15 K, pressure 1 atm). A positive value of a heat of reaction implies an endothermic reaction. Structures and energies for all species were calculated in the gas phase, neglecting solvent effects. This approach seems reasonable as the experimentally used solvent n-hexane has a very low dielectric constant ($\varepsilon = 2$).

3. Results and discussion

We considered the following species as participants of the overall reaction **1** → **2** → **3** (Fig. 2): (a) as reactants the complex

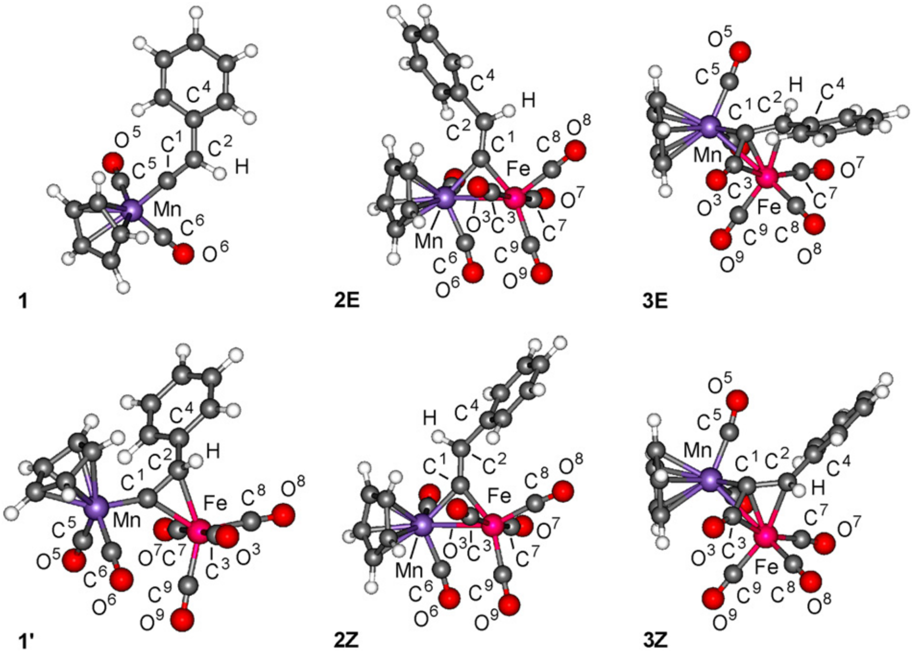

Fig. 2. B3LYP calculated structures of the ground state complexes **1**, **1′**, **2**, **3**. In the variants **E** of **2** and **3**, the moieties Ph and $Fe(CO)_4$ are located in *trans* positions; in the variants Z, these moieties are located in *cis* positions (see text).