



Synthesis, structure and DFT study of cymantrenyl Fischer carbene complexes of group VI and VII transition metals



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ARTICLE INFO

Article history:

Received 11 August 2015

Received in revised form

15 October 2015

Accepted 19 October 2015

Available online 22 October 2015

Keywords:

Fischer carbene

Cymantrenyl

Manganese

Chromium

Molybdenum

Tungsten

DFT

NBO analysis

ABSTRACT

Bi- and trimetallic carbene complexes of group VI and VII transition metals (Cr, Mo, W, Mn and Re), with $\text{CpMn}(\text{CO})_3$ as the initial synthon, have been synthesised according to the classical Fischer methodology. Crystal structures of the novel carbene complexes with general formula $[\text{M}_x(\text{CO})_{y-1}\{\text{C}(\text{OEt})(\text{MnCp}(\text{CO})_3)\}]$, where $x = 1$ then $y = 3$ or 6 ; $x = 2$ then $y = 10$, of the complexes are reported. A density functional theory (DFT) study was undertaken to determine natural bonding orbitals (NBOs) and conformational as well as isomeric aspects of the polymetallic complexes. Application of the second-order perturbation theory (SOPT) of the natural bond orbital (NBO) method revealed stabilizing interactions between the methylene C–H bonds and the carbonyl ligands of the carbene metal moiety. These stabilization interactions show a linear decrease for the group VI metal carbene complexes down the group.

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1. Introduction

The number of classical Fischer carbene complexes containing group VI and group VII transition metals have grown significantly in number since the initial synthesis by Fischer and Maasböl in 1964 [1]. Highly functionalized carbene complexes [2], polymetallic systems [3] and polynuclear biscarbene complexes [4] have all been reported in literature. In particular, complexes where the piano-stool complexes, cymantrene ($\text{CpMn}(\text{CO})_3$) [5,6] and $\text{CpRe}(\text{CO})_3$ [7], are applied as metallating agent have been studied comprehensively. The electronic nature of the carbene ligand's substituents has a direct effect on the bond order of the metal-carbon double bond whilst the steric bulk of these substituents influences the observed bond angles. There is competition for the π -bonding between the three moieties bonded to the carbene carbon centre [8,9].

Intermetallic interactions in complexes containing more than one metal centre are interesting with respect to the potential communication pathways between the metal centres. Communication between metal centres may facilitate electron transfer chemistry, catalysis, molecular electronics and nonlinear optics

applications [10]. Carbene complexes containing transition metals other than Mn or Re, bonded to Cp ligands, have also been reported in literature. Complexes employing $\text{CpFe}(\text{CO})_2\text{Me}$ or $\text{CpFe}(\text{CO})_2\text{Bz}$ as the initial deprotonated synthon have been reported by Butenschön [10] in an attempt to study the influence of a second metal centre, incorporated into the carbene substituent, on the electrochemical nature of the system. Heterometallic carbene complexes of ferrocenyl are numerous in literature [11,12], and often undergo lithiation on both Cp rings to produce trinuclear biscarbene complexes.

Bimetallic complexes where $\text{CpMn}(\text{CO})_3$ and $\text{CpRe}(\text{CO})_3$ are used as the initial building synthons, have been limited to studies published by Fischer [13,14], and Casey [15] on the homonuclear bimetallic monocarbene complexes (Fig. 1) and Sierra [16], who reported heteronuclear monocarbene complexes of group VI metals. To our knowledge, these studies constitute the only examples where deprotonated cymantrenyl moieties served as the nucleophile in carbene synthesis.

Multiple computational studies have been performed on the rate of ligand substitution and stabilities of $\text{CpMn}(\text{CO})_3$ derivatives compared to $\text{TpMn}(\text{CO})_3$. Tp is the scorpionate ligand, hydridotris(1-pyrazolyl)borate and is considered to be an equivalent of the cyclopentadienyl (Cp) ligand. It was observed that the relative displacement rate of a carbonyl ligands from $\text{TpMn}(\text{CO})_3$ was

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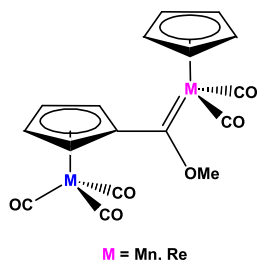


Fig. 1. Homonuclear bimetallic monocarbene complexes containing $\text{CpM}(\text{CO})_3$ ($M = \text{Mn, Re}$) as initial building blocks synthesised by Fischer and Casey.

significantly higher than for the $\text{CpMn}(\text{CO})_3$ analogue. It was concluded that the $\text{TpMn}(\text{CO})_2\text{-L}$ interaction was significantly weaker than that of $\text{CpMn}(\text{CO})_2\text{-L}$ and the bonding enthalpies was found to be 50% lower for the TpMn complex [17]. DFT calculations proved useful in the assignment of a metal-to-ligand charge—transfer transition during a photo slippage process observed by Sierra [16].

Literature ascribes the isomeric differences of group VII complexes, at the point of substitution, to both steric and electronic factors. [18,19]. Nucleophilic attack on either manganese or rhenium carbonyls is expected to be regioselective and occurs on the more electron-poor, equatorial carbonyl position. With bulkier ligands, and in manganese systems with shorter metal–metal bond lengths, axial nucleophilic attack becomes more favourable. Substitution of the carbonyl groups follow a similar reactivity pattern and the equatorial positions are typically favoured for smaller ligands while the axial position becomes favourable with bulkier groups [18,19]. Additional substitution can give rise to at least eight possible isomers [20]. Equatorially substituted $\text{Mn}_2(\text{CO})_9$ -carbene complexes with bulky ligands are, however, also found in literature. In these cases, the alkoxy carbene substituent may be found in the uncommon *syn* conformation relative to the other carbene substituent. Steric hinderance does not allow for the *trans* conformation [21].

In recent studies by Lugan et al. [22] as well as Landman et al. [23] the influence of NBO donor–acceptor interactions in stabilizing a specific carbene conformation was illustrated. These studies involved monometallic carbene complexes where the NBO interactions were observed between carbene substituents (alkoxy or heteroaryl substituent) and a carbonyl ligand of the carbene metal moiety. Based on these reports, a DFT study was initiated to determine whether any of these interactions were present in the novel complexes of this study, which contain an additional metal carbonyl moiety as carbene substituent, *i.e.* $\text{CpMn}(\text{CO})_3$. This study reports the synthesis of the five novel heteroatomic bimetallic and polynuclear complexes of group VI and VII transition metals (Figs. 2 and 3), X-ray crystal structures of four of the complexes and a DFT study.

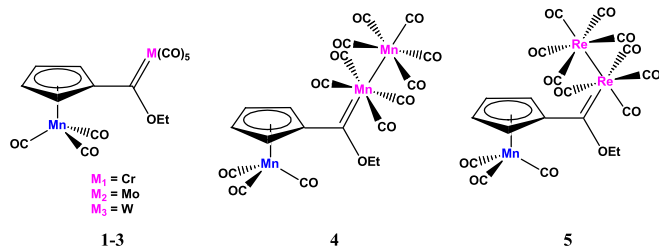


Fig. 2. Heteronuclear bimetallic 1–3 and trimetallic monocarbene complexes 4 and 5.

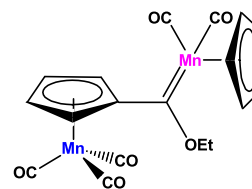


Fig. 3. Homonuclear bimetallic monocarbene complex 6.

2. Experimental

2.1. General

All reactions, unless otherwise noted, were performed under inert nitrogen or argon atmospheres using standard Schlenk techniques [24]. All solvents were freshly distilled, dried and collected under inert conditions, with the exception of toluene. Toluene was not dried, but used after bubbling nitrogen gas through the solvent for 5–10 min. Column chromatography was carried out under inert nitrogen and argon atmospheres using silica gel (particle size 0.063–0.200 mm) as the stationary phase. Percentage yields were calculated relative to the limiting reactant. Crystallization was done using hexane:DCM or hexane:ether diffusion methods. Triethyloxonium tetrafluoroborate [25] was prepared according to a reported literature procedure. The reagents $\text{CpMn}(\text{CO})_3$, $\text{Cr}(\text{CO})_6$, $\text{W}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, $\text{Mn}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$, *n*-butyl lithium (1.6 M solution in hexane) and other commercial reagents were used as purchased. Complex 3 was synthesized according to a literature method [14]. NMR spectra were recorded on a Bruker ARX-300. NMR spectra were recorded in CDCl_3 using the deuterated solvent peak as internal reference. ^1H and ^{13}C NMR spectra were measured at 300.1 and 75.5 MHz, respectively. The numbering of atoms in the NMR assignment is according to the numbers used in Figs. 4–7. IR spectra were recorded on a Perkin Elmer Spectrum RXI FT-IR spectrophotometer as KBr pellets and only the vibration bands in the carbonyl-stretching region (*ca.* 1500–2200 cm^{-1}) are reported.

2.2. Synthesis of complexes 1–6

2.2.1. Synthesis of 1

$\text{CpMn}(\text{CO})_3$ (0.612 g, 3.0 mmol) was dissolved in 40 ml of dry THF. *n*-Butyl lithium (2.00 ml, 3.0 mmol) was added at -30°C and stirred at this temperature for 30 min. The colour of the reaction

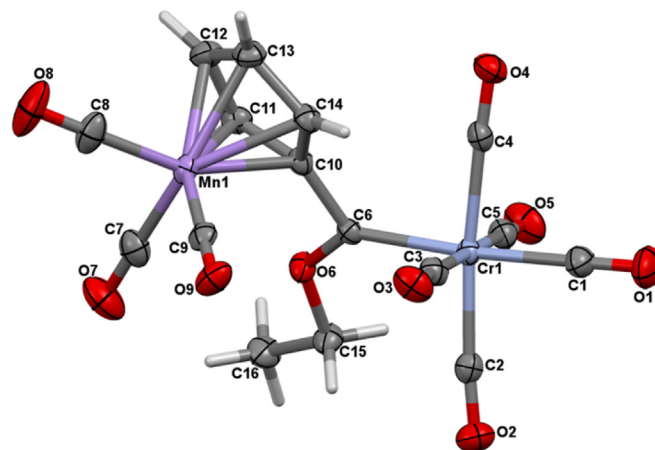


Fig. 4. Perspective view of 1 with thermal ellipsoids drawn at the 50% probability level.

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