



Electrochemical and X-ray photoelectron spectroscopic insights into Molybdenum(0) Fischer ethoxycarbene complexes



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ABSTRACT

The electrochemical analysis, theoretical examination, as well as the first X-ray photoelectron spectroscopic (XPS) study on molybdenum(0) Fischer carbene complexes are presented. The intramolecular communication between the carbene ligand, molybdenum metal centre, and the ancillary ligands is illustrated by linear relationships and trends obtained between experimentally measured redox and XPS binding energy values and theoretically calculated energies and charges. The ease of oxidation of the three series of Mo(0) Fischer carbene complexes presented, namely four pentacarbonyl Mo(0) Fischer carbene complexes of general formula $[(CO)_5MoC(OEt)(Ar)]$, with Ar = 2-thienyl (**1**), 2-furyl (**2**), 2-(N-methyl)pyrrolyl (**3**), 2,2'-bithienyl (**4**), four triphenylphosphine-substituted tetracarbonyl Mo(0) Fischer carbene complexes of general formula $[(CO)_4(PPh_3)MoC(OEt)(Ar)]$, with Ar = 2-thienyl (**5**), 2-furyl (**6**), 2-(N-methyl)pyrrolyl (**7**), 2,2'-bithienyl (**8**), and four triphenylarsine-substituted tetracarbonyl Mo(0) Fischer carbene complexes of general formula $[(CO)_4(AsPh_3)MoC(OEt)(Ar)]$, with Ar = 2-thienyl (**9**), 2-furyl (**10**), 2-(N-methyl)pyrrolyl (**11**), 2,2'-bithienyl (**12**), all showed the same trend, namely (most difficult to oxidize at a higher potential): 2-thienyl \approx 2,2'-bithienyl > 2-furyl > 2-(N-methyl)pyrrolyl. The pentacarbonyl complexes $[(CO)_5MoC(OEt)(Ar)]$ have the highest oxidation potentials, followed by the oxidation potential of $[(CO)_4(PPh_3)MoC(OEt)(Ar)]$, while $[(CO)_4(AsPh_3)MoC(OEt)(Ar)]$ oxidized at a potential 0.12 – 0.15 V lower than the PPh_3 substituted complexes $[(CO)_4(PPh_3)MoC(OEt)(Ar)]$. Substitution of carbonyl ligand(s) in the pentacarbonyl complexes **1–4**, by one (complexes **5–12**) or two ($[(dppe)(CO)_3MoC(OEt)(2-furyl)]$ complex (**13**), dppe = 1,2-bis(diphenylphosphino)ethane) weaker π -acceptor ligands (phosphines/arsines) in Fischer carbene complexes leads to a decrease in the binding energy of the Mo $3d_{5/2}$ photoelectron lines of the X-ray photoelectron spectra of the Fischer carbene complexes and an increase in the binding energy of the carbene carbon C 1s photoelectron lines.

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1. Introduction

The number of literature examples of molybdenum(0) Fischer carbene complexes is strikingly lower than that of chromium(0) and tungsten(0). Fischer carbene complexes based on the latter two metals exhibit higher stability in air [1–3] and are therefore commonly used in academic and industrial processes. Fischer and

his associates noted that pnictogen derivatives (ER_3 with E = P, As, Sb and R = alkyl, aryl) could be employed as ancillary ligands in Fischer carbene complexes to improve the overall air-tolerability [4–6]. These pnictogen ligands can be incorporated into the complex before [4] or after [5,6] carbene synthesis. When carbonyl substitution precedes carbene synthesis, only the *cis* isomer is generated [4], while both *cis*- and *trans* isomers can be obtained when carbonyl substitution follows carbene synthesis [5,6]. Fischer carbene complexes play a pivotal role in synthetic and catalytic processes [7,8]. The work of de Bruin *et al.* showed that carbene radical complexes of Co(II) were produced by an intramolecular electron transfer from the carbene carbon to the metal centre [9]. Carbene radical complexes of Co(II) and Co(III)

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have been employed in the catalytic production of indenenes [10], chromenes [11] and ketenes [12], as well as in alkene cyclopropanation [9,13] and carbon–carbon formation reactions [14]. It is evident from these results that the electronic structure of carbene complexes affects the reactivity of the complexes. Therefore, knowledge of the electronic structure of Fischer carbene complexes may guide in the development and improvement of these complexes as novel catalysts.

The first report on the electrochemical properties of Fischer carbene complexes was made by Lloyd *et al.* in 1973 [15]. Due to the low stability of the Mo(0) Fischer carbene complexes, no electrochemical data of sufficient quality could be obtained [15]. In 1976, Krusic *et al.* demonstrated that $[(\text{CO})_5\text{MoC}(\text{OME})(\text{Me})]$ exhibited a one-electron reduction occurring at the carbene carbon [16]. Casey *et al.* obtained electrochemical data of $[(\text{CO})_5\text{MoC}(\text{OME})(\text{pTol})]$ in their study of the reduction of arylmethoxycarbene complexes of group VIB transition metals [17]. The electrochemical properties of $[(\text{CO})_5\text{MoC}(\text{Y})(\text{C}_4\text{H}_3\text{O})]$, $[(\text{PPh}_3)(\text{CO})_4\text{MoC}(\text{Y})(\text{C}_4\text{H}_3\text{O})]$, and $[(\text{dppe})(\text{CO})_3\text{MoC}(\text{Y})(\text{C}_4\text{H}_3\text{O})]$ ($\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$) for $\text{Y} = \text{OEt}, \text{NH}_2, \text{NHCy}$ were recently reported by our group [18]. The results showed that the ease of oxidation of the metal centre could be systematically tuned by substitution of the carbonyl ligands, and by the alteration of the heteroatom substituent [18]. A similar study on a series of Fischer carbene complexes of type $\text{cis}-[(\text{AsPh}_3)(\text{CO})_4\text{WC}(\text{OEt})(\text{R})]$ for $\text{R} = 2\text{-thienyl}, 2\text{-furyl}, 2\text{-(N-methyl)pyrrolyl},$ and $2,2'\text{-bithienyl}$ were reported by us [19]. The oxidation of the W metal centre and the reduction of the carbene carbon showed dependence on the identity of the heteroaryl carbene substituent [19]. It was also found that the redox properties of $\text{cis}-[(\text{EPh}_3)(\text{CO})_4\text{WC}(\text{OEt})(\text{Ar})]$ with $\text{Ar} = 2\text{-thienyl}, 2\text{-furyl}$ were similar for $\text{E} = \text{P}$ [20] and $\text{E} = \text{As}$ [19]. The influence of different heteroaryl carbene substituents on the ease of oxidation of Mo(0) has not been reported to date. It would thus be interesting to determine whether Mo(0) Fischer carbene complexes exhibit heteroarene-based redox properties, and whether or not the redox properties of the PPh_3 -substituted Fischer carbene complexes of Mo(0) differ from that of the AsPh_3 -substituted analogues.

Based on the success of the above-mentioned studies [18,19], and the lack of similar information for Mo(0) Fischer carbene complexes, an X-ray photoelectron spectroscopic (XPS) study and electrochemical analysis complimented by a theoretical examination of three series' of Mo(0) Fischer carbene complexes are reported here. Series 1: $[(\text{CO})_5\text{MoC}(\text{OEt})(\text{Ar})]$, with $\text{Ar} = 2\text{-thienyl}$ (1) [21], 2-furyl (2) [22], 2-(N-methyl)pyrrolyl (3), 2,2'-bithienyl (4); Series 2: $[(\text{CO})_4(\text{PPh}_3)\text{MoC}(\text{OEt})(\text{Ar})]$, with $\text{Ar} = 2\text{-thienyl}$ (5) [22], 2-furyl (6) [22], 2-(N-methyl)pyrrolyl (7), 2,2'-bithienyl (8); and Series 3: $[(\text{CO})_4(\text{AsPh}_3)\text{MoC}(\text{OEt})(\text{Ar})]$, with $\text{Ar} = 2\text{-thienyl}$ (9), 2-furyl (10), 2-(N-methyl)pyrrolyl (11), 2,2'-bithienyl (12), and $[(\text{dppe})(\text{CO})_3\text{MoC}(\text{OEt})(2\text{-furyl})]$ (13) [23] (Fig. 1).

2. Experimental

2.1. Synthesis

The complexes were synthesized based on classical Fischer methodologies [1,5,6] and literature procedures [20–24]. All of the complexes of this study have been characterized by NMR and IR spectroscopy, mass spectrometry, and X-ray crystallography [21–24]. Bulk purity was confirmed by means of high-resolution mass spectrometry.

2.2. Electrochemistry

Electrochemical analyses by means of cyclic voltammetry (CV) were performed on $0.001 \text{ mol}\cdot\text{dm}^{-3}$ compound solutions in dry acetonitrile containing $0.1 \text{ mol}\cdot\text{dm}^{-3}$ tetra-*n*-butyl ammonium hexafluorophosphate $[\text{tBu}_4\text{N}][\text{PF}_6]$ as supporting electrolyte, under a blanket of purified argon at 25°C utilizing a BAS 100B/W electrochemical analyser. A three-electrode cell, with a glassy carbon working electrode (surface area $7.07 \times 10^{-6} \text{ m}^2$), Pt auxiliary electrode, and an Ag/Ag^+ ($0.010 \text{ mol}\cdot\text{dm}^{-3}$ AgNO_3 in CH_3CN) reference electrode [25] mounted on a Luggin capillary were used [26]. Scan rates were $0.050\text{--}5 \text{ V}\cdot\text{s}^{-1}$. Successive experiments under the same experimental conditions showed that all oxidation and formal reduction potentials were reproducible within 0.010 V . All cited potentials were referenced against the FcH/FcH^+ ($\text{FcH} = \text{Ferrocene}$) couple as suggested by IUPAC [27]. FcH exhibited a peak separation $\Delta E_p = E_{pa} - E_{pc} = 0.070 \text{ V}$ and $i_{pc}/i_{pa} = 1.00$ under our experimental conditions. E_{pa} (E_{pc}) = anodic (cathodic) peak potential and i_{pa} (i_{pc}) = anodic (cathodic) peak current. Ferrocene or decamethylferrocene (Fc^* , -0.508 V vs FcH/FcH^+ under our experimental conditions) was used as internal standard. All CV scans presented are initiated in the positive direction. Scans initiated in the negative direction give the same waves except for waves assigned to the reduction of oxidation products.

2.3. X-ray Photoelectron spectroscopy

X-ray photoelectron spectroscopic (XPS) data was recorded on a PHI 5000 Versaprobe system, with a monochromatic $\text{Al K}\alpha$ X-ray source. Spectra were obtained using the aluminium anode ($\text{Al K}\alpha = 1486.6 \text{ eV}$) operating at $50 \mu\text{m}$, 12.5 W and 15 kV energy (97 X-ray beam). The survey scans were recorded at constant pass energy of 187.85 eV and detailed region scans of C 1s and O 1s at constant pass energy of 29.35 eV , while the Mo 3d, S 2p, P 2p and N 1s was recorded at constant pass energy of 93.90 eV with the analyzer resolution $\leq 0.5 \text{ eV}$. The background pressure was $2 \times 10^{-8} \text{ mbar}$. The XPS data was analyzed utilizing Multipak version 8.2c computer software [28], and applying Gaussian-

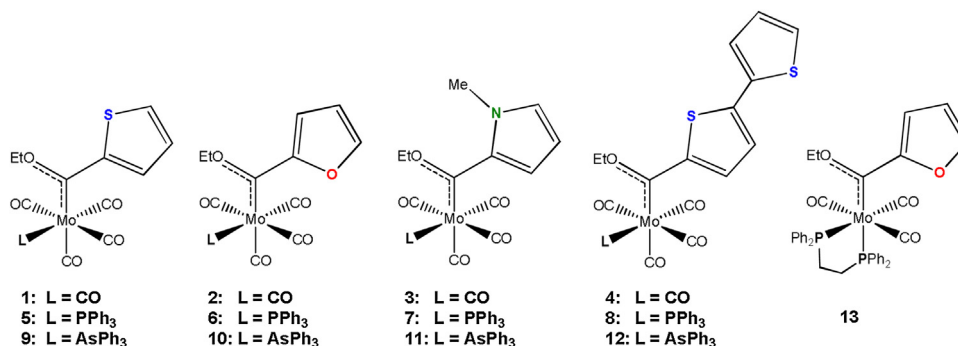


Fig. 1. Molybdenum(0) Fischer ethoxycarbene complexes of this study.

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