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Synthesis and structure of novel triphenylarsine-substituted tungsten(0) Fischer carbene complexes

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ABSTRACT

X-ray crystal structure determination, as well as IR and NMR spectroscopy of four novel triphenylarsine-substituted tetracarbonyl tungsten(0) Fischer carbene complexes of general formula $[(CO)_4(AsPh_3)WC(OEt)(Ar)]$, with Ar = 2-thienyl (**1**), 2-furyl (**2**), 2-(N-methyl)pyrrolyl (**3**), 2,2′-bithienyl (**4**), revealed a *cis*-configuration for the substituted $AsPh_3$ group relative to the carbene ligand for all four novel complexes. All X-ray structures showed that the W—C bond *trans* AsPh3 < W—C bond *trans* carbene < W—C bond *trans* CO. DFT calculations on all possible conformations of each complex due to the different possible positions of the ligands and carbene substituents to each other, correlated with the experimental results.

1. Introduction

In 1964, Fischer and Maasböl synthesized the first carbene complex, $[(CO)_5WC(OMe)(Ph)]$ (Fig. 1), where they described the bonding pattern between the carbene ligand and the metal as a formal carbon-metal double bond [1]. Three years later, Fischer and Klabunde showed that the reaction of $[(CO)_5CrC(OMe)(Me)]$ with ammonia or thiophenol yielded the substitution complexes $[(CO)_5CrC(NH_2)(Me)]$ and $[(CO)_5CrC(SPh)(Me)]$ (Fig. 1), with the liberation of methanol [2]. In 1969 Fischer reported the synthesis of the first ligand-substituted Fischer alkoxycarbene complexes. Complexes of the type *cis*-$[(EPh_3)(CO)_4MC(OMe)(Me)]$ with E = P, As, Sb and M = Cr, Mo, W (Fig. 1) were synthesized from $[(EPh_3)(CO)_5M]$, showing that the ligand sphere around the metal can be altered before carbene synthesis [3]. However, seven years later it was also shown that ligand substitution could also be achieved after carbene formation by substituting a carbonyl ligand of the pentacarbonyl Fischer carbene complex. Fischer and Richter were able to synthesize complexes of the type *cis/trans*-$[(ER_3)(CO)_4CrC(OMe)(Me)]$ with R = Me, Et, Cy, Ph and E = P, As, Sb [4], as shown in Fig. 1.

Arsines are similar to phosphines, neutral σ-donor and π-acceptor ligands. A vast number of tungsten complexes have been synthesized containing the ligand AsR_3, where R is an alkyl or aryl group [5–10]. Fischer *et al.* were successful in synthesizing triphenylarsine-substituted chromium(0) allenylidene complexes, which can be employed in catalytic and stoichiometric organic transformations [5]. Nitrile-substitution with arsines yielded seven-coordinate tungsten(II) complexes, which may find use as precatalysts for olefin metathesis [6]. Further, tungsten(II) complexes with a bidentate arsine-ligand was prepared by Mihichuk in a structural study [8], which may be used similarly as the monodentate analogues of Baker [6]. The steric and electronic properties of ligand EPh_3 in $[(CO)_4M(EPh_3)_2]$ (E = P, As, Sb; M = Mo, W) were investigated by Bergstrom and it was found that the bulkiness of the ligand $AsPh_3$ results in a distorted octahedrons [10]. However, Fischer carbene complexes comprising arsines as ligands are still limited in literature [3–5,11]. Since a number of phosphine-substituted tungsten(0) Fischer alkoxycarbenes with various heteroarene substituents have been synthesized in our laboratories recently [12], we were interested to determine whether the phosphine- and arsine-substituted complexes have similar structural

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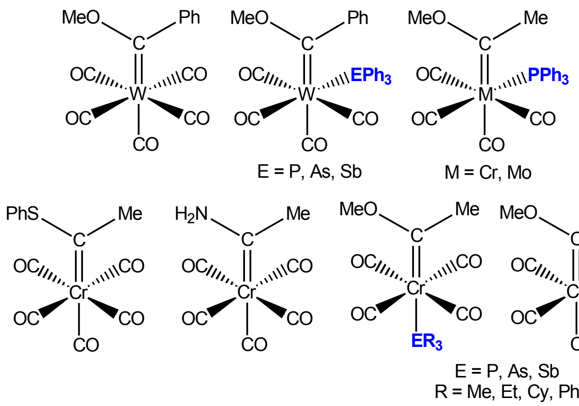

Fig. 1. Selection of Fischer carbene complexes synthesized by Fischer and associates [1–4].

features. Fischer and Richter noted that the substituted complexes exhibited heightened air-stability, in comparison to their parent compounds [4]. This makes the substituted complexes prime candidates for industrial applications studies. Additionally, the stereochemistry of the substituted complexes is primarily *cis*, thus allowing for stereoselective substitution reactions on the arsine-substituted Fischer carbene complexes. Therefore, we report here the synthesis, structural and theoretical study of four novel triphenylarsine-substituted Fischer ethoxycarbene complexes of the type *cis*-[(AsPh$_3$)(CO)$_4$WC(OEt)(Ar)] for Ar = 2-thienyl (**1**), 2-furyl (**2**), 2-(N-methyl)pyrrolyl (**3**) and 2,2′-bithienyl (**4**) shown in Scheme 1. In the DFT computational study, several conformations (Schemes 1 and 2 in Supporting information) of the novel complexes were considered to determine the lowest-energy conformer.

2. Experimental materials and methods

2.1. General

All reactions were performed under inert argon atmospheres using standard Schlenk techniques. All solvents were freshly distilled, dried and collected under inert conditions. 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 diffusion methods. Commercial thiophene was purified [13] and triethyloxonium tetrafluoroborate was prepared according to a reported literature procedure [14]. The reagents [W(CO)$_6$], n-butyl lithium (1.6 M solution in hexane), furan, N-methylpyrrole and triphenylarsine (AsPh$_3$) were used as purchased. The tungsten(0) pentacarbonyl Fischer ethoxycarbene complexes for the hetero-arenes thiophene, **A** [15], furan, **B** [16], N-methylpyrrole, **C** [17], and 2,2′-bithiophene, **D** [18] were synthesized according to literature procedures. NMR spectra were recorded on a Bruker ARX-300. NMR spectra were recorded in CDCl$_3$ using deuterated solvent peaks as the internal references. ^{1}H and ^{13}C NMR spectra were measured at 300.1 and 75.5 M Hz, respectively. Numbering of atoms in the NMR assignment was done according to the numbering system used in Figs. 2–5. Protons are assigned according to the corresponding labelled carbon atoms. 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 (1500–2200 cm^{-1}) are reported. Mass spectra were recorded on a SYNAPT G2 HDMS instrument with the TOF-MS method, with a sampling time of 3 min with direct infusion inlet method. The source was electron-spray ionisation. Melting points were recorded on a Stuart SMP10 instrument.

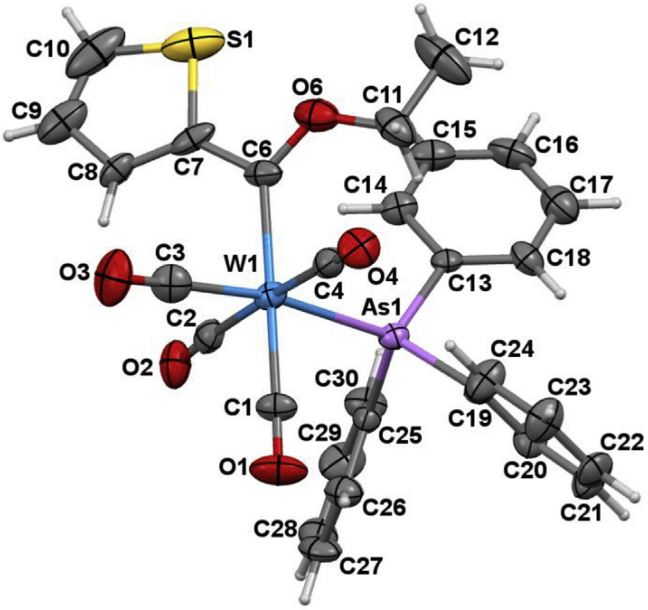

Fig. 2. Perspective view of **1** (*cis-syn* (2) conformer) with thermal ellipsoids drawn at the 50% probability level.

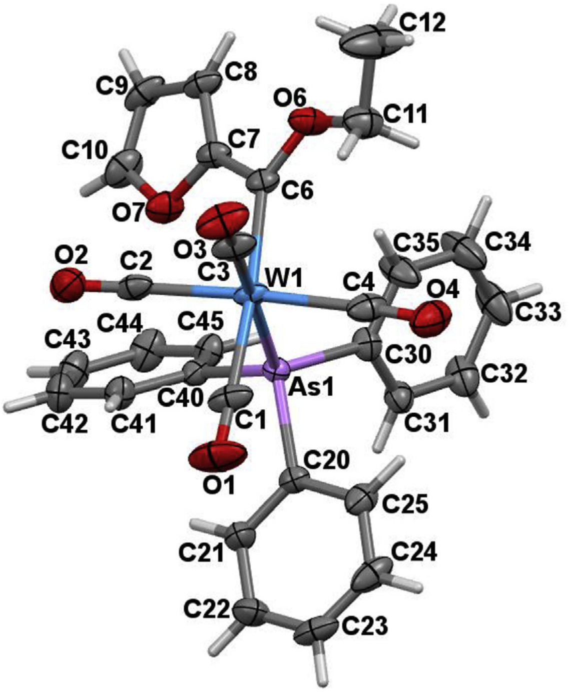

Fig. 3. Perspective view of **2** (*cis-anti* (1) conformer) with thermal ellipsoids drawn at the 50% probability level.

2.2. Synthesis of 1–4

2.2.1. *cis-[(AsPh$_3$)(CO)$_4$WC(OEt)(C$_4$H$_3$S)] (**1**)*

[(CO)$_5$WC(OEt)(C$_4$H$_3$S)], **A**, (0.464 g, 1 mmol) and AsPh$_3$ (0.337 g, 1.1 mmol) were dissolved in hexane (40 mℓ), resulting in a dark red