



Electrochemical behaviour and structure of novel phosphine- and phosphite-substituted tungsten(0) Fischer carbene complexes[☆]



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ABSTRACT

The electrochemical behaviour of a series of sixteen novel Fischer ethoxy- and aminocarbene complexes of the type $[(CO)_4(PPh_3)W=C(X)R]$ with R=2-thienyl or 2-furyl and X=OEt or NHCy, (**1-4**), $[(CO)_3(dppe)W=C(X)R]$ with R=2-thienyl or 2-furyl and X=OEt or NHCy, (**5-8**) (dppe=1,2-bis(diphenylphosphino)ethane) and $[(CO)_4P(OPh)_3W=C(X)R]$ with R=2-thienyl or 2-furyl and X=OEt or NHCy, (**9-12**) is investigated by means of cyclic voltammetry. The complexes all exhibit a two-electron oxidation process that is W-based and a one-electron reduction that is mainly localized on the carbene ligand. Complexes **1-4** and **9-12** are considerably more difficult to oxidize than **5-8** due to the better π -acceptor ability of the $(CO)_4(PR'_3)$ ($R' = Ph$ or OPh) ligand combination than that of $(CO)_3(dppe)$. Density functional theory calculations on the neutral, reduced and oxidized complexes confirmed the role of the frontier orbitals in the oxidation and reduction processes and enabled formulation of mathematical relationships that can be used to predict experimental measured potentials. X-ray crystal structures of **2cis**, **3** and **5** are discussed.

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1. Introduction

Recently, electrochemical studies were reported on the behaviour of Cr(0) [1–3] and W(0) [4] pentacarbonyl Fischer carbene complexes. In these studies, both carbene ligand substituents, i.e. the heteroarene substituent as well as the heteroatom substituent were varied. In this study, this work was extended to determine the effect of modification of the metal ligand environment on the electrochemical behaviour of tungsten Fischer carbene complexes. Towards this end, a series of sixteen novel tungsten(0) Fischer carbene complexes are synthesized in which one or two carbonyl groups are substituted with phosphines or phosphites.

Modification of the ligand sphere of carbonyl carbene complexes was studied not long after the discovery of the first metal carbene complex [5–7]. Substitution of CO ligands while leaving the carbene

ligand intact is achieved with phosphines. It was noted by Fischer that phosphine ligands allowed the complexes higher stability in air than their carbonyl analogues [7]. Two possible reaction pathways are observed for the reaction of phosphines with metal pentacarbonyl carbenes. In the first case, rate limiting dissociation of a carbonyl ligand precedes rapid coordination of the phosphine to the metal in a ligand substitution reaction. In the second case, nucleophilic attack of the phosphine at the carbene carbon leads to ylide formation and subsequent substitution of the carbene ligand by a phosphine to yield $M(CO)_5PR'_3$. Phosphines of low nucleophilicity, e.g. PPh_3 , tend to follow the first pathway while smaller, more basic phosphines, e.g. PMe_3 , follow the second route.

The σ -donor, π -acceptor [8] and steric [9] characteristics of phosphines can be regulated by modification of their substituents. Phosphines have many applications in organometallic chemistry, specifically as ligands in homogenous catalysts [10]. In the case of Fischer carbenes, phosphine “chelates”, which are tethered to the carbene through the substituent on the carbene ligand [11], have been synthesised, as well as examples of carbenes bound to polymers through the phosphorous ligand [12,13]. It was shown that phosphines confer additional reactivity to the carbene complex during reactions with electrophiles, and alter the reactivity pattern during certain organic transformations by varying the

[☆] Dedicated to the memory of Professor Robert Vleggaar (1945–2013), our friend and colleague.

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stereoselectivity of the complex [14]. The change in stereoselectivity was brought about by the use of a chiral phosphine. Barluenga et al. [15] also noted that phosphite ligands can be used to introduce chirality into a Fischer carbene complex. Phosphine carbene complexes were used by Arrieta et al. [16] to alter the reactivity of Fischer carbene complexes during photocarbonylation reactions and to better understand the reaction mechanism. Even though these modifications of Fischer carbene complexes have been known since the late 1960s, not many examples of these complexes were found in literature. This gap was especially noticeable for the diphosphine derivatives [17]. Furthermore, to our knowledge, no examples of heteroaryl phosphine carbenes are known. The combination of altered reactivity of the complex and the catalytic properties of phosphines, motivated this investigation.

In order to design a Fischer carbene of certain reactivity, the influence of different substituents, heteroatoms and groups on the electrochemical properties of the whole molecule has to be quantified. Cyclic voltammetry (CV) is one of the most versatile electroanalytical techniques to study electroactive species [18–20]. The oxidation and reduction potentials of a species can be measured with relative ease over a wide potential range. Electrochemistry thus represents an important experimental tool to the description and understanding of the molecular electronic structure and redox properties of a complex. The electronic influence of the different substituents, heteroatoms and groups on the redox properties of the Fischer carbene can be expressed qualitatively by correlation with electrochemical data. Theoretical density functional theory (DFT) calculation of the energies of the frontier MOs involved in the oxidation and reduction of the complex can be used as a tool to quantitatively correlate experimental and calculated data of a series of related complexes [21–23]. To this extend we hereby present a combined experimental, structural, electrochemical and DFT study of a series of phosphine and phosphite tungsten carbene complexes.

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 to 10 minutes. 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 [25] and triethyloxonium tetrafluoroborate [26] was prepared according to a reported literature procedure. The reagents $W(CO)_6$, *n*-butyl lithium (1.6 M solution in hexane), furan, 1,2-bis(diphenylphosphino)ethane (dppe), PPh_3 , cyclohexyl amine (CHA) and other commercial reagents were used as purchased. NMR spectra were recorded on a Bruker ARX-300. NMR spectra were recorded in $CDCl_3$, CD_3CN or CD_2Cl_2 using deuterated solvent peaks as the internal references. 1H , ^{13}C and ^{31}P NMR spectra were measured at 300.1, 75.5 and 81 MHz, respectively. 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. Mass spectra were recorded on a SYNAPT G2 HDMS with the TOF-MS method with sampling time of 4 minutes, with direct infusion inlet method. The source was electron spray ionization.

2.2. Synthesis of carbene complexes 1–12

The unsubstituted pentacarbonyl carbene precursor complexes **A** [27], **B** [28], **C** [4] and **D** [4] were prepared according to literature procedures and spectroscopic characterization data follow:

A: Yield: 82.6%, bright orange solid. - 1H NMR ($CDCl_3$, ppm): δ 7.80 (dd, H10, 5.0, 0.6 Hz), 8.14 (dd, H8, 4.1, 0.8 Hz), 7.20 (dd, H9, 4.8, 4.3 Hz), 4.98 (q, H11, 7.1 Hz), 1.64 (t, H12, 7.1 Hz). - ^{13}C NMR ($CDCl_3$, ppm): δ 290.7 (C6), 202.5 (s, CO_{trans}), 197.6 (t, CO_{cis} , J_{W-C} = 126.4 Hz), 158.3 (C7), 136.5 (C10), 141.5 (C8), 129.0 (C9), 78.6 (C11), 15.0 (C12). - IR (KBr, cm^{-1}): ν_{CO} = 2066 (m), 1916 (vs).

B: Yield: 73.3%, bright orange solid. - 1H NMR ($CDCl_3$, ppm): δ 7.86 (dd, H10, 1.6, 0.7 Hz), 7.13 (dd, H8, 3.7, 0.7 Hz), 6.60 (dd, H9, 3.7, 1.7 Hz), 4.94 (q, H11, 7.1 Hz), 1.62 (t, H12, 7.1 Hz). - ^{13}C NMR ($CDCl_3$, ppm): δ 284.8 (C6), 203.4 (CO_{trans}), 197.4 (CO_{cis}), 166.2 (C7), 150.0 (C10), 113.4 (C8), 113.4 (C9), 78.4 (C11), 15.1 (C12). - IR (KBr, cm^{-1}): ν_{CO} = 2067 (m), 1920 (vs).

C: Yield: 88.2%, bright orange yellow solid
MS (*m/z*): 433 ($[M]^+ - 3CO$); 280 ($[M]^+ - 5CO - CHA$). - 1H NMR ($CDCl_3$, ppm): Isomer **I**: δ 8.30 (s(b), N-H), 7.50 (dd, H10, 5.1, 1.2 Hz), 7.34 (dd, H8, 3.8, 1.2 Hz), 7.12 (dd, H9, 5.1, 3.8 Hz), 4.35–4.52 (m, H11), 1.10–2.20 (m, **Cyclohexyl-NH**); Isomer **II**: δ 8.64 (s(b), N-H), 7.46 (dd, H10, 5.0, 1.1 Hz), 7.07 (dd, H9, 5.0, 3.7 Hz), 6.93 (dd, H8, 3.7, 1.1 Hz), 3.73–3.86 (m, H11), 1.10–2.20 (m, **Cyclohexyl-NH**). - ^{13}C NMR ($CDCl_3$, ppm): Isomer **I**: δ 235.0 (t, C6, J_{W-C} = 90.8 Hz), 202.8 (t, CO_{trans} , J_{W-C} = 127.1 Hz), 198.2 (t, CO_{cis} , J_{W-C} = 127.0 Hz), 157.0 (C7), 129.5 (C10), 128.1 (C8), 126.9 (C9), 64.9 (C11), 33.0 (C12), 24.9 (C13), 24.4 (C14). Isomer **II**: δ 245.7 (t, C6, J_{W-C} = 90.8 Hz), 203.5 (t, CO_{trans} , J_{W-C} = 127.8 Hz), 198.7 (t, CO_{cis} , J_{W-C} = 127.8 Hz), 150.2 (C7), 127.8 (C10), 127.3 (C8), 124.2 (C9), 59.5 (C11), 33.3 (C12), 24.7 (C13), 24.2 (C14). - IR (KBr, cm^{-1}): ν_{CO} = 2061 (m), 1972 (vw), 1950 (s), 1906 (vs).

D: Yield: 94.6%, bright yellow solid
MS (*m/z*): 280 ($[M]^+ - 5CO - Cyclohexyl$). - 1H NMR ($CDCl_3$, ppm): Isomer **I**: δ 8.93 (s(b), N-H), 7.51 (d, H10, 1.4 Hz), 7.38 (dd, H8, 3.6, 0.5 Hz), 6.57 (dd, H9, 3.6, 0.5 Hz), 4.31–4.42 (m, H11), 1.12–2.15 (m, **Cyclohexyl-NH**); Isomer **II**: δ 8.13 (s(b), N-H), 7.68 (dd, H10, 1.8, 0.6 Hz), 7.25 (dd, H8, 3.6, 0.6 Hz), 6.60 (dd, H9, 3.6, 1.8 Hz), 4.09–4.22 (m, H11), 1.12–2.15 (m, **Cyclohexyl-NH**). - ^{13}C NMR ($CDCl_3$, ppm): Isomer **I**: δ 219.3 (C6), 202.4 (CO_{trans}), 198.4 (t, CO_{cis} , J_{W-C} = 126.9 Hz), 159.1 (C7), 144.1 (C10), 126.3 (C8), 113.7 (C9), 64.3 (C11), 33.1 (C12), 24.5 (C13), 25.3 (C14). Isomer **II**: δ 225.7 (C6), 202.8 (CO_{trans}), 199.1 (t, CO_{cis} , J_{W-C} = 122.2 Hz), 157.6 (C7), 145.8 (C10), 126.4 (C8), 113.3 (C9), 61.1 (C11), 33.2 (C12), 24.3 (C13), 25.3 (C14). - IR (KBr, cm^{-1}): ν_{CO} = 2059 (m), 1966 (vw), 1908 (s), 1882 (vs).

2.2.1. Synthesis of *cis*- and *trans*- $[W(PPh_3)(CO)_4\{C(OEt)C_4H_3S\}]$, (**1cis**) and (**1trans**)

Complex **A** (1.393 g, 3.00 mmol) and PPh_3 (0.945 g, 3.60 mmol) were dissolved in 30 mL of toluene (wine-red solution). This mixture was left to reflux overnight (dark brown solution), and the solvent was removed (dark brown solid). The crude product was purified on silica gel using hexane:DCM gradients. Unreacted carbene **A** (0.285 g, 0.614 mmol, 20.5%) and two products were obtained according to TLC. The two products were identified as the *cis* and *trans* isomers of the product. The *trans* product, **1trans**, is yellow-brown in solution and elutes after the starting carbene **A**. The *cis* product, **1cis**, eluted directly after the *trans* isomer as a dark red-brown solution. The bands corresponding to the isomers could not be completely separated and thus fractions were collected and combined as necessary.

1cis: Yield: 0.590 g, 0.845 mmol, 28.2%, reddish-brown solid
MS (*m/z*): 557 ($[M]^+ - Et - 4CO$); 327 ($[M]^+ - 4Ph - Et - 4CO$). - 1H NMR (CD_2Cl_2 , ppm): δ 7.77 (dd, H8, 4.0, 1.1 Hz), 7.65 (dd, H10, 5.0, 1.1 Hz), 6.97 (dd, H9, 4.8, 4.0 Hz), 7.31–7.46 (m, PPh_3), 4.53 (dq, H11,

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