Electrochemistry of Triphenylarsine-substituted Tungsten(0)

Fischer carbene complexes

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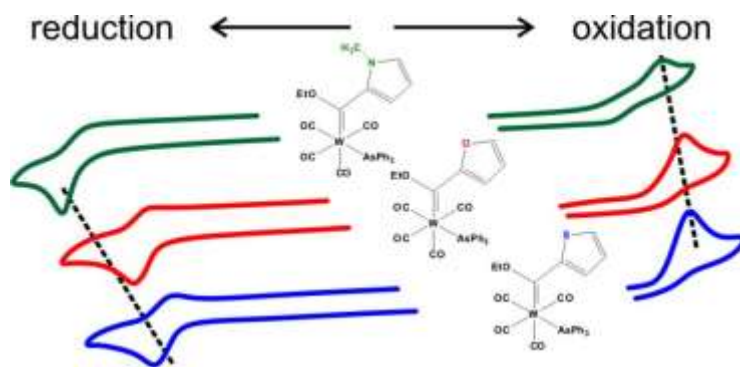
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SYNOPSIS TOC

Highlights

• Order of oxidation for *cis*-[AsPh$_3$(CO)$_4$WC(OEt)(Ar)]: Ar = C$_4$H$_3$S > C$_4$H$_3$O > C$_4$H$_3$NMe.

• Order of reduction for *cis*-[AsPh$_3$(CO)$_4$WC(OEt)(Ar)]: Ar = C$_4$H$_3$S > C$_4$H$_3$O > C$_4$H$_3$NMe.

• Increasing order of oxidation potential $\propto$ decreasing order of the energy of HOMO.

• Increasing order of reduction potential $\propto$ decreasing order of the energy of LUMO.

Abstract

A combined electrochemical and density functional theory study on four 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 that electrochemical properties for these complexes follow the same trend than analogous pentacarbonyl and triphenylphosphine-substituted tetracarbonyl complexes in literature, namely (largest metal oxidation and largest carbene carbon reduction potential) $[(L)(CO)_4WC(OEt)(2\text{-thienyl})]$ > $[(L)(CO)_4WC(OEt)(2\text{-furyl})]$ > $[(L)(CO)_4WC(OEt)(2\text{-(N-methyl)pyrrolyl})]$ (L = CO, PPh$_3$ or AsPh$_3$).

1 Introduction

The electrochemical behaviour of Fischer carbene complexes has attracted much attention in the last decade. Electrochemical analyses of group 6 Fischer carbene complexes reported includes Fischer carbene complexes of the metals chromium(0) [1-3] molybdenum(0) [4,5] and tungsten(0) [6,7]. In a recent study by our group [6], it was shown that the phosphine-substituted Fischer ethoxy carbene complexes of tungsten(0) are more electrochemically active than the non-substituted pentacarbonyl tungsten(0) Fischer ethoxycarbene complexes $[(CO)_5WC(OEt)(Ar)]$ complexes for Ar = 2-thienyl and 2-furyl [7]. Altering the R-groups of the phosphine ligand (PR$_3$) from Ph to OPh, showed to have a negligible effect on the electrochemical behaviour, while substitution of the ethoxy-group on the carbene carbon with various amine substituents [6] showed a marked effect on both the metal oxidation potential (0.08 – 0.19 V) as well as the carbene ligand reduction potential (0.30 – 0.52 V). It was also found that the order of oxidation (and reduction) for monocarbene complexes containing a monomeric heteroarene substituent, a dimeric heteroarene substituent or biscarbene complexes connected with a heteroarene spacer substituent is the same, namely 2-thienyl > 2-furyl > 2-(N-methylpyrrolyl) [8]. To this end we were interested to see whether the electrochemical properties and reactivity patterns of phosphine- and arsine-substituted Fischer carbene complexes of W(0) are similar and also if arsine-substituted Fischer carbene complexes of W(0) containing different

heteroarene substituents show the same order of oxidation as previously reported. Therefore, we report here the electrochemical 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**) (Figure 1). Comparisons between the electrochemical behaviour of these complexes and their literature analogues will be complemented with a DFT study.
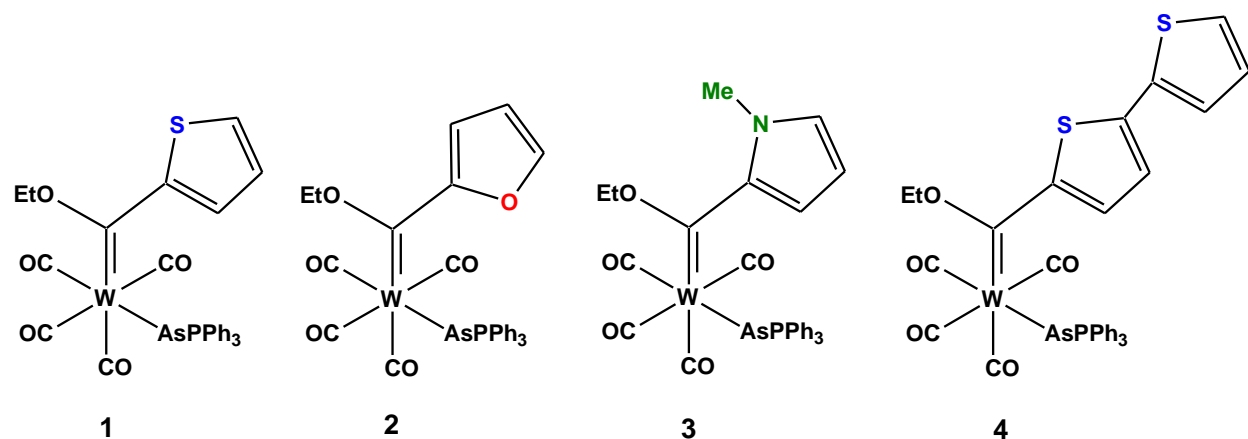
Figure 1. Arsine-substituted Fischer carbene complexes of this study

2   Experimental methods

2.1   *Synthesis*

The complexes were synthesized according to classical Fischer methodology [9,10] and literature procedures [11,12,13,14,15,16,17]. Bulk purity was confirmed with high resolution mass spectroscopy. Characterization data are given below.

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

Yield (37%). ^{1}H-NMR (CDCl$_3$, ppm) δ 7.57 (H10, dd, J = 5.0, 1.1 Hz, 1H), 6.91 (H9, dd, J = 5.0, 4.0 Hz, 1H), 7.86 (H8, dd, J = 4.0, 1.1 Hz, 1H), 4.58 (H11, q, J = 7.0 Hz, 2H), 1.17 (H12, t, J = 7.0 Hz, 3H), 7.24-7.44 (As**Ph$_3$**, m, 15H); ^{13}C-NMR (CDCl$_3$, ppm) δ 294.3 (C6), 210.0 (C1), 202.7 (C2 and C4), 206.8 (C3), 159.3 (C7), 140.0 (C8), 129.8 (C9), 132.7 (C10), 77.2 (C11) 15.1 (C12), 139.6 (C20), 133.7 (C21), 128.9 (C22) 128.6 (C23); IR (KBr, v(CO)/cm^{-1}) 2009 (A_1^1), 1928 (A_1^2), 1898 (B$_1$), 1878 (B$_2$); MS (m/z): Calc. 726.251 [M], Exp. 727.0 [M+1]$^+$; m.p. 118 - 120°C (dec).

2.1.2   *cis*-[(AsPh$_3$)(CO)$_4$WC(OEt)(C$_4$H$_3$O)] (**2**)

Yield (48%). ^{1}H-NMR (CDCl$_3$, ppm) δ 7.32 (H10, d, J = 1.0 Hz, 1H), 6.72 (H9, dd, J = 3.6, 0.8 Hz, 1H), 7.20 (H8, dd, J = 1.7, 0.8 Hz, 1H), 4.78 (H11, q, J = 7.1 Hz, 2H), 1.39 (H12, t, J = 7.1 Hz, 3H), 7.22-7.41 (As**Ph$_3$**, m, 15H); ^{13}C-NMR (CDCl$_3$, ppm) δ 289.0 (C6), 211.0 (C1), 202.7 (C2 and C4), 207.1 (C3), 166.5 (C7), 112.7 (C8), 111.0 (C9), 147.8 (C10), 77.0 (C11) 15.0 (C12), 139.6 (C20), 133.7 (C21), 129.6 (C22) 128.6 (C23); IR (KBr, ν(CO)/cm^{-1}): 2011 (A_1^1), 1921 (A_1^2), 1892 (B$_1$), 1862 (B$_2$); MS (m/z): Calc. 742.318 [M], Exp. 743.0 [M+1]$^+$; m.p. 131 - 132°C (dec).

2.1.3   *cis*-[(AsPh$_3$)(CO)$_4$WC(OEt)(C$_4$H$_3$NMe)] (**3**)

Yield (58%). ^{1}H-NMR (CDCl$_3$, ppm) δ 6.90 (H10, s(br), 1H), 6.26 (H9, dd, J = 4.5, 2.3 Hz, 1H), 7.66 (H8, dd, J = 4.6 Hz, 1.8 Hz, 1H), 4.93 (H11, q, J = 7.1 Hz, 2H), 1.33 (H12, t, J = 7.1 Hz, 3H), 3.78 (H13, s(br)), 7.16 − 7.43 (As**Ph$_3$**, m, 15H); ^{13}C-NMR (CDCl$_3$, ppm) δ 297.5 (C6), 211.0 (C1), 204.1 (C2 and C4), 205.6 (C3), 143.4 (C7), 134.9 (C8), 111.2 (C9), 132.4 (C10), 40.7 (C13), 77.4 (C11) 15.2 (C12), 139.6 (C20), 133.7 (C21), 128.7 (C22) 128.5 (C23); IR (KBr, ν(CO)/cm^{-1}) 2006 (A_1^1), 1917 (A_1^2), 1897 (B$_1$), 1886 (B$_2$); MS (m/z): Calc. 739.293 [M], Exp. 740.0 [M+1]$^+$; m.p. 161 - 163°C (dec).

2.1.4   *cis*-[(AsPh$_3$)(CO)$_4$WC(OEt)(C$_8$H$_5$S$_2$)] (**4**)

Yield (52%). ^{1}H-NMR (CDCl$_3$, ppm) δ 7.21-7.26 (H17, m, 1H), 7.04-7.09 (H16, m, 1H), 7.30-7.33 (H15, m, 1H), 7.01 (H9, d, J = 4.3 Hz, 1H), 7.79 (H8, d, J = 4.3 Hz, 1H) 4.62 (H11, q, J = 7.0 Hz, 2H), 1.24 (H12, t, J = 7.0 Hz, 3H), 7.34-7.43 (As**Ph$_3$**, m, 15H); ^{13}C-NMR (CDCl$_3$, ppm) δ 272.1 (C6), 210.0 (C1), 202.9 (C2 and C4), 207.0 (C3), 125.4 (C7), 128.4 (C8), 124.7 (C9), 137.1 (C10), 136.3 (C14), 124.3 (C15), 128.3 (C16), 125.2 (C17), 77.2 (C11) 14.7 (C12), 139.6 (C20), 133.8 (C21), 128.9 (C22) 128.5 (C23); IR (KBr, ν(CO)/cm^{-1}) 2011 (A_1^1), 1918 (A_1^2), 1895 (B$_1$), 1879 (B$_2$); MS (m/z): Calc. 824.442 [M], Exp. 825.0 [M+1]$^+$; m.p. 149 - 150°C (dec).

2.2   *Cyclic Voltammetry*

Electrochemical studies by means of cyclic voltammetry (CV) were performed on 0.0005 mol dm^{-3} compound solutions in dry acetonitrile containing 0.1 mol dm^{-3} tetra-*n*-butylammonium hexafluorophosphate, [^{n}(Bu$_4$)N][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 (surface area 7.07×10^{-6} m^2) working electrode, Pt auxiliary electrode and an Ag/Ag$^+$ (10 mmol dm^{-3} AgNO$_3$ in CH$_3$CN) reference electrode [18], mounted on a Luggin capillary were used [19]. Scan rates were 0.050-5.000 V 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 Fc/Fc$^+$ couple as suggested by IUPAC [20]. Ferrocene (FcH) exhibited a peak separation $\Delta E_p = E_{pa} - E_{pc} = 0.070$ 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. $E^{\circ\prime}$ (FcH/FcH$^+$) = 0.66(5) V vs SHE in [^{n}(Bu$_4$)N][PF$_6$]/CH$_3$CN [21]. Decamethylferrocene (Fc*, -0.508 V vs FcH/FcH$^+$ under our experimental conditions) were used as internal standard.

2.3 DFT calculations

Density functional theory (DFT) calculations of this study were performed with the hybrid functional B3LYP [22,23] (20% Hartree-Fock exchange) [24] and the as implemented in the Gaussian 09 program package [25]. Geometries of the neutral complexes were optimized in gas phase with the triple-ζ basis set 6-311G(d,p) on all atoms except W, where def2-TZVPP [26] was used. Energies reported are gas phase electronic energies.

3 Results and Discussion

3.1 DFT study

A density functional theory (DFT) computational chemistry study was done to gain insight in the oxidation and reduction processes of complexes **1–4**. Oxidation of the complex in solution occurs when the cell potential is sufficient to allow movement of electrons from the highest occupied molecular orbital (HOMO) of the solution species (analyte) into the metal electrode and reduction occurs when the cell potential is sufficient to promote an electron from the electrode into the lowest unoccupied molecular orbital (LUMO) of the analyte. The character of the HOMO of **1**-**4** thus shows where oxidation takes place, while the character of the LUMO indicates where reduction takes place. **Figure 2** shows the HOMO and LUMO of **1** as

representative example of **1**-**4**. The HOMO is mainly W-d-orbital based, while the LUMO is distributed over the carbene carbon, the heteroatom and the aryl substituent. Oxidation of carbene complexes **1**-**4** is thus metal-based, while the reduction involves the carbene ligand. It is thus expected that electron-donating properties of S *vs* O *vs* NMe of the heteroaryl group in **1**-**4** will influence the ease of reduction. Indeed, for the three heteroarenes of this study, rate studies have shown that the order of reactivity towards electrophiles was found to be: N-methylpyrrole > furan > thiophene. The degree of reactivity was determined more by electron availability than degree of aromaticity [27]. This trend seems to indicate that N-methylpyrrole is the best electron donating substituent and thiophene the worst of the three heteroarenes. The better π-acceptor ability of CO over arsine and carbene ligands is clear from the HOMO of **1** in **Figure 2** where no visual π-back bonding to arsine or the carbene carbon is observed, contrary to the visual π-back bonding to the CO groups.

LUMO   HOMO
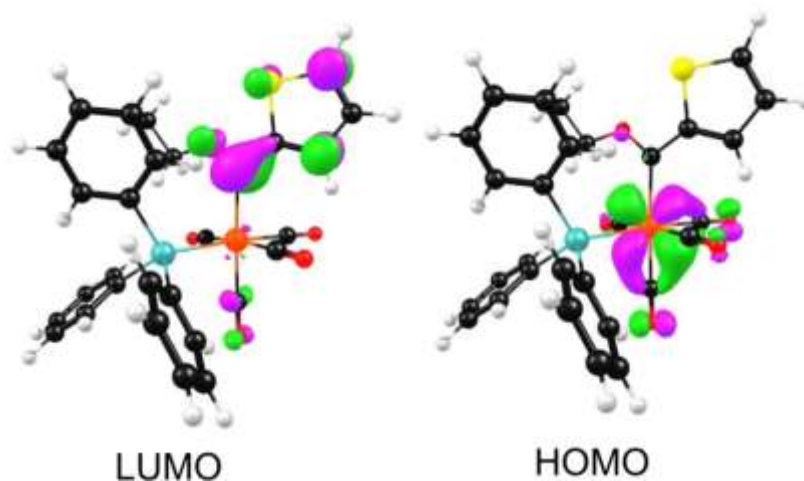
Figure 2. Visualization of the HOMO and LUMO of the neutral complex **1**. The MO plots use a contour of 60 e/nm^3. Colour code (online version): W (orange), C (black), S (yellow), As (blue), O (red) and H (white).

3.2 Electrochemical study

We report here the electrochemical behaviour of triphenylarsine-substituted Fischer ethoxycarbene complexes of W(0). The cyclic voltammograms (CVs) of carbene complexes **1**-**4** at scan rates $0.050 - 0.300$ V s^{-1} are given in Figure 3, scan rates $0.050 - 5.000$ V s^{-1} in Figure S1 (supplementary Information) and the data summarized in Table 1.

The DFT study presented above, in agreement with previously published results [6,7], shows that the first oxidation process observed for **1**-**4** can be ascribed to the oxidation of the

W(0) metal centre. The first oxidation process observed for **1**, **2** and **4** is irreversible at all scan rates. The first oxidation process observed for **3** show two near overlapping peaks at 0.260 and 0.315 V *vs* FcH/FcH$^+$. The AsPh$_3$ group in **1**-**4** can be in a position *cis* or *trans* relative to the carbene ligand, leading to *cis* and *trans* isomers of **1**-**4**. Experimentally only *cis* isomers have been collected from column chromatography and characterized by X-ray crystallography for **1**-**4**. [17]. The *cis* isomers are generally more stable, although it was possible to isolate the *trans* isomer for related phosphine-substituted Fischer ethoxy carbene tungsten (0) complexes [6,11]. Upon dissolving the isolated *cis* complexes of **1**-**4** in dichloromethane or chloroform, only **3** formed small amounts of the *trans* isomer in solution as observed on TLC and NMR spectroscopy. Thus, in solution, mainly *cis*, but also the *trans* isomer is observed only for **3**. This is consistent with the CVs of **1**-**4** where only the CV of **3** shows the oxidation of the *trans* isomer in addition to the oxidation of the *cis* isomer. The first oxidation peak is assigned to the oxidation of the *trans* isomer, since DFT calculated energy of the HOMO of the *trans* isomer is less stable (higher energy) than the HOMO of the *cis* isomer, see **Table 1**. An electron will thus be more easily removed (oxidation) from the higher energy HOMO of the *trans* isomer, than from the lower energy, more stable, HOMO of the *cis* isomer, implying that the *trans* isomer will be more easily oxidized at a lower potential.

The reduction process is ascribed to the one electron reduction of the carbene carbon, as described in the DFT section above, as well as for related carbene complexes of tungsten [6,7,28]. The reduction process of **1**-**2** is enhanced at higher scan rates, with a peak current separation, ΔE, of 0.070-0.075 V. This implies that the radical anion that forms upon reduction is stabilized long enough on the timescale of the CV to be oxidized back to the neutral complex. The reduction process of **3** is irreversible at all scan rates.

The first reduction process of **4** is reversible with a peak current ratio i_{pa}/i_{pc} of 0.4-0.5 and $\Delta E = 0.074$ V at all scan rates 0.050-5.000 V s^{-1}. The enhanced stabilization of the radical anion of **4** on the timescale of the CV experiment, is brought by the extended dimeric heteroarene five-membered ring system of **4**. The added electron during the first reduction of **4** is distributed over the carbene carbon and the two five-membered rings, as can be seen by the singly occupied molecular orbital (SOMO) of the reduced complex (q = -1) in Figure 4. Two further irreversible reduction processes are observed after the first reversible reduction of **4**, due to the stability of the radical anion of the first reduction process of **4**. The lowest singly unoccupied molecular

orbital (SUMO) of the DFT optimized radical anion of the first reduction process (q = -1) indicates that the second reduction also predominantly involves the carbene carbon atom and the heteroarene ring system, see Figure 4.

Peak currents of the CVs at different scan rates of **1**, **2** and **4** are given in **Table 2**. Since the oxidation peaks of the oxidation wave (peak a in **Figure 3**) and the reduction peaks of the reduction wave (peak b in **Figure 3**) of complexes **1**-**4** have true Nernstian shapes, the Randles-Sevcik equation $i_p = (2.69 \times 10^5) n^{1.5} A D^{0.5} C v^{0.5}$ (n = the number of exchanged electrons, A = electrode area (cm^2), D = diffusion coefficient (cm^2 s^{-1}), C = bulk concentration (mol cm^{-3}) of the electroactive species [29]), can be applied to the oxidation peak a and the reduction peak b. The peak current ratios, $i_{pa,ox \text{ (peak a)}}/i_{pc,red \text{ (peak b)}}$, is thus indicative of the amount of electrons involved in the oxidation process of peak a relative the reduction process of peak b. The peak current ratios, $i_{pa,ox}/i_{pc,red}$, given in **Table 2** for **1**, **2** and **4** indicate a two-electron transfer (or most likely two closely overlapping one electron transfer) for the oxidation process relative to a one electron reduction process. This result is in agreement with results obtained on related Fischer carbene complexes [6] and results of Licandro *et. al.* [28] for a series of five alkoxy-, amino- and hydrazinocarbene complexes of tungsten, who also proposed a two-electron metal-based oxidation process for the first oxidation. It is not possible to determine reliable peak current ratios, $i_{pa,ox}/i_{pc,red}$, for complex **3** due to the overlapping of the oxidation of the *cis* and *trans* isomers.
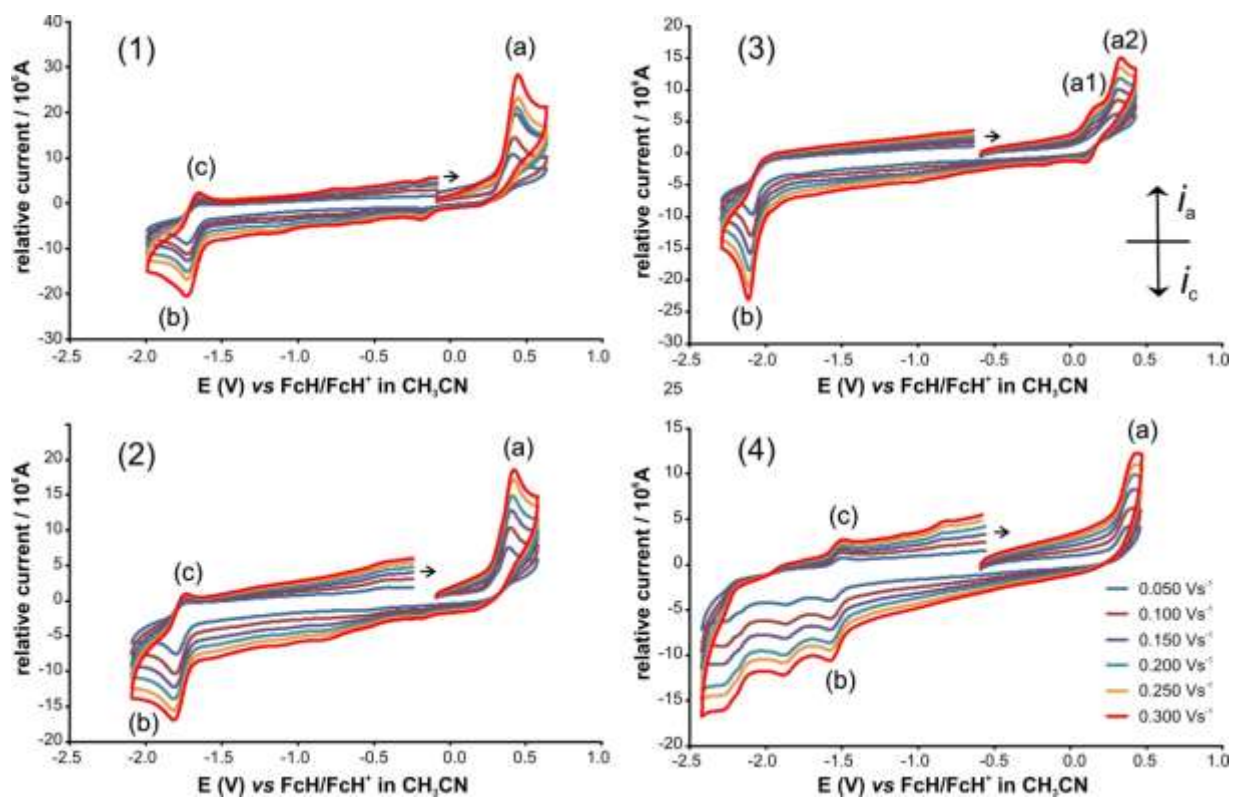
Figure 3. Cyclic voltammograms of *ca* 0.0005 mol dm^{-3} or saturated solutions of **1−4** at scan rates of 0.050−0.300 V s^{-1}. Measurements were performed in 0.1 M [^{n}(Bu$_4$)N][PF$_6$]/CH$_3$CN on a glassy carbon working electrode at 20 °C. Scans were initiated in the positive direction, as indicated by the arrow.
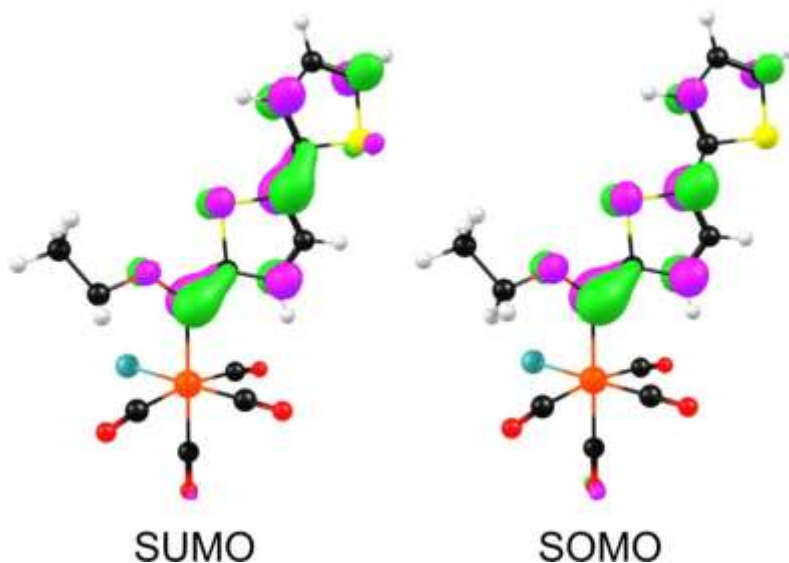
Figure 4. Visualization of the SUMO (β) and SOMO (α) of the radical anion (q = -1, S = ½) of complex **4**. The MO plots use a contour of 60 e/nm^3. Colour code (online version): W (orange), C (black), S (yellow), As (blue), O (red) and H (white).

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The oxidation potential of the AsPh$_3$-containing complexes **1**-**3** is *ca* 0.300 V lower than that of the related pentacarbonyl complexes [(CO)$_5$WC(OEt)(Ar)] (Ar = 2-thienyl (**1′**), 2-furyl (**2′**), 2-(N-methyl)pyrrolyl (**3′**)) [8], see **Figure 5** and Table 1. This is expected, since the AsPh$_3$ is a weaker π-acceptor ligand than CO [30], see **Figure 2**. More electron density is thus donated to five CO groups from W in **1′**-**3′** than to four CO and one AsPh$_3$ group in **1**-**3**. W is thus more electron-poor in the pentacarbonyl complexes **1′**-**3′** and more difficult to oxidize (oxidize at a higher more positive potential). The influence on the reduction potential is less pronounced, the reduction potential of **1**-**3** is 0.100 - 0.160 V lower than that of **1′**-**3′**. This is expected, since the reduction is not metal-based. However, the oxidation and reduction potentials of **1**-**2** and that of the related *cis*-[PPh$_3$(CO)$_4$WC(OEt)(Ar)] (Ar = 2-thienyl (**1‴**), 2-furyl (**2‴**)) and *cis*-[P(OPh$_3$)(CO)$_4$WC(OEt)(Ar)] (Ar = 2-thienyl (**1⁗**), 2-furyl (**2⁗**)) complexes are the same, although PPh$_3$ and P(OPh$_3$) are better σ donor and π acceptors than AsPh$_3$ [30,31,32,33], see Table 1.

The order of oxidation and of reduction of **1**-**3** is:
Largest $E_{pa(ox)}$ and largest $E_{pc(red)}$: *cis*-[AsPh$_3$(CO)$_4$WC(OEt)(C$_4$H$_3$S)] > *cis*-[AsPh$_3$(CO)$_4$WC(OEt)(C$_4$H$_3$O)] > [AsPh$_3$(CO)$_4$WC(OEt)(C$_4$H$_3$NMe)] (smallest $E_{pa(ox)}$ and $E_{pc(red)}$)

This is exactly the same order observed for the pentacarbonyl complexes [(CO)$_5$WC(OEt)(Ar)] **1′**-**3′**, as well as for related Cr-pentacarbonyl complexes [(CO)$_5$CrC(OEt)(Ar)] (Ar = 2-thienyl (**1″**), 2-furyl (**2″**), 2-(N-methyl)pyrrolyl (**3″**)) [1], see **Figure 5**.

The oxidation of **4**, however, is within 0.014 V of the oxidation of **1**. This shows than the W-metal based oxidation of **4** is insensitive to the influence of the second ring of the dimeric heteroarene five-membered ring. A similar result was obtained when comparing the oxidation potentials of [(CO)$_5$CrC(OEt)(Ar)] where Ar = 2-thienyl, 2-(2'-thienyl)-5-furyl, and N-methyl-2-(2'-thienyl)-5-pyrrolyl [1]. The influence of the second thienyl ring of **4** on the first reduction of **4** is more pronounced. The first reduction of **4** occurs at a potential 0.149 V more positive than that of **1**. The higher (less negative) reduction of **4** relative to that of **1** is ascribed to the

stabilisation of the extended dimeric heteroarene five-membered ring system of **4**, making it easier to add an electron to **4** than to **1**.
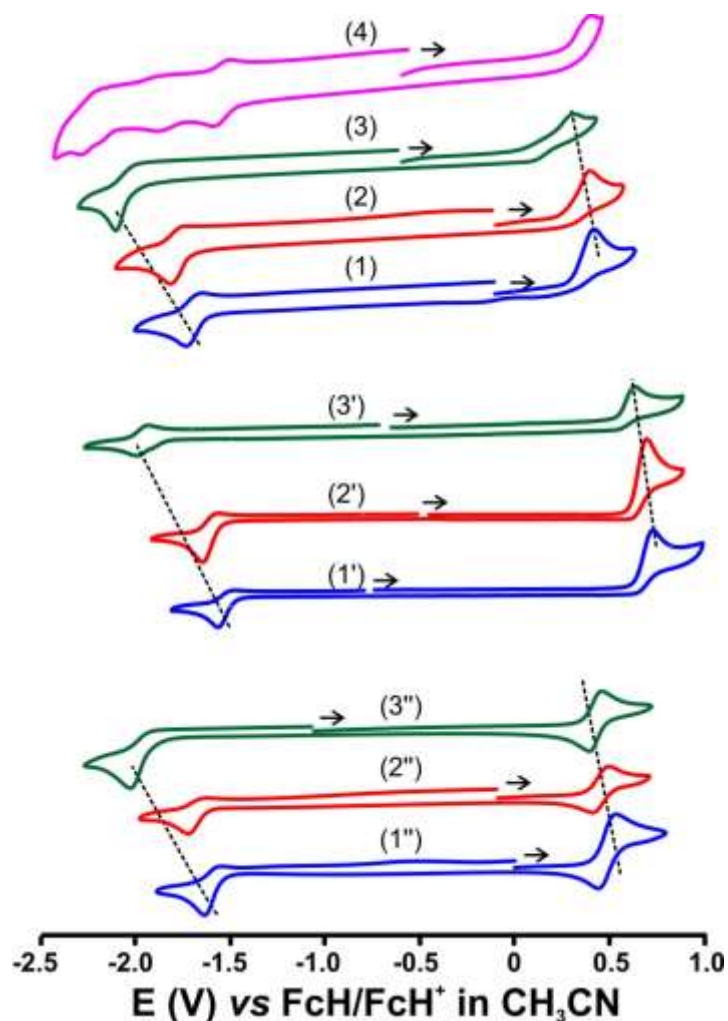
Figure 5. Comparative cyclic voltammograms of **1-4**, [(CO)$_5$WC(OEt)(Ar)] (Ar = 2-thienyl (**1′**), 2-furyl (**2′**), 2-(N-methylpyrrolyl) (**3′**)) and [(CO)$_5$CrC(OEt)(Ar)] (Ar = 2-thienyl (**1″**), 2-furyl (**2″**), 2-(N-methylpyrrolyl) (**3″**)) in CH$_3$CN / 0.1 mol dm^{-3} [^{n}(Bu$_4$)N][PF$_6$] on a glassy carbon-working electrode at a scan rate of 0.100 V s^{-1}. Scans were initiated in the positive direction as indicated by the arrow. The dotted lines highlight the effect of the aryl substituent on the oxidation and reduction potential.

Table 1. Electrochemical and DFT data for **1-4** and related carbene complexes. Cyclic voltammetry data obtained for *ca* 0.0005 mol dm^{-3} solutions of the indicated carbene complexes in CH$_3$CN containing 0.1 mol dm^{-3} [^{n}(Bu$_4$)N][PF$_6$], as supporting electrolyte at a scan rate of 0.100 V s^{-1} and 20 °C. Potentials are reported in V relative to the FcH/FcH$^+$ couple.

	Complex	Oxidation	Reduction				DFT energy[a]	
		E_{pa} / V	E_{pc} / V	E_{pa} / V	ΔE / V	$E^{0'}$/ V	E_{HOMO} / eV	E_{LUMO} / eV
1	*cis*-[(CO)$_4$(AsPh$_3$)WC(OEt)(C$_4$H$_3$S)]	0.422	-1.727	-1.652	0.075	-1.690	-5.347	-2.442
2	*cis*-[(CO)$_4$(AsPh$_3$)WC(OEt)(C$_4$H$_3$O)]	0.400	-1.808	-1.738	0.070	-1.773	-5.250	-2.326
3	*cis*-[(CO)$_4$(AsPh$_3$)WC(OEt)(C$_4$H$_3$NMe)]	0.315	-2.095	-	-	-	-	-5.105	-1.982
	trans-[(CO)$_4$(AsPh$_3$)WC(OEt)(C$_4$H$_3$NMe)]	0.260	-	-	-	-	-4.983	-1.724
4	*cis*-[(CO)$_4$(AsPh$_3$)WC(OEt)(C$_8$H$_4$S$_2$)]	0.408	-1.578	-1.504	0.074	-1.541	-5.273	-2.644
1′	[(CO)$_5$WC(OEt)(C$_4$H$_3$S)][b]	0.728	-1.564	-1.478	0.086	-1.521	-5.907	-2.873
2′	[(CO)$_5$WC(OEt)(C$_4$H$_3$O)][b]	0.697	-1.645	-1.559	0.086	-1.602	-5.798	-2.725
3′	[(CO)$_5$WC(OEt)(C$_4$H$_3$NMe)][d]	0.632	-1.994	-1.932	0.062	-1.963	-5.670	-2.366
1″	[(CO)$_5$CrC(OEt)(C$_4$H$_3$S)][c]	0.538	-1.625	-1.552[a]	-1.589	0.073	-6.074	-2.754
2″	[(CO)$_5$CrC(OEt)(C$_4$H$_3$O)][c]	0.494	-1.719	-1.649	-1.684	0.070	-5.962	-2.583
3″	[(CO)$_5$CrC(OEt)(C$_4$H$_3$NMe)][c]	0.463	-2.019	-1.938	-1.979	0.081	-5.833	-2.204
1‴	*cis*-[(CO)$_4$(PPh$_3$)WC(OEt)(C$_4$H$_3$S)][b]	0.421	-1.715	-1.683	0.068	-1.717	-5.297	-2.382
2‴	*cis*-[(CO)$_4$(PPh$_3$)WC(OEt)(C$_4$H$_3$O)][b]	0.383	-1.837	-1.767	0.07	-1.802	-5.212	-2.280
1⁗	*cis*-[(CO)$_4$(P(OPh)$_3$)WC(OEt)(C$_4$H$_3$S)][b]	0.419	-1.827	-1.903	0.076	-1.865	-5.584	-2.592
2⁗	*cis*-[(CO)$_4$(P(OPh)$_3$)WC(OEt)(C$_4$H$_3$O)][b]	0.384	-1.954	-2.022	0.068	-1.988	-5.478	-2.468

[a] Energies obtained with the B3LYP functional and the 6-311G(d,p) basis set on all atoms except W and Cr, where def2-TZVPP was used.
[b] Data from reference [6].
[c] Data from reference [1].
[d] Data from reference [8].

Table 2. Peak currents and peak current ratios obtained from the CVs of **1**, **2** and **4** at the indicated scan rates. Cyclic voltammetry data obtained for *ca* 0.0005 mol dm^{-3} or saturated solutions of the indicated carbene complexes in CH$_3$CN containing 0.1 mol dm^{-3} [^{n}(Bu$_4$)N][PF$_6$], as supporting electrolyte at 20 °C.

Scan rate V s^{-1}	$10^6\, i_{pc(red)}$/ A	$10^6\, i_{pa(red)}$/ A	$10^6\, i_{pa(oks)}$/ A	$i_{pa,ox}/i_{pc,red}$	$i_{pa,red}/i_{pc,red}$
Complex 1					
0.050	5.2	2.4	7.8	1.5	0.45
0.100	6.5	2.6	10.6	1.6	0.40
0.150	7.8	3.3	13.1	1.7	0.42
0.200	8.1	3.9	15.4	1.9	0.48
0.250	8.9	4.3	17.9	2.0	0.49
0.300	10.7	5.2	20.9	2.0	0.49
0.500	12.4	7.7	25.1	2.0	0.62
1.000	17.1	11.8	35.0	2.0	0.69
5.000	33.3	24.2	56.5	1.7	0.73
Complex 2					
0.050	3.3	1.3	5.5	1.7	0.40
0.100	4.8	1.6	7.2	1.5	0.32
0.150	5.9	1.8	9.2	1.6	0.31
0.200	6.6	2.1	10.5	1.6	0.32
0.250	6.8	2.4	11.8	1.7	0.35
0.300	7.2	2.8	13.1	1.8	0.38
0.500	8.4	3.9	15.7	1.9	0.47
1.000	11.1	6.4	22.3	2.0	0.58
5.000	25.3	14.4	45.9	1.8	0.57
Complex 4					
0.050	1.3	0.6	2.6	2.0	0.45
0.100	1.8	0.8	3.6	2.0	0.43
0.150	2.3	1.0	4.6	2.0	0.44
0.200	2.6	1.2	5.1	2.0	0.45
0.250	2.9	1.3	5.9	2.0	0.43
0.300	3.2	1.4	6.4	2.0	0.44
0.500	4.1	1.8	8.3	2.0	0.44
1.000	5.1	2.3	10.5	2.1	0.45
5.000	11.5	5.0	22.1	1.9	0.43

Oxidation of a complex involves the removal of electron(s) from the HOMO of the neutral complex. The ease of oxidation or the oxidation potential from a theoretical point of view is thus related to the DFT calculated energy of the HOMO, E_{HOMO}, of the neutral complex. Less

energy or a lower experimental oxidation potential is needed to remove an electron from a higher energy HOMO (such as complex **3**) than an electron from a lower more stable energy HOMO (such as complex **1**), see **Figure 6**. In evaluating the energies of the HOMOs of complexes **1-4** in **Figure 6**, we observe that E_{HOMO} increases in going from complex **1** to **4** to **2** to **3**, exactly the opposite (expected) order as the increase of the oxidation potential of these complexes. The same expected inverse trend is observed for other Fischer carbene complexes containing a carbene ligand of the type =C(OEt)(Ar) with Ar = 2-thienyl, 2-furyl or a 2-(N-methyl)pyrrolyl given in **Table 1**, see **Figure 7** (a).

The ease of electrochemical reduction (the reduction potential) relates to the DFT calculated energy of the LUMO, E_{LUMO}, of the neutral complex, the orbital the electron is added to upon reduction. An electron is more easily added to a lower (more stable) energy LUMO, such as the LUMO of complex **4**, than to the higher energy LUMO of complex **3**. Thus, a less negative reduction potential is associated with the reduction of complex **4** relative to that of complex **3**. The order of the increase of E_{LUMO} for complexes **1 – 4** is: **4 < 1 < 2 < 3**, and the order of decrease of the reduction potential, Epc (red), is **4 > 1 > 2 > 3.** This inverse trend is found to be consistent for all the complexes given in given in **Table 1**, see **Figure 7** (b).
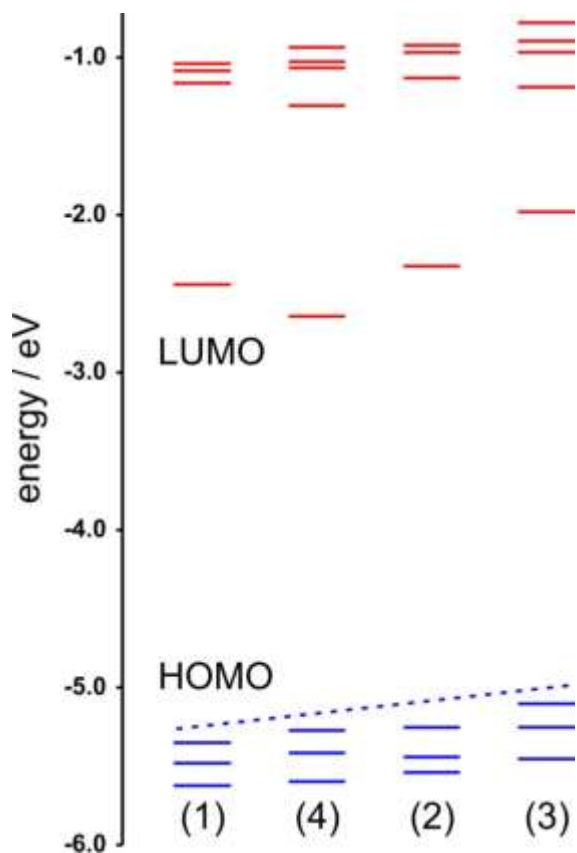
Figure 6. Molecular orbital energy levels (eV) of **1-4**.
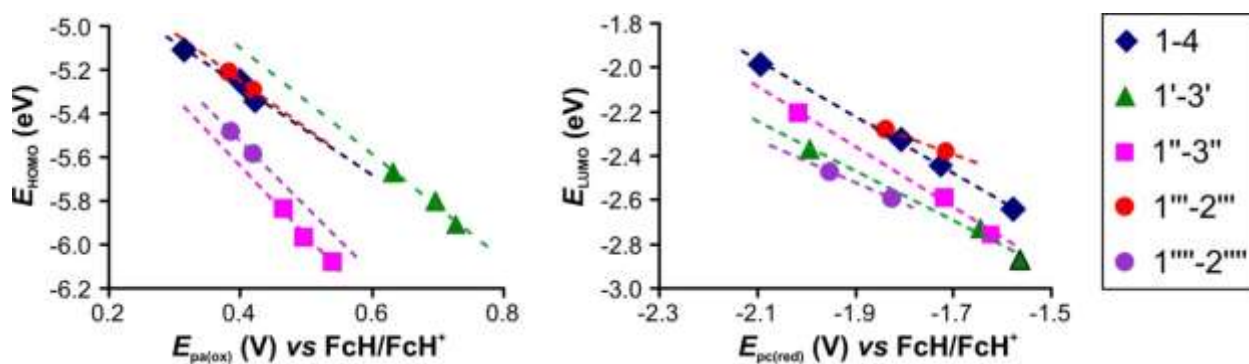
Figure 7. Relationship between (a) E_{pa} of the metal oxidation and E_{HOMO} and (b) E_{pc} of the carbene carbon reduction and E_{LUMO} of selected Fischer carbene complexes containing a carbene ligand of the type =C(OEt)(Ar) with Ar = 2-thienyl, 2-furyl or a 2-(N-methyl)pyrrolyl. See Table 1 for the complex numbering.

4   Conclusions

An electrochemical study showed that the order of metal oxidation and carbene carbon reduction is the same for *cis*-[(AsPh$_3$)(CO)$_4$WC(OEt)(Ar)], [(CO)$_5$WC(OEt)(Ar)] and

[(CO)$_5$CrC(OEt)(Ar)] complexes, where Ar = 2-thienyl has the largest metal oxidation potential and the largest carbene carbon reduction potential and Ar = 2-(N-methyl)pyrrolyl the lowest. This trend is in agreement with the electron donating properties of the heteroarene substituents. For all these complexes the order of increasing oxidation/reduction potential is linearly related to the decreasing order of the DFT calculated energy of the HOMO/LUMO.

Disclosure statement

The authors declare no conflict of interest.

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Supplementary data

Cyclic voltammmetry
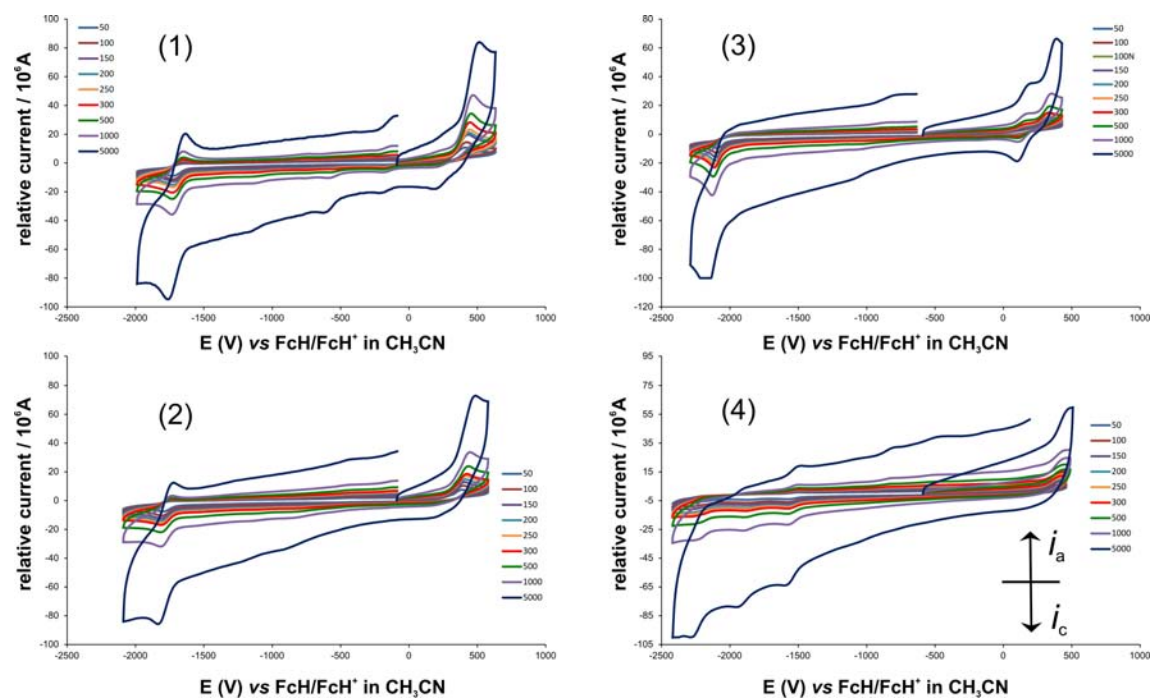
Figure S1. Cyclic voltammograms of *c.a.* 0.0005 mol dm^{-3} or saturated solutions of **1-4** in CH$_3$CN / 0.1 mol dm^{-3} [^{n}(Bu$_4$)N][PF$_6$] on a glassy carbon-working electrode at a scan rate of 0.050 – 0.500 V s^{-1} (0.05 V s^{-1} increments), 1.000 and 5.000 V s^{-1}. Scans initiated in the positive direction as indicated by the arrow.

Optimized Cartesian coordinates (Å)

Density functional theory (DFT) calculations of this study were performed with the hybrid functional B3LYP [1,2] as implemented in the Gaussian 09 program package [3]. Geometries of the neutral complexes were optimized in gas phase with the triple-ζ basis set 6-311G(d,p) on all atoms except W, where def2-TZVPP [4] was used. Energies reported are gas phase electronic energies.

1   *cis* [W(AsPh3)(CO)4C(OEt)(2-thienyl)]

As	-1.342639000	0.226229000	0.166625000
C	0.056781000	2.653728000	0.966231000
C	0.294495000	4.022409000	1.071103000
C	0.513080000	-1.387886000	-2.455084000
C	1.040895000	-1.519065000	1.614489000
C	1.368922000	1.586407000	-2.438207000
C	1.569795000	3.002611000	-2.939978000
C	2.269444000	0.329960000	-0.530096000
C	2.340974000	-2.616158000	-0.664255000
C	3.423239000	0.485985000	0.350964000
C	3.984110000	-0.396502000	1.257568000
C	5.128059000	0.105844000	1.916683000
C	5.447597000	1.378061000	1.518755000
C	-0.454429000	-2.948846000	-0.366162000
C	-0.580446000	4.931614000	0.478009000
C	-1.067184000	2.181048000	0.279293000
C	-1.694457000	4.466399000	-0.216207000
C	-1.941223000	3.096601000	-0.313450000
C	-2.146514000	-0.133731000	1.935105000
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C	-2.473788000	-1.454746000	2.261727000
C	-2.802994000	-0.091682000	-2.346651000
C	-2.950917000	0.125450000	-0.973876000
C	-2.961343000	0.578316000	4.100595000
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C	-4.235289000	0.275960000	-0.440473000
C	-5.197865000	0.005866000	-2.640667000
C	-5.352184000	0.215980000	-1.272004000
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H	0.751894000	1.956667000	1.420963000
H	0.885918000	3.194567000	-3.770766000
H	1.166553000	4.375320000	1.609875000
H	1.365367000	3.727908000	-2.150485000
H	1.560241000	0.854342000	-3.223695000
H	2.592005000	3.147517000	-3.295815000
H	3.597801000	-1.388503000	1.426752000
H	5.690439000	-0.451119000	2.653768000
H	6.261458000	1.995253000	1.869824000
H	-0.392334000	5.996626000	0.554753000
H	-1.820373000	-0.232863000	-2.777133000
H	-2.146616000	1.909253000	2.628529000
H	-2.288476000	-2.258524000	1.559516000

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H        -2.815085000     2.748422000    -0.850412000
H        -3.145068000     1.374055000     4.814056000
H        -3.296086000    -2.778876000     3.736300000
H        -3.729213000    -0.970160000     5.381816000
H        -3.792522000    -0.321824000    -4.238685000
H        -4.369743000     0.431796000     0.622970000
H        -6.068344000    -0.045430000    -3.284927000
H        -6.343355000     0.328907000    -0.846872000
O         0.334117000    -1.513387000    -3.588725000
O         1.162873000    -1.688433000     2.745537000
O         2.323295000     1.362137000    -1.379607000
O         3.222423000    -3.354020000    -0.768052000
O        -1.141200000    -3.876078000    -0.344600000
S         4.374061000     1.978926000     0.316157000
W         0.809400000    -1.345997000    -0.425775000
```

    2   *cis* [W(AsPh3)(CO)4C(OEt)(2-furyl)]

```
As        1.195026000     0.041460000     0.164432000
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C         0.376619000     1.496063000     4.063324000
C         1.380056000     0.583074000     2.056491000
C         1.592495000     1.379815000     4.732636000
C         1.897967000     1.631379000    -0.770441000
C         1.919266000     1.624370000    -2.169222000
C         2.341688000     2.764381000    -0.085226000
C         2.388136000     2.731778000    -2.871881000
C         2.588866000    -2.489531000     0.522025000
C         2.598316000     0.467152000     2.733889000
C         2.701742000     0.863496000     4.066111000
C         2.728122000    -1.194699000     0.009723000
C         2.803988000     3.875543000    -0.791326000
C         2.830236000     3.861378000    -2.183603000
C         3.642874000    -3.395340000     0.440894000
C         3.934077000    -0.823621000    -0.590261000
C         4.843300000    -3.021425000    -0.160698000
C         4.985696000    -1.736589000    -0.676536000
C        -0.154584000    -2.466187000    -1.623857000
C        -1.123276000    -2.176637000     1.054209000
C        -1.195634000     0.008268000    -2.428131000
C        -1.431847000     3.745240000    -1.204406000
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C        -2.368407000     0.633510000     0.261050000
C        -2.487662000     4.243407000    -0.494920000
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C        -3.044757000     3.139361000     0.198950000
C        -3.757916000    -0.622852000     1.832512000
C        -4.985508000    -0.295744000     2.660115000
H         1.568076000     0.758110000    -2.717185000
H         1.659961000    -2.799899000     0.985777000
H         1.674373000     1.684676000     5.769917000
H         2.328067000     2.787766000     0.997367000
H         2.403200000     2.712272000    -3.955848000
H         3.145665000     4.750438000    -0.249144000
H         3.193482000     4.724265000    -2.730645000
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H         3.521356000    -4.395798000     0.840408000
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H       -0.492342000       1.892434000       4.576722000
H       -0.684687000       1.177667000       2.226220000
H       -0.706410000       4.189987000      -1.865082000
H       -2.819443000       5.269303000      -0.476704000
H       -2.940118000      -0.984154000       2.457810000
H       -3.894182000       3.136244000       0.861079000
H       -3.974123000      -1.371218000       1.070206000
H       -4.760658000       0.464788000       3.411290000
H       -5.330704000      -1.195796000       3.175031000
H       -5.796322000       0.069545000       2.026261000
O        0.386070000      -3.294312000      -2.213148000
O       -1.058580000      -2.910315000       1.943645000
O       -1.196724000       0.486462000      -3.472903000
O       -1.302122000       2.420015000      -1.000200000
O       -3.338753000       0.598724000       1.188710000
O       -3.829704000      -2.527867000      -1.465111000
W       -1.191783000      -1.003341000      -0.624592000


    3   cis [W(AsPh3)(CO)4C(OEt)(2-(N-methylpyrrolyl))]


As       -1.311217000       0.210287000       0.151142000
C        0.085943000       2.490724000       1.309865000
C        0.395635000       3.830867000       1.530750000
C        0.576171000      -1.482355000      -2.427720000
C        0.979284000      -1.585640000       1.651340000
C        1.398055000       1.485685000      -2.411560000
C        1.554457000       2.887228000      -2.969096000
C        2.281931000       0.311002000      -0.452197000
C        2.347496000      -2.675086000      -0.602117000
C        3.388309000       0.474403000       0.467601000
C        3.914305000      -0.477990000       1.356026000
C        4.101816000       2.915490000      -0.059792000
C        5.024748000       0.068412000       2.003491000
C        5.171667000       1.358136000       1.518577000
C       -0.294661000       4.831768000       0.846768000
C       -0.450430000      -2.996373000      -0.359962000
C       -0.933782000       2.136257000       0.418076000
C       -1.298550000       4.484693000      -0.053182000
C       -1.621808000       3.142986000      -0.263773000
C       -2.265567000      -0.194838000       1.835506000
C       -2.610945000       0.797644000       2.756840000
C       -2.616729000      -1.523591000       2.097569000
C       -2.637728000       0.032166000      -2.452525000
C       -2.843283000       0.292087000      -1.095162000
C       -3.298247000       0.464548000       3.924209000
C       -3.307813000      -1.850994000       3.261457000
C       -3.648535000      -0.858409000       4.178265000
C       -3.700770000       0.098105000      -3.352635000
C       -4.130932000       0.606805000      -0.647209000
C       -4.978834000       0.417687000      -2.902257000
C       -5.191997000       0.669560000      -1.548083000
H        0.384820000       1.311731000      -2.050584000
H        0.639741000       1.722037000       1.837775000
H        0.884194000       3.012749000      -3.823370000
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H        1.174951000        4.092098000        2.238347000
H        1.297040000        3.639871000       -2.221170000
H        1.637483000        0.732561000       -3.163046000
H        2.576465000        3.062810000       -3.312760000
H        3.093580000        3.313277000        0.039005000
H        3.540420000       -1.477540000        1.480954000
H        4.346081000        2.844368000       -1.118670000
H        4.803612000        3.592294000        0.428799000
H        5.653841000       -0.410099000        2.736701000
H        5.893550000        2.117349000        1.778501000
H       -0.051680000        5.874717000        1.016692000
H       -1.655230000       -0.239856000       -2.814862000
H       -1.839698000        5.256587000       -0.589385000
H       -2.345952000        1.831288000        2.573272000
H       -2.356624000       -2.309798000        1.400010000
H       -2.413892000        2.888483000       -0.957484000
H       -3.527951000       -0.112345000       -4.402049000
H       -3.557594000        1.242949000        4.633417000
H       -3.573801000       -2.884491000        3.452317000
H       -4.181098000       -1.116103000        5.086813000
H       -4.312262000        0.793211000        0.404443000
H       -5.806980000        0.461609000       -3.600670000
H       -6.186748000        0.909487000       -1.189089000
N        4.212085000        1.613515000        0.593813000
O        0.429383000       -1.635117000       -3.564169000
O        1.055481000       -1.764768000        2.785448000
O        2.323889000        1.335721000       -1.317063000
O        3.229432000       -3.414962000       -0.693548000
O       -1.141811000       -3.923093000       -0.351772000
W        0.813015000       -1.406371000       -0.395052000

    4   trans [W(AsPh3)(CO)4C(OEt)(2-(N-methylpyrrolyl))]

As      -1.722641000        0.042385000       -0.023604000
C        0.739459000       -1.856874000        1.325561000
C        0.915184000       -1.516483000       -1.490978000
C        0.952248000        0.951625000        1.797917000
C        1.025940000        1.379394000       -1.184609000
C        3.132336000       -0.214641000        0.121647000
C        3.546026000       -2.638043000        0.164062000
C        3.586995000        2.295410000        0.423742000
C        3.955279000        0.986185000        0.084411000
C        4.706919000        3.126899000        0.314232000
C        4.786159000       -3.509325000        0.089365000
C        5.753812000        2.326697000       -0.107885000
C        6.201105000       -0.008834000       -0.745942000
C       -1.767121000        2.938103000        0.424227000
C       -2.122290000       -0.620966000       -2.827284000
C       -2.263346000        4.238001000        0.339396000
C       -2.443217000        1.879776000       -0.189626000
C       -2.649057000       -0.814499000       -1.545770000
C       -2.660688000       -1.967306000        1.876357000
C       -2.739272000       -1.191634000       -3.937223000
C       -2.782249000       -0.622917000        1.505613000
C       -3.364020000       -2.462371000        2.971642000
C       -3.435153000        4.494165000       -0.368307000
C       -3.608719000        0.218755000        2.254455000
C       -3.619758000        2.143780000       -0.898197000
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C      -3.799422000     -1.592287000     -1.391556000
C      -3.883906000     -1.970669000     -3.777669000
C      -4.110808000      3.445025000     -0.987789000
C      -4.186914000     -1.618182000      3.715154000
C      -4.305511000     -0.278618000      3.355695000
C      -4.410768000     -2.170315000     -2.504653000
H       2.606245000      2.595648000      0.744422000
H       2.867828000     -2.843266000     -0.663622000
H       3.013634000     -2.793788000      1.101138000
H       4.495233000     -4.560732000      0.156422000
H       4.756706000      4.185199000      0.514318000
H       5.318229000     -3.364131000     -0.853509000
H       5.468472000     -3.291919000      0.914269000
H       5.733868000     -0.531980000     -1.578652000
H       6.439285000     -0.733758000      0.030760000
H       6.775368000      2.585874000     -0.339947000
H       7.119224000      0.463801000     -1.095928000
H      -0.851478000      2.755300000      0.972351000
H      -1.228735000     -0.022895000     -2.965887000
H      -1.728861000      5.048946000      0.821471000
H      -2.015912000     -2.633967000      1.317331000
H      -2.320691000     -1.033071000     -4.924704000
H      -3.260725000     -3.505840000      3.247356000
H      -3.713890000      1.262007000      1.984449000
H      -3.817267000      5.506289000     -0.440708000
H      -4.153723000      1.338348000     -1.387411000
H      -4.223374000     -1.751068000     -0.407811000
H      -4.360212000     -2.421129000     -4.641271000
H      -4.728877000     -2.002612000      4.571946000
H      -4.941374000      0.385395000      3.930874000
H      -5.021233000      3.637295000     -1.544841000
H      -5.301062000     -2.775411000     -2.372610000
N       5.324583000      1.043276000     -0.238340000
O       0.577691000     -2.785503000      1.995553000
O       0.888705000     -2.259326000     -2.372739000
O       0.967426000      1.589397000      2.757122000
O       1.042146000      2.257125000     -1.927712000
O       3.975461000     -1.263299000      0.102317000
W       0.947858000     -0.226033000      0.109255000
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   5   *cis* [W(AsPh3)(CO)4C(OEt)(2,2'-bithienyl)]

```
As      2.087361000      0.525028000      0.227425000
C       1.198368000     -2.046227000     -2.143613000
C       2.068698000     -2.819096000      0.385839000
C      -0.073706000     -1.434749000      1.713162000
C      -0.261233000      0.562175000     -2.980588000
C      -0.609339000     -3.309402000     -0.357733000
C      -0.630786000      1.798911000     -3.775577000
C      -1.241178000     -0.499072000     -0.991026000
C      -2.560587000     -0.507685000     -0.382856000
C      -3.072908000     -1.285588000      0.643360000
C      -4.421934000     -1.035256000      0.939670000
C      -4.988195000     -0.051291000      0.147726000
C      -6.342628000      0.453607000      0.185128000
C      -7.038080000      1.137452000     -0.787746000
C      -8.363403000      1.472763000     -0.407619000
C      -8.677516000      1.045046000      0.851530000
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```
H     0.157549000     2.015212000    -4.501215000
H     0.658003000     0.707501000    -2.414194000
H    -0.143471000    -0.308752000    -3.627456000
H    -0.741569000     2.662804000    -3.117708000
H    -1.565810000     1.647383000    -4.319102000
H    -2.495031000    -2.043687000     1.146357000
H    -4.976257000    -1.576538000     1.694927000
H    -6.613525000     1.369165000    -1.755656000
H    -9.058249000     2.001300000    -1.046319000
H    -9.606759000     1.159278000     1.387976000
O     1.608240000    -2.352438000    -3.178459000
O     2.926669000    -3.510553000     0.730182000
O    -0.385251000    -1.372155000     2.818702000
O    -1.262677000    -4.260670000    -0.386008000
O    -1.344281000     0.293030000    -2.068217000
S    -3.826860000     0.573265000    -0.989639000
S    -7.349586000     0.230323000     1.603928000
W     0.516759000    -1.656365000    -0.248391000
```

Characterization Data of complexes

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

Yield (37%). ^{1}H-NMR (CDCl$_3$, ppm) δ 7.57 (H10, dd, J_{H-H} = 5.0, 1.1 Hz, 1H), 6.91 (H9, dd, J_{H-H} = 5.0, 4.0 Hz, 1H), 7.86 (H8, dd, J_{H-H} = 4.0, 1.1 Hz, 1H), 4.58 (H11, q, J_{H-H} = 7.0 Hz, 2H), 1.17 (H12, t, J_{H-H} = 7.0 Hz, 3H), 7.24-7.44 (As**Ph$_3$**, m, 15H); ^{13}C-NMR (CDCl$_3$, ppm) δ 294.3 (C6), 210.0 (C1), 202.7 (C2 and C4), 206.8 (C3), 159.3 (C7), 140.0 (C8), 129.8 (C9), 132.7 (C10), 77.2 (C11) 15.1 (C12), 139.6 (C20), 133.7 (C21), 128.9 (C22) 128.6 (C23); IR (KBr, v(CO)/cm^{-1}) 2009 (A_1^1), 1928 (A_1^2), 1898 (B$_1$), 1878 (B$_2$); MS (m/z): Calc. 726.251 [M], Exp. 727.0 [M+1]$^+$; m.p. 118-120°C (dec).

2. cis-[(AsPh$_3$)(CO)$_4$WC(OEt)(C$_4$H$_3$O)] (2)

Yield (48%). ^{1}H-NMR (CDCl$_3$, ppm) δ 7.32 (H10, d, J_{H-H} = 1.0 Hz, 1H), 6.72 (H9, dd, J_{H-H} = 3.6, 0.8 Hz, 1H), 7.20 (H8, dd, J_{H-H} = 1.7, 0.8 Hz, 1H), 4.78 (H11, q, J_{H-H} = 7.1 Hz, 2H), 1.39 (H12, t, J_{H-H} = 7.1 Hz, 3H), 7.22-7.41 (As**Ph$_3$**, m, 15H); ^{13}C-NMR (CDCl$_3$, ppm) δ 289.0 (C6), 211.0 (C1), 202.7 (C2 and C4), 207.1 (C3), 166.5 (C7), 112.7 (C8), 111.0 (C9), 147.8 (C10), 77.0 (C11) 15.0 (C12), 139.6 (C20), 133.7 (C21), 129.6 (C22) 128.6 (C23); IR (KBr, v(CO)/cm^{-1}): 2011 (A_1^1), 1921 (A_1^2), 1892 (B$_1$), 1862 (B$_2$); MS (m/z): Calc. 742.318 [M], Exp. 743.0 [M+1]$^+$; m.p. 131-132°C (dec).

3. cis-[(AsPh$_3$)(CO)$_4$WC(OEt)(C$_4$H$_3$NMe)] (3)

Yield (58%). ^{1}H-NMR (CDCl$_3$, ppm) δ 6.90 (H10, s(br), 1H), 6.26 (H9, dd, J_{H-H} = 4.5, 2.3 Hz, 1H), 7.66 (H8, dd, J_{H-H} = 4.6 Hz, 1.8 Hz, 1H), 4.93 (H11, q, J_{H-H} = 7.1 Hz, 2H), 1.33 (H12, t, J_{H-H} = 7.1 Hz, 3H), 3.78 (H13, s(br)), 7.16 – 7.43 (As**Ph$_3$**, m, 15H); ^{13}C-NMR (CDCl$_3$, ppm) δ 297.5 (C6), 211.0 (C1), 204.1 (C2 and C4), 205.6 (C3), 143.4 (C7), 134.9 (C8), 111.2 (C9), 132.4 (C10), 40.7 (C13), 77.4 (C11) 15.2 (C12), 139.6 (C20), 133.7 (C21), 128.7 (C22) 128.5 (C23); IR (KBr, v(CO)/cm^{-1}) 2006 (A_1^1), 1917 (A_1^2), 1897 (B$_1$), 1886 (B$_2$); MS (m/z): Calc. 739.293 [M], Exp. 740.0 [M+1]$^+$; m.p. 161-163°C (dec).

4. cis-[(AsPh$_3$)(CO)$_4$WC(OEt)(C$_8$H$_5$S$_2$)] (4)

Yield (52%). ^{1}H-NMR (CDCl$_3$, ppm) δ 7.21-7.26 (H17, m, 1H), 7.04-7.09 (H16, m, 1H), 7.30-7.33 (H15, m, 1H), 7.01 (H9, d, J_{H-H} = 4.3 Hz, 1H), 7.79 (H8, d, J_{H-H} = 4.3 Hz, 1H) 4.62 (H11, q, J = 7.0 Hz, 2H), 1.24 (H12, t, J_{H-H} = 7.0 Hz, 3H), 7.34-7.43 (As**Ph$_3$**, m, 15H); ^{13}C-NMR (CDCl$_3$, ppm) δ 272.1 (C6), 210.0 (C1), 202.9 (C2 and C4), 207.0 (C3), 125.4 (C7), 128.4 (C8), 124.7 (C9), 137.1 (C10), 136.3 (C14), 124.3 (C15), 128.3 (C16), 125.2 (C17), 77.2 (C11) 14.7 (C12), 139.6 (C20), 133.8 (C21), 128.9 (C22) 128.5 (C23); IR (KBr, v(CO)/cm^{-1}) 2011 (A_1^1), 1918 (A_1^2), 1895 (B$_1$), 1879 (B$_2$); MS (m/z): Calc. 824.442 [M], Exp. 825.0 [M+1]$^+$; m.p. 149-150°C (dec).

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