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Stabilization of 17-electron metal-centered species. Electrochemical study of [WX(CO)$_3$(η^5-C$_5$H$_5$)] (X = Cl, Br, I) and [WI(CO)$_2$(PCy$_3$)(η^5-C$_5$H$_5$)]

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Abstract

The electrochemical study of [WX(CO)$_3$(η^5-C$_5$H$_5$)] (X = Cl, Br, I) (**1**–**3**) is reported. The reductions follow ECE mechanisms, yielding the anion [W(CO)$_3$(η^5-C$_5$H$_5$)]$^-$ (**7**$^-$). The stability of **1**–**3** towards reduction increases with the increasing electronegativity and decreasing size of the halide. **7**$^-$ reoxidizes to the unstable 17-electron radical [W(CO)$_3$(η^5-C$_5$H$_5$)] (**7**), which readily dimerizes. The oxidations of **1**–**3** follow EC mechanisms, leading to the cations [WX(CO)$_3$(η^5-C$_5$H$_5$)]$^+$, which are very unstable and readily decompose. [WI(CO)$_2$(PCy$_3$)(η^5-C$_5$H$_5$)] has been prepared and characterized as a mixture of *cis* (**4**) and *trans* (**5**) isomers (ratio *cis*:*trans* 95:5). The electrochemical reduction of the *cis* isomer (**4**) is also an ECE process, but takes place at a potential significantly more negative than **3**. An anion [W(CO)$_2$(PCy$_3$)(η^5-C$_5$H$_5$)]$^-$ (**8**$^-$) is formed which reoxidizes to **8**. This new 17-electron radical is considerably more stable than **7** due to the presence of the bulky PCy$_3$ ligand. A similar effect is observed in the oxidation of **4**, where the 17-electron product **4**$^+$ is significantly more stable than the analogue **3**$^+$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cyclopentadienyl; Tungsten; Carbonyl complexes; Electrochemistry

1. Introduction

The chemistry of 17- and 19-electron organotransition-metal radicals has been extensively investigated during the last decade [1]. The group 6 radicals [M(CO)$_3$(η^5-C$_5$H$_5$)]$^\bullet$ (M = Cr, Mo, W) and substituted derivatives are some of the most intensely studied neutral organometallic radicals. Such species can be produced via either photolysis of metal–metal bonded 18-electron dimeric compounds [2] or electron transfer reactions of 18-electron monomers [3]. They have been seen to engage in atom abstraction, [2]e; [4] and in the frequently coupled ligand substitution and disproportionation reactions [5]. These radicals have also been proposed as intermediates in a variety of reactions involving organometallic compounds [6]. They are nonetheless usually very unstable with respect to dimerization. However, there are now several known examples of 17-electron compounds which are significantly stabilized towards dimerization to the 18-electron metal–metal bonded analogues by substitution of small ligands with more sterically demanding ones (e.g. CO by tertiary phosphines [7], and η^5-C$_5$H$_5$ by η^5-C$_5$Me$_5$ [7]h and η^5-C$_5$Ph$_5$ [8]).

The electrochemistry of the organometallic halides [MX(CO)$_m$(η^5-C$_5$R$_5$)$_n$] (R = H, Me; X = halogen atom) has received relatively little attention [9], whereas the electrochemical reactivities of the organometallic dimers [M(CO)$_m$(η^5-C$_5$R$_5$)$_n$]$_2$ have been subjects of active research [10]. As part of our ongoing studies on the

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redox chemistry of organotransition-metal compounds [11], we report here the electrochemical study of [$WX(CO)_3(\eta^5\text{-}C_5H_5)$] (X = Cl (**1**), Br (**2**), I (**3**)). The electrochemical reduction of **1**–**3** had been previously reported [12] using a mercury working electrode. In that case, the electrode material participates significantly in the mechanism, forming an intermediate complex, [$W(CO)_3(\eta^5\text{-}C_5H_5)$]$_2$Hg. The formation of such an intermediate complex is not possible when using a platinum working electrode in the present study and, therefore, the reduction path must be different.

In order to stabilize 17-electron metal-centered radicals, we have prepared and studied elctrochemically the new compound [$WI(CO)_2(PCy_3)(\eta^5\text{-}C_5H_5)$] (**4**), in which there is a tricyclohexylphosphine ligand (PCy_3) with a great steric requirement (cone angle = 170°).

2. Experimental section

2.1. Reagents and general techniques

All manipulations were carried out by using standard Schlenk vacuum-line and syringe techniques under an atmosphere of oxygen-free argon. All solvents for synthetic use were reagent grade. Diglyme, pentane, tetrahydrofurane (THF), diethyl ether and hexane were dried and distilled over sodium in the presence of benzophenone ketyl under an Ar atmosphere. Also under Ar atmosphere, carbon tetrachloride, dichloromethane (DCM), dichloroethane (DCE), and toluene were dried and distilled over $MgSO_4$, CaH_2, and sodium, respectively. Propylene carbonate (PC) was stored over molecular sieves (5 Å) under an Ar atmosphere. All solvents were bubbled with argon for 1 h after distillation and then stored under Ar, or degassed by means of at least three freeze-pump-thaw cycles after distillation and before use.

The compounds [$W(CO)_3(\eta^5\text{-}C_5H_5)$]$_2$, [$WH(CO)_3(\eta^5\text{-}C_5H_5)$] and [$WX(CO)_3(\eta^5\text{-}C_5H_5)$] (X = Cl, Br, I) were prepared according to literature procedures [13–15]. The halo-derivatives were purified by thin-layer chromatography (TLC) using CH_2Cl_2/hexane (1:2) as eluent. The ^{1}H-NMR spectra were recorded on a Bruker AMX-300 instrument. Chemical shifts were measured relative to an internal reference of tetramethylsilane or to residual protons of the solvents for ^{1}H and H_3PO_4 for ^{31}P. Infrared spectra were measured on a Perkin-Elmer 1650 infrared spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the University Autónoma of Madrid on a Perkin-Elmer 240 B microanalyser. Electronic spectra were recorded on a Pye Unicam SP 8-100 UV-visible spectrophotometer. Mass spectra were measured on a VG-Autospec mass spectrometer for FAB or AIE by the Mass Laboratory of the University Autónoma of Madrid.

2.2. Preparation of [$WI(CO)_2(PCy_3)(\eta^5\text{-}C_5H_5)$]. Separation of two isomers

A solution of PCy_3 (0.05 g, 0.18 mmol) in THF (15 ml) was added to a solution of [$WI(CO)_3(\eta^5\text{-}C_5H_5)$] (0.05 g, 0.11 mmol) in the same solvent (30 ml). The solution was heated at 50°C to produce a mixture of *cis* (**4**) and *trans* (**5**) isomers. The reaction was monitored by FTIR spectroscopy. Upon filtration and removal of the solvent under reduced pressure, a reddish-brown solid was obtained which was extracted with DCM, and the *cis* and *trans* mixture was separated and purified by TLC using DCM/hexane (1:2) as eluent. Yield: 95% *cis*, 5% *trans*. IR (THF) ν_{CO} 1942 (vs), 1859 (s) cm^{-1}; (THF-toluene) ν_{CO} 1948, 1936 (sh), 1864, 1855 (sh) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.51 (s, 5H, *cis*), 5.40 (d, 5H, J_{PH} 1.4Hz, *trans*), 1.84 (m, 15H$_{ec}$), 1.24 (m, 18H$_{ax}$). ^{31}P ($CDCl_3$) 65.24 (s, *trans*), 51.31 (s, *cis*). MS: *m*/*e* 684 (M^+ –CO). UV (THF) λ_{max} 474 nm. Anal. Calcd. for $C_{25}H_{38}WO_2PI$: C, 42.2; H 5.4. Found: C 42.3; H 5.6.

2.3. Preparation of [$W(CO)_2(PCy_3)(\eta^5\text{-}C_5H_5)$]$_2$ (**6**) via reduction of [$WI(CO)_2(PCy_3)(\eta^5\text{-}C_5H_5)$] and oxidation of resulting Li[$W(CO)_2(PCy_3)(\eta^5\text{-}C_5H_5)$]

An 1 M solution of $LiEt_3BH$ in THF was added dropwise to a red solution of [$WI(CO)_2(PCy_3)(\eta^5\text{-}C_5H_5)$] (0.1 g, 0.14 mmol) in THF (30 ml) at 0°C until the colour turned pale yellow. Gas was evolved during the reaction. The mixture was filtered in a Schlenk tube and an IR spectrum was recorded. Complete conversion to Li[$W(CO)_2(PCy_3)(\eta^5\text{-}C_5H_5)$] ($\nu_{CO}$ 1920 (vs) and 1831 (s) cm^{-1}) was observed. An aqueous solution of $Fe_2(SO_4)_3$ (0.06 g) and glacial acetic acid (0.1 ml) was added by syringe, the colour turned orange-red instantly. Degassed hexane (30 ml) was added via cannula and the two-phase mixture was shaken vigorously, allowed to separate and then quickly cooled to -78°C. This caused the aqueous layer to freeze and the hexane-THF layer was then decanted via cannula into a Ar-filled, 250 ml flask containing anhydrous Na_2SO_4 (20 g). The clear orange-red solution was decanted via cannula from the drying agent into a Schlenk flask. Upon removal of the solvent under reduced pressure, a reddish-orange solid was obtained which was recrystallized from hexane-DCM at -15°C. Yield 85%. IR (THF) ν_{CO} 1912 (m), 1859 (sh), 1824 (vs) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.02 (s, 5H), 1.86 (m, 15H$_{ec}$), 1.25 (m, 18H$_{ax}$). ^{31}P ($CDCl_3$) 52.1 (s). MS: *m*/*e* 585 (1/2 M^+). UV (THF) λ_{max} 500, 363 nm. Anal. Calcd. for $C_{50}H_{76}W_2O_4P_2$: C, 51.3; H 6.5. Found: C 51.1; H 6.6.

2.4. Electrochemical measurements

A computer-driven PAR Mo. 273 electrochemistry system with positive feedback iR compensation was employed. All experiments were carried out in a three electrode cell under N_2 atmosphere in anhydrous deoxygenated solvent. Temperature was maintained constant at 25°C. Solutions contained 0.2 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte, and either DCE or PC as solvent.

Cyclic voltammetry studies were made on a pc–Pt working electrode (0.05 cm^2 real surface area, as calculated in a separate experiment through the H-adatom charge in 0.5 M H_2SO_4 solution [16]). The counter electrode was a Pt gauze. The reference electrode was an Ag wire quasi-reference electrode (QRE), pretreated by immersion in 10 M HNO_3 for 5 min before use. After a series of experiments, the QRE potential was calibrated by adding ferrocene (Fc) to the solution and taking voltammograms of the ferrocenium/ferrocene system. Potentials in this paper are then referred to this couple, Fc^+/Fc, which has been recommeded as a standard reference in nonaqueous solvents [17]. It can be related to a SCE reference electrode by using a value of $+0.307$ V vs SCE for Fc^+/Fc [18]. Controlled potential coulometry studies were made on a large area Pt working electrode.

3. Results and discussion

*3.1. Synthesis and characterization of cis- and trans-[WI(CO)$_2$(PCy$_3$)(η^5-C$_5$H$_5$)] (**4** and **5**)*

The reaction of **3** with the unidentate phosphorus ligand PCy_3 in refluxing THF gives the monosubstituted derivative $[WI(CO)_2(PCy_3)(\eta^5\text{-}C_5H_5)]$ in quantitative yield (98%) as a mixture of *cis* and *trans* isomers. The relative proportion of these isomers in related compounds depends markedly on the nature of phosphorus ligands, the method of preparation as well as the solvent [19]. The identity of the isomers was proven according to well-established infrared and NMR criteria [19]a; [20]. The ^{1}H-NMR spectrum shows that the monosubstituted complex exists as a mixture of these two isomers, the resonances due to the cyclopentadienyl protons of *cis* isomer are a singlet at 5.51 ppm, while those due to the *trans* isomer consist of 1:1 doublet at 5.40 ppm ($J_{PH} = 1.4$ Hz). Integrals of the *cis* and *trans* resonances suggest a *cis*:*trans* ratio of ca. 95:5. This ratio also depends on the solvent, thus when the polarity of the solvent increases the percentage of *cis* isomer increases ($CDCl_3$ *cis*:*trans* 95:5; acetone-d_6 *cis*:*trans* 98:2).

The ^{31}P NMR spectrum at room temperature exhibits two singlets at 51.31 ppm (*cis*) and 65.24 ppm (*trans*). The ratio of *cis*:*trans* isomers obtained from the integrals of these resonances agreed reasonably well with that obtained from ^{1}H-NMR data.

The IR spectrum in THF exhibits two absorption bands at 1942 (vs) and 1859 (s) cm^{-1} associated with terminal W–CO stretching (ν_{CO}) modes, the higher frecuency (sym) more intense than the lower one (antisym), whilst the IR spectrum in THF-toluene shows four bands at 1948, 1936 (sh), 1864, 1855 (sh) cm^{-1}. This supports the assignment made from the ^{1}H-NMR data [20]a.

The separation of this isomeric mixture into their components is essential to the electrochemical study and is described in the Experimental Section. The complexes are stable with respect to isomerization both in the solid state and in solution at low temperature.

*3.2. Synthesis and characterization of [W(CO)$_2$(PCy$_3$)(η^5-C$_5$H$_5$)]$_2$ (**6**)*

The photochemical reactions of $[W(CO)_3(\eta^5\text{-}C_5H_5)]_2$ with phosphines lead to disproportionation and/or substitution products [1,21]. The ratio of substitution to disproportionation products depends on the size and concentration of the ligand. When the size of the ligand increases, the monosubstituted dimer is formed preferentially to the disubstituted dimer or disproportionation products. Thus, bulky ligands (e.g. PCy_3, $\theta = 170°$) yield only monosubstituted products [22]. We therefore prepared **6** from reduction of the PCy_3-substituted halide with $LiEt_3BH$ to yield the Li^+ salt, $Li[W(CO)_2(PCy_3)(\eta^5\text{-}C_5H_5)]$. The IR spectrum of this compound (1920 and 1831 cm^{-1}) is similar to that of $Li[W(CO)_3(\eta^5\text{-}C_5H_5)]$ [23]. Acidification of the salt with glacial acetic acid and oxidation by $Fe_2(SO_4)_3$ produce the disubstituted dimer **6**, isolated as a light reddish-orange powder. This new compound exhibits IR, ^{1}H and ^{31}P NMR spectra very similar to those of the disubstituted dimer $[W(CO)_2L(\eta^5\text{-}C_5H_5)]_2$ (M = Mo, W) (L = P-donor ligands) [24]. These data can only be explained in terms of the existence of two isomers (*cis* and *trans*) in solution.

3.3. Electrochemical studies

*3.3.1. Reduction of **1**, **2** and **4***

The voltammetric reductions of **1**, **2** and **3** show similar characteristics. An irreversible cathodic wave is observed for each of the compounds, and the solvent dependent peak potentials, E_{pc}, are assembled in Table 1. In the reduction process, a reduced species is formed which reoxidizes upon scan reversal at a much more positive potential, E_{reox} (Fig. 1, Table 1). When the anodic scan following the reduction of **1**–**3** is extended

Table 1
Electrochemical data for the reduction of **1**, **2** and **3** in solvents DCE and PC

	1		**2**	**3**
	DCE	PC	PC	PC
E_{pc} (V vs Fc$^+$/Fc)[a]	−1.73	−1.53	−1.49	−1.46
i_{pc}/C (mA cm^{-2} M^{-1})[a, b]	208	162	150	145
E_{pc} vs log v slope (mV)	—	65	75	74
α (from E_{pc} vs log v)	—	0.46	0.40	0.41
$\lvert E_{pc}-E_{p/2}\rvert$ (mV)	—	100	110	115
α (from $\lvert E_p-E_{p/2}\rvert$)	—	0.48	0.43	0.41
E_{reox} (V vs Fc$^+$/Fc)[a]	−0.68	−0.47	−0.45	−0.46
i_{pa}/C (mA cm^{-2} M^{-1})[a, c]	32	65	72	73
E_{add}(V vs Fc$^+$/Fc)[a, d]		0.49	0.07; 0.38; 0.49	0.04; 0.37; 0.49

[a] Data at $v = 0.1$ Vs^{-1}.
[b] Reduction peak current density/C.
[c] Reoxidation peak current density/C.
[d] Additional peaks in the anodic scan. Peak for [WX(CO)$_3$(η^5-C$_5$H$_5$)] oxidation is omitted.

until 1 V vs Fc$^+$/Fc, additional oxidation peaks can be observed in the voltammograms of the three compounds (Fig. 2, solid line). One of them, at around 0.65 V, corresponds to the oxidation of **1**–**3** and will be further discussed in the following section. The other peaks do not appear when the cell is switched at −0.6 V (a potential value less negative than that necessary to reduce **1**–**3**) and scanned in the positive direction (Fig. 2, dashed line); therefore, they must be due to the oxidation of species produced by the reduction of **1**–**3** or by the subsequent reoxidation at ca. 0.46 V. One of these peaks, at +0.49 V, is common to the three compounds; the remaining ones are dependent on the nature of the halogen atom (E_{add} in Table 1).

The overall number of electrons transferred in the reduction process was determined by controlled potential coulometry. Thus, weighted amounts of **1**–**3** were dissolved in 0.2 M TBAPF$_6$ in PC (yielding red solutions) and reduced at −2.15 V vs Fc$^+$/Fc, a potential well within the diffusion-limited region of the reduction waves. The amount of electricity consumed when the current decayed to background (after ca. 1 h) (the colours of the end solutions were very pale), indicated that all the reductions were two-electron processes. Cyclic voltammograms recorded inmediately after the electrolyses did not show any reduction peaks when the sweeps started at −0.6 V in the cathodic direction, indicating that **1**–**3** had disappeared from the solutions. However, when the scans began at −0.8 V in the positive direction, an anodic peak at −0.46 V ($v = 0.1$ Vs^{-1}) appeared, with a current density higher than that for the starting solutions of **1**–**3**.

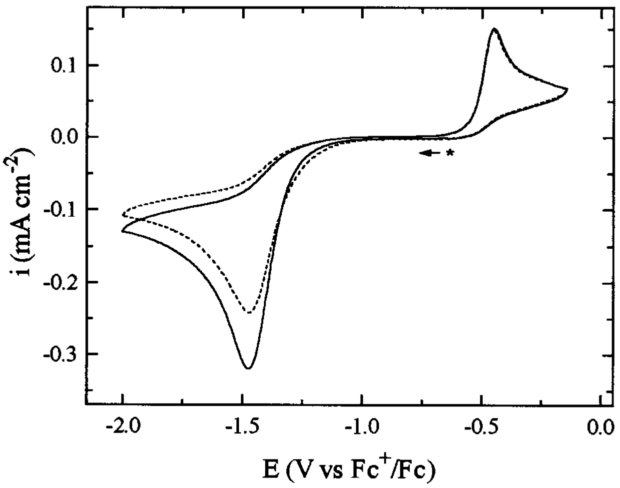

Fig. 1. Cyclic voltammogram for the reduction of a 2.1 × 10^{-3} M solution of **2** in PC containing 0.2 M TBAPF$_6$ at 0.1 Vs^{-1} and 25°C. The first (——) and second (– – –) scans are shown. An asterisk indicates the start of a cycle.

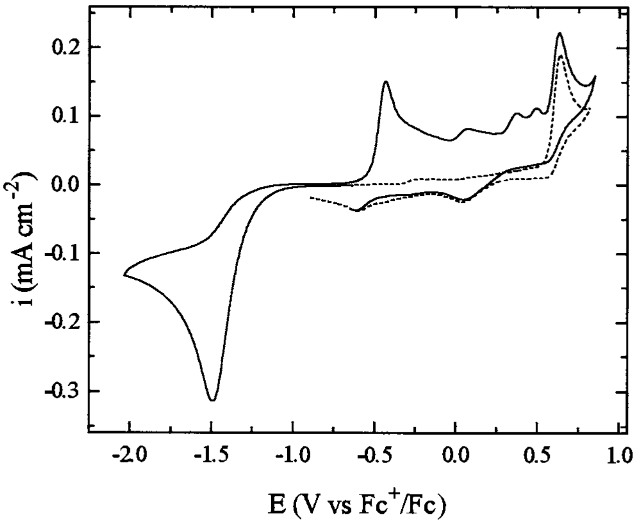

Fig. 2. Cyclic voltammogram of a 2.1 × 10^{-3} M solution of **2** in PC containing 0.2 M TBAPF$_6$ at 0.1 Vs^{-1} and 25°C. Scans started at −0.6 V in the cathodic direction (——) and in the anodic direction (– – –).

Reoxidations of the previously formed reduced species were also attempted by controlled potential coulometry. However, the current intensity decayed to the background value with less than 1 F mol^{-1} (ca. 0.75) being consumed, although the colour of the solutions turned red. Cyclic voltammograms recorded inmediately after such reoxidations were significatively different from the original ones, showing several cathodic peaks that are poorly defined and difficult to identify.

The voltammetric study at different sweep rates (v) reveals that, for the three compounds, the reduction peak current density (i_{pc}) is a linear function of $v^{1/2}$ in the range $0.01 < v < 10$ Vs^{-1}. A systematic shift in the peak potentials with scan rate was observed, and the plots of E_{pc} vs log v are linear for v up to 1 Vs^{-1}. The slopes of these plots are assembled in Table 1. The width of the waves were also studied. Experimentally observed $|E_{\text{p}} - E_{\text{p}/2}|$ values, where $E_{\text{p}/2}$ is the potential at half-height, are also shown in Table 1 for the reduction processes. They are always greater than 30 mV, the value which would correspond to a reversible, diffusion-controlled, two-electron transfer.

The linear dependency of E_{p} on log v, with slopes greater than 60 mV per decade, as well as the width of the waves, are indicative of irreversible charge transfer processes. The transfer coefficient, α, can be calculated from the E_{p} vs log v plot according to [25]:

$$E_{\text{p}} = (2.3RT/2\alpha n_{\alpha}F) \log v + \text{constant}, \quad (1)$$

where n_{α} is the number of electrons transferred in the rate limiting step. Calculated α values assuming $n_{\alpha} = 1$ are assembled in Table 1. Alternatively, α can be calculated from the width of the wave [25]:

$$|E_{\text{p}} - E_{\text{p}/2}| = 1.857(RT/\alpha n_{\alpha}F) \quad (2)$$

Table 1 also lists α values calculated by this method, which are consistent with those obtained from the E_{p} vs log v slope.

All the above data, the shapes of the voltammograms, and the reported studies on related compounds [26], suggest that the reduction follows an ECE type mechanism according to Eqs. (3)–(5), where M = $W(CO)_3(\eta^5\text{-}C_5H_5)$.

$$\text{M–X} + e^- \rightarrow [\text{M–X}]^- \quad (3)$$

$$[\text{M–X}]^- \rightleftarrows \text{M}^{\cdot} + \text{X}^- \quad (4)$$

$$\text{M}^{\cdot} + e^- \rightleftarrows \text{M}^- \quad (5)$$

In the first electrochemical step, an electron is transferred to the LUMO of the compound, which is probably an antibonding W-halide orbital. Eq. (3) is rate determining and yields an anion radical with a very weak W–X bond [26]. As a result of this, an homogeneus chemical reaction readily takes place Eq. (4) in which the weakened W–X bond is broken, yielding X^- anions and $M^{\cdot}$ radicals ($[W(CO)_3(\eta^5\text{-}C_5H_5)]^{\cdot}$ (**7**)). **7** has an unpaired electron in a W-centered orbital of less energy than the starting W–X antibonding orbitals. Therefore, the introduction of a new electron is now more favourable than in **1**–**3**, and reduction takes place more easily; that is, $M^{\cdot}$ is readily electroreducible at the reduction potential of M–X and an overall two electron transfer is observed, yielding the anion M^- ($[W(CO)_3(\eta^5\text{-}C_5H_5)]^-$ (**7**$^-$)).

7$^-$ is also the final product of the reduction of the dimer $[W(CO)_3(\eta^5\text{-}C_5H_5)]_2$, in which there is a W–W bond, and which has been voltammetrically studied by Anderson et al. [10]d. Reoxidation of the anion was found to follow Eqs. (6) and (7):

$$[W(CO)_3(\eta^5\text{-}C_5H_5)]^- \rightleftarrows [W(CO)_3(\eta^5\text{-}C_5H_5)]^{\cdot} + e^- \quad (6)$$

$$2[W(CO)_3(\eta^5\text{-}C_5H_5)]^{\cdot} \rightarrow [W(CO)_3(\eta^5\text{-}C_5H_5)]_2 \quad (7)$$

Thus, the final product is $[W(CO)_3(\eta^5\text{-}C_5H_5)]_2$. This process was studied in DCM, THF and acetonitrile [10]e, and both the potential for dimer reduction and the potential for anion reoxidation were found to depend on the solvent. In order to have exactly the same experimental conditions, we have also studied voltammetrically $[W(CO)_3(\eta^5\text{-}C_5H_5)]_2$ in PC, finding that it is reduced at −1.61 V vs Fc^+/Fc, and that the resulting anion is reoxidized at $E_{\text{reox}} = -0.46$ V. This E_{reox} is practically the same as that obtained for **1**, **2** and **3** (Table 1), in agreement with the proposed mechanism. On the other hand, we have found that $[W(CO)_3(\eta^5\text{-}C_5H_5)]_2$ is oxidized at +0.49 V in PC, the potential value of the additional peak found in the voltammograms of the three compounds when reduction of **1**–**3** was initially performed. This corroborates that reduction of **1**–**3** leads to **7**$^-$, and that reoxidation of this anion yields the dimer $[W(CO)_3(\eta^5\text{-}C_5H_5)]_2$, which is absent in the starting solution.

X^- is also a product of the reduction process, and can be oxidized in the subsequent anodic scan. In order to clearly identify the peaks due to this process, small amounts of KX were added to the solutions, and scans performed from −0.6 V in the positive direction. For X = Br, a complex oxidation peak at ca. 0.38 V is observed. For X = I two new peaks appear at 0.04 V and at 0.37 V. All these halide oxidation peaks are observed in the voltammograms of the corresponding solutions of **2** and **3** after initial reduction (see E_{add} in Table 1). No extra peaks appear for X = Cl in the potential range studied, in accordance with the higher value of E^0 for the Cl_2/Cl^- couple.

The anodic peak at 0.07 V, which is seen after the reduction of **2**, is not due to the oxidation of Br^- or $[W(CO)_3(\eta^5\text{-}C_5H_5)]_2$. It could be due to the oxidation of the product of a different kind of reaction of the radicals formed after reoxidation of **7**$^-$, probably with solvent molecules involved [1]m.

The diffusion coefficients, D, of **1**–**3** were obtained in PC from the chronoamperometric i–t transients according to [27]:

$$it^{1/2} = nFAC(D/\pi)^{1/2}, \qquad (8)$$

where n is the overall number of electrons transferred per molecule ($n = 2$), A is the electrode area and C is the bulk concentration of electroactive species. Several of these transients were recorded at different constant potentials in the range of -1.8 to -2.1 V vs Fc$^+$/Fc, i.e. where the charge transfer is diffusion controlled. The plots of i vs $t^{-1/2}$ were always linear and the slopes almost coincident, but best results were obtained at ca. -2.0 V vs Fc$^+$/Fc. From the slope of these plots, D is 1.50×10^{-6}, 1.45×10^{-6} and 1.43×10^{-6} cm^2 s^{-1}, for **1**, **2** and **3**, respectively. These values are in very good agreement with those expected from the direct application of the following equation [18]:

$$i_p = (2.99 \times 10^5)n(\alpha n_\alpha)^{1/2}ACD^{1/2}v^{1/2} \qquad (9)$$

which is valid for irreversible processes. Considering $n = 2$ and $n_\alpha\alpha = 0.47$ for **1** and 0.41 for **2** and **3** (Table 1), and averaging the results in the $0.01 < v < 1$ Vs^{-1} range, (9) yields $D = 1.52 \times 10^{-6}$, 1.50×10^{-6} and 1.40×10^{-6} cm^2 s^{-1} for **1**, **2** and **3**, respectively.

When the values of E_{pc} in PC are compared for **1**, **2** and **3**, a trend to less negative E_{pc} is found from the Cl to the I compound. A more negative E_{pc} is indicative of a greater difficulty to reduce the compound, i.e. a greater stability towards this process as the electrons transferred occupy orbitals of a higher energy. As discussed above, in [WX(CO)$_3$(η^5-C$_5$H$_5$)] these LUMO are probably W–X antibonding orbitals. A higher energy W–X antibonding orbital corresponds to a more stable W–X bonding orbital when W = Cl, as a result of the stronger and more efficient interaction between W and Cl. Thus, the stability of **1**–**3** towards reduction increases with the increasing electronegativity and decreasing size of the halide. A previous work on the reduction of [WX(CO)$_3$(η^5-C$_5$H$_5$)] was reported by Denisovich et al. [12]c in 1968. The working electrode material, Hg, actively participated in the reduction mechanism, as the intermediate radical [W(CO)$_3$(η^5-C$_5$H$_5$)], formed after electron transfer and W–X bond breaking, reacted with Hg to yield [W(CO)$_3$(η^5-C$_5$H$_5$)]$_2$Hg. This latter species was reduced in a second wave to [W(CO)$_3$(η^5-C$_5$H$_5$)]$^-$. Although the conditions were different from those of the present study, the same trend in the reduction potential with the nature of X was found.

Changing the solvent significantly influences the value of E_{pc}. For **1**, the reduction peak is ca. 0.2 V more negative in DCE than in PC. The direction of the shift agrees with what might be expected from the higher dipole moment and dielectric constant of PC respect to DCE. The polar molecules of PC stabilize both the intermediate anion radical and the anion formed after total reduction, making this process easier. The change in i_{pc} when the solvent is DCE or PC is in agreement with the different viscosities of both media (2.53 cP for PC and 0.785 cP for DCE). According to Walden's ($D\eta = D'\eta'$), D_{DCE} ca. $3.22D_{CP}$ and, consequently, i_{pc} is higher in DCE, as observed.

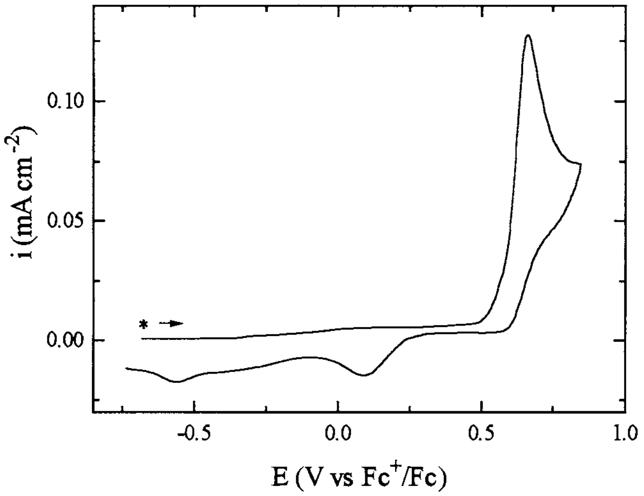

Fig. 3. Cyclic voltammogram for the oxidation of a 1.4×10^{-3} M solution of **3** in PC containing 0.2 M TBAPF$_6$ at 0.1 Vs^{-1} and 25°C. An asterisk indicates the start of the run.

3.3.2. *Oxidation of* ***1****,* ***2*** *and* ***3***

The electrochemical oxidation of **1**, **2** and **3** was studied in PC. An irreversible anodic wave with two associated cathodic processes (at ca. 0.1 V and ca. -0.6 V) is found for the three compounds (Fig. 3). Peak potentials and peak currents are assembled in Table 2. Coulometry of the oxidation wave was attempted, but the results were not conclusive. The currents decayed to background long before 1 F mol^{-1} had been transferred. This kind of problem seems to be common in the coulometric determination for the oxidation of related compounds [11,28]. Poisoning of the electrode and compound decomposition are probably taking place.

Lau et al. [9]f,g reported the oxidation of [MoX(CO)$_3$(η^5-C$_5$H$_5$)] (X = Cl, Br, I) in DCM and acetonitrile on a Pt working electrode. They observed monoelectronic irreversible waves (the oxidation of the

Table 2
Electrochemical data for the oxidation of **1**, **2** and **3** in PC

Compound	1	2	3
E_{ox} (V vs Fc$^+$/Fc)[a]	0.62	0.64	0.66
i_{pa}/C (mAcm^{-2} M^{-1})[a, b]	150	90	88

[a] Data at $v = 0.1$ Vs^{-1}.

[b] Oxidation peak current density/C.

iodine compound was reversible at 5 Vs^{-1} in DCM). The process follows Eqs. (10) and (11):

$$[MoX(CO)_3(\eta^5-C_5H_5)] \rightarrow [MoX(CO)_3(\eta^5-C_5H_5)]^+ + e^- \quad (10)$$

$$[MoX(CO)_3(\eta^5-C_5H_5)]^+ \rightarrow \text{decomposition} \quad (11)$$

Based on the above results with compounds closely related to **1**–**3**, together with the similarity of the reported waves, we think that the oxidations of **1**, **2** and **3** are also one electron processes, leading to the cations $[WX(CO)_3(\eta^5\text{-}C_5H_5)]^+$, which are very unstable and readily decompose. The assignment of $n = 1$ is in agreement with the current density of the oxidation peak as compared with that of the reduction peak (where $n = 2$) for **2** and **3**. However, for **1** $(i_p)_{ox}$ is higher than expected for $n = 1$, and the process may be more complicated. One possibility is that the follow-up chemical reaction of $\mathbf{1}^+$ produces a species that can be further oxidized at $E_{ox}(\mathbf{1})$, thus yielding an ECE global mechanism.

In the present study, none of the compounds showed any sign of coupled cathodic processes on the reverse scan with sweep rates as high as 80 Vs^{-1}, which establishes the existence of follow-up chemical reactions that are fast on the time scale of the cyclic voltammetry experiment.

A comparison of E_{ox} values in Table 2 reveals that the oxidation potential increases when X changes from Cl to Br to I. The observed differences are small, but significant and in agreement with the trend found for the above mentioned $[MoX(CO)_3(\eta^5\text{-}C_5H_5)]$ [9]f,g (in DCM at $v = 0.2$ Vs^{-1}: +0.63, +0.64 and +0.68 V vs Fc^+/Fc for X = Cl, Br, I, respectively). The order is opposite to what would be expected if only the halogen electronegativity (decreasing from Cl to I) is considered. Decreasing X electronegativity would involve increasing electron density on the metal atom, thus decreasing E_{ox}. The opposed trend, called 'inverse halide order' by Zietlow et al. [29], was attributed to metal-d to halogen-d backbonding. Many other similar systems have been reported in the literature [30]. Using such explanation, iodine is the best π-aceptor and allows the most effective backbonding. This gives the order Cl < Br < I, the same as found in E_{ox}.

The oxidation of **1** has also been studied in DCE. An anodic peak at +0.66 V vs Fc^+/Fc ($i_p/C = 166$ mA cm^{-2} M^{-1} at 0.1 Vs^{-1}), analogous to that found in PC, is obtained (Fig. 4). However, it is followed by a second peak at +0.96 V (71 mA cm^{-2} M^{-1} at 0.1 Vs^{-1}), which could be a further oxidation of a product of the chemical reaction following the first charge transfer.

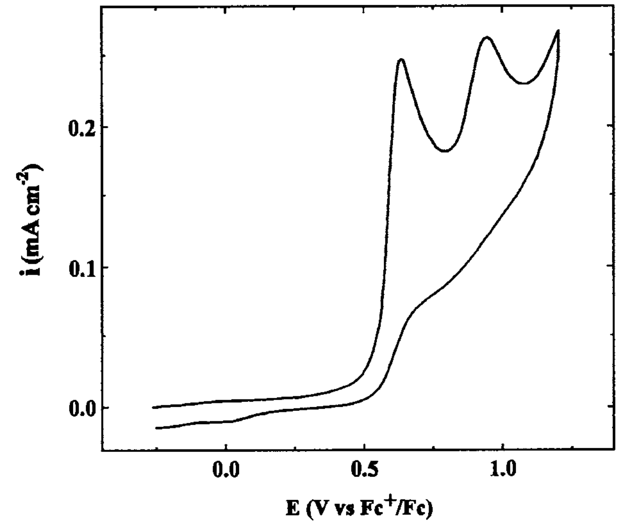

Fig. 4. Cyclic voltammogram for the oxidation of a 1.5×10^{-3} M solution of **1** in DCE containing 0.2 M $TBAPF_6$ at 0.1 Vs^{-1} and 25°C. An asterisk indicates the start of the run.

3.3.3. Electrochemistry of 4

The voltammetric reduction of **4** in PC gives rise to an irreversible cathodic wave (Fig. 5) with E_{pc} significantly more negative than that of **3** (−1.94 V as compared to −1.46 V). Upon scan reversal, a reoxida-

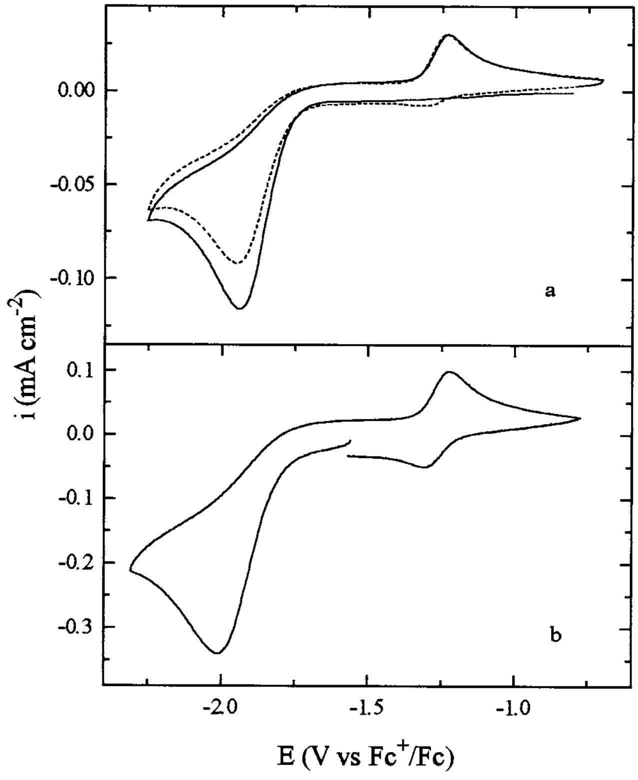

Fig. 5. Cyclic voltammograms for the reduction of a 8.5×10^{-4} M solution of **4** in PC containing 0.2 M $TBAPF_6$ at 25°C. The first (——) and second (– – –) scans are shown in a. The sweep rate is 0.1 Vs^{-1} in a, and 1 Vs^{-1} in b. An asterisk indicates the start of a cycle.

Table 3
Electrochemical data for the reduction and oxidation of **4** in PC

	$\mathbf{4}\rightarrow\mathbf{8}^-$	$\mathbf{8}^-\rightarrow\mathbf{8}$	$\mathbf{4}\rightarrow\mathbf{4}^+$
E_p (V vs Fc^+/Fc)[a]	-1.94	-1.24[c]	0.23[d]
i_p/C (mA cm^{-2} M^{-1})[a, b]	130	30	110
E_p vs log v slope (mV)	75		
α (from E_p vs log v)	0.40		

[a] Data at $v = 0.1$ Vs^{-1}.

[b] Peak current density/C.

[c] Anodic peak potential, $E_{1/2} = -1.27$ V.

[d] Anodic peak potential, $E_{1/2} = 0.20$ V.

tion peak at -1.24 V ($v = 0.1$ Vs^{-1}) is found. The general shape of the waves is similar to those obtained with **1**–**3** solutions. Peak potentials, peak currents (i_{pc} is a linear function of $v^{1/2}$ in the range $0.01 < v < 10$ Vs^{-1}) and wave parameters are assembled in Table 3. All these data imply that the reduction process must follow a path analogous to that of Eqs. (3)–(5).

The negative shift in E_{pc} when a CO ligand is substituted by PCy_3 is in agreement with the greater basicity of PCy_3, as reflected by the decrease of the value of the higher frequency ν_{CO} in **4** (1942 cm^{-1}) with respect to **3** (2032 cm^{-1}). The substitution increases the electron density on the W atom and stabilizes **4** towards reduction. The final product of the reduction process is the anion $[W(CO)_2(PCy_3)(\eta^5\text{-}C_5H_5)]^-$ ($\mathbf{8}^-$), which is oxidized to the radical species $[W(CO)_2(PCy_3)(\eta^5\text{-}C_5H_5)]$ (**8**) at -1.24 V ($v = 0.1$ Vs^{-1}). In the related compound **3**, the radical **7** readily dimerizes and no cathodic peak is found upon scan reversal, indicating that the rate constant of the dimerization reaction Eq. (7) is large. However, when the scan is reversed at -0.6 V in a solution of **4** (Fig. 5a) a reduction peak is observed even at a sweep rate as slow as 0.05 Vs^{-1}. The peak current ratio i_{pc}/i_{pa} for the $\mathbf{8}/\mathbf{8}^-$ system approaches 1 as v increases (Fig. 5b). On the other hand $\Delta E_p = E_{pa} - E_{pc}$ parallels that of ferrocene under the same conditions (it is 58 mV at 0.1 Vs^{-1}, but increases slightly with scan rate; the behaviour of ferrocene was analogous). All these data indicate that the oxidation of $\mathbf{8}^-$ follows an EC scheme. A reversible charge transfer yielding the radical **8** is followed by a homogeneous chemical reaction whose rate constant is rather small. Therefore, the presence of the bulky PCy_3 ligand greatly stabilizes the 17-electron radical species **8**.

The chemical reaction could be a dimerization to $[W(CO)_2(PCy_3)(\eta^5\text{-}C_5H_5)]_2$ (**6**), and an independent experiment was carried out in order to check this idea. Thus, a solution of **6** was prepared, and cyclic voltammetry performed. **6** is oxidized at $+0.1$ V by an EC process (at $v = 10$ Vs^{-1}, a cathodic peak is obtained upon scan reversal). When the anodic sweep after reduction of **4** was extended to $+1$ V (Fig. 6), some additional peaks appear in the voltammogram; one of them takes place at $+0.04$ V and is observed as a shoulder of the main oxidation peak at $+0.23$ V. This peak is due to the oxidation of I^- produced in the reduction of **4**, as confirmed by in situ addition of a small amount of KI to the solution. No clear peak for the oxidation of **6** is observed, but it could easily be masked by the peaks at 0.04 and 0.23 V. Therefore, there is no evidence of dimerization taking place, but it cannot be discarded.

Other possibilities apart from dimerization can account for the chemical reaction in the EC mechanism. Seemingly, the introduction of a solvent molecule would yield a 19-electron species which could be responsible for the small oxidation peaks that appear at -0.47 and at -0.23 V in the voltammogram (Fig. 6).

The voltammetric oxidation of **4** gives rise to two peaks, at $+0.23$ V and at ca. $+0.5$ V ($v = 0.1$ Vs^{-1}). The second peak is completely irreversible even at 80 Vs^{-1}. However, a coupled cathodic peak is obtained for the first one at $v \geq 0.02$ Vs^{-1}. The reversibility is more clearly appreciated when the scan is reversed before the second peak (Fig. 7). The peak current ratio i_{pc}/i_{pa}, although not accurately determined due to the vicinity of the peak at $+0.5$ V, clearly approaches 1 as v increases (Fig. 7b). ΔE_p parallels that of ferrocene under the same conditions.

The irreversible peak at ca. 0.5 V seems to have at least two components. The more anodic one becomes comparatively more important as v increases (compare Fig. 7a and b). It has two associated reduction waves, at -0.1 V and at -0.75 V. The latter eventually disappears as v increases, indicating that it is related to the less anodic component of the complex irreversible oxidation peak.

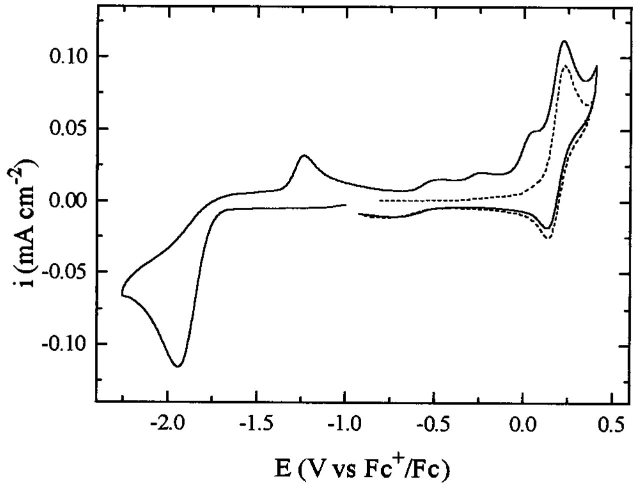

Fig. 6. Cyclic voltammogram of a 8.5×10^{-4} M solution of **4** in PC containing 0.2 M $TBAPF_6$ at 0.1 Vs^{-1} and 25°C. Scans started at ca. -1.0 V in the cathodic direction (——) and in the anodic direction (– – –).

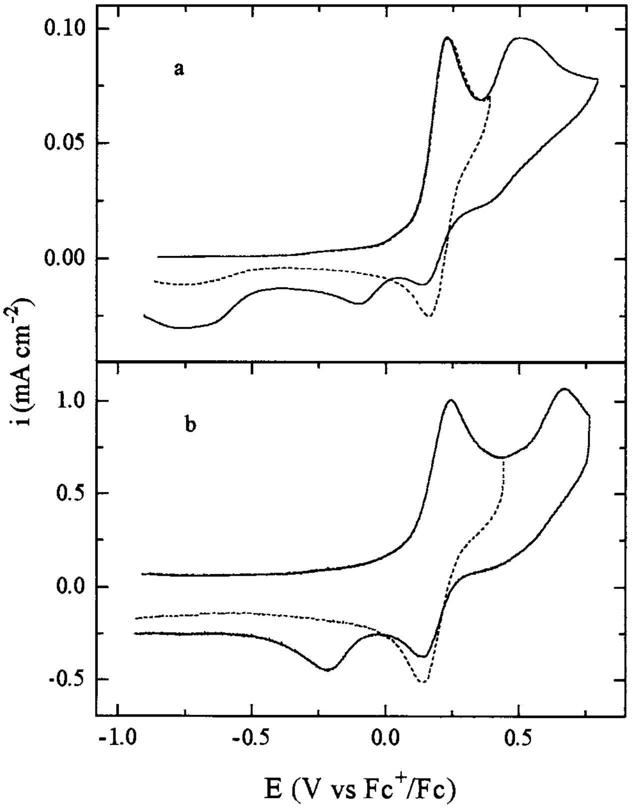

Fig. 7. Cyclic voltammograms for the oxidation of a 8.5×10^{-4} M solution of **4** in PC containing 0.2 M $TBAPF_6$ at 25°C. Switching potential after (——) and before (– – –) the second anodic peak. The sweep rate is 0.1 Vs^{-1} in a, and 10 Vs^{-1} in b.

All the above data indicate that the oxidation of **4** follows an EC mechanism similar to that of **1**–**3**. A first reversible charge transfer yields the cation $\mathbf{4}^+$, which suffers a follow-up chemical reaction. However, this chemical step is not too fast on the time scale of the cyclic voltammetry experiment, as indicated by the presence of the coupled cathodic peak. The product of the chemical reaction undergoes a further irreversible oxidation at the potential of the second peak. The complexity of this wave seems to indicate the existence of more than one product.

The substitution of a CO ligand by PCy_3 results in a significant stabilization of the 17-electron species $\mathbf{4}^+$ as compared to $\mathbf{3}^+$. At the same time, oxidation of **4** is also easier than that of **3**, taking place at a potential 0.43 V less positive. The shift in the oxidation potential reflects the greater basicity of PCy_3. Thus, the substitution of the π-bonding CO ligand by the the strong σ-donating phosphine leads to a much higher electron density on the W atom in **4** than in **3**, consequently the abstraction of one electron to yield the cation becomes an easier process. On the other hand, the greater chemical stability of $\mathbf{4}^+$ should be related to the steric demand of the bulky PCy_3 ligand.

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