# Water-soluble $Co_3C$ and $Co_2C_2$ Clusters; Redox Chemistry and Electrochemical Reactions in Water

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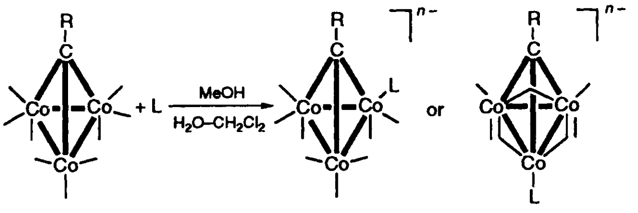
The water-soluble clusters $[Co_3(CR)(CO)_8L]^{n-}$ {$n$ = 1 or 3, L = $[PPh_{3-n}(C_6H_4SO_3\text{-}m)_n]^{n-}$; R = Ph, Me, Cl or Br} and $[Co_2\{C_2(CO_2Me)_2\}(CO)_5\{P(C_6H_4SO_3\text{-}m)_3\}]^{3-}$ (two isomers) have been prepared and characterised. Attempts were also made to sulfonate the capping aryl group of $[Co_3(CPh)(CO)_9]$. The redox processes of these complexes in water, 'wet' and 'dry' solvents have been investigated; $\vec{E}C\vec{E}$ and $\vec{E}C\overleftarrow{E}$ mechanisms, similar to those elucidated for non-aqueous solvents, operate in water but the large sulfonated ligands influence the kinetic parameters. The need to use dry solvents for electrochemical studies of these clusters may not be as important as previously thought.

Electron-transfer processes in non-aqueous media have been defined for a number of transition-metal carbonyl clusters and their derivatives.[1–3] It is standard in these investigations for strictly anhydrous conditions to be used for electrochemical and redox studies. While a change in non-aqueous solvent from say acetone to dichloromethane does not appear to effect the overall electron-transfer mechanism it is not clear what role, if any, the solvent plays in $\vec{E}C\overleftarrow{E}$ or $\vec{E}C\vec{E}$ processes. The $\vec{E}C\overleftarrow{E}$ processes are particularly important[4–6] for phosphine or phosphite[7] derivatives of $Co_3C$ clusters and $\vec{E}C\overleftarrow{E}/\vec{E}C\vec{E}$ with $[Co_2(C_2R_2)(CO)_6]$ (R = Ph, Bu or $CF_3$) clusters.[8] Facile ligand dissociation or metal–metal bond cleavage activated by the formation of a cluster radical anion is the critical kinetic parameter.[6] It is known that donor solvents such as MeCN can compete, albeit unsuccessfully, with phosphines for the vacant site on a co-ordinatively unsaturated cobalt atom in the cluster radical anion but there are no studies on the competitiveness of other nucleophiles with poor π-acceptor properties. In addition, investigations into the possible use of clusters as ETC (electron transfer catalysed) ($\vec{E}C\overleftarrow{E}$) hydroformylation catalysts would be easier in aqueous medium as the catalyst is phase-separated from the organic substrate.[9] Accordingly, synthetic routes to water-soluble $Co_3C$ and $Co_2C_2$ clusters and phosphine complexes were examined and the redox chemistry of the phosphine derivatives in aqueous medium investigated.

## Results and Discussion

$Co_3C$ *Complexes*.—Reaction of the clusters $[Co_3(CR)(CO)_9]$ **1** (R = Ph **1a**, Me **1b**, Cl **1c** or Br **1d**) with the sulfonated ligands[10] $[PPh_{3-n}(C_6H_4SO_3\text{-}m)_n]^{n-}$ ($n$ = 1 or 3) in a water–$CH_2Cl_2$ solvent system, either at elevated temperatures or with sonication at ambient temperatures, or in boiling methanol, gave the water-soluble substituted clusters $[Co_3(CR)(CO)_8\{PPh_2(C_6H_4SO_3\text{-}m)\}]^-$ (R = Ph **3**, Me **5**, Cl **7** or Br **9**) and $[Co_3(CR)(CO)_8\{P(C_6H_4SO_3\text{-}m)_3\}]^{3-}$ (R = Ph **4**, Me **6**, Cl **8** or Br **10**), in good yield as their $Na^+$ or $K^+$ salts (Scheme 1). Crystalline salts obtained with $AsPh_4^+$ as the counter ion provided non-hygroscopic samples for analysis and compounds for a comparative electrochemical study in non-aqueous solution, but both the $AsPh_4^+$ and $Na^+/K^+$ salts crystallised with a differing amount of water of crystallisation (IR spectra all showed strong water bands). Ready oxidation of the ligand is a problem during these reactions and anaerobic conditions are necessary; whether the clusters assist this oxidation is uncertain but transition-metal compounds are known[11] to catalyse the oxidation of $P(C_6H_4SO_3\text{-}m)_3^{3-}$. To obviate this problem, syntheses based on ligand exchange with $[Co_3(CPh)(CO)_8(PPh_3)]$ in a biphasic medium were tried, but without success.



1 a b

3–10

**Scheme 1** L = $[PPh_{3-n}(C_6H_4SO_3\text{-}m)_n]^{n-}$ ($n$ = 1 or 3); R = Ph, Me, Cl or Br

The physicochemical properties of these water-soluble derivatives are very similar to those of the classical tertiary phosphine $Co_3C$ complexes.[12] The sodium salts of **3–10** are soluble in water and alcohols but insoluble in acetone, dichloromethane, benzene and hexane. They were characterised by analysis, conductivity and spectroscopy (Table 1). The $^{31}P\text{-}\{^1H\}$ NMR data were typical of those for other $PPh_2(C_6H_4SO_3\text{-}m)^-$ or $P(C_6H_4SO_3\text{-}m)_3^{3-}$ ligands bound to transition-metal clusters[13] with the chemical shift in the range δ 49–60. The high $\delta_P$ value for the $AsPh_4^+$ salt of $[Co_3(CCl)(CO)_8\{P(C_6H_4SO_3\text{-}m)_3\}]^{3-}$ **8** is notable as it suggests that the presence of an electron-withdrawing substituent on the carbyne cap perturbs the donation of the lone pair to the cluster, *i.e.* affects the s character of the Co–P bond. The $^1H$ and $^{13}C$ NMR data were also compatible with the proposed structures. The totally symmetric $A_1$ ν(CO) bands for **3–10** are ≈20 $cm^{-1}$ lower in energy than the comparable modes in the parent clusters indicating that the σ-donor/π-acceptor characteristics of the sulfonated ligands match those of $PPh_3$ derivatives.[12] No ν(CO) bands attributable to bridging carbonyl groups were seen in the IR spectra of crystalline samples when R = Ph, Cl or Br. For these complexes the ligand most likely occupies an equatorial co-ordination site (structure **a**, Scheme 1) with their molecular conformation being identical to that of $[Co_3(CPh)(CO)_8(PPh_3)]$, but the co-ordination of a large ligand in an equatorial conformation will cause significant 'bending back' of the capping apical substituent R.[14] A strong bridging ν(CO) band at 1846 $cm^{-1}$ in the IR spectrum of the sodium salt of $[Co_3(CMe)(CO)_8\{P(C_6H_4SO_3\text{-}m)_3\}]^{3-}$ **6** suggests an axial co-ordination site (structure **b**, Scheme 1) for the phosphane as found in $[Co_3(CMe)(CO)_8\{P(C_6H_{11})_3\}]$.[15] These results are

**Table 1** Representative analytical[a] and physical data for $[Co_3(CR)(CO)_8L]^{n-}$ ($n$ = 1 or 3) and $[Co_2\{C_2(CO_2Me)_2\}(CO)_5L]^{3-}$ **11**

| Anion | Salt | R | L | $H_2O$[b] | Analysis (%) C | H | $\nu(CO)$[c]/$cm^{-1}$ | $\delta_P$[d,e] |
|---|---|---|---|---|---|---|---|---|
| 3 | $AsPh_4^+$ | Ph | $PPh_2(C_6H_4SO_3\text{-}m)^-$ | 3 | 53.2<br>(54.0) | 3.4<br>(3.6) | 2075, 2033<br>2006, 1950 | 50.2 |
| 4 | $AsPh_4^+$ | Ph | $P(C_6H_4SO_3\text{-}m)_3^{3-}$ | 3 | 57.9<br>(57.5) | 3.8<br>(3.8) | 2075, 2033<br>2006, 1964 | 50.8 |
| 5 | $AsPh_4^+$ | Me | $PPh_2(C_6H_4SO_3\text{-}m)^-$ | 2 | 54.8<br>(54.8) | 4.3<br>(3.3) | 2072, 2029<br>2002 | — |
| 6 | $AsPh_4^+$ | Me | $P(C_6H_4SO_3\text{-}m)_3^{3-}$ | 3 | 56.6<br>(56.4) | 3.7<br>(3.8) | 2072, 2029<br>2002 | 51.5 |
| 8 | $AsPh_4^+$ | Cl | $P(C_6H_4SO_3\text{-}m)_3^{3-}$ | 0 | 57.7<br>(56.7) | 4.1<br>(3.5) | 2079, 2041<br>2014 | 59.6 |
| 10 | $AsPh_4^+$ | Br | $P(C_6H_4SO_3\text{-}m)_3^{3-}$ | 0 | 56.1<br>(55.5) | 3.9<br>(3.4) | 2083, 2035<br>2018 | 50.3 |
| 6 | $Na^+$ | Me | $P(C_6H_4SO_3\text{-}m)_3^{3-}$ | 3 | 31.4<br>(32.0) | 2.0<br>(2.0) | 2081, 2031<br>1846 | 49.2 |
| 11 | $Na^+$ | — | $P(C_6H_4SO_3\text{-}m)_3^{3-}$ | 3 | 32.7<br>(32.9) | 2.7<br>(2.7) | 2084, 2033<br>1988 | 53.0 |

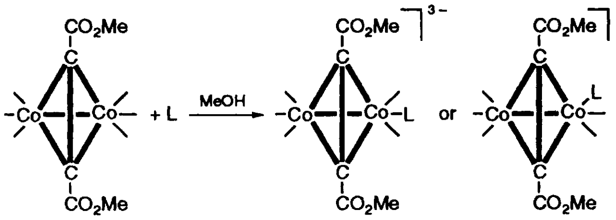
[a] Required values are given in parentheses; S analyses were also in agreement. [b] Water of crystallisation. [c] KBr disc. [d] In water for $Na^+$ salts and acetone–water for $AsPh_4^+$. [e] $^1H$ and $^{13}C$ NMR data, which are relatively uninformative but consistent with the stoichiometry, are available from the authors.

consistent with the observation[12] that the bridged conformation is adopted by derivatives of **1b** when the phosphane has a large cone angle. Weak bridging ν(CO) bands were found in the solution spectra of all complexes and the non-bridged (equatorial) ⟶ bridged (axial) interconversion elucidated for phosphane complexes[16] clearly occurs in aqueous as well as non-aqueous media.

There was no IR evidence for higher substitution products in any of the reactions. This is not unexpected as the sulfonated ligands have a very large cone angle (170°)[17] compared to 145° for $PPh_3$[18] and it has been demonstrated that there are severe intramolecular steric interactions within the $Co_3C$ cluster unit which restricts the degree of substitution.[19]

The success in increasing the aqueous solubility of these carbonyl clusters led us to consider directly sulfonating the aryl group of $[Co_3(CPh)(CO)_9]$ **1a**. Sulfonation by chlorosulfonic acid destroyed the cluster, $[Co_3(CPh)(CO)_9]$ is protonated in sulfuric acid[20] and the required trichloromethyl precursor[21] for reaction with $Co_2(CO)_8$, $p\text{-}Cl_3CC_6H_4SO_3H$, could not be synthesised.

*$Co_2C_2$ Complexes.*—Substitution of CO in $[Co_2\{C_2(CO_2Me)_2\}(CO)_6]$ **2** by $P(C_6H_4SO_3\text{-}m)_3^{3-}$ was achieved in methanol to give two water-soluble red-brown products. Analytical and conductivity data were consistent with the stoichiometry $K_3[Co_2\{C_2(CO_2Me)_2\}(CO)_5\{P(C_6H_4SO_3\text{-}m)_3\}]$ for the major **11a** and minor product **11b** (Scheme 2). On standing in solution **11b** rapidly converts into **11a** so pure samples of **11b** were not obtained. In addition **11a** and **11b** had similar ν(CO) spectra both with a symmetrical in-phase $A_1$ mode at 2080 $cm^{-1}$ which is indicative[22] of a mono-substituted $Co_2C_2$ cluster; but the respective $^{31}P$ chemical shifts were δ 53.1 and 33.2, the latter being extremely broad. The steric and π-acceptor requirements of both the ligand and alkyne have considerable influence on whether pseudoaxial or pseudo-equatorial co-ordination is adopted in complexes of $[Co_2(C_2R_2)(CO)_6]$. Pseudoaxial co-ordination is found in $[Co_2(C_2H_2)(CO)_4(PMe_3)_2]$[23] and $[Co_2\{C_2(CO_2Me)_2\}(CO)_5\{Fe(\eta^5\text{-}C_5H_4PPh_2)_2\}]$[24] and equatorial in $[Co_2\{C_2(CF_3)_2\}(CO)_5(MeCN)]$.[25] The spectroscopic data are consistent with the view that **11a** and **11b** are co-ordination isomers {**11b** is not an oxide complex as $\delta_P$ for $[P(O)(C_6H_4SO_3\text{-}m)_3]^{3-}$ is seen as a weak sharp resonance at δ 34.1}, the thermodynamically preferred **11a** having a pseudoaxial conformation; $^{31}P$ NMR shifts for $P(C_6H_4SO_3\text{-}m)_3^{3-}$ complexes can move to low field in constrained structural environments.[26]



**2** **11a** **11b**

**Scheme 2** L = $P(C_6H_4SO_3\text{-}m)_3^{3-}$

*Electrochemistry of $Co_3C$ Complexes in Aqueous Solution.*—As a reference point for the aqueous electrochemistry, the sulfonated phosphine derivatives as the $AsPh_4^+$ salts were studied in dry acetone in order to compare their behaviour with the tertiary phosphine analogues in non-aqueous solution. A cyclic voltammogram at a glassy carbon electrode (GCE) for $[Co_3(CPh)(CO)_8\{PPh_2(C_6H_4SO_3\text{-}m)\}]^-$ **3**, which is typical of those for the $AsPh_4^+$ salts, is shown in Fig. 1(*a*). The primary electrode process on the first scan at room temperature is the $3^{0/-}$ couple [A/B in Fig. 1(*a*)]. Apart from this couple there are small features D and $Co(CO)_4^-$ (not shown in Fig. 1) on the oxidation scan, with no evidence for an exergonic ETC reaction producing the disubstituted complex $[Co_3(CPh)(CO)_7\{PPh_2(C_6H_4SO_3\text{-}m)\}_2]^{2-}$, as is found[5–7] with the $PPh_3$ analogue. On the second and subsequent scans there is a decrease in the current due to $3^{0/-}$, the largest decrease occurring at fast scan rates. More significant is the appearance of a reduction wave C due to the formation of the radical anion[27] $[Co_3(CPh)(CO)_9]^{\bullet-}$ (this was confirmed by reducing **1a** in a separate experiment) and an increase in D on the oxidation scan. For **3** and other salts in acetone the current functions for features A–D are dependent on the scan rate, presence of dissolved CO and the temperature. These observations are consistent with the $\vec{E}C\overleftarrow{E}$ mechanism previously proposed for $[Co_3(CR)(CO)_8L]$ complexes in which the electrochemical profiles are the result of competition between ligand and CO dissociation (Scheme 3).[6,7] But there are some notable differences between the sulfonated and non-sulfonated phosphine analogues. First, the absence of an ETC component; given the known dependence of these reactions on steric factors, this is probably a consequence of the large cone angles of $PPh_2(C_6H_4SO_3\text{-}m)^-$ and $P(C_6H_4SO_3\text{-}m)_3^{3-}$. Secondly, the appearance of $[Co_3(CPh)(CO)_9]^{\bullet-}$ in the follow-up scans at scan rates > 200 mV $s^{-1}$ is accompanied by a small

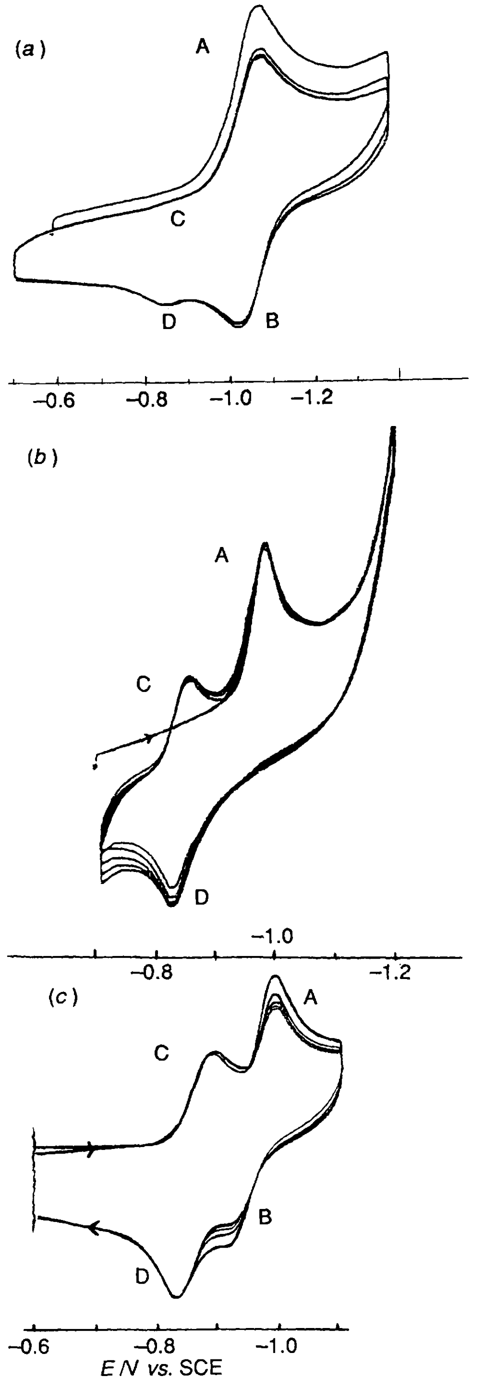
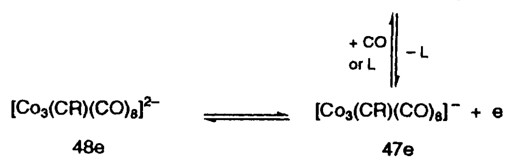


**Fig. 1** Cyclic voltammograms of (*a*) **3** as its AsPh$_4^+$ salt in acetone; 200 mV s$^{-1}$, 0.1 mol dm$^{-3}$ NEt$_4$ClO$_4$, GCE; (*b*) **3** as its Na$^+$ salt in water, 200 mV s$^{-1}$, 0.1 mol dm$^{-3}$ NaClO$_4$, GCE; and (*c*) **1a** plus PPh$_2$(C$_6$H$_4$SO$_3$-*m*)$^-$ (1:5 mol ratio) in water–methanol, 500 mV s$^{-1}$, NaClO$_4$, GCE



**Scheme 3**

current function for D. Feature D could be ascribed to oxidation of the 48e dianion or the 49e radical anion but the former couple is normally only seen for the PPh$_3$ analogue in the presence of extraneous CO.[7] Recombination of the sulfonated ligand is therefore slower than the reaction with CO for these larger phosphines.

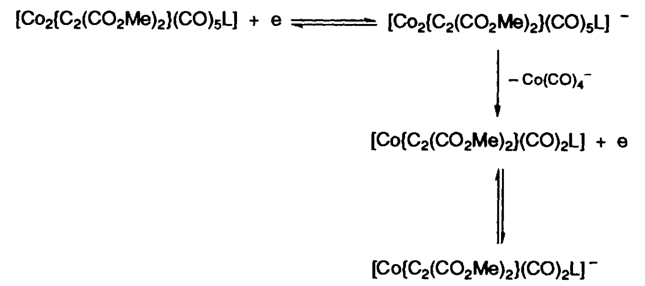
Electrochemical investigation of the water-soluble Na$^+$/K$^+$ salts was carried out at a GCE in water and in 'wet' solvents; comparative data for **3** in water are given in Fig. 1(*b*). In water, and 'wet' solvents, the initial cathodic scan again displays the reduction wave A close to the potential of the equivalent process for the AsPh$_4^+$ salt of **3** in acetone. However, there is no companion oxidation wave of **3**$^-$ (*i.e.* B) but the oxidation feature D is now more significant. On subsequent scans a new reduction wave C due to **1a**$^-$ appears (reduction of **1a** occurs at this potential in acetone–water) while the current of **3**$^-$ decreases; a steady-state current distribution is achieved after the second scan. Cyclic voltammogram profiles for the other complexes **4**–**10** were similar and, in all cases, varying the scan rates had little effect on the current functions for the major species. It was interesting that a small oxidation current due to [Co(CO)$_3$L]$^-$ was seen as well as that for the oxidation of Co(CO)$_4^-$. Although it has been suggested[6] that the fragmentation pathway is facilitated in wet solvents there was little difference in the current functions for the mononuclear species in the different solvents.

It is clear that, while the change from a non-aqueous solvent to water does not alter the overall $\overrightarrow{E}C\overleftarrow{E}$ process in Scheme 3, it does change the relative rate of ligand and CO elimination/recombination reactions with the 49e and/or 47e cluster species (our data are consistent with either being involved). The impression is that the dissociation of the large sulfonated ligand is fast in either a non-aqueous or aqueous medium but recombination of the ligand is both slower in all solvents compared to PPh$_3$ and in water compared to acetone. Furthermore, CO combination is faster in water. This would explain the presence of [Co(CO)$_3$L]$^-$ in the diffusion layer and the increased current function for the [Co$_3$(CR)(CO)$_9$]$^{\bullet-}$ radical anion. Emphasis on steric rather than electronic control of the kinetic regime is justified given that the spectroscopic data indicate that the σ-donor/π-acceptor properties of PPh$_3$ are similar to the sulfonated ligands.

Because of the similarity of the electrode processes in aqueous and non-aqueous solution it was of interest to see if ETC synthesis was feasible using water-soluble phosphines. Compound **1a** was chosen as the substrate because of the stability of its radical anion and preliminary SNIFTIRS (subtractive normalised interfacial Fourier infrared spectroscopy) studies had shown[28] that in 'wet' solvents the formation of the radical anion is still the initial step at the electrode process in the diffusion layer. Fig. 1(*c*) gives the responses for the addition of PPh$_2$(C$_6$H$_4$SO$_3$-*m*)$^-$ to a water–methanol solution of **1a**. On the first sweep the reduction of **1a** at C is followed by the appearance of a new wave A due to the reduction of **3**; on the oxidation scan the companion waves for both **1a**$^{\bullet-}$ (B) and **3**$^{\bullet-}$ (D) are seen. As expected for an $\overrightarrow{E}C\overleftarrow{E}$ reaction the relative magnitude of the A/B and C/D couples is dependent on scan rates and temperature, and the electrochemical profiles are similar to those already described[7] for $\overrightarrow{E}C\overleftarrow{E}$ reactions involving **1a** and PPh$_3$. Unfortunately, a suitable solvent system could not be found to achieve efficient bulk electrochemical ETC syntheses.

*Electrochemistry of* Co$_2$C$_2$ *Complexes in Aqueous Solution.*—For dicobalt alkyne complexes in non-aqueous solvents the primary electrode process is the formation of the radical anion but the subsequent behaviour of the radical anion is dependent on both the alkyne substituent and ligand[8] (Scheme 4.)

The (previously unreported) electrochemistry of the parent complex **2** is similar to that of [Co$_2$(C$_2$Ph$_2$)(CO)$_6$]. For **11**, the formation of **11**$^{\bullet-}$ is still the primary electrode process manifested by the cathodic wave A at $E_{pc} = -1.17$ V [Fig. 2(*a*)]. Anodic scan profiles are influenced by scan rate and the presence of excess CO. At scan rates up to 500 mV s$^{-1}$ the



**Scheme 4** L = $P(C_6H_4SO_3\text{-}m)_3^{3-}$

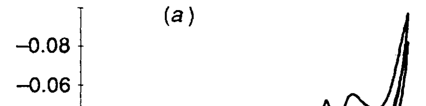


**Fig. 2** Cyclic voltammograms for **11** at a GCE (0.1 mol dm$^{-3}$ $NaClO_4$): (*a*) scan rate 500 mV s$^{-1}$, in water; (*b*) scan rate 10 V s$^{-1}$, in water; (*c*) scan rate 500 mV s$^{-1}$, in acetone–water, addition of 5 mol equivalents of $P(C_6H_4SO_3\text{-}m)_3^{3-}$

primary reduction process is irreversible with only two small oxidation features E and C due to $Co(CO)_4^-$ and $[Co(CO)_3\{P(C_6H_4SO_3\text{-}m)_3\}]^{4-}$ respectively; the current function of E exceeds that of C. A steady-state situation is reached after two scans with the only new cathodic feature being D (presumably the reduction of $[Co(CO)_3\{P(C_6H_4SO_3\text{-}m)_3\}]^{3-}$). At scan rates above 500 mV s$^{-1}$ [Fig. 2(*b*)] a new oxidation wave B appears at −1.05 V and E disappears. Wave B could be due to the oxidation of **11**$^{\bullet-}$ (the companion of the primary reduction wave A, $\Delta E$ = 120 mV) or a mononuclear species $[Co\{C_2(CO_2Me)_2\}(CO)_2\{P(C_6H_4SO_3\text{-}m)_3\}]^{4-}$ produced by the fragmention pathway in Scheme 4. The latter is the dominant process for phosphane or arsane complexes in non-aqueous media[8] and, given the similarity between $P(C_6H_4SO_3\text{-}m)_3^{3-}$ and $PPh_3$ in these systems, this is the preferred assignment for B.

With **2** in aqueous solution $\vec{E}C\overleftarrow{E}$ reactions also occurred as shown in Fig. 2(*c*); the addition of $Na_3[P(C_6H_4SO_3\text{-}m)_3]$ to a water–acetone solution of **2** produced a new reduction wave ≈0.2 V cathodic of $\mathbf{2}^{0/-}$ which corresponds to $\mathbf{11}^{4-}$. However, as with the $Co_3C$ system, electrochemically initiated ETC reactions are not a viable method for the preparation of **11**.

## Conclusion

These results show that the basic electrochemical processes are the same in aqueous and non-aqueous solvents although the kinetics of the ECE processes may be dependent on solvent. Whether a scrupulously dry solvent is used is a judgement for the researcher but, practically, our experience is that the electrode responses are often more Nernstian in behaviour when 'wet' solvents are used; in particular, the passivation of the electrode surface, which is often a feature of cluster electrochemistry, is negated. Preliminary SNIFTIRS data[28] indicate that a layer of unbound and cluster-bound CO may be responsible for the surface effects and that water reduces this layer. Counter ions also influence the configuration of the cluster at the surface and subsequent electrode responses; thus $NBu_4PF_6$ often gives better responses than the perchlorate. Details of these surface effects will be given elsewhere but it is clear that electrosynthesis involving $Co_3C$ derivatives can be carried out in aqueous media. For $Co_2C$ clusters the same conclusion holds providing radical anions with long-lifetimes, *e.g.* $[Co_2\{C_2(CF_3)_2\}(CO)_6]^{\bullet-}$ are used.

## Experimental

The clusters $[Co_3(CR)(CO)_9]$ (R = Ph **1a**, Me **1b**, Cl **1c** or Br **1d**),[29] and $[Co_2\{C_2(CO_2Me)_2\}(CO)_6]$[30] and the sulfonated phosphines[11] $PPh_2(C_6H_4SO_3\text{-}m)^-$ ($K^+$ or $Na^+$ salts) and $P(C_6H_4SO_3\text{-}m)_3^{3-}(K^+)$ were prepared by literature methods. All reactions were carried out under nitrogen using clean distilled solvents and sonication was achieved with an Ultrasonics 380 with a microtip probe. The IR and $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded on Digilab and Varian 300 VXR spectrometers respectively. Aqueous ν(CO) spectra were recorded in solution cells with $CaF_2$ windows. Electrochemical measurements were performed with a three-electrode cell using an EG & G PAR 270 instrument at scan rates 0.05–10 V s$^{-1}$. A polished GCE was used for aqueous solutions and a Pt or GCE for non-aqueous solvents; the reference was a saturated calomel electrode (SCE) uncorrected for junction potentials, the supporting electrolyte 0.1 mol dm$^{-3}$ $NaClO_4$ or $NEt_4ClO_4$ and the substrate ≈1 × 10$^{-3}$ mol dm$^{-3}$. Minor adsorption pre-waves in the cyclic voltammograms were dependent on the electrode history but consistent data were obtained for the major features.

*Preparation of* $Co_3C$ *Derivatives* **3**–**10**.—The preparation of the complex from **1a** is typical. The salt $Na[PPh_2(C_6H_4SO_3\text{-}m)]$ (0.103 g, 0.29 mmol) in water (8 cm$^3$) was added *via* a cannula to a stirred solution (25 cm$^3$, 1:4 $CH_2Cl_2$–MeOH) of $[Co_3(CPh)(CO)_9]$ (0.100 g, 0.18 mmol). The mixture was heated to 50 °C for 2.5 h at which time TLC analysis showed a small amount of unreacted cluster plus a single product. Alternatively, the mixture was sonicated for 15 min; although shorter reaction times are required, the disadvantage of this procedure was the logistical difficulty of keeping oxygen from the reaction solution. Organic solvents were stripped *in vacuo*, water (20 cm$^3$) was added and the aqueous layer extracted with $CH_2Cl_2$ until the washings were colourless. The water was stripped *in vacuo* to give $[Co_3(CPh)(CO)_8\{PPh_2(C_6H_4SO_3\text{-}m\}]^-$ **3** as its $Na^+$ salt as a red-purple solid. The product was recrystallized from hot methanol to give red-purple crystals; yield 140 mg (70%).

Other $Na^+$ or $K^+$ salts were prepared in a similar manner with slight differences in reaction conditions (compound number, salt/ligand/capping group R and different reaction conditions without sonication): **4** $K^+/P(C_6H_4SO_3\text{-}m)_3^{3-}$/Ph, 50 °C, 1.5 h; **5** $Na^+/PPh_2(C_6H_4SO_3\text{-}m)^-$/Me, 1:3 $CH_2Cl_2$–MeOH, 5 cm$^3$ $H_2O$, no acid, 50 °C, 3.5 h then 75 °C for 1.5 h; **6** $K^+/P(C_6H_4SO_3\text{-}m)_3^{3-}$/Me, 1:3 $CH_2Cl_2$–MeOH, $P(C_6H_4SO_3\text{-}m)_3^{3-}$ added in 0.1 mol dm$^{-3}$ HCl, 80 °C, 2.5 h; **7** $Na^+/PPh_2(C_6H_4SO_3\text{-}m)^-$/Cl, as for **5**, 50 °C, 1 h; **8** $K^+/P(C_6H_4SO_3\text{-}m)_3^{3-}$/Cl, as for **6**, 50 °C, 2.5 h; **9**

$Na^+/PPh_2(C_6H_4SO_3$-*m*$)^-$/Br, as for **5**; **10** $K^+/P(C_6H_4SO_3$-*m*$)_3{}^{3-}$/ Br, as for **6**, 50 °C, 3 h.

A different procedure could be used for the $P(C_6H_4SO_3$-*m*$)_3{}^{3-}$ complexes. To a solution of **1b** (0.85 g, 1.86 mmol) in dry methanol (60 $cm^3$) was added excess solid $P(C_6H_4SO_3$-*m*$)_3{}^{3-}$ ($Na^+$ salt) (2.00 g). The mixture was stirred for 20 min and then heated to reflux for 1.5 h; at this stage the solution was red-brown and a brown solid had precipitated. The solvent was removed and the solid washed with ethyl acetate to remove unreacted cluster. The residue was dissolved in methanol and filtered through a silica gel pad. Solvent was stripped *in vacuo* and the product recrystallised from methanol (2 × ) to give **6** as its $Na^+$ salt (yield 55%).

A typical preparation of the $AsPh_4{}^+$ salts is as follows. A solution of $AsPh_4Cl{\cdot}HCl$ (2.5 g) in water (10 $cm^3$) was added to the $Na^+$ salt of **3** (0.375 g) dissolved in water (7 $cm^3$) and HCl (4 mol $dm^{-3}$, 2 $cm^3$). Precipitation of a dark solid occurred immediately. The light brown solution was decanted from the solid and the precipitate washed with water. The resulting product was dried under dynamic vacuum to yield 0.436 g of **3**$\cdot 3H_2O$ as its $AsPh_4{}^+$ salt (82%).

*Preparation of* $[Co_2\{C_2(CO_2Me)_2\}(CO)_5\{P(C_6H_4SO_3$-*m*$)_3\}]^{3}$ **11**.—The salt $Na_3[P(C_6H_4SO_3$-*m*$)_3]$ (1.50 g, 2.6 mmol) was added to **2** (0.93 g, 2.16 mmol) in dry methanol (25 $cm^3$). As the cluster is heat sensitive the mixture was stirred at ambient temperature for 3–5 d. Analysis by TLC showed that a small amount of cluster remained unreacted. The solution was filtered through a silica gel pad and the solvent stripped *in vacuo*. Unreacted cluster was removed by washing with $CH_2Cl_2$ until the washings were clear, leaving a red solid which was recrystallised from hot MeOH–$EtO_2CMe$ to give **11** as its $Na^+$ salt; yield 450 mg (21%). Solvent was stripped from the washings, water added and the aqueous solution extracted with $CH_2Cl_2$. The water was removed and the orange solid chromatographed on silica gel plates (MeOH–$CH_2Cl_2$ 1 : 1). The red band of lower $R_f$ was **11a**, yield 200 mg (10%); the upper orange band on work-up gave **11b**. However, TLC analysis of samples of **11b** always showed the presence of **11a**.

To prepare the $AsPh_4{}^+$ salt, **11a** as its $Na^+$ salt was dissolved in the minimum volume of water and an aqueous solution of $AsPh_4Cl$ added until precipitation of the orange solid was complete. The precipitate was extracted into $CH_2Cl_2$, the extracts dried over $MgSO_4$ and the solvent removed to give the salt as a red oil.

*Ligand-exchange Reactions*.—A mixture of $[Co_3(CPh)(CO)_8(PPh_3)]$ in $CH_2Cl_2$ and $P(C_6H_4SO_3$-*m*$)_3{}^{3-}$ ($K^+$ salt) in water were either stirred for many hours, or sonicated for 15 min. No red-purple colouration appeared in the aqueous layer. Other unsuccessful procedures including adding a phase-transfer agent, $NBu_4OH$, and using a homogeneous solvent system of propanol–methanol.

*Attempted Preparations of Sulfonated* **1a**.—(*a*) To chlorosulfonic acid (2 $cm^3$) was added **1a** (50 mg) under a dynamic vacuum. The mixture was stirred for 30 min, the acid removed *in vacuo* and water (50 $cm^3$) distilled onto the residue with the flask cooled to 0 °C. The aqueous solution was removed from the brown solid, the solid dissolved in $CH_2Cl_2$ (25 $cm^3$) and the solvent stripped *in vacuo*. No ν(CO) bands or $^1H$ NMR resonances were found in the product.

(*b*) Compound **1a** (50 mg) was added to fuming $H_2SO_4$ (125 mg) and the mixture stirred for 15 min. Triisooctylamine and water (1 : 1, 100 $cm^3$) were cautiously added to 0 °C. The phases were separated and the amine layer titrated with 8% NaOH, then 3% NaOH until neutral. Work-up of the aqueous layer gave only decomposition products.

(*c*) To trichloroacetaldehyde hydrate (25 g) in benzene (24 $cm^3$) was slowly added $H_2SO_4$ (65 $cm^3$) whilst maintaining the temperature at 28 °C. The mixture was then stirred at room temperature for 3 h. After work-up ($Na_2CO_3$, $H_2O$), recrystallisation from ethanol yielded 11 g of 1,1,1-trichloro-2,2-diphenylethane, m.p. 66 °C (lit.,[31] 67 °C) (Found: C, 58.25; H, 3.80; Cl, 37.95. $C_{14}H_{12}Cl_3$ requires: C, 58.65; H, 4.20; Cl, 37.10%). Chlorosulfonic acid (6.2 $cm^3$) was added in small quantities over 5 min to this product (1.5 g) and the mixture stirred for 15 min. The mixture was poured into water (42 $cm^3$) and NaCl (8 g) and the aqueous layer extracted with ether (2 × ). Work-up gave no product with the appropriate mass spectrum for $Cl_3CC_6H_4SO_3H$.

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