

THE UNUSUAL ELECTROCHEMICAL BEHAVIOUR OF $[\text{Co}_8(\text{CO})_{18}\text{C}]^{2-}$ COMPARED TO $[\text{M}_6(\text{CO})_{15}\text{C}]^{2-}$ ($\text{M} = \text{Co}, \text{Rh}$) AND $[\text{Fe}_6(\text{CO})_{16}\text{C}]^{2-}$ CARBIDO CLUSTERS

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Summary

A variety of electrochemical reactions has been observed for the carbido-carbonyl clusters $[\text{Co}_8(\text{CO})_{18}\text{C}](\text{NMe}_3\text{CH}_2\text{C}_6\text{H}_5)_2$, $[\text{Co}_6(\text{CO})_{15}\text{C}](\text{NMe}_3\text{CH}_2\text{C}_6\text{H}_5)_2$, $[\text{Rh}_6(\text{CO})_{15}\text{C}](\text{Et}_4\text{N})_2$ and $[\text{Fe}_6(\text{CO})_{16}\text{C}](\text{Et}_4\text{N})_2$. The hexanuclear clusters undergo irreversible electrochemical oxidation and reduction steps, whereas the octacobalt species exhibits three electrochemically reversible one-electron steps. The relation between the redox properties and the structure of these clusters is discussed.

There have been very few studies of the electrochemistry of carbide clusters [1–5]. The electrochemical (and chemical) reduction of $[\text{M}_5(\text{CO})_{15}\text{C}]$ clusters ($\text{M} = \text{Fe}$ [2], Ru or Os [3]) was shown to produce the corresponding $[\text{M}_5(\text{CO})_{14}\text{C}]^{2-}$ anion. Ferrocene tricobalt carbide clusters $[(\text{R})\text{FcCCo}_3(\text{CO})_{9-n}\text{Ln}]$ [4] ($\text{R} = \text{H}$, $n = 0$ and 1 for $\text{L} = \text{PPh}_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$ and $\text{P}(\text{OR})_3$; $n = 2$ for $\text{L} = \text{P}(\text{OR})_3$; and $n = 0$ for $\text{R} = \text{Ac}$) or tricobalt-carbon Lewis base derivatives [5] have been extensively studied. We present here new results on carbido-carbonyl clusters $[\text{Co}_8(\text{CO})_{18}\text{C}](\text{R}_4\text{N})_2$ or $[\text{Co}_8(\text{CO})_{18}\text{C}](\text{NMe}_3\text{CH}_2\text{C}_6\text{H}_5)_2$ (I), $[\text{Co}_6(\text{CO})_{15}\text{C}](\text{R}_4\text{N})_2$ or $[\text{Co}_6(\text{CO})_{15}\text{C}](\text{NMe}_3\text{CH}_2\text{C}_6\text{H}_5)_2$ (II), $[\text{Rh}_6(\text{CO})_{15}\text{C}](\text{R}_4\text{N})_2$ (III) ($\text{R} = \text{Et}$ or Bu) and $[\text{Fe}_6(\text{CO})_{16}\text{C}](\text{Et}_4\text{N})_2$ (IV) (metallic cores in Fig. 1).

Experimental

The salts of compounds I [6], II [7], III [8] and IV [9] were prepared by previously reported methods with Bu_4N^+ or $(\text{NMe}_3\text{CH}_2\text{C}_6\text{H}_5)^+$ as counterion for I and II and Et_4N^+ for III and IV. Each of the species I to IV was characterized by its IR

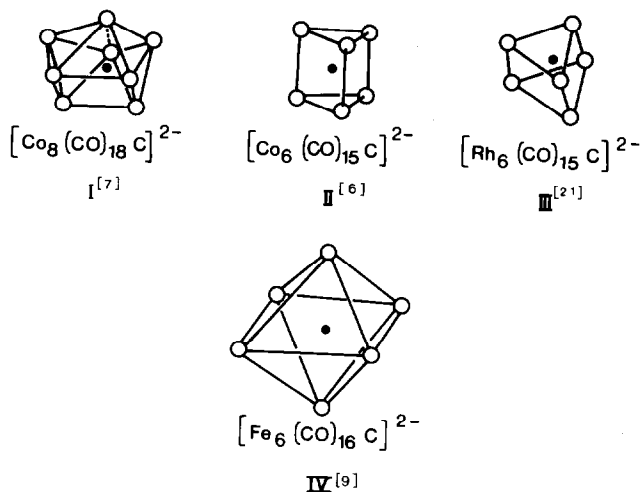


Fig. 1. Metallic core of the studied clusters according to references 6, 7, 9, and 21. ● C; ○ M (Co, Rh, Fe).

spectrum in tetrahydrofuran (THF) and by microanalysis. All experiments were carried out under argon. The apparatus used for electrochemical measurements has been described previously [1]. For electrochemical experiments, the solutions of the studied complexes were prepared by dissolving the solid complexes in thoroughly degassed 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ containing 0.1 M Bu_4NClO_4 as supporting electrolyte. Studies by rotating disc electrode (RDE) and by cyclic voltammetry (CV) were made on a platinum disc electrode (area 3.14 mm²). All potentials were measured versus a saturated calomel electrode (SCE) for which the ferrocene/ferrocinium couple had $E_{1/2} + 0.54$ V (RDE voltammetry). This value includes the unknown constant junction potential between KCl saturated water and 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ containing 0.1 M Bu_4NClO_4 .

The electroactive range of the solvent was +1.8 to -1.8 V/SCE. The electrochemical results were independent of the nature of the alkyl or aryl ammonium cations in the studied clusters and in the supporting electrolyte. ESR spectra were recorded with frozen solutions (110 K), after exhaustive potential controlled oxidation or reduction, with a Bruker ER 200-D spectrometer using a conventional X-band (9.63 GHz) accessory, and a special electrolysis cell allowing combined coulometry - ESR [10]. Infrared studies were performed with a Perkin-Elmer 225 spectrophotometer.

Results

The electrochemical results are listed in Table 1.

Electrochemical behaviour of $[\text{Co}_8(\text{CO})_{18}\text{C}]^{2-}$ (Cluster I)

This cluster undergoes two well-defined reversible reductions at $E_{1/2} - 0.81$ V and $E_{1/2} = -1.35$ V vs. SCE, respectively (Fig. 2). Potential controlled coulometry and comparisons between the RDE limiting currents corresponding to the reduction

TABLE 1
ELECTROCHEMICAL RESULTS

Cluster	Reduction				Oxidation						
	$E_{1/2}^{\text{red}}$ (V/SCE)	n^a	$\log i/(i_1 - i)$ (mV/log)	ΔE_p^b (mV)	k_s^c (10^{-3} cm^{-1})	$E_{1/2}^{\text{ox}}$ (V/SCE)	n^a	$\log i/(i_1 - i)$ (mV/log)	ΔE_p^b (mV)	$i_{\text{pc}}/i_{\text{pa}}$	ESR ^d
$(\text{Co}_8(\text{CO})_{18}\text{C})^{2-}$	-0.81	1	66	80	1.2 ± 0.2	-0.01	1	74	80	0.71	$g = 1.825$
	reversible					reversible					
$(\text{Co}_8(\text{CO})_{15}\text{C})^{2-}$	-1.35	1	68	80	(1.3 ± 0.2)	≈ 0.50	$= 2$	electrode passivation			
	reversible					irreversible					
$(\text{Rh}_6(\text{CO})_{15}\text{C})^{2-}$	-1.76	2	irreversible								
						$E_{\text{pa}_1} = 0.00$	1	irreversible			
$(\text{Fe}_8(\text{CO})_{16}\text{C})^{2-}$						$E_{\text{pa}_2} = 0.15$	1	irreversible			
						$\approx +0.34$	2	irreversible			
						$\approx +1.10$	electrode passivation				
$(\text{Fe}_8(\text{CO})_{16}\text{C})^{2-}$	-1.50	2	irreversible			$+0.20$	1	irreversible			
						$+0.50$	1	irreversible			
						$+1.20$	2	irreversible			

^a Number of electron(s) exchanged. ^b $E_{\text{pa}} - E_{\text{pc}}$ determined at a potential scan rate $v = 0.1 \text{ V s}^{-1}$. ^c Determined by Nicholson's method [11]. ^d Temperature 110 K.

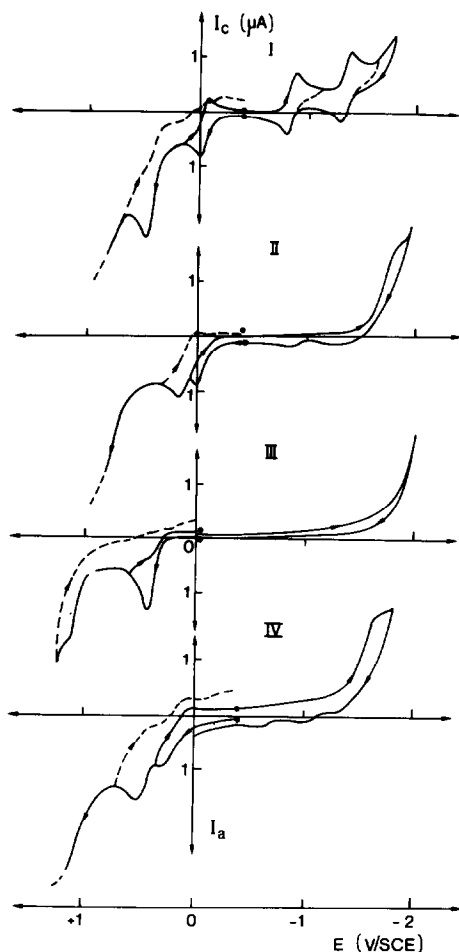


Fig. 2. Cyclic voltammetry of the studied clusters. Cluster concentration $2.5 \times 10^{-4} M$ in $1,2\text{-C}_2\text{H}_4\text{Cl}_2 + 0.1 M \text{Bu}_4\text{NClO}_4$; Pt electrode, $\nu 0.1 \text{ V s}^{-1}$, $T 20^\circ\text{C}$. * Start of the scan.

steps of the clusters and to the oxidation of ferrocene, both indicate that the complex undergoes two one-electron reductions, with the following characteristics for each reduction step:

(a) On the rotating disc electrode (RDE) the limiting current $I_{\text{lim}} = f(c)$ is a straight line crossing the origin of the axes. The plot $1/I_{\text{lim}} = f(1/\omega^{1/2})$ has similar characteristics (ω = angular frequency of rotation). Thus, the limiting current is diffusion controlled.

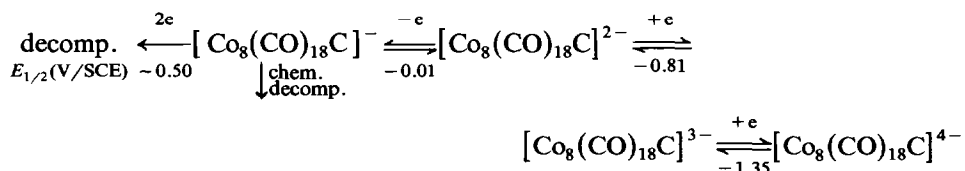
(b) In cyclic voltammetry the current peak ratio $I_{\text{pa}}/I_{\text{pc}} = 1$ for $0.1 \leq \nu \leq 1 \text{ V s}^{-1}$, $I_{\text{pc}} = f(\nu^{1/2})$ is a straight line crossing the origin of the axes, and E_{pc} (E_{pc} = cathodic peak potential) is independent of the potential scan rate, ν ; thus the two reduction steps are electrochemically reversible.

The value of the standard heterogeneous rate constant, k_s , calculated for the two reduction steps by the Nicholson method [11], was $(1.2 \pm 0.2) 10^{-3} \text{ cm s}^{-1}$ for each step. The value of $\Delta G^\ddagger = (9.5 \pm 0.5) \text{ kcal mol}^{-1}$ calculated as described by Marcus

[12] from the k_s obtained in reduction ($k_s = K z \exp -\Delta G^\ddagger / RT$) is reasonably close to that of ΔG^\ddagger previously determined (8 kcal mol⁻¹) [1] for the electron transfer to the tetranuclear clusters $[\text{Co}_4(\text{CO})_{12-2n}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_n]$ ($n = 0, 1, 2$). ΔG^\ddagger value of 11.6 kcal mol⁻¹ was recently observed at 298 K for the one-electron process $[\text{Os}_6(\text{CO})_{18}]^e \rightarrow [\text{Os}_6(\text{CO})_{18}]^{-1}$ [13]. After controlled potential electrolysis at -1.0 V/SCE of the solution of $[\text{Co}_8(\text{CO})_{18}\text{C}]^{2-}$, a paramagnetic species was obtained, as indicated by an ESR signal ($g = 2.087$) with no hyperfine structure at 110 K. When the solution was allowed to warm up the ESR signal disappeared. A second electrolysis carried out at -1.6 V/SCE on a solution of $[\text{Co}_8(\text{CO})_{18}\text{C}]^{2-}$ generated an ESR-inactive species. Nevertheless, after exhaustive electrolysis either at -1.0 V/SCE or at -1.6 V/SCE it was impossible to regenerate the starting material by inverse coulometry, although both reduction steps were electrochemically reversible.

The cluster $[\text{Co}_8(\text{CO})_{18}\text{C}]^{2-}$ undergoes also two oxidation steps, at $E_{1/2} - 0.01$ V and $E_{1/2} + 0.50$ V vs. SCE, respectively. In cyclic voltammetry, the first oxidation is reversible, whereas the second is irreversible (no reduction peak). The peak current for the second oxidation is nearly twice that for the first. Furthermore, the polarographic wave obtained by RDE voltammetry for the second step is distorted by electrode passivation probably owing to cluster decomposition. For the first oxidation step, in which one electron is exchanged, potential controlled coulometry at $+0.15$ V/SCE, reveals that a plot of I_{lim} (RDE voltammetry) against $f(c)$ is a straight line passing through the origin. The log plot of the wave observed in RDE voltammetry is also a straight line, with a slope of 74 mV/log units.

The additional observations consistently indicate that this first one-electron oxidation involves a chemical step following the electron transfer; thus in cyclic voltammetry the current peak ratio $I_{\text{pc}}/I_{\text{pa}}$ decreases with v (0.95 at 1 V s^{-1} and 0.71 at $v = 0.1 \text{ V s}^{-1}$), and $I_{\text{pa}}/v^{1/2}$ is constant as v changes whereas E_{pa} shifts towards more positive values as v increases, although E_{pa} is not proportional to $\log v$. On the other hand, after exhaustive oxidation followed by reduction, the starting material could not be recovered. However, a paramagnetic species was generated in the first oxidation step as revealed by the ESR signal ($g = 1.825$, no hyperfine structure) obtained with a frozen (110 K) oxidized solution. It was not possible to ascertain whether the species exhibiting this ESR signal was the primary product of the oxidative electron transfer or a species resulting from a subsequent chemical step. The following reaction scheme may be proposed on the basis of the above analysis of the experimental results:



Electrochemical behaviour of $[\text{Co}_8(\text{CO})_{15}\text{C}]^{2-}$ (Cluster II)

This carbide cluster shows two oxidation steps at $E_{\text{pa}} 0.00$ V and $E_{\text{pa}} + 0.15$ V/SCE, respectively (at $v 0.10 \text{ V s}^{-1}$). The half-wave potentials for these two steps are too close to be distinguished by RDE voltammetry, which therefore exhibits a

single oxidation wave. The limiting current for this unique wave is proportional to the concentration of the cluster. Cyclic voltammetry for the first oxidation step shows that $I_{pa}/v^{1/2}$ is constant at low v but increases for higher values of v , corresponding to a weak adsorption of the reactant $[\text{Co}_6(\text{CO})_{15}\text{C}]^{2-}$ on the electrode.

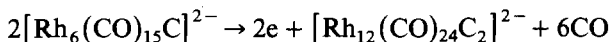
After oxidative coulometry at +0.20 V (2 F/mol) the anion $[\text{Co}_6(\text{CO})_{14}\text{C}]^-$ was identified among the oxidation products by comparison of its reduction peak (-0.72 V/SCE) with an authentic sample, and from the IR spectrum of the oxidized solution ($\nu(\text{CO})$ 2060w, 2015s, 1850m cm^{-1}) [6]. During this oxidative electrolysis of $[\text{Co}_6(\text{CO})_{15}\text{C}]^{2-}$, $\text{Co}_4(\text{CO})_{12}$ was produced in the solution as a result of chemical step(s) following the electron transfer, as evidenced by the appearance of its reduction peak at -0.35 V/SCE [1] in cyclic voltammetry.

The cluster $[\text{Co}_6(\text{CO})_{15}\text{C}]^{2-}$ also undergoes an irreversible reduction at $E_{1/2} \approx -1.75$ V/SCE. This reduction is a two electron process as shown by comparison of wave heights with $[\text{Co}_8(\text{CO})_{18}\text{C}]^{2-}$ and exhaustive coulometry at a controlled potential (-1.75 V/SCE). After coulometry at -1.75 V, $[\text{Co}(\text{CO})_4]^-$ anions were identified by IR spectroscopy ($\nu(\text{CO})$ 1886 cm^{-1}) and by their oxidation peak at +0.20 V [14]. Among the reduction products, the IR absorption bands obtained (1960s, 1940sh, 1800w cm^{-1}) [15] may correspond to the $[\text{Co}_{13}(\text{CO})_{24}\text{C}_2]^{4-}$ cluster.

Electrochemical behaviour of $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$ (Cluster III)

The cluster undergoes an irreversible oxidation at $E_{1/2} + 0.34$ V/SCE (rotating disc electrode voltammetry). Logarithmic analysis of the wave $E = f(\log I/I_{\text{lim}} - I)$ gives two straight lines with slopes 94 and 106 mV/log units, respectively. Polarographic wave height comparison with $[\text{Co}_8(\text{CO})_{18}\text{C}]^{2-}$ and controlled potential coulometry at +0.6 v shows the oxidation to be a two-electron process. In oxidative coulometry carried out under argon several uncharacterized products were obtained. In contrast, controlled potential electrolysis at +0.6 V vs. SCE under a CO atmosphere led mainly to a single species which could, from the observed IR spectrum of the solution ($\nu(\text{CO})$ 2043sh, 2020s, 1985sh, 1870w, 1815vw), be $[\text{Rh}_{12}(\text{CO})_{24}\text{C}_2]^{2-}$, [16].

The following oxidation scheme may thus be proposed:



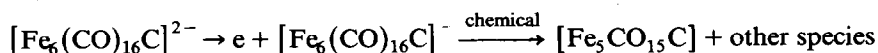
It is noteworthy that chemical oxidation of the cluster III $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$ in a CO atmosphere and under mild conditions leads to the $\text{Rh}_8(\text{CO})_{19}\text{C}$ cluster [7].

No reduction step was observed for $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$ up to -1.80 V/SCE.

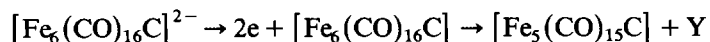
Electrochemical behaviour of $[\text{Fe}_6(\text{CO})_{16}\text{C}]^{2-}$ (Cluster IV)

The octahedral carbide cluster [9], $[\text{Fe}_6(\text{CO})_{16}\text{C}]^{2-}$ (IV), has a core structure different from that of compounds II and III, and, not unexpectedly, it displays a different electrochemical behaviour. Complex IV undergoes two irreversible one-electron (wave height comparisons with $[\text{Co}_8(\text{CO})_{18}\text{C}]^{2-}$ and controlled potential coulometries) oxidation steps, at $E_{1/2} + 0.20$ V and +0.50 V/SCE, followed by a further two-electron irreversible oxidation wave at +1.20 V/SCE. Controlled potential electrolysis at +0.30 V/SCE on a gold electrode (the platinum electrode passivated) leads to the known cluster $[\text{Fe}_5\text{CO}_{15}\text{C}]$, which was identified by com-

parison of the IR spectrum with that of an authentic sample [17]. The following scheme is proposed for this first oxidation reaction:

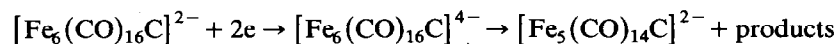


When oxidative electrolysis was carried out at +0.60 V/SCE, the neutral cluster $[\text{Fe}_5(\text{CO})_{15}\text{C}]$ was also obtained as a product of the second oxidation step, which is consistent with previous conclusions that the chemical oxidation of the cluster IV generates the $[\text{Fe}_5(\text{CO})_{15}\text{C}]$ cluster [15]:



The species $[\text{Fe}_5(\text{CO})_5\text{C}]$ is chemically stable. For instance, 80 mg of pure $[\text{Fe}_5\text{C}(\text{CO})_{15}]$ were isolated after electrolysis at +0.60 V of 0.5 g of $[\text{Fe}_6(\text{CO})_{16}\text{C}](\text{Et}_4\text{N})_2$ (25% global yield). Electrolysis of cluster IV at +1.30 V/SCE led to cluster decomposition (no $\nu(\text{CO})$ IR absorption in the resulting solution).

The cluster IV $[\text{Fe}_6(\text{CO})_{16}\text{C}]^{2-}$ also undergoes an irreversible reduction at -1.50 V/SCE. Exhaustive coulometric reduction at -1.60 V/SCE on a platinum electrode in 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ 0.1 M TBAP requires two electrons per mole of complex; the IR spectrum of the resultant brown solution is inconclusive ($\nu(\text{CO})$ 2020m, 1945s, 1910s, 1870vs, 1730w). The coulometric reduction was also carried out at -1.60 V/SCE on a gold electrode (-20°C) in CH_3CN and monitored by IR spectroscopy. During the electrolysis an IR band at 1870 cm^{-1} first increases and then progressively disappears as new bands grow ($\nu(\text{CO})$ 2025w, 1970s, 1950sh cm^{-1}), providing evidence for slow formation of $[\text{Fe}_5(\text{CO})_{14}\text{C}]^{2-}$ [18]. The decrease of the IR band at 1870 cm^{-1} together with the development of the IR spectrum of $[\text{Fe}_5(\text{CO})_{14}\text{C}]^{2-}$ suggests that the 1870 cm^{-1} band belongs to the reduction product $[\text{Fe}_6(\text{CO})_{16}\text{C}]^{4-}$, thus indicating the following reduction scheme:



Discussion

The electrochemical behaviour of four carbide clusters (I–IV) has been examined on solid electrodes in 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ containing 0.1 M TBAP. The cluster Co_8 (I) undergoes three one-electron reversible steps whereas the Co_6 (II) and Rh_6 (III) clusters show irreversible reduction and oxidation steps. This difference may be ascribed to the different structures of these compounds, since the $[\text{Co}_8(\text{CO})_{18}\text{C}]^{2-}$ cluster is a tetragonal antiprism [19] with 114 valence electrons [20] whereas Co_6 (and Rh_6) clusters have a trigonal prismatic structure with 90 valence electrons. According to Lauher [20], the latter is an open structure in which there are fewer close metal–metal interactions than in the close-packed structure of $[\text{Co}_8(\text{CO})_{18}\text{C}]^{2-}$. The structure of $[\text{Co}_8(\text{CO})_{18}\text{C}]^{2-}$ is derived from the prismatic cluster of $[\text{Co}_6(\text{CO})_{15}\text{C}]^{2-}$ by introduction of two extra-cobalt atoms on the rectangular (Fig. 1) faces of the prism, giving a bicapped prism which is a tetragonal antiprism [19]. The Co–Co distances in $[\text{Co}_8(\text{CO})_{18}\text{C}]^{2-}$ are all of the same order of magnitude, whereas in $[\text{Co}_6(\text{CO})_{15}\text{C}]^{2-}$ those for bonds in the basal triangle of the prism differ from those for inter-basal linkages. In the latter cluster, the metallic core offers more basic Co sites on the basal triangles by localization of the charge density,

according to Martinengo et al. [6]. It was thus expected that the reduction of the metallic core should be easier in the octa-cobalt cluster I than in $[\text{Co}_6(\text{CO})_{15}\text{C}]^{2-}$ (III), as experimentally observed.

Also, the charge distribution and the open geometry for $[\text{Co}_6(\text{CO})_{15}\text{C}]^{2-}$ may be responsible for the lower stability of the oxidized and reduced clusters compared with that of $[\text{Co}_8(\text{CO})_{18}\text{C}]^{2-}$ which has a close-packed structure. The electrochemical results are thus in agreement with the structural parameters of the cobalt clusters I and II. In the case of the isostructural clusters $[\text{Co}_6(\text{CO})_{15}\text{C}]^{2-}$ and $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$ (trigonal prismatic, 90 valence electrons), the cobalt complex is easier to reduce than the rhodium complex as expected from the increase of the metal-metal interaction and of the metal basicity from Co to Rh, which shifts the anti-bonding LUMO level to higher energy as shown previously for Co_4 and Rh_4 clusters [1].

Further studies on the electrochemistry of clusters are in progress.

References

- 1 (a) J. Rimmelin, P. Lemoine, M. Gross and D. de Montauzon, *Nouv. J. Chim.*, 7 (1983) 453; (b) J. Rimmelin, P. Lemoine, M. Gross, A. Bahsoun and J.A. Osborn, *Nouv. J. Chim.*, 9 (1985) 181.
- 2 A. Gourdon and Y. Jeannin, *C.R. Hebd. Séances Acad. Sci., Ser. II*, 295 (1982) 1101.
- 3 B.F.G. Johnson, J. Lewis, W.J.H. Nelson, J.N. Nicholls, J. Puga, P.R. Raithby, M.J. Rosales, M. Schröder and M.D. Vargas, *J. Chem. Soc., Dalton Trans.*, (1983) 2447.
- 4 S.B. Colbran, B.H. Robinson and J. Simpson, *Organometallics*, 2 (1983) 943.
- 5 A.M. Bond, P.A. Dawson, B.M. Peake, P.H. Rieger, B.H. Robinson and J. Simpson, *Inorg. Chem.*, 18 (1979) 1413.
- 6 S. Martinengo, D. Strumolo and (the late) P. Chini, V.G. Albano and D. Braga, *J. Chem. Soc., Dalton Trans.*, (1985) 35.
- 7 V.G. Albano, P. Chini, S. Martinengo, M. Sansoni and D. Strumolo, *J. Chem. Soc., Chem. Commun.*, (1974) 229.
- 8 S. Martinengo, D. Strumolo and P. Chini, *Inorg. Synth.*, 20 (1980) 212.
- 9 M.R. Churchill, J. Wormald, J. Knight and M.J. Mays, *J. Am. Chem. Soc.*, 93 (1971) 3073.
- 10 G. Cros, J.P. Costes and D. de Montauzon, *Polyhedron*, 3 (1984) 585.
- 11 R.S. Nicholson, *Anal. Chem.*, 37 (11) (1965) 1351.
- 12 R.A. Marcus, *J. Chem. Phys.*, 43 (2) (1965) 679 and references therein.
- 13 B. Tulyathan and W.E. Geiger, *J. Am. Chem. Soc.*, 107 (1985) 5960.
- 14 P. Lemoine, A. Giraudeau, M. Gross, R. Bender and P. Braunstein, *J. Chem. Soc., Dalton Trans.*, (1981) 2059; W.F. Edgell, M.T. Yong and N. Koizumi, *J. Am. Chem. Soc.*, 87 (1965) 2563.
- 15 V.G. Albano, D. Braga, P. Chini, G. Ciani and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, (1982) 645.
- 16 V.G. Albano, D. Braga, P. Chini, D. Strumolo and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, (1983) 249.
- 17 R.P. Stewart, U. Anders and W.A.G. Graham, *J. Organomet. Chem.*, 32 (1971) C49.
- 18 C.G. Cooke and M.J. Mays, *J. Organomet. Chem.*, 88 (1975) 231.
- 19 V.G. Albano, P. Chini, G. Ciani, S. Martinengo and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, (1978) 463.
- 20 J.W. Lauher, *J. Am. Chem. Soc.*, 100 (1978) 5305.
- 21 V.G. Albano, M. Sansoni, P. Chini and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, (1973) 651.