Redox Behaviour of Triangular Platinum–Cobalt Clusters.† Electrochemically induced Generation of the Tetranuclear Cluster $[Pt_2Co_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]$ ‡

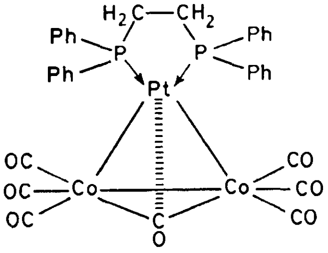
By **Paul Lemoine, Alain Giraudeau,** and **Maurice Gross,** Laboratoire d'Électrochimie et de Chimie Physique du Corps Solide, E.R.A. au C.N.R.S. No. 468, Université Louis Pasteur, 4, rue Blaise Pascal, 67000 Strasbourg, France
Robert Bender and **Pierre Braunstein,** Laboratoire de Chimie de Coordination, E.R.A. au C.N.R.S. No. 670, Université Louis Pasteur, 4, rue Blaise Pascal, 67000 Strasbourg, France

The redox behaviour of two trimetallic platinum–cobalt clusters $[PtCo_2(\mu\text{-}CO)(CO)_6(dppe)]$ (1) [dppe = 1,2-bis(diphenylphosphino)ethane] and $[PtCo_2(\mu\text{-}CO)(CO)_7(PPh_3)]$ (2) was studied on both solid and mercury electrodes in aprotic medium by polarography, cyclic voltammetry, and potentiostatic coulometry. The reduction of the two clusters occurs *via* a one-electron irreversible step which further results in the release of one $[Co(CO)_4]^-$ anion per mol of cluster. The cluster $[Pt_2Co_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]$ (3) was isolated in good yield from the reduction of (2). Each of the clusters (1) and (2) undergoes two one-electron oxidation steps. The first oxidation step is reversible at high potential scans, whereas the second step leads to electrode passivation. The redox potentials corresponding to the studied reactions are compared with those previously obtained for the linear trimetallic complex $[(OC)_4Co(PtL_2)Co(CO)_4]$ (4) (L = *cyclo*-CNC_6H_{11}).

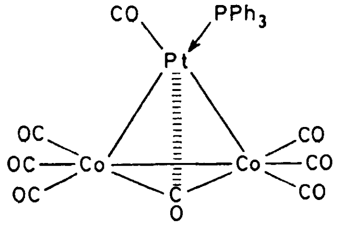
IN previous electrochemical investigations on linear metal–metal bonded complexes,[1-3] the reduction scheme shown in equation (1) has been proposed for complex

$$[(OC)_4Co(PtL_2)Co(CO)_4] + e^- \longrightarrow [Co(CO)_4]^- + [(PtL_2)Co(CO)_4]^{\bullet} \quad (1)$$

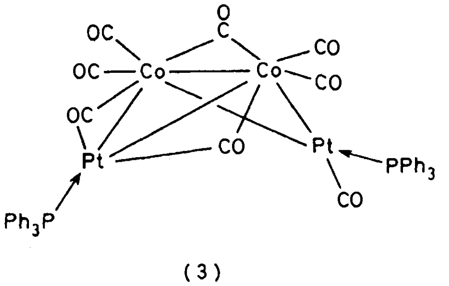
$[(OC)_4Co(PtL_2)Co(CO)_4]$ (L = *cyclo*-CNC_6H_{11}) (4), whose half-wave potential is close to −1.20 V § in propylene carbonate (pc) containing 0.1 mol dm^{-3} tetraethylammonium perchlorate, on a gold electrode. In order to analyse the effect of structure on the redox properties of this and other similar complexes, it was of interest to study the electrochemical behaviour of clusters containing the same metal atoms as complex (4), but with a closed metallic skeleton, as shown below. Previously, reversible oxidation–reduction of carbonyl clusters of Fe, Co, and Ni [4-9] has been reported, whose reversibility suggests that the 'electron reservoir' concept [10] holds in such clusters.



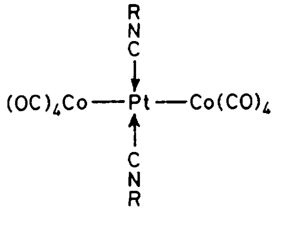
(1)



(2)



(3)



(4)

The difference between the linear complex (4) and the studied clusters (1) and (2) arises from the ligands coordinated to the platinum [1,2-bis(diphenylphosphino)ethane (dppe) in (1), CO and PPh_3 in (2), isocyanide in (4)]. In contrast to complex (4), which is partly ionized in pc solutions,[2,3] the cluster (1) is not dissociated in pc or in CH_2Cl_2, as verified by polarography. The cluster (2), however, is ionized to some extent (20%) in pc. This dissociation depends markedly on the solvent; in CH_2Cl_2, no dissociation is observed for (2), whereas it is rapidly destroyed in dimethylformamide (dmf) as

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† Part 3 in the series 'Electrochemistry of Platinum(II) Coordination Compounds.' Part 2 is ref. 3.

‡ 1,2;1,3;2,3-Tri-μ-carbonyl-2,2,3,3,4-pentacarbonyl-1,4-bis(triphenylphosphine)diplatinumdicobalt(4*Pt*–*Co*)(*Co*–*Co*).

§ All voltages *versus* a standard calomel electrode (s.c.e.).

evidenced from the disappearance of the polarographic wave at -0.75 V and the simultaneous increase of waves at -1.20 and $+0.20$ V respectively. The extent of the dissociation in pc was calculated from the ratio of the wave heights corresponding respectively to the oxidation of $[Co(CO)_4]^-$ (at $+0.20$ V) and to the reduction of the cluster (2). This paper reports on the reactivity of clusters (1) and (2) in aprotic medium, on gold, platinum, or mercury electrodes. The results will be compared with those previously obtained [1-3] on the linear complex (4).

EXPERIMENTAL

The complexes were studied by stationary voltammetry (solid electrodes or dropping-mercury electrode), by cyclic voltammetry, and coulometry. Attempts were made to identify the reduction products obtained after exhaustive coulometry. The three-electrode cells, the electrochemical device, and the experimental procedure have been described in preceding papers of the series.[2,3] The clusters (1) and (2) were prepared according to published procedures.[11,12] The solvents used were purified propylene carbonate (pc) and dichloromethane. Different conducting electrolytes were used due to solubility considerations: $[NEt_4][ClO_4]$ was used in pc, and $[N(n\text{-}C_6H_{13})_4][ClO_4]$ in CH_2Cl_2.

Electroreduction of Clusters (1) *and* (2).—(*a*) *Reduction of* $[PtCo_2(\mu\text{-}CO)(CO)_6(dppe)]$, (1). On a rotating-disc electrode (platinum or gold) in pc, the cluster (1) exhibits a well defined cathodic wave at $E_{\frac{1}{2}} = -1.20$ V. The limiting current is proportional to the concentration in the range 10^{-4}—10^{-3} mol dm^{-3} and the Levich equation holds for rotation rates of the electrode ranging from 1 000 to 5 000 r.p.m. Logarithmic analysis of this wave gave a straight line with a slope of 59 mV. Potentiostatic coulometric measurements indicate that one electron is exchanged per mol of cluster in this reduction.

Cyclic voltammetry on platinum at low-potential scan rates (up to 1 V s^{-1}) gives a single, cathodic, irreversible peak at $E_{pc} = -1.20$ V [Figure 1(*a*) and (*b*)], but at higher scan rates (50—100 V s^{-1}), on mercury electrodes, an anodic peak becomes observable on the backwards scan of the cyclic voltammogram, Figure 1(*c*). These results indicate that the reduction product of (1) undergoes subsequent chemical reaction. Also, Figure 1(*a*) and (*b*) show that in addition to the cathodic peak at -1.20 V an anodic peak is observed at $E_{pa} = +0.20$ V. This peak corresponds to the oxidation potential of $[Co(CO)_4]^-$ (yielding $[Co(CO)_4]^{\bullet}$), as previously demonstrated.[2,3] The presence of $[Co(CO)_4]^-$ in the reduced solution was also confirmed by i.r. spectroscopy [ν(CO) 1 885vs cm^{-1}]. Thus, $[Co(CO)_4]^-$ is a stable fragmentation product of the reduced form of cluster (1). After coulometric reduction of (1), the polarographic oxidation wave height of generated $[Co(CO)_4]^-$ was measured and found consistent with one $[Co(CO)_4]^-$ anion liberated per mol of cluster (1). Also, when multiple-potential scans were taken [Figure 1(*b*)] from $+0.3$ to -1.6 V and back, a new cathodic peak was observed at $E_p = -0.45$ V. This peak corresponds [1-3] to the reduction of $[Co_2(CO)_8]$ produced by dimerization of $[Co(CO)_4]^{\bullet}$ radicals anodically generated at $+0.20$ V.

However, after multiple-potential sweeps, the platinum electrode became passivated. No carbonyl-containing species other than $[Co(CO)_4]^-$ could be identified by i.r. spectroscopy, and attempts failed to isolate and identify the remaining, platinum-containing fragment(s). The above electrochemical and spectrochemical results are consistent with an irreversible reduction pathway for the cluster (1), according to the electrochemical reduction (2), followed by chemical step (3).

$$[PtCo_2(\mu\text{-}CO)(CO)_6(dppe)] + e^- \longrightarrow [PtCo_2(\mu\text{-}CO)(CO)_6(dppe)]^- \quad (2)$$

$$[PtCo_2(\mu\text{-}CO)(CO)_6(dppe)]^- \longrightarrow [Co(CO)_4]^- + \text{unidentified products} \quad (3)$$

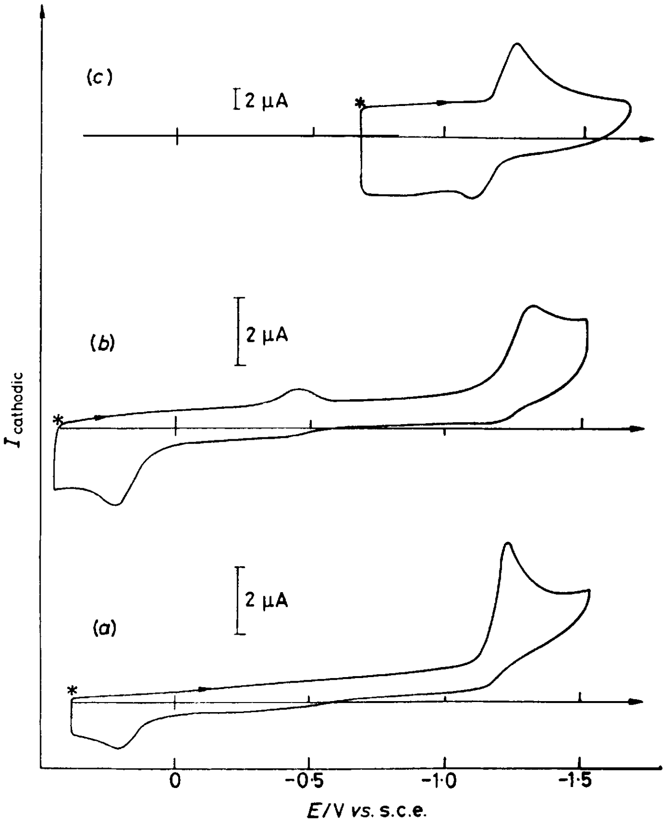


FIGURE 1 Cyclic voltammetry of cluster (1). $c = 8.8 \times 10^{-4}$ mol dm^{-3} in pc + 0.1 mol dm^{-3} $[NEt_4][ClO_4]$ on a solid gold electrode (area 3.14 mm^2), (*a*) at 0.1, (*b*) at 1 V s^{-1} (multiple-potential scans); (*c*) saturated solution, on a mercury electrode, at 100 V s^{-1}. Start of the scan marked (*)

(*b*) *Reduction of* $[PtCo_2(\mu\text{-}CO)(CO)_7(PPh_3)]$, (2). By stationary voltammetry on a rotating gold-disc electrode in pc, the cluster (2) is reduced in a well defined wave at $E_{\frac{1}{2}} = -0.75$ V, whose limiting current is proportional to the concentration (in the range 10^{-3}—10^{-4} mol dm^{-3}). Logarithmic analysis of the wave is linear and the correponding slope is 95 mV. In these measurements by stationary voltammetry, it was observed that successive potential scans at cathodic potentials passivated the solid working electrode; the electrode was therefore polished between two runs.

In pc, potentiostatic coulometry of (2) and comparison between the cathodic limiting currents of (1) and (2) indicate one electron exchanged per mol in the reduction of the cluster (2). Cyclic voltammetry (Figure 2) provides clear-cut evidence of the irreversibility of the reduction step. In Figure 2, the peak A corresponds to the reduction of (2),

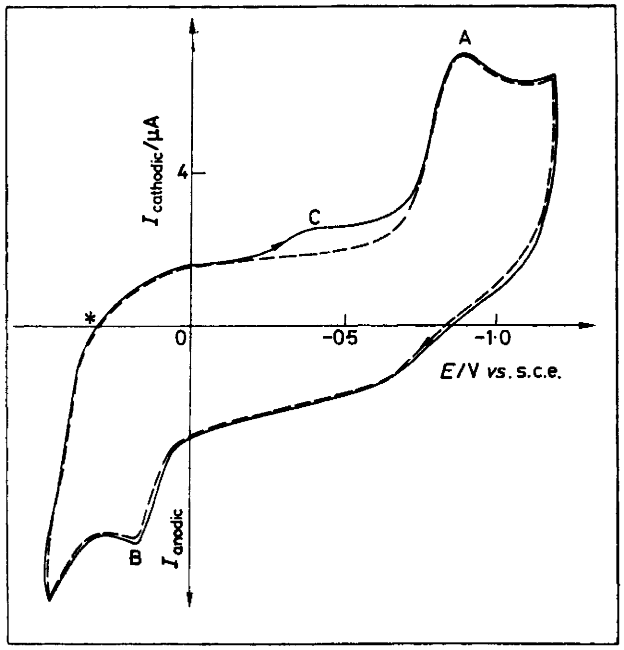


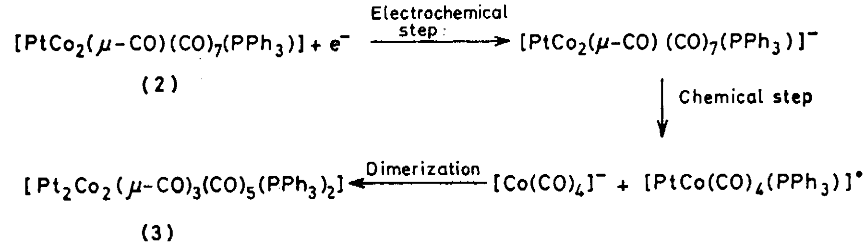
FIGURE 2 Cyclic voltammetry of cluster (2). $c = 4 \times 10^{-4}$ mol dm^{-3} on a solid gold electrode in pc + 0.1 mol dm^{-3} [NEt_4][ClO_4]; single scan (— — —), multiple-potential scan (——). Start of the scan marked (*)

peak B corresponds to the oxidation of $[Co(CO)_4]^-$ yielding $[Co(CO)_4]^•$, and peak C is ascribed to the reduction of $[Co_2(CO)_8]$ resulting from dimerization of $[Co(CO)_4]^•$. Even at fast scan rates (10 V s^{-1} on the solid electrode, and 100 V s^{-1} on the mercury electrode) the overall reduction process remains irreversible.

On the mercury electrode in pc, the reduction of cluster (2) exhibits characteristics only slightly different from those described above on gold. Although a single polarographic wave is also observed at $E_{\frac{1}{2}} = -0.70$ V, cyclic voltammetry produces two cathodic peaks at $E_{pc1} = -0.88$ V and $E_{pc2} = -1.18$ V (100 V s^{-1}) respectively. The cathodic peak at -1.18 V is well accounted for by an adsorption of the reduction products on mercury (negative temperature coefficient from -30 to $+60$ °C). This is consistent with the observation reported above that solid electrodes become increasingly passivated in pc after the first cathodic potential scan. Also, exhaustive reduction of (2) followed by a polarographic checking of the reduced solution (from -1 to $+0.5$ V) revealed that one $[Co(CO)_4]^-$ anion is quantitatively liberated per mol of reduced cluster.

After exhaustive reduction of (2) in CH_2Cl_2 at -1 V, i.r. spectroscopy of the reduced solution in the ν(CO) region identified $[Co(CO)_4]^-$ and $[Pt_2Co_2(CO)_8(PPh_3)_2]$ by analogy with the frequencies of an authentic sample.[13]

Furthermore, the cluster (3) was isolated from the reduced solution after CH_2Cl_2 removal and extraction of the solid residue with toluene–hexane (1 : 10). From this solution maintained at -30 °C, complex (3) was crystallized in 68% yield. It has been verified that (3) is reducible at $E_{\frac{1}{2}} = -1.25$ V (CH_2Cl_2, Pt electrode). From the above results, the reduction scheme shown below may be proposed for complex (2).



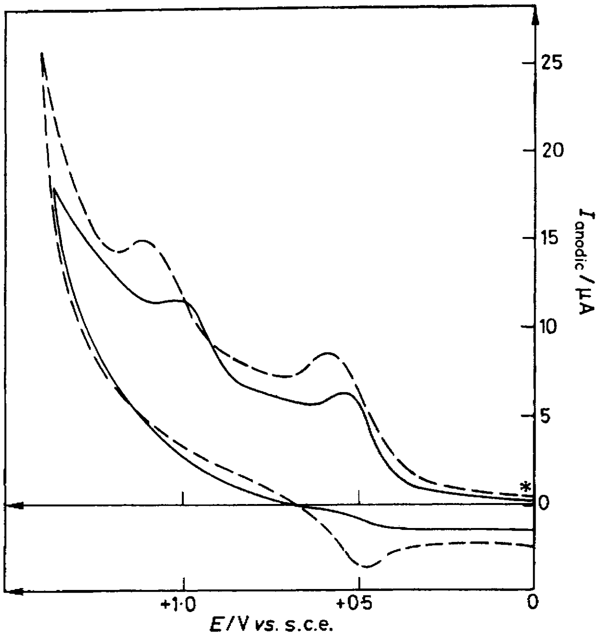


FIGURE 3 Electro-oxidation of cluster (1). Cyclic voltammetry on a gold electrode, in pc + 0.1 mol dm^{-3} [NEt_4][ClO_4]; at 400 mV s^{-1} (——), at 1 V s^{-1} (— — —). Start of the scan marked (*)

The presence of (3) among the stable reduction products of the cluster (2) leads to the reasonable assumption that the intermediate product is $[PtCo(CO)_4(PPh_3)]^•$, which further rapidly dimerizes into (3) (see Discussion section). E.s.r. coulometry, *in situ* at 298 K, revealed no signal during the reduction of (2).

Electro-oxidation of Clusters (1), (2), *and* (3).—(*a*) *Oxidation of cluster* (1). On a rotating platinum-disc electrode, two oxidation waves are observed, at $E_{\frac{1}{2}} = +0.47$ V and $E_{\frac{1}{2}} = +0.85$ V (see Table). These two waves have the same limiting currents as the cathodic wave of (1) at -1.20 V. It may be observed from cyclic voltammograms (Figure 3) that the first anodic step becomes more reversible as the

Half-wave potentials of the studied complexes in propylene carbonate containing 0.1 mol dm^{-3} $[NEt_4][ClO_4]$

Studied species	Electro-reduction		Electro-oxidation first step		Electro-oxidation second step	
	$E_{\frac{1}{2}}$/V	n	$E_{\frac{1}{2}}$/V	n	$E_{\frac{1}{2}}$/V	n
(1)	-1.20 [a] -1.22 [b]	1	$+0.47$ [a]	1	$+0.85$ [a]	1
(2)	-0.75 [a] -0.70 [b]	1	$+0.71$ [a]	1	$+0.95$ [a]	1
(3)	-1.25 [c]		$+1.75$ [a]			
(4) [d]	-1.25 [a]	1	$+0.66$ [a]	1	$+1.18$ [a]	1

[a] Platinum rotating-disc electrode (2 000 r.p.m.). [b] Dropping-mercury electrode. [c] Platinum rotating-disc electrode (2 000 r.p.m.); in CH_2Cl_2 + 0.1 mol dm^{-3} $[N(n\text{-}C_6H_{13})_4][ClO_4]$. [d] Data for the trimetallic linear complex $[(OC)_4Co(PtL_2)Co(CO)_4]$ (4) (L = *cyclo*-CNC_6H_{11}) are given for comparison. For more details see refs. 1—3.

potential scan increases up to 1 V s^{-1}, whereas the second oxidation step remains irreversible, even at scan rates up to 10 V s^{-1}. Also, controlled-potential coulometry revealed that each of the two anodic steps involves one electron.

(*b*) *Oxidation of cluster* (2). In the experimental conditions indicated in the Table, two oxidation steps are observed for (2) at $E_{\frac{1}{2}} = +0.71$ V and $E_{\frac{1}{2}} = +0.95$ V. These waves are followed by a passivation peak at +1.85 V. Both anodic steps are monoelectronic and irreversible.

(*c*) *Oxidation of cluster* (3). The cluster (3), electrosynthesized by reduction of (2), could be electro-oxidized at +1.75 V only, in a one-electron step (Table).

DISCUSSION

The results gathered in the Table reveal that the cluster (1) is more difficult to reduce and easier to oxidize than (2). The origin of this difference lies probably in the higher electron density on Pt in (1) than in (2), due to the higher electron-donating effect from dppe than from both PPh_3 and CO. This higher electron density on platinum in (1) than in (2) is reflected in the stretching frequencies of the unique bridging carbonyl [1 729 cm^{-1} in (1) and 1 768 cm^{-1} in (2)]. The 39 cm^{-1} difference between (1) and (2) has also been related to the change in basicity between the 14-electron fragments Pt(dppe) and $Pt(CO)(PPh_3)$.[12] These observations parallel well the measured values of the half-wave potentials for (1) and (2) in their electroreduction as well as in their electro-oxidation.

The reduction products of (1) and (2) are the $[Co(CO)_4]^-$ anion and a Pt–Co fragment. In the electroreduction of (1), no compound other than $[Co(CO)_4]^-$ was identified, whereas after electroreduction of (2), the cluster $[Pt_2Co_2(CO)_8(PPh_3)_2]$ (3) was identified and isolated, in addition to $[Co(CO)_4]^-$. Thus the overall electroreduction process seems to occur *via* analogous schemes for (1) and (2); the ultimate chemical fate of the Pt–Co fragment is nevertheless different in (1) and in (2), due to the difference in the nature of the ligands surrounding the platinum. This is documented from the results of cyclic voltammetry at 100 V s^{-1}, which revealed that $[PtCo_2(\mu\text{-}CO)(CO)_6(dppe)]^-$ is generated in the electroreduction of (1) whereas $[PtCo_2(\mu\text{-}CO)(CO)_7(PPh_3)]^-$ is not detected in the reduction of (2), under identical experimental conditions. This indicates that the chemical step consecutive to the electrochemical step leading to the formation of $[Co(CO)_4]^-$ and the Pt–Co fragment is slower in the case of $[PtCo_2(\mu\text{-}CO)(CO)_6(dppe)]^-$ than in the case of $[PtCo_2(\mu\text{-}CO)(CO)_7(PPh_3)]^-$. These results suggest that the rate of dimerization of the speculated intermediate $[PtCo(CO)_4(PPh_3)]^{\bullet}$, yielding $[Pt_2Co_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]$ (3) from the initial reduction product of (2), is very fast.

When comparing the redox properties of the linear complex $[(OC)_4Co(PtL_2)Co(CO)_4]$ (4) previously studied[1,3] with those of (1) in the same experimental conditions (Table), it may be observed that the reduction potential of (1) is close to that of (3) and (4). An analogy in the electroreduction of (1), (2), and (4) lies in the number (one) of electrons transferred in the reduction step and in the common species produced ($[Co(CO)_4]^-$). The above observations lead to the reasonable assumption that the overall electroreduction scheme of the complexes (1), (2), and (4) is very similar whether the metallic skeleton is open [as in (4)] or closed [as in (1) and (2)], and occurs through intermediate generation of radicals.[1] However, *in situ* e.s.r. experiments carried out in this study failed to detect radicals, probably due to their short lifetime.

Also, the present paper reports for the first time the synthesis of a heterotetranuclear cluster, (3), in good yield (68%) by electroreduction of an heterotrinuclear cluster, (2). A similar effect was recently observed in homonuclear ruthenium clusters, where chemical reduction of $[Ru_3(CO)_{12}]$ yielded $[Ru_4(CO)_{13}]^{2-}$ (ref. 14) through partial or total fragmentation of $[Ru_3(CO)_{12}]$. Further studies on the electrochemical behaviour of transition-metal clusters are in progress.

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