Oxidative Electrochemistry of the Cluster $[Co_4(CO)_9\{HC(PPh_2)_3\}]$. Reactivity with the Nucleophiles PPh_3 and $P(OMe)_3$†

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The one-electron-oxidized cluster $[Co_4(CO)_9\{HC(PPh_2)_3\}]^{\cdot+}$ reacts with PPh_3 and $P(OMe)_3$. The reaction mechanisms involve the substitution of CO by PR_3. The $P(OMe)_3$ substituted cluster is stable, whereas the PPh_3 substituted cluster undergoes an intramolecular electron transfer which regenerates the initial cluster. A general reaction scheme is proposed for the one-electron-oxidized and the one-electron-reduced cluster.

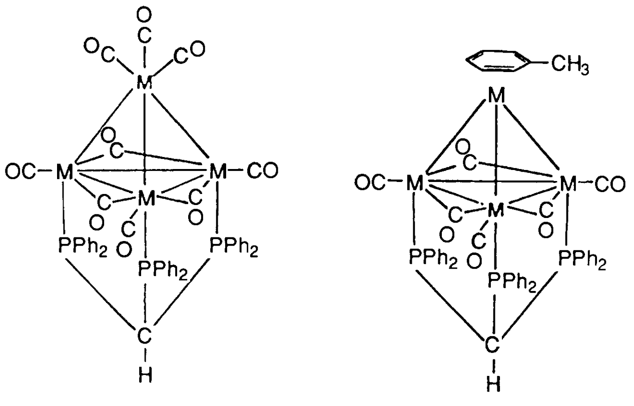
Ligand-substitution processes in polynuclear carbonyl species, especially in tetranuclear clusters akin to $[Co_4(CO)_{12}]$, have attracted much interest in recent years. Studies consistently demonstrated that the ability of carbon monoxide to undergo displacement reactions was a critical feature in such reactions.[1–6]

Electroreductive studies on $[Co_4(CO)_{12}]$ and analogues, including phosphine derivatives[7–10] confirmed the importance of CO lability in substitution reactions. These electrochemical studies also demonstrated that (*i*) clusters may undergo electron-induced nucleophilic substitution reactions;[9,10] in some cases the yield of the substitution processes was increased by electron transfer catalysis (e.t.c.);[8,11] (*ii*) the stability of electrogenerated cluster monoanion radicals was enhanced when bis- or tris-phosphine capping moieties were liganded to the cluster.[7,8]

The cluster $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ [Figure 1(*a*)] deserves special attention regarding these characteristics as it is remarkably stabilized towards fragmentation by the presence of the tripod $HC(PPh_2)_3$[12] and its anion radical undergoes e.t.c. substitution in the presence of nucleophiles. The reductive e.t.c. nucleophilic substitution of CO by phosphine involved the apical cobalt, and occurred *via* a CO-dissociation step preceding the phosphine co-ordination.[8] This cluster $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ was also reported[8] to oxidize reversibly through a $1e^-$ process: in $1,2\text{-}C_2H_4Cl_2$ + 0.1 mol dm^{-3} tetrahexylammonium perchlorate, at a platinum electrode, this cluster was oxidized at $E_{\frac{1}{2}}^{ox} = +0.82$ V *vs.* saturated calomel electrode (s.c.e.) whereas the reduction occurred at $E_{\frac{1}{2}}^{red} = -0.89$ V *vs.* s.c.e. Cross-analysis of experimental parameters led[8] to the conclusion that both redox steps were fast (k_s being about 4×10^{-3} cm s^{-1} in both steps) and one-electron charge transfers, with no detectable chemical steps on the electrochemical timescale. In the oxidative step, however, the reactivity with nucleophiles of the cation radical obtained remained to be checked. The purpose of the present study was to clarify this behaviour.

Experimental

The clusters (Figure 1) were synthesized by published procedures.[12] All experiments were carried out with carefully deaerated solutions.



(*a*) (*b*)

Figure 1. The clusters studied:[12b] (*a*) $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ and (*b*) $[Co_4(CO)_6\{HC(PPh_2)_3\}(\eta\text{-}C_6H_5Me)]$

The redox characteristics were determined on platinum disc electrodes (area: 3.14 mm^2), in dichloroethane $1,2\text{-}C_2H_4Cl_2$ containing 0.1 mol cm^{-3} tetrahexylammonium perchlorate $N(C_6H_{13})_4ClO_4$ as supporting electrolyte. The reference electrode was a saturated calomel electrode (s.c.e.) electrically connected to the study solution by a glass frit and a bridge filled with $1,2\text{-}C_2H_4Cl_2$ + 0.1 mol dm^{-3} $N(C_6H_{13})_4ClO_4$. Other experimental devices and procedures have been described elsewhere.[7,8]

Results and Discussion

Electrochemical Oxidation of $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ *in the Presence of* PPh_3.—In the presence of PPh_3 (cluster/PPh_3 = 1:1) cyclic voltammograms exhibited the following general trends (Figure 2): (*i*) the known[8] one-electron reversible oxidation of $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ remained observed around +0.85 V *vs.* s.c.e. with, however, an enhancement of the oxidation peak, whilst the corresponding reduction peak [equation (1)] disappeared; (*ii*) a new couple of

$$[Co_4(CO)_9\{HC(PPh_2)_3\}]^{\cdot+} + e \longrightarrow [Co_4(CO)_9\{HC(PPh_2)_3\}] \quad (1)$$

peaks, indicative of a reversible system, became observable at potentials less positive ($E_p^{\,c} = +0.39$ V and $E_p^{\,a} = +0.45$ V *vs.*

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† *Non-S.I. unit employed:* atm = 101 325 Pa.

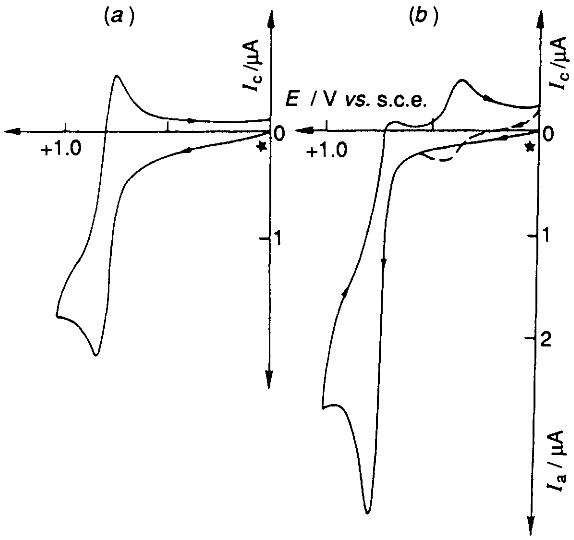

Figure 2. Cyclic voltammograms documenting the electrochemical oxidation of the cluster $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ in the presence of PPh_3; $v = 0.1$ V s^{-1}, 1,2-$C_2H_4Cl_2$ + 0.1 mol dm^{-3} $N(C_6H_{13})_4ClO_4$, platinum electrode, 20 °C. Asterisk indicates start of the scan, (*a*) cluster only ($\approx 2 \times 10^{-4}$ mol dm^{-3}); (*b*) cluster + PPh_3 (each $\approx 2 \times 10^{-4}$ mol dm^{-3}); (– – –), second cycle immediately following the first one

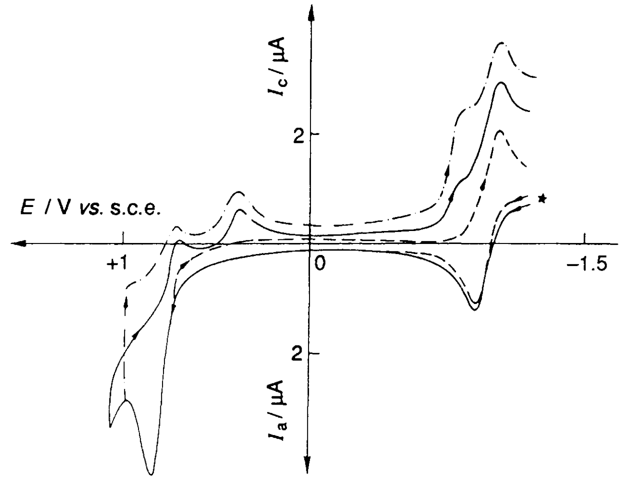

Figure 3. Cyclic voltammetry of $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ in the presence of PPh_3. Conditions as in Figure 2 except concentrations of cluster and PPh_3 were *ca.* 2×10^{-4} mol dm^{-3} (——). First polarization cycle, from -1.3 to $+1$ V *vs.* s.c.e. and back; (– – – –) second polarization cycle, from -1.3 to $+0.7$ V *vs.* s.c.e and back; (— · — · —) third cycle, from -1.3 to $+0.95$ V *vs.* s.c.e. and back; during the cycle the electrode potential was held constant for 60 s at $+0.95$ V *vs.* s.c.e.

s.c.e. at $v = 0.1$ V s^{-1}) than those corresponding to the couple $[Co_4(CO)_9\{HC(PPh_2)_3\}]^{\cdot +}$–$[Co_4(CO)_9\{HC(PPh_2)_3\}]$.

When cyclic voltammetry experiments were carried out from -1.3 V *vs.* s.c.e. to positive potentials, and backwards to -1.3 V *vs.* s.c.e. again, the following results were gathered (Figure 3) in the presence of PPh_3. (*a*) On scanning the potential from -1.3 V *vs.* s.c.e. until oxidation of $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ occurred (*i.e.* beyond about $+0.85$ V), the backwards scan exhibited [Figure 3(*a*)], besides the other peaks described above, one cathodic, irreversible, peak at $E_p^c = -0.75$ V *vs.* s.c.e. ($v = 0.1$ V s^{-1}). This peak corresponded to the known[13] reduction of $[PPh_3H]^+$ to PPh_3. It was authenticated by the comparison with the reduction signal of an authentic sample of $[PPh_3H]^+$. ($[PPh_3H^+]ClO_4$ was prepared as a white precipitate upon dropwise addition of $HClO_4$ to PPh_3 dissolved in 1,2-$C_2H_4Cl_2$). (*b*) When the anodic scan was stopped before the oxidation of $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ [Figure 3(*b*)] the reduction signals at -0.75 V *vs.* s.c.e. was absent on the backwards scan (as well as, of course, the reduction peak around $+0.4$ V). (*c*) After holding the electrode potential at $+0.95$ V *vs.* s.c.e. on the anodic (onwards) scan [Figure 3(*c*)] the reduction peaks on the backwards scan were the same as that without potential hold [Figure 3(*a*)], except that the reduction peak current on $[PPh_3H]^+$ at -0.75 V *vs.* s.c.e. increased.

The following experiments provided additional insights on the reactions generating the above results. An exhaustive oxidation of $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ was performed by controlled-potential coulometry at $+0.9$ V *vs.* s.c.e., successively in the absence and in the presence of PPh_3. (Oxidation of PPh_3 does not occur at this potential.) In the absence of PPh_3 the oxidation of $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ required 1 F mol^{-1} ($n = 1$). In the presence of PPh_3, if N is the concentration ratio $[PPh_3]$/ [cluster], the exhaustive oxidation at $+0.9$ V required ($n = N + 1$) F mol^{-1} of cluster and, therefore, the amount of electricity consumed was directly proportioned towards the concentration of PPh_3 in the solution. This linear relationship levelled off for $N > 5$. Also, after exhaustive oxidation at $+0.9$ V *vs.* s.c.e., for instance at $[Co_4(CO)_9\{HC(PPh_2)_3\}]/[PPh_3] = 1:1$ (and therefore consumption of 2 F per mol of cluster), the resulting solution still exhibited the reduction signal of $[PPh_3H]^+$ at -0.75 V *vs.* s.c.e., whereas the reversible couple of peaks around $+0.4$ V was no longer present. The absence of the latter peaks indicates that these peaks likely result from a combination of the oxidized cluster with PPh_3 which did not exist when the cluster had been exhaustively oxidized.

The temperature had significant effects on the oxidation of the cluster in the presence of PPh_3 as evidenced from the following. Cyclic voltammetry under an argon atmosphere in solutions [1,2-$C_2H_4Cl_2$ + 0.1 mol dm^{-3} $N(C_6H_{13})_4ClO_4$] containing the cluster $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ and PPh_3 (1:1) was initially irreversible at 20 °C [Figure 2(*b*)], and became gradually reversible when T decreased: at -20 °C, the couple of peaks (around $+0.85$ V *vs.* s.c.e.) corresponding to the system $[Co_4(CO)_9\{HC(PPh_2)_3\}]^{\cdot +}$–$[Co_4(CO)_9\{HC(PPh_2)_3\}]$ was reversible again in spite of the presence of PPh_3, and the peak currents corresponded to a one-electron transfer,* while the couple of peaks around $+0.4$ V disappeared. These temperature effects provided clear-cut evidence that PPh_3 reacted with the cation radical $[Co_4(CO)_9\{HC(PPh_2)_3\}]^{\cdot +}$, and that this endothermic reaction generated a species reversibly reducible around $+0.4$ V *vs.* s.c.e. ($v = 0.1$ V s^{-1}).

In addition, at 20 °C, the partial pressure of CO† in the solution ($0 < P_{CO} < 2$ atm) had no effect on the voltammetric oxidation figures (shape of peak, current and potential), at striking variance with the observations made for the reduction[8] of the cluster in the presence of phosphines. Thus, dissociation of CO from the cluster cation radical was not an initial critical step in the chemical reaction of this cation radical with PPh_3.

Thus, in the presence of PPh_3 and on the basis of the above results, the electrochemical oxidation of $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ and the subsequent reactions may be described as an electrochemical heterogeneous one-electron step at the electrode (E_1) followed by a chemical reaction (C_1) and by an electrochemical homogeneous reaction (E_2) [equations (2)—(4)]. The homogeneous reaction E_2 is indeed consistent with the known

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* This result was obtained by comparison with cyclic voltammetric peaks obtained at 20 °C, for the same solution, in the presence of the cluster only, and corrected for the temperature effect on the peak current parameters, *i.e.* 15% attenuation of the currents from 20 to -20 °C.

† The CO partial pressure in the solution was taken as equal to the static, equilibrated CO pressure maintained above the liquid surface after bubbling CO through the solution.

$$\mathrm{E_1}\quad [\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}}] \rightleftharpoons [\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}}]^{\bullet +} + \mathrm{e} \quad (2)$$

$$\mathrm{C_1}\quad [\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}}]^{\bullet +} + \mathrm{PPh_3} \longrightarrow [\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}(PPh_3)}]^{\bullet +} \quad (3)$$

$$\mathrm{E^2}\quad [\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}(PPh_3)}]^{\bullet +} \xrightarrow{\mathrm{H_2O}} [\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}}] + [\mathrm{PPh_3H}]^{+} \quad (4)$$

reactivity of $\mathrm{PPh_3}^{\bullet +}$ with traces of water.[13] It is also consistent with the absence of CO predissociation (documented by the above reported effect of P_{CO}). It implies the occurrence of an internal charge transfer in $[\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}(PPh_3)}]^{\bullet +}$.

The chemical step $\mathrm{C_1}$ actually involves the co-ordination of $\mathrm{PPh_3}$ to the cluster radical cation, followed by an internal charge transfer in the resulting species in which the phosphine actually bears the positive charge and may therefore react with water in step $\mathrm{E_2}$. As a result, *each* $\mathrm{PPh_3}$, after co-ordination with $[\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}}]^{\bullet +}$ and subsequent reactions, regenerates *one* neutral cluster. The loss of linearity observed beyond $N = 5$ in the coulometric experiments may very well be ascribed to other chemical reactions of the intermediate species.

In the above mechanism, as the redox potential of the transient species, in which $\mathrm{PPh_3}$ is co-ordinated to the cluster, is less positive than that of the couple $[\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}}]^{\bullet +}$–$[\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}}]$ it precludes any possible electrocatalysed oxidation of the cluster by the resulting species whose E° is around +0.4 V *vs.* s.c.e. This is a striking difference with respect to the results obtained for the reduction.[8]

The site of the chemical interaction between $[\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}}]^{\bullet +}$ and $\mathrm{PPh_3}$ may reasonably be speculated to be the apical cobalt, based on the experimental observations that, in clusters obtained from $[\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}}]$ by partial or total substitution of strongly bonded ligands for the CO initially co-ordinated to the apical cobalt, the cation radical did not react with $\mathrm{PPh_3}$. This observation was made in the following clusters, where apical CO was replaced by other ligands: $[\mathrm{Co_4(CO)_6\{HC(PPh_2)_3\}(\eta\text{-}C_6H_5Me)}]$ [Figure 1(*b*)], $[\mathrm{Co_4(CO)_8\{P(OMe)_3\}\{HC(PPh_2)_3\}}]$ and $[\mathrm{Co_4(CO)_8(dppm)_2}]$ [dppm = bis(diphenylphosphino)methane].

Electrochemical Oxidation of $[\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}}]$ *in the Presence of* $\mathrm{P(OMe)_3}$.—Cyclic voltammograms revealed that, for the reversible couple $[\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}}]^{\bullet +}$–$[\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}}]$, the reduction peak disappeared in the presence of $\mathrm{P(OMe)_3}$, as observed in the presence of $\mathrm{PPh_3}$. However, the following additional results were obtained.

When the concentration ratio in the studied solution was such that $[\mathrm{cluster}]/[\mathrm{P(OMe)_3}] = 1:1$ a new reversible system (1) was observed, characterized by $E_{\mathrm{p}}{}^{\mathrm{c}}{}_{1} = +0.46$ V and $E_{\mathrm{p}}{}^{\mathrm{a}}{}_{1} = +0.58$ V vs. s.c.e. Further addition of $\mathrm{P(OMe)_3}$ led to cyclic voltammograms in which the reduction peak current of the system (1) decreased, whereas a new reduction peak (2) appeared at $E_{\mathrm{p}}{}^{\mathrm{c}}{}_{2} = +0.27$ V *vs.* s.c.e. As the ratio $[\mathrm{cluster}]/[\mathrm{P(OMe)_3}]$ increased beyond 1:1, the peak current $I_{\mathrm{p}}{}^{\mathrm{c}}{}_{2}$ increased and it was even possible to detect a third, new reduction peak (3) at $E_{\mathrm{p}}{}^{\mathrm{c}}{}_{3} = +0.09$ V *vs.* s.c.e. (reversible couple). The temperature effects clearly illustrated the occurrence of chemical steps in this global reduction process in the presence of $\mathrm{P(OMe)_3}$: at −20 °C, no matter whether the $[\mathrm{cluster}]/[\mathrm{P(OMe)_3}]$ concentration ratio was equal to or higher than 1:1, the system (1) remained almost unchanged, whereas the reduction signal (2) was dramatically decreased, and (3) disappeared. These results provided convincing clues that the monoreduced cluster underwent substitution of one CO by one $\mathrm{P(OMe)_3}$ to generate the reversible system (1), while the characteristics of the systems (2) and (3) were consistent with further chemical substitutions of CO by $\mathrm{P(OMe)_3}$ in the cluster.

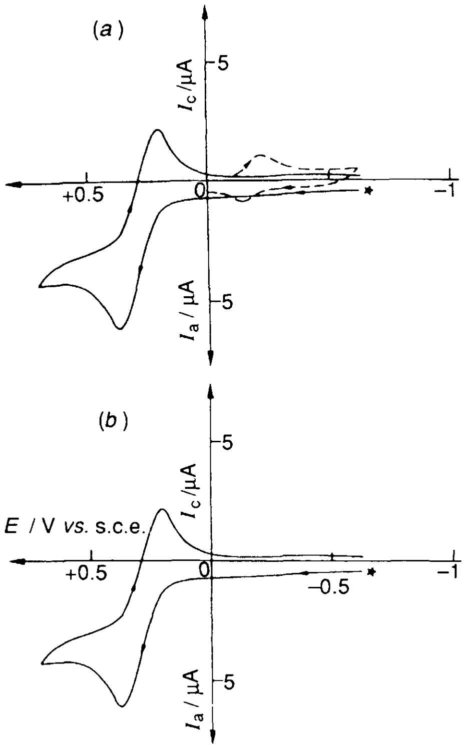


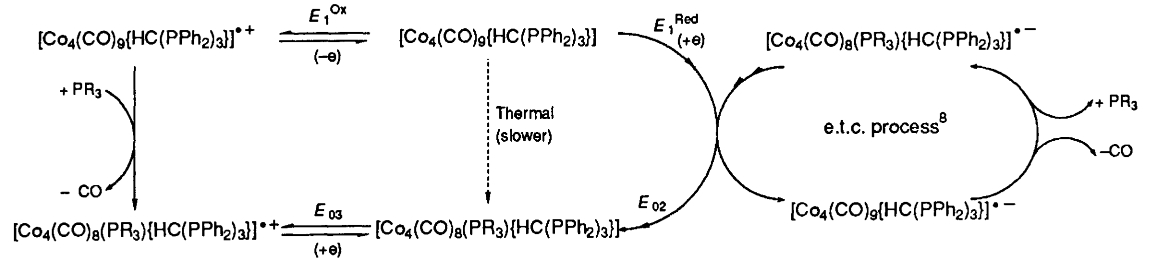
Figure 4. Electrochemical oxidation of the capped cluster $[\mathrm{Co_4(CO)_6\{HC(PPh_2)_3\}(\eta\text{-}C_6H_5Me)}]$ (*ca.* 5×10^{-4} mol dm^{-3}). Conditions as in Figure 2. (*a*) (——) In the absence of $\mathrm{P(OMe)_3}$ and under argon, (– – – –) in the presence of $\mathrm{P(OMe)_3}$ and under argon, $[\mathrm{P(OMe)_3}]/[\mathrm{cluster}] > 1:1$. (*b*) Under CO and in the presence of $\mathrm{P(OMe)_3}$; $[\mathrm{P(OMe)_3}]/[\mathrm{cluster}] > 1:1$, $P_{\mathrm{CO}} = 1$ atm.

These electrochemical results were insensitive to the partial pressure of CO in the solution ($0 < P_{\mathrm{CO}} < 2$ atm), like those reported in the presence of $\mathrm{PPh_3}$. Also, the new reduction peaks (1)—(3) observed in the presence of $\mathrm{P(OMe)_3}$ were not present unless prior electrochemical oxidation of the neutral cluster $[\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}}]$ occurred at the electrode: these peaks therefore correspond to the reduction of species resulting from chemical reactions of the cluster radical cation with $\mathrm{P(OMe)_3}$. At variance with the observations made in the presence of $\mathrm{PPh_3}$, the peak current corresponding to the electrochemical oxidation of $[\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}}]$ was not changed after $\mathrm{P(OMe)_3}$ was introduced in the solution. This result precluded possible regeneration of the neutral cluster through a reaction scheme similar to that proposed above in the presence of $\mathrm{PPh_3}$.

Electrochemical measurements were also performed on a solution of an authentic $\mathrm{P(OMe)_3}$-substituted cluster: $[\mathrm{Co_4(CO)_8\{P(OMe)_3\}\{HC(PPh_2)_3\}}]$ in which $\mathrm{P(OMe)_3}$ substituted one CO on the apical cobalt. On oxidation, the solution of this compound exhibited one reversible couple of peaks whose potentials ($E_{\mathrm{p}}{}^{\mathrm{a}} = +0.58$ V and $E_{\mathrm{p}}{}^{\mathrm{c}} = +0.46$ V *vs* s.c.e.) were the same as for system (1) above, whereas the signals (2) and (3) were absent.

Therefore, when electrochemical oxidation of $[\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}}]$ was performed in the presence of $\mathrm{P(OMe)_3}$ the substituted cluster $[\mathrm{Co_4(CO)_8\{P(OMe)_3\}\{HC(PPh_2)_3\}}]$ was produced by the chemical reaction of $[\mathrm{Co_4(CO)_9\{HC(PPh_2)_3\}}]^{\bullet +}$ with $\mathrm{P(OMe)_3}$.

The electrochemical oxidation of the apically capped cluster $[\mathrm{Co_4(CO)_6\{HC(PPh_2)_3\}(\eta\text{-}C_6H_5Me)}]$ [Figure 1(*b*)], in which all three apical CO were replaced by toluene, revealed an



unexpected reactivity. From the observed inertness of its radical anion towards substitution by phosphines,[8] and from the above reported low reactivity (if any) of its radical cation towards PPh_3, similar observations could be expected in the presence of $P(OMe)_3$. However, oxidative cyclic voltammograms of $[Co_4(CO)_6\{HC(PPh_2)_3\}(\eta\text{-}C_6H_5Me)]$ in the presence of $P(OMe)_3$ $\{[P(OMe)_3]/[\text{cluster}] > 1:1\}$ revealed the generation of a new species reversibly reduced and oxidized at respectively $E_p^c = -0.23$ V and $E_p^a = -0.15$ V *vs.* s.c.e. [Figure 4(*a*)]. This new couple of peaks observed around −0.19 V *vs.* s.c.e. was about 400—450 mV more cathodic with respect to the couple of peaks corresponding to the original cluster redox system $[Co_4(CO)_6\{HC(PPh_2)_3\}(\eta\text{-}C_6H_5Me)]^{\bullet+}$–$[Co_4(CO)_6\{HC(PPh_2)_3\}(\eta\text{-}C_6H_5Me)]$. This potential shift was much higher than that observed ($\Delta E \approx 250$ mV) between the couple $[Co_4(CO)_9\{HC(PPh_2)_3\}]^{\bullet+}$–$[Co_4(CO)_9\{HC(PPh_2)_3\}]$ and its apically substituted derivatives $[Co_4(CO)_8\{P(OMe)_3\}\{HC(PPh_2)_3\}^{\bullet+}$–$[Co_4(CO)_8\{P(OMe)_3\}\{HC(PPh_2)_3\}]$. The substitution inertness of the capping apical toluene [Figure 1(*b*)] in chemical reactions as well as in the cluster radical cation in the presence of PPh_3 prompted us to speculate that the reaction observed with $P(OMe)_3$ could involve a basal, rather than apical, cobalt. Chemical degradation of the oxidized cluster on the time-scale of exhaustive coulometric preparation precluded isolation and further identification of the substituted species.

However, on the cyclic voltammetric time-scale, the following observations support this speculation: oxidative cyclic voltammograms were recorded for $[Co_4(CO)_6\{HC(PPh_2)_3\}(\eta\text{-}C_6H_5Me)]$ in the presence of $P(OMe)_3\{[P(OMe)_3]/[\text{cluster}] > 1:1$ [Figure 4(*a*)]. First under argon and in carefully deaerated solution, the curve (*a*) was observed, with the new reduction signal around −0.19 V *vs.* s.c.e. On the other hand, under $P_{CO} = 1$ atm, the curve (*b*) was observed, no other signals being detectable other than the oxidation/reduction couple of the original cluster. Further recording, after careful degassing of the solution by argon, restored the initial pattern [Figure 4(*a*)].

It is therefore clear that dissociation of CO from the cluster is involved in the reaction of $P(OMe)_3$ with the oxidized form of the cluster. These results are consistent with the observation[6] that, for the studied cluster [Figure 1(*b*)], the basal cobalts are less positive than the apical one. Therefore, for this toluene-capped cluster, one may reasonably speculate that the oxidation site is on the basal cobalt triangle, and therefore that $P(OMe)_3$ did not co-ordinate on the same site on reacting with $[Co_4(CO)_9\{HC(PPh_2)_3\}]^{\bullet+}$ as with $[Co_4(CO)_6\{HC(PPh_2)_3\}(\eta\text{-}C_6H_5Me)]^{\bullet+}$.

The above results led to the conclusion that the electrochemical oxidation of $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ in the presence of the nucleophiles PPh_3 and $P(OMe)_3$ was always followed by reactions of the nucleophile with the cluster cation radical. The fate of the moieties generated was different with PPh_3 and with $P(OMe)_3$. With $P(OMe)_3$ the species obtained were stable on the voltammetric time-scale. In the presence of PPh_3 no stable substitution product was obtained owing to the high reactivity of the intermediate species: the final stable species obtained were $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ and $[PPh_3H]^+$. With both nucleophiles, the redox characteristics of the stable products, and of the detectable intermediate, prevented any possible catalytic enhancement of the substitution yield, at striking variance with the results obtained for the reduction.[8]

It might be added that, in the presence of $P(OMe)_3$, electroreduction of $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ yields results quite similar and consistent with those already reported[8] in the presence of phosphines. When reductive cyclic voltammetry was performed under the same conditions as those above, with $P(OMe)_3$ added to the solution containing the cluster (stoicheiometry 1:1), the curves obtained exhibited an additional reduction peak ($E_p^c = -1.225$ V *vs.* s.c.e. at 0.1 V s^{-1}) and this new reduction peak, 220 mV more cathodic than that of the original cluster, increased at the expense of the original reduction signal of the cluster. The observed peak-potential shift ($\Delta E_p^c = -220$ mV) corresponds exactly to the value expected when one carbon monoxide is replaced by one monodentate phosphine.[7,8] In addition, it was observed that increasing the partial pressure of CO in the solution hinders the substitution.

The algebraic sequence of the reduction potentials, for the original cluster and the new species detected, matches the required conditions for electron-transfer-catalysed substitution, as in the presence of phosphines.[8]

Thus, taking into account the present results and those known for the reduction, a general reaction scheme may be drawn for the cluster $[Co_4(CO)_9\{HC(PPh_2)_3\}]$ in the presence of PR_3 nucleophiles. In this scheme, the e.t.c. substitution at the cathode is triggered by the algebraic sequence $E_{02} < E_1^{red}$, whereas the sequence $E_{03} < E_1^{ox}$ observed at the anode prevents any similar catalytic turnover.

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