Synthesis, Reactivity, and Electrochemical Behaviour of New Five-co-ordinate Nitrosyl Cobalt Complexes

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The synthesis and characterization of some new five-co-ordinate mononitrosyl cobalt complexes of the type $[CoL_4(NO)][BPh_4]_2$ [L = $P(OMe)_3$, $P(OEt)_3$, or $PPh(OEt)_2$] is described. The reactivity of these compounds with π-acceptor ligands such as NO, CO, phosphite, and isocyanide is discussed. Furthermore, the reaction with molecular oxygen and with halide ions (X^-) has been investigated and a new method of obtaining the cations $[CoXL_3(NO)]^+$ has been achieved. The cathodic and anodic behaviour of the complex $[Co\{P(OEt)_3\}_4(NO)][BPh_4]_2$ at a platinum electrode in acetonitrile is also reported.

ALTHOUGH a large number of studies on nitrosyl cobalt complexes has been made,[1,2] few of them are concerned with five-co-ordinate mononitrosyl derivatives. Beside compounds containing chelate ligands, of formula $[CoL_2(NO)]^{n+}$ (L = diarsine,[3] dimethylglyoxime,[2a] or dithioacetylacetonate;[4] n = 2 or 0) or of formula [CoL(NO)] [L = *NN'*-ethylenebis(acetylacetoneiminate) or *NN'*-ethylenebis(salicylideneiminate)],[5] only two examples of complexes with unidentate phosphine ligands of the type $[CoX_2L_2(NO)]$ (X = Cl, Br, or I; L = tertiary phosphine)[6] and $[CoXL_3(NO)]^+$ (L = phosphite)[7] have been reported. However, no example of a cobalt compound with the donor-atom set $L_4(NO)$ is known. As an extension of our studies dealing with nitrosyl cobalt complexes, we report here the synthesis and reactivity of the first derivatives of the type $[CoL_4(NO)][BPh_4]_2$ (L = phosphite).

An electrochemical study of the complex $[Co\{P(OEt)_3\}_4(NO)][BPh_4]_2$ has been undertaken in order to determine its redox properties and to correlate the data obtained with those previously reported for the cations $[CoXL_3(NO)]^+$ [X = Cl or I; L = $P(OEt)_3$ or $P(OMe)_3$].[8]

EXPERIMENTAL

Materials.—All the solvents used were purified by standard techniques and distilled and stored under nitrogen. The compounds $Co[NO_3]_2{\cdot}6H_2O$, $Co[ClO_4]_2{\cdot}6H_2O$, and $Co[BF_4]_2{\cdot}6H_2O$ were Baker products and were used as received. Diethoxyphenylphosphine was prepared by the method reported in ref. 9 while triethyl phosphite and trimethyl phosphite, again Baker products, were purified by distillation under nitrogen. Nitric oxide (Baker) was purified by passing it through a trap cooled to −80°C. 4-Tolyl isocyanide was obtained by the 'phosgene method' of Ugi *et al.*[10] All other reagents were used as received.

All chemicals and reagents employed in the electrochemical experiments were prepared as reported in ref. 8.

Apparatus.—Infrared spectra of KBr pellets and 1,2-dichloroethane solutions were obtained by using a Perkin-Elmer model 457 spectrophotometer. Hydrogen-1 n.m.r. spectra were recorded with a Varian EM 390 spectrometer with tetramethylsilane as internal standard. Electronic spectra at room temperature were recorded on a Varian model 219 spectrophotometer. Magnetic susceptibilities in solution were measured by the Evans' method.[11] Conductivities of 10^{-3} mol dm^{-3} solutions of the complexes were measured with a Haloisis bridge at 25 ± 0.1 °C. Measurements of gas uptake were carried out in a glass vacuum system following the procedure described previously.[7]

The apparatus employed in the voltammetric, chronoamperometric, and coulometric tests has been described elsewhere.[8] All the electrochemical tests were performed at 20 ± 0.1 °C.

Synthesis of the Complexes.—$[CoL_4(NO)][BPh_4]_2$ [L = $P(OEt)_3$, $PPh(OEt)_2$, or $P(OMe)_3$]. The appropriate phosphite (60 mmol) was added to a solution of $Co[NO_3]_2{\cdot}6H_2O$ (2.91 g, 10 mmol) in ethanol (60 cm^3) or methanol, under nitrogen. The reaction mixture was stirred for 15—20 min and then nitric oxide was bubbled through the solution for 30 min. The addition of $Na[BPh_4]$ (6.6 g, 20 mmol) caused the precipitation of a pink solid which was filtered off and recrystallized from dichloromethane–ethanol. The yield obtained was ⩾40% (Found: C, 62.45; H, 7.25; N, 1.00. $C_{72}H_{100}B_2CoNO_{13}P_4$ requires C, 62.1; H, 7.25; N, 1.00%. Found: C, 69.75; H, 6.55; N, 1.00. $C_{88}H_{100}B_2CoNO_9P_4$ requires C, 69.55; H, 6.65; N, 0.90%. Found: C, 58.85; H, 6.20; N, 1.00. $C_{60}H_{76}B_2CoNO_{13}P_4$ requires C, 58.9; H, 6.25; N, 1.15%).

The compounds $Co[ClO_4]_2{\cdot}6H_2O$ or $Co[BF_4]_2{\cdot}6H_2O$ can also be used as starting cobalt(II) salts, but in these cases lower yields were obtained. Sometimes, the synthesis of the trimethyl phosphite derivative leads to a compound which is insoluble in any solvent; however, its elemental analysis and i.r. spectrum are identical to those of the well characterized complex $[Co\{P(OMe)_3\}_4(NO)][BPh_4]_2$.

$[CoX\{P(OEt)_3\}_3(NO)][BPh_4]$ (X = Cl, Br, or I). The complex $[Co\{P(OEt)_3\}_4(NO)][BPh_4]_2$ (1.39 g, 1.0 mmol) was added to ethanol (30 cm^3) together with the appropriate lithium halide (1.1 mmol). Stirring of the reaction mixture for 24 h gave a green solid which was filtered off and recrystallized from dichloromethane–diethyl ether. The yield was ⩾80% (Found; C, 53.6; H, 7.00; N, 1.35. Calc. for $C_{42}H_{65}BClCoNO_{10}P_3$: C, 53.55; H, 6.95; N, 1.50%. Found: C, 51.2; H, 6.55; N, 1.45. $C_{42}H_{65}BBrCoNO_{10}P_3$ requires C, 51.15; H, 6.65; N, 1.40%. Found: C, 48.65; H, 6.40; N, 1.40. Calc. for $C_{42}H_{65}BCoINO_{10}P_3$: C, 48.8; H, 6.35; N, 1.35%).

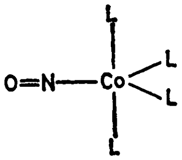
RESULTS AND DISCUSSION

Synthesis and Reactivity.—The synthesis of the new five-co-ordinate mononitrosyl complexes $[CoL_4(NO)]^{2+}$ [L = $P(OEt)_3$, $PPh(OEt)_2$, or $P(OMe)_3$] has been achieved by bubbling, at room temperature and 1 atm,* gaseous NO through a $Co[NO_3]_2\cdot 6H_2O$ solution containing an excess of phosphite.

Selected properties of these complexes which are all crystalline pink solids, stable in the solid state but rather unstable in polar organic solvents, are given in the Table. The complexes are diamagnetic and the conductivity values (Λ in the range 130.6—118.8 S cm^2 mol^{-1} in nitromethane) are in agreement with those reported for 1 : 2 electrolytes containing BPh_4^- as anion.[12]

The i.r. spectra of the complexes $[CoL_4(NO)][BPh_4]_2$ show, in the NO stretching region, only one strong band in the range 1 819—1 835 cm^{-1} in 1,2-dichloroethane solution and at 1 810—1 842 cm^{-1} in the solid state. According to the empirical rules proposed by Haymore and Ibers[13] the observed and corrected NO stretching frequencies, falling above 1 620 cm^{-1}, are characteristic of a linear MNO group.

The room-temperature ^{1}H n.m.r. spectra of the derivatives $[Co\{P(OEt)_3\}_4(NO)][BPh_4]_2$ and $[Co\{PPh(OEt)_2\}_4(NO)][BPh_4]_2$ show a triplet at τ 8.58 and 8.83 due to the methyl protons, and in the methylene region a multiplet at τ 5.64 and 6.32 respectively. On cooling the solutions to −60 °C, the methylene protons resonance splits into two broad signals, at τ 5.74 and 5.62 [for L = $P(OEt)_3$] and at τ 6.26 and 6.39 [for L = $PPh(OEt)_2$], with an intensity ratio of 1 : 1, indicating that the four phosphite groups are in two sets of two equivalent positions. On this basis a trigonal-bipyramidal geometry with a linear MNO group in an equatorial position can be proposed



for the cations $[CoL_4(NO)]^{2+}$. Such a configuration agrees with the theoretical studies of Hoffmann *et al.*,[14] which suggest that the presence of good π-acceptor ligands in five-co-ordinate mononitrosyl d^8 complexes favours the proposed structure rather than a tetragonal-pyramidal geometry with a strongly bent co-ordinated NO group.

The cations $[CoL_4(NO)]^{2+}$ are relatively unstable in solution and decompose spontaneously at room temperature with a rate depending on the nature of the phosphite group, decreasing in the order $PPh(OEt)_2 > P(OMe)_3 > P(OEt)_3$. This process can be satisfactorily followed by i.r. and ^{1}H n.m.r. techniques and the results show that whereas the triethyl phosphite derivative decomposes in acetone or 1,2-dichloroethane solution so slowly that after 1 d the extent of decomposition is *ca.* 10%, the decomposition of the other derivatives is much faster (half-lives of 4—5 h).

Physical constants and selected i.r., ^{1}H n.m.r., and visible spectral data

Compound	Colour	M.p.[a] (θ_c/°C)	Λ[b]/ S cm^2 mol^{-1}	$\tilde{\nu}$(NO)/cm^{-1} ClCH$_2$CH$_2$Cl	KBr	Visible spectra[c] $\lambda_{max.}$/nm	Chemical shift (τ)[d] CH$_2$	CH$_3$
$[Co\{P(OEt)_3\}_4(NO)][BPh_4]_2$	Pink	111	130.6	1 835s	1 842s	306 (2 700), 478 (153)	5.64 (m)[e]	8.58 (t)
$[Co\{PPh(OEt)_2\}_4(NO)][BPh_4]_2$	Pink	99	118.8	1 819s	1 810s	306 (sh), 342 (5 000), 502 (290)	6.32 (m)	8.83 (t)[f]
$[Co\{P(OMe)_3\}_4(NO)][BPh_4]_2$	Pink	109	122.1	1 831s	1 828s	316 (3 300), 456 (138)		6.14 (m)
$[CoBr\{P(OEt)_3\}_3(NO)][BPh_4]$	Green	100	48.3	1 782s	1 779s	338 (3 000), 580 (303)	5.71 (m)	8.67 (t)

[a] Melting points were determined in capillaries and are uncorrected. [b] Molar conductances (Λ) were determined in 10^{-3} mol dm^{-3} nitromethane solutions at 25 ± 0.1 °C. [c] In ClCH$_2$CH$_2$Cl. Molar absorption coefficients (ϵ/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [d] In $(CD_3)_2CO$. [e] At −60 °C there are two signals at τ 5.64 and 6.32. [f] In CD_2Cl_2 this resonance occurs at τ 8.84.

The i.r. spectra of the $PPh(OEt)_2$ derivative show that the band at 1 819 cm^{-1} decreases in intensity within a few hours and is replaced by two new peaks at 1 858 and 1 806 cm^{-1} which are identical in position and intensity ratio with those observed for a pure sample of $[Co\{PPh(OEt)_2\}_2(NO)_2][BPh_4]$. The formation of the dinitrosyl compound can also be followed by ^{1}H n.m.r. spectra, which show the disappearance of the signal at τ 8.83 [in $(CD_3)_2CO$] due to the starting complex and the appearance of two new signals at τ 8.63 and at 8.46. The resonance at τ 8.63 is attributed to the compound $[Co\{PPh(OEt)_2\}_2(NO)_2]^+$. The dinitrosyl complex is recovered from the solution in good yield (45% based on the starting cobalt cation) but we were not able to isolate any other product. A diamagnetic cobalt(III) derivative such as $[Co\{PPh(OEt)_2\}_6]^{3+}$ could have been expected to form in a disproportionation reaction of the mononitrosyl starting complex producing $[Co\{PPh(OEt)_2\}_2(NO)_2]^+$ and $[Co\{PPh(OEt)_2\}_6]^{3+}$. However, the reduction of the starting cobalt(II) compound to the dinitrosyl cobalt(I) final complex by the phosphite ligand cannot be excluded.

Likewise, $[Co\{P(OEt)_3\}_2(NO)_2][BPh_4]$ and $[Co\{P(OMe)_3\}_2(NO)_2][BPh_4]$ are formed from the decomposition of $[Co\{P(OEt)_3\}_4(NO)][BPh_4]_2$ and $[Co\{P(OMe)_3\}_4(NO)][BPh_4]_2$ respectively.

The complexes $[CoL_4(NO)]^{2+}$ react with NO at room temperature and at a pressure of 1 atm to give, quantitatively after 1 d, the dinitrosyl derivatives $[CoL_2(NO)_2]^+$, equation (1).

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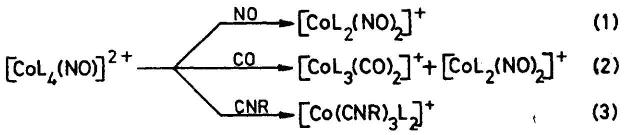
* Throughout this paper: 1 atm = 101 325 Pa.

A slow reaction takes place when the five-co-ordinate mononitrosyl compounds are allowed to react with carbon monoxide and, after 1 d, the complexes $[CoL_4(CO)]^+$ and $[CoL_2(NO)_2]^+$ are obtained in good yield and in a 1 : 1 ratio, equation (2). If the reaction mixture is kept under carbon monoxide for some days, whereas the dinitrosyl compounds remain unchanged, the monocarbonyl derivatives $[CoL_4(CO)]^+$ react further with CO to give $[CoL_3(CO)_2]^+$ as final products.

4-Tolyl isocyanide reacts with the cations $[CoL_4(NO)]^{2+}$ to give the mixed-ligand cobalt(I) derivatives $[Co(CNR)_3L_2]^+$ in quantitative yield, equation (3). These reactions, summarised in Scheme 1, show that reduction of $[CoL_4(NO)]^{2+}$ takes place in the presence of ligands such as NO, CO, and CNR to give cobalt(I) complexes and that only the isocyanide ligand gives rise to complete substitution of the nitrosyl group.



SCHEME 1

The reactivity of the cations $[CoL_4(NO)]^{2+}$ towards phosphite was also studied, by varying the complex to phosphite molar ratio in the range 1 : 1—1 : 100, but in no case was there any reaction and the complexes can be recovered unchanged. However, after several hours the cations $[CoL_2(NO)_2]^+$ can be detected, presumably due to the decomposition of the starting mononitrosyl derivatives.

These complexes exhibit an unexpected stability towards phosphite since the similar compounds $[CoXL_3(NO)]^+$,[7] in which one phosphite ligand has been replaced by a halide, react rapidly with the free $P(OR)_3$ or $PPh(OR)_2$ affording the reduced products $[CoL_2(NO)_2]^+$, $[CoXL(NO)_2]$, and $[CoL_3(NO)]$.

The reaction of an equimolar amount of lithium halide with a suspension of $[CoL_4(NO)]^{2+}$ in ethanol leads to the derivatives $[CoXL_3(NO)]^+$, which were isolated and characterized. The substitution reaction (4) is quantitative (yield ⩾95%) and allows the preparation of pure samples of the bromo-derivative $[CoBr\{P(OEt)_3\}_3(NO)][BPh_4]$ (Table 1) which cannot be obtained by the reaction of the cation $[CoBrL_4]^+$ with NO.[7]

$$[CoL_4(NO)]^{2+} + X^- \longrightarrow [CoXL_3(NO)]^+ + L \quad (4)$$

Furthermore, it can be observed that hydrohalogenic acid can be used as a source of X^- in reaction (4).

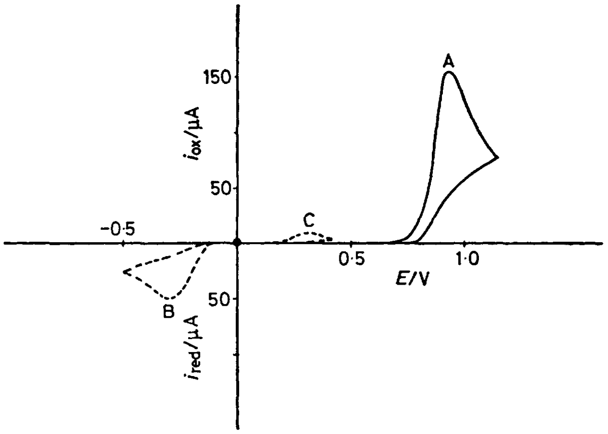
Reaction (4) does not seem to be a true equilibrium since, as mentioned above, an excess of phosphite causes the reduction of $[CoXL_3(NO)]^+$ to cobalt(I) derivatives and no $[CoL_4(NO)]^{2+}$ compounds are formed. Furthermore, the $[CoXL_3(NO)]^+$ complexes initially produced in the presence of an excess of halide later decompose to the $[CoXL(NO)_2]$ and $[CoL_3(NO)]$ final products.

The reactivity of the mononitrosyl cobalt compounds $[CoL_4(NO)][BPh_4]_2$ towards molecular oxygen has also been tested. While in 1,2-dichloroethane solvent no reaction is observed, by exposing to the air or to pure oxygen a dichloromethane solution containing $[CoL_4(NO)][BPh_4]_2$ a fast colour change from pink to green is observed. Measurements of gas uptake indicate that the ratio of starting complexes to the oxygen adsorbed falls in the range 0.6—0.8. From the resulting green solutions the complexes $[CoClL_3(NO)]^+$ (yield 90%) can be isolated and phosphite oxide is detected by i.r. spectroscopy. These data can be rationalized in terms of the reaction (5)

$$[CoL_4(NO)]^{2+} \xrightarrow[CH_2Cl_2]{O_2} [CoClL_3(NO)]^+ + PO(OR)_3 \quad (5)$$

in which molecular oxygen does not react with the complex or with the co-ordinated NO group [5e] but with the phosphite ligand. The chlorine in the final cobalt product comes from the CH_2Cl_2 solvent.

Electrochemical Properties of $[Co\{P(OEt)_3\}_4(NO)][BPh_4]_2$.—The Figure shows the cyclic voltammetric behaviour at a platinum electrode of a 0.1 mol dm^{-3} tetraethylammonium perchlorate–acetonitrile solution of $[Co\{P(OEt)_3\}_4(NO)][BPh_4]_2$, which has been chosen as a typical example of the class of compounds $[CoL_4(NO)][BPh_4]_2$.



Cyclic voltammetric curves recorded on an acetonitrile solution containing 3.5 × 10^{-3} mol dm^{-3} $[Co\{P(OEt)_3\}_4(NO)][BPh_4]_2$ and 0.1 mol dm^{-3} tetraethylammonium perchlorate. Platinum working microelectrode; potential scan rate 0.2 V s^{-1}. Potential scan is initially anodic in direction (——), initially cathodic in direction (– – –); starting potential (●)

In the anodic scan an oxidation process (A) is evident; at a potential scan rate (v) of 0.2 V s^{-1} the peak potential value, $(E_p)_A$, is equal to 0.93 V *vs.* s.c.e. (saturated calomel electrode). No associated cathodic response is recorded up to the direct reduction of the starting compound. The current peak relative to the cathodic process (B) is characterized by an E_p value of −0.30 V *vs.* s.c.e. at the same sweep rate. By reversing the potential scan just beyond this peak an associated anodic peak (C) is recorded before the response due to the oxidation of $[Co\{P(OEt)_3\}_4(NO)][BPh_4]_2$; it is rather low in height and increases by stopping the potential for a few seconds in correspondence to the reduction peak (B).

Data from chronoamperometric tests carried out on solutions of $[Co\{P(OEt)_3\}_4(NO)][BPh_4]_2$ at a potential of -0.85 V *vs.* s.c.e., beyond the cathodic peak, allow us to conclude that a one-electron reduction occurs on the chronoamperometric and hence on the voltammetric time scales, by comparison with data from the one-electron oxidation of bis(cyclopentadienyl)iron(II). Only at the longest times do the apparent numbers of electrons involved in the electrode process become higher than unity. On the other hand, controlled-potential coulometric experiments reveal that two electrons per molecule of starting compound are involved in the overall reduction process. It must be deduced, therefore, that the one-electron reduction product, initially formed at the electrode, undergoes a slow chemical reaction leading to a species which is further reducible at the same potential. No particularly useful information can be gained from cyclic voltammetric experiments at different scan rates, which only allow us to establish the non-reversible character of the first charge-transfer process.

The final reduction product has been identified from elemental analysis, i.r., and ^1H n.m.r. data as the compound $[Co\{P(OEt)_3\}_3(NO)]$ which can be recovered in almost quantitative yield ($\geqslant 95\%$ with respect to the starting compound).

On the basis of the above reported results the mechanism in Scheme 2 can be proposed [$L = P(OEt)_3$].

$$[CoL_4(NO)]^{2+} + e^- \longrightarrow [CoL_4(NO)]^+ \qquad (6)$$

$$[CoL_4(NO)]^+ \xrightarrow{\text{slow}} [CoL_3(NO)]^+ + L \qquad (7)$$

$$[CoL_3(NO)]^+ + e^- \longrightarrow [CoL_3(NO)] \qquad (8)$$

SCHEME 2

A comparison of the cathodic behaviour of $[Co\{P(OEt)_3\}_4(NO)]^{2+}$ and $[CoX\{P(OEt)_3\}_3(NO)]^+$ ($X = Cl$ or I)[8] shows that in both cases the four-co-ordinate $[Co\{P(OEt)_3\}_3(NO)]$ is formed *via* an electron transfer–chemical step–electron transfer mechanism. However, the one-electron reduction products initially formed, $[Co\{P(OEt)_3\}_4(NO)]^+$ and $[CoXL_3(NO)]$ respectively, have different stoicheiometries and total charge but both are unstable and undergo a chemical reaction to form the four-co-ordinate complex $[CoL_3(NO)]^+$. The loss of one phosphite ligand in the former case and of X^- in the latter one[8] thus appears to be necessary to reach four-co-ordination which is more stable than five-co-ordination in d^9 cobalt species.

The complex $[Co\{P(OEt)_3\}_3(NO)][BPh_4]$ cannot be recovered from the solution, because it is reduced, according to equation (8), at the potential at which its formation occurs *via* equations (6) and (7).

Cyclic voltammograms on the electrolysed solution show the presence of an anodic peak at the same potential as peak C in the Figure. The presence in the solution of a stoicheiometric amount of $P(OEt)_3$ does not change significantly the voltammetric picture which is typical of the $[Co\{P(OEt)_3\}_3(NO)]$ complex, nor the nature of the major product resulting from its anodic oxidation.[8] Also in this case 2 mol of electrons per mol of starting complex are used and i.r., ^1H n.m.r., and voltammetric data indicate the formation of the dinitrosyl cobalt complex $[Co\{P(OEt)_3\}_2(NO)_2]^+$ with an almost quantitative yield, based on nitrosyl content. The resulting solution is diamagnetic and phosphite oxide is present. Since triethyl phosphite is oxidizable at the electrode only at potentials more anodic than 1.90 V *vs.* s.c.e., the occurrence of homogeneous redox reactions must be taken into account.

It can be noted that the anodic oxidation of the species $[Co\{P(OEt)_3\}_3(NO)]$, when carried out in the presence of a stoicheiometric amount of chloride ions, leads to a small amount of $[CoCl\{P(OEt)_3\}_3(NO)]^+$;[8] whereas the complex $[Co\{P(OEt)_3\}_4(NO)]^{2+}$ is totally absent from the solution obtained by anodic oxidation of the same cobalt complex performed in the presence of a stoicheiometric amount of $P(OEt)_3$.

By chronoamperometric tests at a potential of 1.50 V *vs.* s.c.e., well beyond $(E_p)_A$, the constancy of the number of electrons involved in the anodic oxidation has been checked over a time range of 2×10^{-3}—5 s. By comparison with the data from the one-electron oxidation of bis(cyclopentadienyl)iron(II), it can be deduced that the compound studied undergoes a two-electron oxidation on the chronoamperometric and the voltammetric time scales. Controlled-potential coulometric experiments allow us to extend this conclusion over a wider time span, leading us to conclude that 2 mol of electrons per mol of starting compound are involved in the overall oxidation process.

Cyclic voltammetric tests have been performed at potential scan rates ranging from 0.05 to 200 V s^{-1}. Both the $(E_p - E_{p/2})_A$ and the $\partial(E_p)_A/\partial\log v$ values, which increase with the potential scan rate, indicate the quasi-reversible character of the charge transfer. From these tests, however, it is not possible to determine conclusively whether the fast chemical reaction follows the charge transfer[15] or is interposed between two subsequent one-electron charge transfers, since at sufficiently high scan rates the degree of reversibility of the electrode charge transfer becomes too low.

Analyses performed on the products recovered from the exhaustively electrolyzed solution reveal the presence of a small amount (*ca.* 10% based on the parent compound) of $[Co\{P(OEt)_3\}_2(NO)_2]^+$.[7] Moreover, phosphite oxide (strong i.r. absorption band at 1 260 cm^{-1}), which again must arise from homogeneous chemical reactions, and species containing no nitrosyl ligands are present in the solution.

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REFERENCES

[1] B. F. G. Johnson and J. A. McCleverty, *Prog. Inorg. Chem.*, 1966, **7**, 277; W. P. Griffith, *Adv. Organomet. Chem.*, 1968, **7**, 211; N. G. Connelly, *Inorg. Chim. Acta Rev.*, 1972, **6**, 48; K. G. Caulton, *Coord. Chem. Rev.*, 1975, **14**, 317; J. A. McCleverty, *Chem. Rev.*, 1979, **79**, 53, and refs. therein.

[2] (*a*) C. B. Ungermann and K. G. Caulton, *J. Am. Chem. Soc.*, 1976, **98**, 3862; (*b*) P. L. Johnson, J. H. Enemark, R. D. Feltham, and K. B. Swedo, *Inorg. Chem.*, 1976, **15**, 2989; (*c*) J. A. Kaduk and J. A. Ibers, *ibid.*, 1977, **16**, 3283, and refs. therein; (*d*) M. Di Vaira, C. A. Ghilardi, and L. Sacconi, *ibid.*, 1976, **15**, 1555; (*e*) S. Bhaduri, K. Grundi, and B. F. G. Johnson, *J. Chem. Soc., Dalton Trans.*, 1977, 2085.

[3] R. D. Feltham and R. S. Nyholm, *Inorg. Chem.*, 1965, **4**, 1334; J. H. Enemark, R. D. Feltham, J. Riker-Nappier, and K. F. Bizot, *ibid.*, 1975, **14**, 624.

[4] A. R. Hendrickson, R. K. Y. Ho, and R. L. Martin, *Inorg. Chem.*, 1974, **13**, 1279, and refs. therein.

[5] (*a*) M. Tamaki, I. Masuda, and K. Shinra, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 2858; (*b*) F. Calderazzo, C. Floriani, R. Henzi, and F. L'Eplattenier, *J. Chem. Soc. A*, 1969, 1378; (*c*) A. Earnshaw, P. C. Hewlett, and L. F. Larkworthy, *J. Chem. Soc.*, 1965, 4718; (*d*) J. H. Enemark and R. D. Feltham, *J. Chem. Soc., Dalton Trans.*, 1972, 718; (*e*) S. G. Clarkson and F. Basolo, *Inorg. Chem.*, 1973, **12**, 1528.

[6] G. Booth and J. Chatt, *J. Chem. Soc.*, 1962, 2099; J. P. Collman, P. Farnham, and G. Dolcetti, *J. Am. Chem. Soc.*, 1971, **93**, 1788.

[7] G. Albertin, E. Bordignon, L. Canovese, and A. A. Orio, *Inorg. Chim. Acta*, 1980, **38**, 77.

[8] R. Seeber, G. A. Mazzocchin, G. Albertin, and E. Bordignon, *J. Chem. Soc., Dalton Trans.*, 1980, 979.

[9] R. Rabinowitz and J. Pellon, *J. Org. Chem.*, 1961, **26**, 4623.

[10] I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, and K. Offermann, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 472.

[11] D. F. Evans, *J. Chem. Soc.*, 1959, 2003; R. A. Bailey, *J. Chem. Educ.*, 1972, **49**, 297.

[12] W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

[13] B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 3060.

[14] R. Hoffmann, M. M. L. Chen, M. Elian, A. R. Rossi, and D. M. P. Mingos, *Inorg. Chem.*, 1974, **13**, 2666, and refs. therein.

[15] D. H. Evans, *J. Phys. Chem.*, 1972, **76**, 1160.