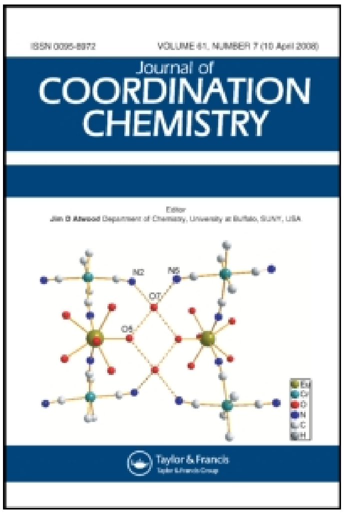

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE INFLUENCE OF TERTIARY PHOSPHINE CONE ANGLES ON CHEMICAL AND ELECTROCHEMICAL PROPERTIES OF COBALT DIMETHYLGLYOXIMATO COMPLEXES WITH TERTIARY PHOSPHINE AXIAL LIGANDS

C. W. Smith[a]; G. W. Vanloon[a]; M. C. Baird[a]
[a] Department of Chemistry, Queen's University, Kingston, Ontario, Canada

To cite this Article Smith, C. W. , Vanloon, G. W. and Baird, M. C.(1976) 'THE INFLUENCE OF TERTIARY PHOSPHINE CONE ANGLES ON CHEMICAL AND ELECTROCHEMICAL PROPERTIES OF COBALT DIMETHYLGLYOXIMATO COMPLEXES WITH TERTIARY PHOSPHINE AXIAL LIGANDS', Journal of Coordination Chemistry, 6: 2, 89 — 95

To link to this Article: DOI: 10.1080/00958977608079891

URL: http://dx.doi.org/10.1080/00958977608079891

J. Coord. Chem.
1976, vol. 6, pp. 89–95

THE INFLUENCE OF TERTIARY PHOSPHINE CONE ANGLES ON CHEMICAL AND ELECTROCHEMICAL PROPERTIES OF COBALT DIMETHYLGLYOXIMATO COMPLEXES WITH TERTIARY PHOSPHINE AXIAL LIGANDS

C. W. SMITH, G. W. VANLOON† and M. C. BAIRD

Department of Chemistry, Queen's University, Kingston, Ontario, Canada

(*Received December 3, 1975; in final form June 14, 1976*)

Details of the formation of the complexes *trans*-$[Co(DH)_2(PR_3)_2]^+$ (PR_3 = PPh_3, $PMePh_2$, PMe_2Ph, PBu_3) from the reactions of the free phosphines with *trans*-$[Co(DH)_2(H_2O)_2]^+$ are studied polarographically. The ease of formation and the ease of reduction of the bisphosphine complexes correlate better with the cone angles of the phosphines than with their expected relative donor properties. The complexes behave as weak acids (pK_a 9.9–10.6) in 95% ethanol, there being no apparent correlation with the nature of the axial ligands.

INTRODUCTION

We have recently reported a study of physical and chemical properties of cobalt(III) complexes of the types $[CosalenPR_3]X$, *trans*-$[Cosalen(PR_3)_2]X$, *trans*-$[Co(DH)_2(PR_3)_2]X$ and *trans*-$[Co(DH)_2PR_3X]$ (salen = N,N′-ethylenebis salicylideneiminato, DH = dimethylgloximato, PR_3 = tertiary phosphine, X = anion).[1] It was shown, *inter alia*, that phosphine steric requirements, conveniently expressed in terms of cone angles,[2–4] appeared to determine both the ease of addition of a second phosphine to the complexes $[CosalenPR_3]^+$ (PR_3 = PPh_3, $PMePh_2$, PMe_2Ph, PBu_3), and the kinetic dissociative liability of the axial phosphines in the complexes $[Cosalen(PR_3)_2]^+$ and $[Co(DH)_2PPh_3X]$.

In this paper, we report the results of a similar study of the cobaloxime complexes *trans*-$[Co(DH)_2(PR_3)_2]^+$ (PR_3 = PPh_3, $PMePh_2$, PMe_2Ph, PBu_3). The work also complements earlier polarographic work on complexes of the type $[Co(DH)_2L_2]^+$ (L = N, S donors)[5,6] and $[Co(DH)_2PR_3L]$ (L = Cl^-, H_2O)[7–9], and is the first systematic study of the polarographic characteristics of 2:1 tertiary phosphine cobaloxime complexes.

EXPERIMENTAL

The cationic complexes were prepared as described previously,[1] the oxime deprotonated forms by evaporation of the eluent from a Dowex 1 exchange resin (OH^- form) when 9.5 g of the ion pair $[Co(DH)_2(PR_3)_2][Co(DH)_2Cl_2]$ in 100 ml of 70% ethanol were passed through the column (1 x 10 cm).[12] Analytical data are presented in Table I.

Polarographic experiments were done using a Beckman Electroscan 30 instrument. The dropping mercury electrode (DME) employed has a measured capillary constant of 1.94_3 $sec^{1/2}$ $mg^{-1/3}$. A three

TABLE I
Analytical data

Complex	Calculated C	Calculated H	Calculated N	Found C	Found H	Found N
$[Co(D)(DH)(PMe_2Ph)_2]\cdot H_2O$	49.5	6.40	9.62	49.8	6.38	9.49
$[Co(D)(DH)(PBu_3)_2]\cdot H_2O$	54.1	9.78	7.88	54.8	9.66	7.98

---

†Author to whom correspondence should be sent.

electrode cell – DME, platinum counter electrode and saturated calomel reference electrode was used. All experiments were done under purified nitrogen in 0.10 M lithium nitrate/95% ethanol solvent.

"pH" measurements were done in the ethanolic solutions using a conventional glass/calomel combination electrode (Fisher 13-639-92) in conjunction with an Orion Ionalyzer Model 801 meter. A convenient operational approach for measuring acidity in mixed solvents has been described by Bates *et al.*[10] This involves calibrating the electrodes in a standard aqueous buffer and then after a thirty minute equilibration in 95% ethanol, taking measurements in the ethanolic solutions. A term δ which is a function of solvent composition and has been determined experimentally over the range of ethanol/water mixtures is subtracted from the pH reading to give pH*, a measure of the proton concentration in the solvent used. δ has been found to be –0.55 for 95% ethanol (93.7 weight percent).[10]

RESULTS AND DISCUSSION

The polarographic characteristics of the four complexes in 95% ethanol depend greatly on the nature of the phosphine and the pH* of the solvent (Table II). Interestingly, the values of $E_{1/2}$ of the complexes, in both acidic and basic solution, become more cathodic in the approximate order $PPh_3 < PMePh_2 < PBu_3 < PMe_2Ph$. The trend does not reflect the expected order of σ donor properties of the axial phosphines, as has been generally observed with other systems,[5,6,8] but rather the order of decreasing cone angles.[2–4] It appears that it is the smaller phosphines which best donate electron density to the metal atom. Possible precedents for this type of behaviour are the complexes $\{Co(DH)_2[P(c{-}C_6H_{11})_3]H_2O\}^{+}$[8] and $[Co(DH)_2(c{-}C_6H_{11}NH_2)_2]^{+}$[6], for which the values of $E_{1/2}$ do not correlate well with other phosphine and amine complexes, respectively, when only electronic factors are considered. The bulky cyclohexyl groups in these compounds appear to make the $E_{1/2}$ values much more anodic, as is observed here.

The complexes studied in this work may be divided into two categories on the basis of the polarographic behaviour under "neutral" or acidic conditions:

1) Complexes exhibiting two reduction steps (assigned as Co(III)–Co(II) and Co(II)–Co(I) on the basis of their diffusion current and coulometric characteristics). These comprise the complex with PPh_3 (either in the presence or absence of excess ligand), and the complex with PPh_2Me in the absence of excess ligand.

2) Complexes exhibiting one reduction step (Co(III)–Co(I); i_d/c values are approximately twice those of the individual steps above). These include the complexes with PBu_3 and PMe_2Ph, and the complex with $PMePh_2$ when excess ligand is present.

All waves are polarographically irreversible, with "log plot" slopes in the range 60 to 90 mV as opposed to the values for reversible reductions of 59 and 29 mV for one and two electron reductions, respectively.

Formation of the axial phosphine-substituted species upon titration of the complex $[Co(DH)_2(H_2O)_2]^+$ with PR_3 was followed polarographically, pH* being maintained below eight. Under these conditions the diaquo complex exhibits two

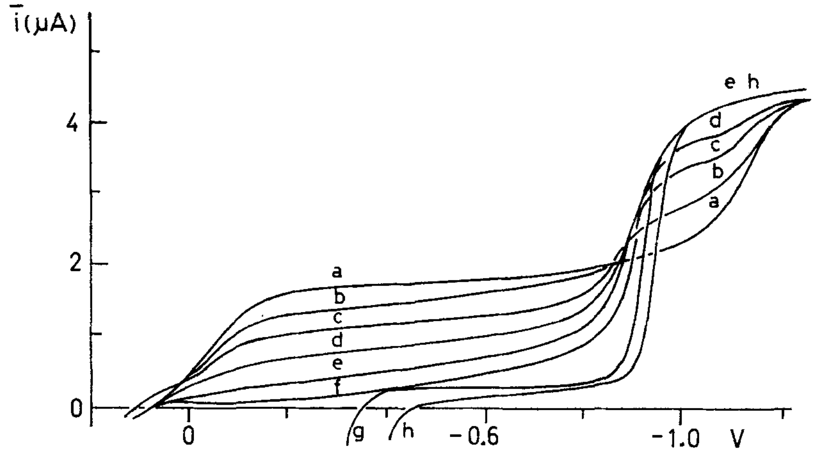

FIGURE 1 Polarographic titration of $[Co(DH)_2(H_2O)_2]NO_3$, 0.989 mM, with PMe_2Ph. Moles PMe_2Ph: moles complex (a) 0, (b) 0.37, (c) 0.74, (d) 1.03, (e) 1.40, (f) 1.76, (g) 3.22, (h) 17.9.

irreversible but well-defined one electron reduction steps with $E_{1/2}$ of −0.05 V (hereafter referred to as wave I) and −1.15 V (wave II).

Figure 1 shows the polarographic changes during the titration with PMe_2Ph. As the phosphine concentration is increased, waves I and II are systematically diminished to yield a single two-electron wave (wave III) with $E_{1/2}$ of −0.9 V corresponding to the complex, $[Co(DH)_2(PMe_2Ph)_2]^+$ (Table II). There is no evidence of any intermediate species. Figure 2 shows that the new wave grows linearly at the expense of waves I and II, formation being complete at the phosphine:cobalt ratio of 2:1. The titration with PBu_3 occurs in an analogous manner, the two-electron cathodic wave observed in the polarogram of $[Co(DH)_2(PBu_3)_2]ClO_4$ being formed systematically at the expense of the aquo complex waves.

With $PMePh_2$ the titration indicates more complex changes (Figure 3). Waves I and II are initially replaced by two one-electron reduction waves (III and IV) which do not correspond to those observed for $[Co(DH)_2(PMePh_2)_2]ClO_4$. As more phosphine is added, wave III disappears to yield a more negative wave (V), and wave IV shifts slightly in the positive direction (now called wave VI). Waves V and VI cor-

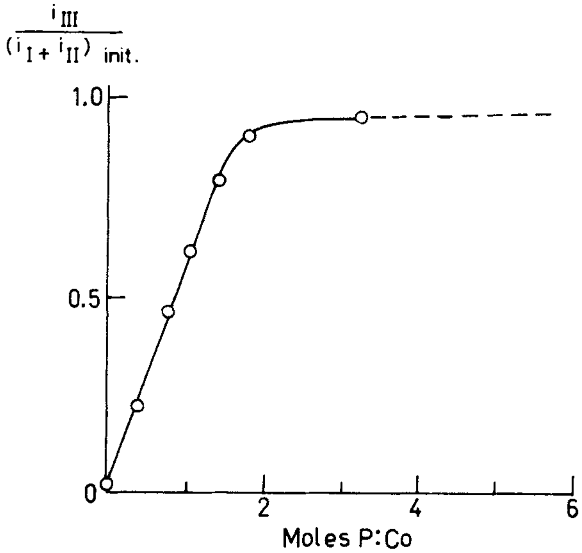

FIGURE 2 Polarographic titration curve, $[Co(DH)_2(H_2O)_2]^+$, 0.958 mM, with PMe_2Ph. Ratio $i_{III}/(i_I + i_{II})_{initial}$ = fraction of Co(III) in the form giving rise to i_{III}.

TABLE II
Polarographic data for $[Co(DH)_2(PR_3)_2]X^a$

PR_3	pH*	$E_{1/2}$ (V)	"Rev. plot"[b] (mV)	i_dc (μA/mM)	Process	$\frac{[PR_3]\ excess}{[complex]}$
PPh_3	8.55	−0.14 −0.70	90 64	1.83 1.90	III–II II–I	0
$PMePh_2$	6.79	−0.61 −0.75		1.45 1.83	III–II II–I	0
PMe_2Ph	5.47	−0.90	58	4.27	III–I	0
PBu_3	6.52	−0.74	80	3.90	III–I	0
PPh_3	8.66	−0.13 −0.70	80 64	1.85 1.85	III–II II–I	21
$PMePh_2$	6.89	−0.75	90	3.4	III–I	42
PMe_2Ph	6.28	−0.90	86	4.1	III–I	52
PBu_3	7.23	−0.74	75	4.0	III–I	59
PPh_3	11.65	−0.70	85		III–I	21
$PMePh_2$	11.31	−0.77	65	3.2	III–I	42
PMe_2Ph	11.55	−1.13	(Obscured by maximum)	4.0	III–I	52
PBu_3	12.17	−0.90	57	3.7	III–I	59

[a] Solvent medium, 95% ethanol, 0.10 M $LiNO_3$; all solutions 1 ± 0.2 mM with respect to complex.

[b] $E/\log[i/(i_d - i)]$.

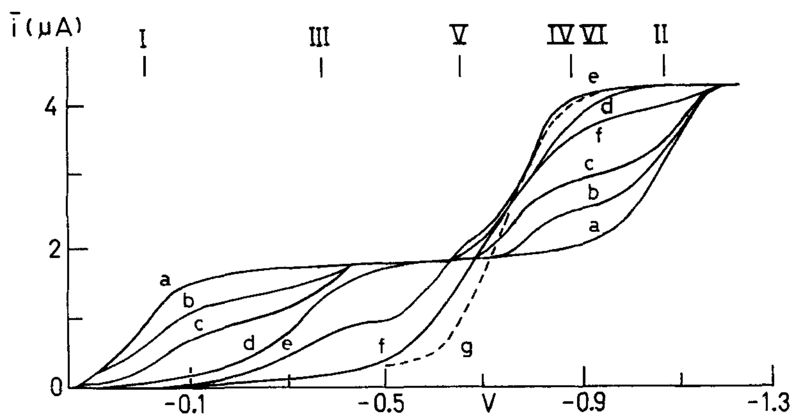

FIGURE 3 Polarographic titration of $[Co(DH)_2(H_2O)_2]^+$ with $PMePh_2$. Moles $PMePh_2$: moles complex: (a), 0, (b) 0.26, (c) 0.52, (d) 0.94, (e) 1.36, (f) 2.09, (g) 12.5.

respond closely to those observed for the bisphosphine complex in a solution containing no excess phosphine. At phosphine:cobalt ratios greater than 2:1 wave V merges into wave VI and the process appears to be a two-electron reduction as previously observed. The negative shift of wave V (Co(III) to Co(II)) as excess ligand concentration is increased is indicative of a system where the reduction process is accompanied by ligand loss. Using the approach of Meites,[11] the number of ligands lost in this case was found to be 0.96 (i.e. approximately 1). In contrast, the Co(II) to Co(I) (wave VI) reduction is insensitive to excess concentration of the axial ligand, indicating no ligand loss during the reduction step.

The titration behaviour is consistent with stepwise formation of the bisphosphine complex (waves V and VI) via the monophosphine species $[Co(DH)_2(PMePh_2)H_2O]^+$ (waves III and IV). Formation of the species corresponding to waves III and IV is essentially complete at the phosphine:cobalt ratio of 1:1 (Figure 4); the complex rapidly diminishes as the species giving rise to waves V and VI is formed, the formation of the latter being complete at the 2:1 ratio.

The polarographic changes observed upon titration with PPh_3 are shown in Figure 5. Analysis of these polarograms is complicated by the occurrence of an oxidation wave in the Co(III)–Co(II) region due to the presence of free PPh_3. However, some tentative observations may be made. Waves at about –0.20 V and –0.70 V completely replace the waves of the diaquo species at phosphine:cobalt ratios in excess of 1:1. Significant further changes do not occur above this ratio, except that the waves become less drawn out. It may be concluded that the monophosphine complex is formed, but that it is not possible to polarographically observe the stepwise formation of the bisphosphine complex, the wave positions apparently being close to those of the one-to-one species.

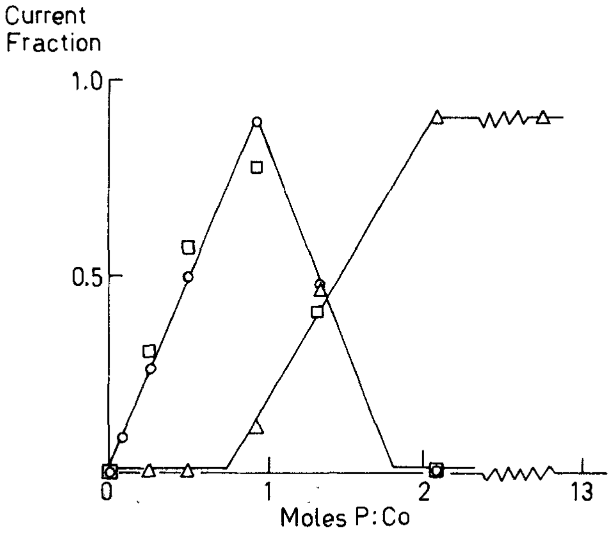

FIGURE 4 Polarographic titration curve, $[Co(DH)_2 \cdot (H_2O)_2]^+$ with $PMePh_2$: ○ $i_{III}/i_{II(initial)}$, □ $i_{IV}/i_{II(initial)}$, △ $i_{VI}/2i_{II(initial)}$.

These latter polarographic data could also be interpreted as indicating that a bisphosphine complex is not formed with PPh_3. However, the complex $[Co(DH)_2(PPh_3)_2]^+$ was synthesized and its uv-visible spectrum was measured. There is no spectral evidence of its dissociation in ethanol solution; it gives an absorbance maximum at 540 nm which does not shift on addition of up to twenty fold excess of phosphine. Furthermore, the triplet signals for dimethylglyoxine and phosphorus methyl protons in the nmr spectrum were measured to assess evidence of exchange of the axial phosphines. Spectra were monitored at temperatures up to 450°K using nitrobenzene and benzonitrile

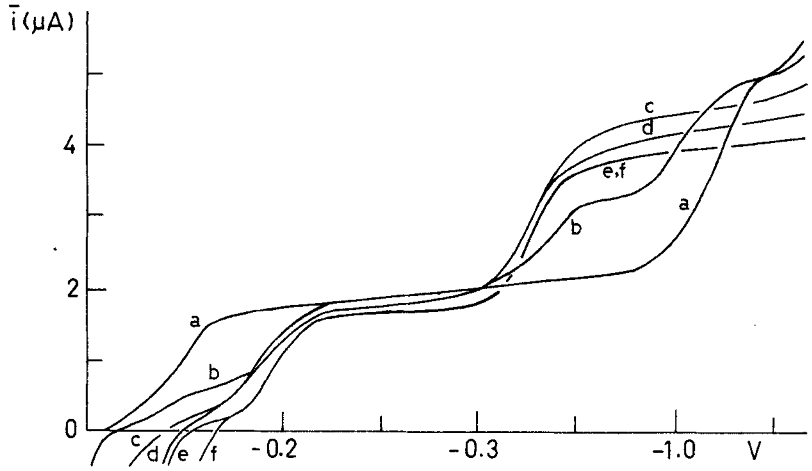

FIGURE 5 Polarographic titration of $[Co(DH)_2(H_2O_2)_2]^+$, 1.07 mM, with PPh_3. Moles PPh_3: moles complex: (a) 0, (b) 0.42, (c) 0.94, (d) 2.2, (e) 5.4, (f) 14.8.

as solvents. No evidence of incipient triplet collapse was observed for PPh_3 or for the other bisphosphine complexes up to this temperature. Decomposition began to occur above 400°K.

In summary, the bisphosphine complexes with PBu_3 and $PPhMe_2$ are apparently formed directly without a stable monophosphine form being observed while the complexes with $PMePh_2$ and PPh_3 exhibit stable monophosphine intermediates. Some of these findings are seemingly at variance with results obtained by Costa *et al.* who reported polarographic behaviour of $[Co(DH)_2(PBu_3)H_2O]^+$, which exhibited two one-electron reduction steps ($E_{1/2}$ −0.525 and −0.752 V) in 95% ethanol.[7] This species was not observed in the present work. However, the polarographic behaviour of the bis-PBu_3 and both mono- and bis-PPh_3 species, as described by these authors, is in reasonable agreement with the polarograms observed in the present work.

An attempt was made to synthesize $[Co(DH)_2(PMe_2Ph)H_2O]^+$ by reacting less than stoichiometric amounts of PMe_2Ph with the diaquo-cobaloxime complex in a methanolic medium using methods described by Costa *et al.*[12] The ^1H nmr spectrum, however, indicated that only the bisphosphine complex was formed; this supports the polarographic evidence that there is no monophosphine intermediate.

A similar situation arises in the work of Costa *et al.*[12] during attempts to isolate species $[Co(DH)_2PR_3X]$ (X is halogen or nitrate); in this case the ion-pair $[Co(DH)_2(PR_3)_2][Co(DH)_2X_2]$ is often isolated instead. The ion-pair is isolated exclusively when PBu_3 is used, but a mixed product containing in part the neutral monophosphine species is obtained when PPh_3 is used. The different behaviour has been ascribed to the relative kinetic trans effects of the two PR_3 groups. In the present experiments, coordination of the first PBu_3 or PMe_2Ph group appears to exert a strong symbiotic influence[13] on the complex, greatly favouring coordination of the second phosphine group as opposed to the solvent molecule in the trans site. The results suggest that the dismutation equilibrium

$$2[Co(DH)_2(PR_3)H_2O]^+ \rightleftharpoons [Co(DH)_2(PR_3)_2]^+ + [Co(DH)_2(H_2O)_2]^+$$

lies far to the right, implying that the equilibrium constant for the reaction

$$[Co(DH)_2(PR_3)H_2O]^+ + PR_3 \rightleftharpoons [Co(DH)_2(PR_3)_2]^+ + H_2O$$

is greater than that for the reaction

$$[Co(DH)_2(H_2O)_2]^+ + PR_3 \rightleftharpoons [Co(DH)_2(PR_3)H_2O]^+ + H_2O$$

The reverse appears to be true for PPh_3 and $PMePh_2$, a conclusion which perhaps suggests an important role for steric as well as electronic factors. We have previously shown[1] that the equilibrium constants for the reaction

$$[CosalenPR_3]^+ + PR_3 \rightleftharpoons [Cosalen(PR_3)_2]^+$$

increase as the cone angles of the tertiary phosphines decrease, irrespective of phosphine donor strengths. In contrast, equilibrium constants for the coordination of the relatively small nitrite ion to similar five-coordinated species[14] increase as the expected electronic *trans* influence of PR_3 decreases, steric effects apparently being unimportant. In the systems under study here it is likely that the large *trans* effects of all four tertiary phosphines[1] would labilize the water (a hard Lewis base) of $[Co(DH)_2(PR_3)H_2O]^+$ towards substitution by the soft phosphorus donors on the soft cobalt(III) Lewis acid.[1] Formation of the bis-phosphine complexes with relatively small PBu_3 and PMe_2Ph would then occur much more readily than with the relatively large $PMePh_2$ and PPh_3.[2,3]

As shown in Table II, all four complexes in the presence of excess ligand undergo single two electron reductions in basic solution at potentials cathodic of those exhibited at lower pH*. Again all waves are polarographically irreversible. The change in polarographic behaviour may be interpreted in terms of dissociation of one oxime proton at low activities of solvated proton, as has been reported for similar complexes with nitrogen and sulphur donors.[15–17]

A conventional pH titration with standardized KOH solution shows for each compound a single inflection, which corresponds to a mole ratio of hydroxide: complex of approximately 1:1. The data are shown in Table III, with calculated pK_a^* values. As was observed for similar complexes of nitrogen donors,[16] no apparent correlation exists between the values of pK_a^* and the donor properties of the axial ligands.

Changes in the electronic spectra of the complexes also occur as the pH* is increased,[15–17] a band in the region 27 to 30 kK shifting to higher frequency (Table IV). These spectrophotometric changes are not sufficiently large to permit calculation of pK_a^*.

A deprotonated complex, $[Co(D)(DH)(PMe_2Ph)] \cdot H_2O$, was obtained from the methanolic eluent of an anion exchange resin using a method described by Costa *et al.*[12] As expected, because of the decrease in formal charge of the complex on deprotonation, the DH and the phosphine methyl resonances in the ^1H n.m.r. spectrum occur 0.29 and 0.12 p.p.m. upfield from the corresponding resonances in the spectrum of

TABLE III

pK_a^* values for oxime–proton dissociation from $[Co(DH)_2(PR_3)_2]^+$ species[a]

PR_3	Protons titrated[b]	pK_a^* [c]
PPh_3	1.05	10.24
$PMePh_2$	0.97	9.89
PMe_2Ph	1.10	10.43
PBu_3	1.05	10.63

[a] Approximately 0.1 m moles of complex + 200 mg excess PR_3 titrated with 0.389 M KOH in 95% EtOH, 0.1 M $LiNO_3$.

[b] Moles (OH^-)/moles (complex) at end point.

[c] pK_a^* = pH* at 0.5 volume of base added to end point.

TABLE IV

Electronic spectra in acidic and basic solutions in 95% EtOH, 0.10 M $LiNO_3$

Complex	pH*	Energy (kK)	log ε
$[Co(DH)_2(PPh_3)_2]^+$	5.24	26.7	4.70
	11.21	29.0	4.73
$[Co(DH)_2(PMePh_2)_2]^+$	5.66	29.4	4.56
	11.83	31.1	4.60
$[Co(DH)_2(PMe_2Ph)_2]^+$	6.08	30.7	4.28
	12.45	31.5	4.22
$[Co(DH)_2(PBu_3)_2]^+$	5.85	30.4	4.04
	12.53	31.1	4.08

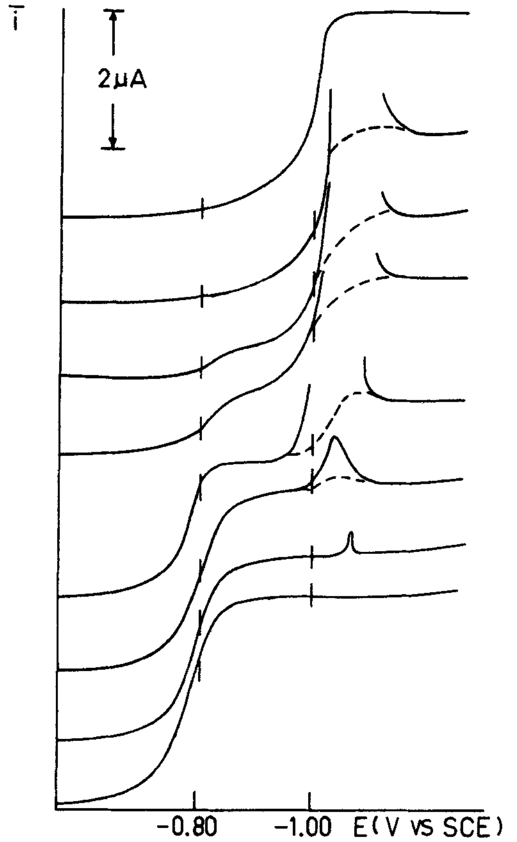

FIGURE 6 Dependence of polarogram of $[Co(DH)_2(PMe_2Ph)_2NO_3$ (0.685 mM) on pH* in 95% ethanol. pH* (bottom to top): 5.47, 9.64, 10.04, 10.36, 11.12, 11.82, 12.58. 12.58 (maximum suppressor added to solution of uppermost polarogram).

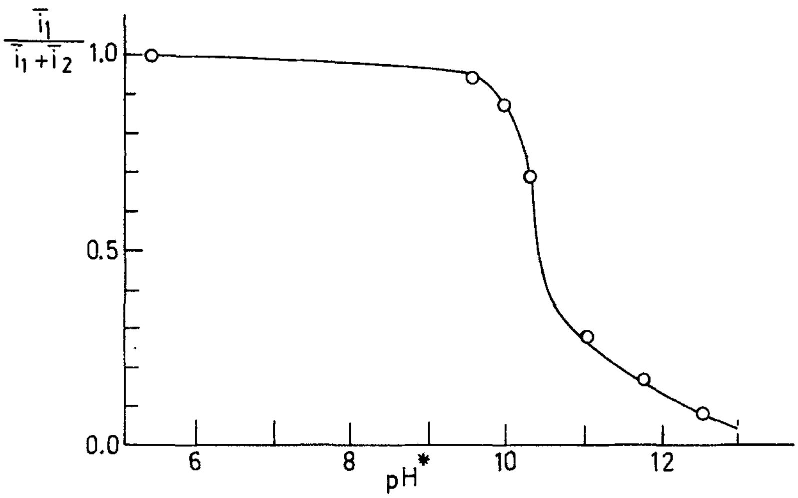

FIGURE 7 Acid dissociation of $[Co(DH)_2(PMe_2Ph)_2]NO_3$ followed polarographically. i_1 corresponds to the diffusion current of the more anodic of the reduction waves, i_2 to the more cathodic wave. Curve corresponds to polarograms of Figure 6.

the cationic complex. The oxime proton resonance could not be observed in CD_3NO_2, but was seen in $CDCl_3$, where integration confirmed that the complex remains in the deprotonated form in this medium. Analogous results were obtained with the deprotonated PBu_3 complex.

Changes in the polarogram of $[Co(DH)_2(PMe_2Ph)_2]NO_3$ as the acidity of the ethanolic solution is varied are shown in Figure 6. Under acidic conditions the polarogram reveals a single cathodic wave (Co(III)–Co(I), see above). As pH* is increased, this wave is systematically diminished at the expense of a more cathodic wave which is reasonably assigned to the corresponding reduction of the species $[Co(D)(DH)_2(PMe_2Ph)_2]$ in view of the above supporting evidence. Employing the relative diffusion currents (i_d) as an estimate of the relative concentrations of the two forms, pK_a^* is obtained as in Figure 7, the value being 10.50. This is in reasonable agreement with that measured potentiometrically (10.43), supporting the wave assignments.

It was not possible to repeat these experiments for the other three complexes because reduction was a two-step process in some cases in the acidic solution.

ACKNOWLEDGEMENT

The National Research Council of Canada is thanked for financial support of this work, including a scholarship to C.W.S.

REFERENCES

1. C. W. Smith, G. W. vanLoon and M. C. Baird, *Can. J. Chem.*, **54**, 1875 (1976).
2. C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).
3. C. A. Tolman, W. C. Seidel and L. W. Gosser, *J. Amer. Chem. Soc.*, **96**, 53 (1974).
4. W. C. Trogler and L. G. Marzilli, *J. Amer. Chem. Soc.*, **96**, 7589 (1974).
5. G. Costa, G. Mestroni, A. Puxeddu and E. Reisenhofer, *J. Chem. Soc. (A)*, 2870 (1970).
6. R. H. Prince and M. G. Segal, *Inorg. Chim. Acta*, **11**, L35 (1974).
7. G. Costa, A. Puxeddu and G. Tauzher, *Inorg. Nuc. Chem. Letters*, **4**, 319 (1968).
8. G. Costa, G. Tauzher and A. Puxeddu, *Inorg. Chim. Acta*, **3**, 41 (1969).
9. G. Costa, A. Puxeddu and E. Reisenhofer, *Coll. Czech. Chem. Comm.*, **36**, 1065 (1971).
10. R. G. Bates, M. Paabo and R. A. Robinson, *J. Phys. Chem.*, **67**, 1883 (1963).
11. L. Meites, *Polarographic Techniques*, Second Edition, John Wiley and Sons, 1965, p. 279.
12. G. Costa, G. Tauzher and A. Puxeddu, *Inorg. Chim. Acta*, **3**, 45 (1969).
13. R. G. Pearson, *Inorg. Chem.*, **12**, 712 (1973).
14. G. Tauzher, G. Mestroni, A. Puxeddu, R. Costanzo and G. Costa, *J. Chem. Soc. (A)*, 2504 (1971).
15. A. V. Ablov and M. P. Filippov, *Rus. J. Inorg. Chem.*, **5**, 1311 (1960).
16. A. V. Ablov and M. P. Filippov, *Rus. J. Inorg. Chem.*, **7**, 525 (1962).
17. A. V. Ablov, B. A. Bovykin and N. M. Samus, *Rus. J. Inorg.*, **11**, 31 (1966).