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Electrochemical Reduction of Protonated Cyclopentadienylcobalt Phosphine Complexes

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Cobalt complexes $CpCo(PR_3)_2$ (M; Cp = η^5-C_5H_5; R = Ph (**1**), Et (**2**), OMe (**3**)) and $CpCoPh_2PXPPh_2$ (X = C_2H_4 (**4**), C_2H_2 (**5**), CH_2 (**6**)) were transformed into the respective protonated salts $[\mathbf{2}H]PF_6$–$[\mathbf{6}H]PF_6$ with NH_4PF_6 in toluene/methanol. The electrochemistry of M as well as $[MH]^+$ was studied at Pt, vitreous-carbon, and Hg electrodes in methylene chloride and propylene carbonate. Equilibrium constants $K_B = 3 \times 10^6$ M and 1.4×10^5 M were determined for the protonation of **3** and **5**, respectively. In all cases a well-defined, chemically irreversible (EC_i), reduction peak, cathodic from the $M^{+/0}$ couple but anodic from the reduction of protons at comparable concentration, was observed for the reduction of $[MH]^+$. The reduction product MH either decays to M and H_2 or can give H_2 via proton–hydride reaction. In the presence of acid, M is reprotonated and a catalytic cycle for hydrogen evolution is formed. Thus, complex **3** is shown to act as a catalyst for hydrogen production at −1.15 V on a Hg cathode from an aqueous solution buffered to pH 5.

Introduction

In view of decreasing energy resources, production of hydrogen by proton reduction, ultimately from water (water splitting) by some cheap energy source like sunlight is still one of the most attractive concepts in the search for an economically and ecologically feasible fuel provision. Chemical cycles based on the conversion of light into redox energy, stored in suitable molecules, besides many other difficulties, face the problem of transferring the redox energy onto protons. A solution has been sought in using colloidal Pt as a microheterogeneous electron-transfer catalyst in solution. An alternative approach consists of binding the proton to be reduced to a Brønstedt base M and transferring the redox energy onto the protonated complex with concomitant opening or weakening of the bond to hydrogen.

In Scheme I a cycle based on this concept is shown. A species M is protonated, giving $[MH]^+$, which is subsequently reduced to an intermediate MH, which may release hydrogen and re-form directly or re-form via M^+, the starting complex M. The route designated by steps d and e appears particularly attractive since it avoids a second-order reaction (of MH) or the intermediacy of hydrogen radicals and partitions the two electrons necessary to form H_2 from H^+ between two separate redox steps.

The requirements for such a cycle to work successfully are severalfold:

(i) $[MH]^+$ and at least one member of the redox pair $M^{0/+}$ (where M of course may be positively or negatively charged by its own) must possess sufficient chemical stability to persist in dilute solution.

(ii) M must possess at least two closely spaced oxidation levels.

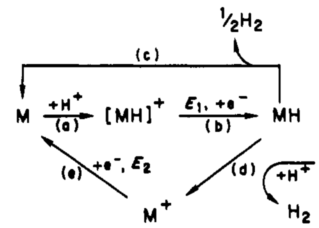
(iii) M should be strong enough a base to be protonated by moderately strong to weak acids.

(iv) None of the redox potentials associated with reduction steps e and b in Scheme I must be too negative; i.e., both M^+ and $[MH]^+$ should be easily reducible species.

Though in principle any base of suitable strength could serve as M, it is evident from the above, in particular from condition ii, that M will be preferably a transition-metal complex ML_n. Many such complexes are known to be readily and reversibly protonated by moderate to strong acids.[1] Moreover, the basicity as well as the redox potentials E_1 and E_2 and finally the protic/hydridic nature of the hydrogen in ML_nH and $[ML_nH]^+$, respectively,[2] may be predictably varied by the choice of suitable ligands L and metals M.

The literature covers a number of reports on the electrochemistry of hydride complexes $[ML_nH]^{p+}$. Complexes studied frequently show redox potentials for $[ML_nH]^+$ near or even to the cathodic side of −2 V (vs. SCE) like the $[M(dppe)_2H_2]^+$ cations (dppe = bis(diphenylphosphino)ethane) with M = Co or Ir.[3]

Scheme I



Similar negative potentials are necessary to reduce $Fe(dppe)_2H$.[4] In this case the anionic reduction product protonates in the presence of proton donors to give stable *cis*-$Fe(dppe)_2H_2$. $[Pt(PEt_3)_3H]^+$ has been supposed to act, after initial reduction to a neutral species adsorbed at the electrode surface, as a catalyst for proton reduction at Hg near −2 V.[5] The iron phosphine complex is an example of those hydrides that are protonated to give stable polyhydrides similar to the metallocene derivatives Cp_2ReH and Cp_2WH_2, which form the cations $[Cp_2ReH_2]^+$ and $[Cp_2WH_3]^+$.

As a first entry into the field we have undertaken a study of the electrochemical reduction of complexes $[CpCo(PR_3)_2H]^+$. Cyclopentadienylcobalt complexes $CpCo(PR_3)_2$ are readily accessible with a variety of phosphine and phosphite ligands and are reported as moderately air-sensitive compounds. Some derivatives have been chemically[6] and electrochemically[7] oxidized to the respective cations $[CpCo(PR_3)_2]^+$, and those with the more basic phosphine ligands have been protonated to stable cationic hydrides $[CpCo(PR_3)_2H]^+$ by mild acids in organic solvents.[1,8] The principal objective of this work was to collect information about the variation of redox potentials E_1 and E_2 with the ligand PR_3 and to get an insight into the course of the follow-up reactions to be expected after electrochemical reduction of $[MH]^+$, in particular, whether a closed cycle for proton reduction via routes c or d/e of Scheme I can be effected with this system.

Experimental Section

All manipulations were carried out under an atmosphere of pure nitrogen with absolute and nitrogen-saturated solvents. The spectrometer used for ^1H NMR measurements was a Bruker SY 80 FT. Electrochemical equipment was EG&G/PAR and has been described previously.[9]

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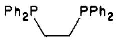
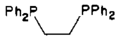
Table I. ^1H NMR Absorptions (δ) of Complexes $CpCo(PR_3)_2$ (**1–6**) (C_6D_6) and $[CpCo(PR_3)_2H]PF_6$ ($[\mathbf{2}H]PF_6$–$[\mathbf{6}H]PF_6$) (CD_2Cl_2)

compd	ligand	lit.	Cp ($^3J_{H-P}$, Hz)	other (J_{H-P}, Hz)	$[Co-H]^+$ ($^2J_{H-P}$, Hz)
1	PPh_3	11	4.40 (0.7)		
$[\mathbf{2}H]PF_6$	PEt_3	8d	5.05^a		−15.1 (75)
3	$P(OMe)_3$	12	4.93 (0.7)	3.54 (5.9) OMe	
$[\mathbf{3}H]PF_6$	$P(OMe)_3$	12	5.20^a	3.65 (6.0) OMe	−13 (80)
4		13	4.70 (0.95)	~1.9 m CH_2	
$[\mathbf{4}H]PF_6$			4.80^a	~2.3 m CH_2	−15.3 (69)
5		14	4.58 (0.52)	6.8–8 m Ph and CH=CH	
$[\mathbf{5}H]PF_6$			4.80^a	6.8–8 m Ph and CH—CH	−15.5 (75)
6			4.80 (0.9)	3.35 (20) CH_2	
$[\mathbf{6}H]PF_6$			5.30^a	3.45 (20) CH_2	−11.7

^{a}Due to the larger sweep width necessary for the protonated complexes digital resolution is insufficient for resolution of the P–H coupling.

Table II. Electrochemical Parameters for the Redox Transitions $M^{+/0}$ and $[MH]^{+/0}$ in Propylene Carbonate (PC) and Methylene Chloride (MC)

		MC			PC			MC	PC
compd	ligand	$\bar{E}(M^{+/0})^a$	ΔE_p, mV	i_a/i_c (v = 100)	$\bar{E}(M^{+/0})^a$	ΔE_p, mV	i_a/i_c (v = 100)	$E_p{}^c([MH]^{+/0})^b$	$E_p{}^c([MH]^{+/0})^b$
1	PPh_3	−0.73^c	60	1.0	−0.74	65	1.0		−0.99^d
2	PEt_3	−1.01^e	60						−1.40
3	$P(OMe)_3$	−0.32	70	1.0	−0.37	100	1.0	−1.3	−1.27
4		−0.575	70	1.0	−0.53	75	1.0	−1.54	−1.44
5		−0.50	70	1.0	−0.49^e	65	0.7	−1.45	−1.34
6		−0.42	60	0.83	−0.44	65	1.0	−1.33	−1.34

^{a}Potentials are in V vs. SCE referred to the ferrocene(+/0) couple; see text. ^{b}Cathodic peak potential for the irreversible (EC_i) reduction of $[MH]^+$ at v = 100 mV/s. ^{c}From a solution of $[M]^+$ (see text). ^{d}Follow-up peak of the reduction of M^+ in the presence of H^+. ^{e}Follow-up peak of a solution of $[MH]^+$ after reduction at −1.40 V.

Phosphine Complexes $CpCo(PR_3)_2$. Compounds $CpCo(PR_3)_2$ have been prepared by various methods (cf. literature given in Table I). We have used the readily accessible ethylene derivative $CpCo(C_2H_4)_2$[10] as the starting compound and have found the following procedure satisfactory for preparing complexes **1–6**.

A 1.8-g (10-mmol) sample of $CpCo(C_2H_4)_2$ was heated together with 20 mmol of the phosphine or phosphite or 10 mmol of the bisphosphine in 10 mL of toluene slowly to reflux. Refluxing was continued for an additional 30 min after the evolution of ethylene had ceased. The dark red solution, after cooling, was filtered through a 2.5 × 10 cm alumina column (4% water) and the filtrate covered with the same volume of pentane. When the pentane diffused into the toluene phase at −30 °C, the complexes crystallized (80–100%). They were purified by repeated recrystallization form toluene/pentane until sharp melting points and satisfactory ^1H NMR spectra were obtained.

Complex **3**, after filtration over alumina and evaporation of the solvent, was crystallized from pentane. Complexes **4** and **5** were chromatographed over alumina with pentane/toluene 10:1 v/v as the eluent.

Protonated Complex Salts $[CpCo(PR_3)_2H]PF_6$. A saturated solution of the phosphine/phosphite complex in toluene was diluted with an equal volume of methanol. Excess NH_4PF_6 was added. When the solutions had been cooled to −30 °C, the protonated salts slowly separated as yellow crystals. They were filtered, washed with toluene, and recrystallized from toluene/methanol 1:1 at low temperature. Yields are near quantitative. ^1H NMR absorptions are given in Table I. Anal. Calcd for $C_{30}H_{27}CoP_2$ (**6**; M_r = 508.4): C, 70.87; H, 5.35. Found: C, 71.08; H, 5.48. Calcd for $C_{31}H_{30}CoF_6P_3$ ($[\mathbf{4}H]PF_6$; M_r = 668.4): C, 55.70; H, 4.52. Found: C, 55.62; H, 4.46. Calcd for $C_{31}H_{28}CoF_6P_3$ ($[\mathbf{5}H]PF_6$; M_r = 666.4): C, 55.87; H, 4.23. Found: C, 55.70; H, 4.38.

The salt $[\mathbf{6}H]PF_6$, after purification, according to its ^1H NMR spectrum, contained a small amount of $[Cp_2Co]PF_6$ that could not be removed. Due to this impurity, which does not interfere with the electrochemistry of the compound, no elemental analysis was effected.

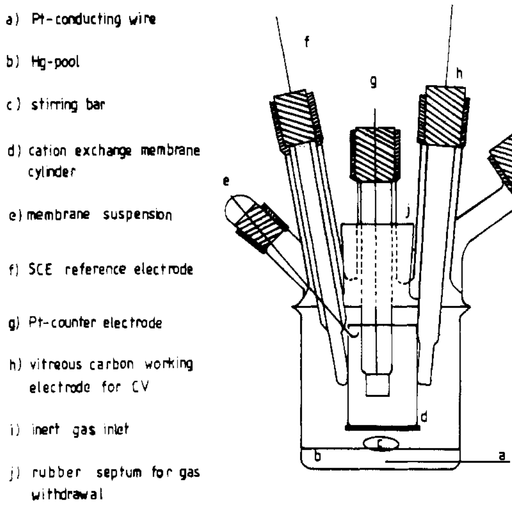


Figure 1. Ion-exchange membrane-divided electrolysis cell for the catalytic decomposition of acids.

Reaction of $[\mathbf{4}H]PF_6$ with Cp_2Co. A 300-mg (0.4-mmol) sample of $[\mathbf{4}H]PF_6$ was stirred with 200 mg (1.06 mmol) of Cp_2Co in 20 mL of methylene chloride at 0 °C for 2 h, during which time the dark solution slowly turned brown-red. The solvent was stripped and the residue extracted with pentane. The pentane solution was filtered through 1 cm of CuCl to remove unreacted Cp_2Co. Concentrating and cooling the solution to −80 °C made the product, $CpCo(C_5H_6)$, crystallize. Yields are about 80%.

Electrochemical Experiments. Cyclic voltammetry at a Pt-bead or vitreous-carbon electrode was done in methylene chloride and propylene carbonate with 0.1 M Bu_4NPF_6 as the supporting electrolyte. Potentials were recorded against the ferrocene/ferrocenium couple and referred to an aqueous SCE by adding some ferrocene to the solution at the end of each measurement and recording the cyclic voltammogram of the $Fc^{+/0}$ couple in the same solution. $E_{1/2}(Fc^{+/0})$ vs. SCE was found as +0.40 V in methylene chloride and +0.370–+0.375 V in propylene carbonate.

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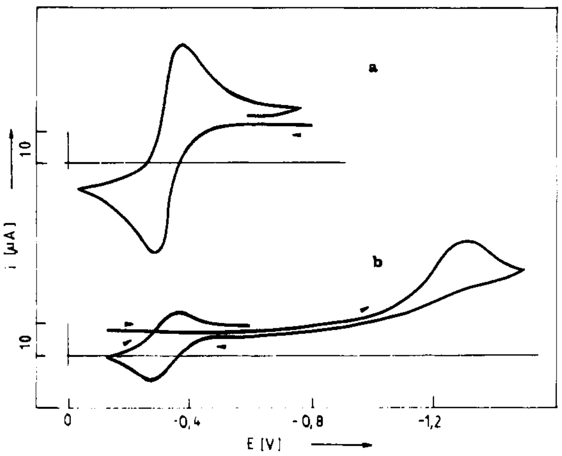

Figure 2. Cyclic voltammogram of (a) **3** and (b) [**3**H]PF_6 (10^{-3} M in methylene chloride, Pt-bead electrode, TBAH supporting electrolyte, v = 100 mV/s).

Potentials given in Table II and referred to in the text are recalculated setting $E_{1/2}(Fc^{+/0})$ as +0.40 V vs. SCE in either solvent.

For polarography at the DME and cyclic voltammetry at the HMDE a PAR SMDE 303, modified to operate with the same SCE as the CV solution, was used.

Bulk electrolysis with demonstration of sustained hydrogen evolution was performed in a vacuum-tight round-bottom cell on a Hg-pool cathode. The anode compartment was made from a small round-bottom vessel suspended in the cell consisting of a cation-exchange membrane. Details of the cell construction with provisions for gas withdrawal and CV scans during and after electrolysis are depicted in Figure 1. Hydrogen evolution was monitored by removing portions of the gas volume with a syringe and injecting it onto a Porapack GC column.

Complex [**5**H]PF_6 was reduced with excess NaHg in propylene carbonate. From 0.11 mmol of complex salt, 1.08 mL of H_2 (theoretically 1.26 mL) was evolved and measured volumetrically.

A 3 × 10^{-4} M solution of [**5**H]PF_6 in propylene carbonate was electrolyzed at −1.5 V. After passage of 8.5 C (one-fourth of theoretical), the current began to decrease and hydrogen evolution, as monitored by GC, became slow. CF_3COOH was then added to make the solution 5 × 10^{-3} M in acid and the electrolysis continued. There was an increase in current, and hydrogen gas was formed again.

A 50-mL sample of an aqueous solution buffered to pH 5 with citrate (pH 4.95 before and pH 5.15 at the end of the experiment) and containing 8 × 10^{-5} mol of **3** was electrolyzed at −1.15 V at a Hg-pool cathode with an initial current of 20 mA. Gas samples were withdrawn periodically and GC-analyzed for hydrogen. A linear increase of the hydrogen concentration with the charge consumed was noted. The experiment was stopped after the passage of 160 C, which corresponds to about 20 cycles/molecule.

Results

Redox Behavior of Unprotonated (M) and Protonated ([MH]$^+$) Complexes. It was found that CpCo(phosphine) complexes in dilute solution, as required for electroanalytical experiments, are of considerable air sensitivity. Moreover, the triphenylphosphine derivative, **1**, tends to dissociate in solution. Only compounds **3**, **4**, and **6** could be handled as the neutral complexes in dilute solution. **1** was studied by starting from the cation salt [**1**]PF_6,[6] which appeared thermally more stable than the neutral complex. **2** and **5** in electrochemical experiments were generated in situ from the protonated salts [**2**H]$^+$ and [**5**H]$^+$, respectively. The protonated salts were well-behaved in dilute solution in all cases except the triphenylphosphine derivative, **1**, where salt [**1**H]X has never been isolated and [**1**H]$^+$ is only generated as a transient species in electrochemical cycles. Treatment of bulk quantities of **1** with acid led to unidentifiable products (other than [**1**]$^+$).

From either M$^+$ (**1**) or M (**3**, **4**, **6**) as the bulk solution species, a chemically and electrochemically reversible redox couple at a potential between −0.35 and −0.7 V, henceforth designated E_1, as given in Table II and shown in Figure 2a, is assigned to the M$^{+/0}$ transition. A corresponding peak pair (anodic/cathodic) appears in the cyclic voltammograms of [**2**H]$^+$–[**6**H]$^+$ after having swept through the more cathodic peak at potential E_2 (Figure 2b). The variation of E_1 roughly follows the trend to be expected from the σ-donor capacity of the phosphine ligands. Note the rather cathodic value for the triphenylphosphine derivative, **1**. Obviously the steric strain, which causes this complex to partially dissociate in solution, also facilitates the removal of an electron beyond what could be expected from the effect of ligand basicity.

Starting a cathodic sweep with a solution of [MH]$^+$ ([**2**H]$^+$–[**6**H]$^+$) gives no peak or only a minor peak at E_1 and an irreversible (EC_i) peak at E_2. The peak at E_1 develops at the ensuing anodic sweep, and cycling around E_1 shows the peak pair due to M$^{+/0}$ decreasing by diffusion (Figure 2b). A similar pattern is obtained when the neutral complexes M are studied in the presence of acid. Adding increasing proportions of e.g. CF_3COOH leads to the disappearance of the pair at E_1 and the growing of the peak at E_2. It was confirmed by scanning the acidified supporting electrolyte that no peak near E_2 is due to the acid itself and that the onset of proton reduction is well beyond (cathodic of) E_2 at the respective electrode material. It was found in all cases that the direct reduction of protons in the concentration range in question did not yield a peak but rather a continuous rise in current.[15] These observations are combined evidence that the peak at E_2 is due to the reduction of [MH]$^+$ rather than protons (CF_3COOH or H^+_{solv}[16]) in solution. As seen from Table II the reduction of [MH]$^+$ in any case is distinctly negative and well separated from the M$^{+/0}$ electron transition. At moderate scan rates this reduction appears totally irreversible, and in the absence of extra acid neutral M is regenerated as seen from the appearance of the relevant peak pair (eq 1a). In the presence of extra acid,

$$[MH]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} MH \xrightarrow{k_2} M + {}^1/_2H_2 \tag{1a}$$

$$M + H^+ \xrightarrow{k_1} [MH]^+ \tag{1b}$$

neutral M, generated cathodic from E_1, is reprotonated (eq 1b) and [MH]$^+$ accumulates near the electrode surface when the potential is between E_1 and E_2; thus, no follow-up anodic peak near E_1 is observed when the acid concentration is sufficiently high.

Finally, the same sequence is obtained in the case of **1**, starting with [**1**]$^+$. Neutral **1** is generated cathodic from E_1, and the cyclic voltammogram is as expected for **1**. In the presence of acid, **1** is protonated near the electrode surface and gives rise to the peak for the reduction of [**1**H]$^+$ at E_2 and a diminished or completely absent peak for the oxidation of **1** at E_1.

Reaction 1a was further substantiated by electrochemical or chemical reduction of e.g. [**5**H]$^+$ where **5** was regenerated (see below).

Protonation Equilibrium of CpCo(P(OMe)$_3$)$_2$ (3) and CpCo-(Ph$_2$P(CH)$_2$PPh$_2$) (5). Since protonation of **2**–**6** is effected with NH_4^+ as the acid, K_B values for these complexes in the solvent mixture utilized must be greater than that of ammonia in the same solvent, which can be estimated to be around 10^5 M.[16] This has been proven for **3** and **5** in an experiment where 1 equiv of the neutral complex was added to a 10^{-3} M solution of NH_4PF_6 in propylene carbonate. The reduction peak due to the reduction of protons at −0.95 V disappears on addition of the phosphine or respective phosphite complex, and the peak at the respective potential E_2 for the reduction of [MH]$^+$ instead is seen.

However, it was noted in polarographic and CV experiments that isolated and purified salts [MH]PF_6 always exhibited a small but significant wave due to the unprotonated complex M (Figure 3), indicating a finite dissociation of [MH]$^+$ in solution. Provided protonation/deprotonation of M is not a fast reaction on the time scale of the experiment, as shown below, then starting the scan between E_1 and E_2 the anodic (peak) current, due to the M$^{+/0}$ couple, measures the concentration of M in solution, whereas the cathodic current, pertaining to the reduction of [MH]$^+$, is a measure of the concentration of this species.[17] Thus, the ratio

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[15] The onset of proton reduction at Hg in 5 × 10^{-3} M CF_3COOH in propylene carbonate is at about −1.5 V vs. SCE.

[16] Barretts, W. C., Jr.; Johnson, H. W., Jr.; Sawyer, D. T. *Anal. Chem.* **1984**, *56*, 1890.

Table III. Peak Current Ratios i_a/i_c at E_2 Employing Rapid Scan Rates with Varying Proton Concentration

expt no.	syst	c_{H^+}, M	v, V/s: 1	2	5	10	20
1	$[5H]^+$/vitr C	0	0.30	0.55	0.63	0.70	0.70
2	$[5H]^+$/vitr C	5×10^{-4}	0.30	0.35	0.35		0.50
3	$[5H]^+$/Pt	0	~0	0.2	0.42	0.40	0.74
4		5×10^{-4}	0.24	0.33	0.53	0.60	0.68
5		$\sim 10^{-3}$	...	...	0.57	0.62	...
6	$[5H]^+$/Hg	0	0.4	0.43	0.58		
7		5×10^{-4}			no reoxidation peak		
8	$[4H]^+$/vitr C	0	0.28	0.31	0.40	0.57	0.53
9	$[4H]^+$/vitr C	5×10^{-4}	0	0.32	0.33	0.53	0.50

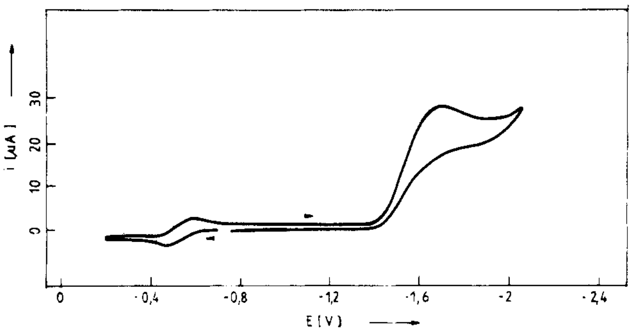
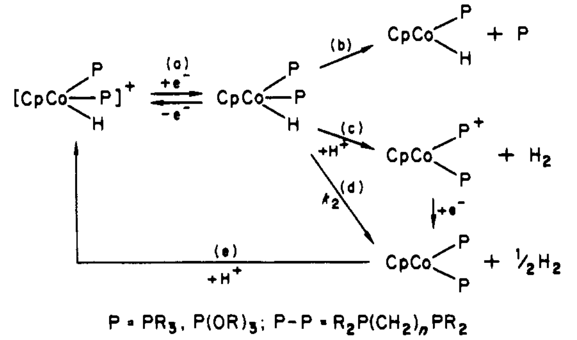


Figure 3. Cyclic voltammogram of $[5H]PF_6$, 6×10^{-4} M in methylene chloride, showing the dissociation of the protonated cation.

Scheme II



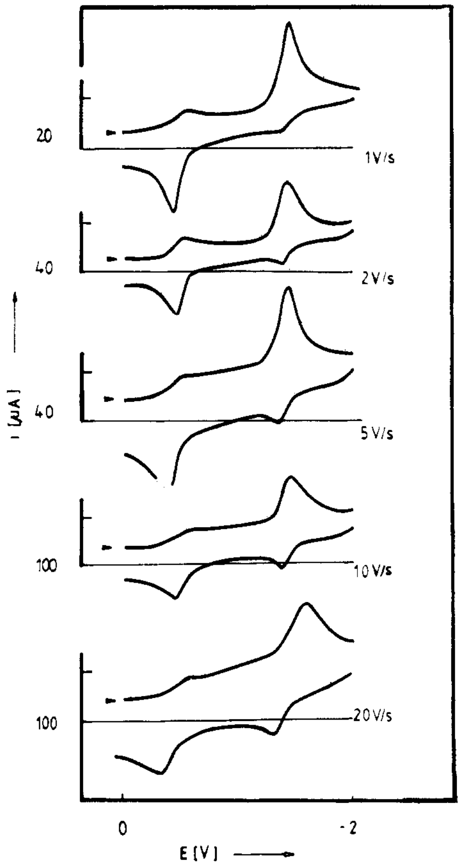


Figure 4. Rapid-scan cyclic voltammograms of $[4H]PF_6$ (8×10^{-4} M in propylene carbonate, Pt-bead electrode, TBAH supporting electrolyte).

Table IV. Peak Current Ratio i_a/i_c for Reduction of $[5H]PF_6$ (Vitreous-Carbon Electrode, Propylene Carbonate, v = 10 V/s) at Different Concentrations of Complex

c, M	i_a/i_c[a]	c, M	i_a/i_c[a]
7.8×10^{-3}	0.36	1.4×10^{-3}	0.44
3.9×10^{-3}	0.43	8.4×10^{-4}	0.48

[a] Average of several experiments.

of these two peak currents or the ratio of the respective polarographic waves gives access to the equilibrium constant K_B of the protonation equilibrium (2). Values of $K_B = 1.4 \times 10^5$ and 3

$$H^+ + M \rightleftarrows [MH]^+ \qquad K_B = c_{[MH]^+}/c_{M^2} \qquad (2)$$

$\times 10^6$ M^{-1} were determined from the dissociation of $[5H]^+$ and $[3H]^+$, respective, in methylene chloride.

Reduction of $[MH]^+$ at Rapid Scan Rates. The lifetime of the neutral species [MH] and the mode of its decomposition were evaluated from rapid-scan experiments at Pt and vitreous-carbon electrodes and at the HMDE. As mentioned above, the reduction of $[MH]^+$ at any electrode material, though diffusion-controlled, has the characteristics of a rapid EC_i process giving rise to an oxidation peak due to M at scan rates up to about 1 V/s. From comparison of the peak heights at E_1 and E_2 a monoelectronic process can be inferred for the reaction at E_2 too generating a transient species MH. The possible reaction paths of MH are detailed for a complex of the type in question in Scheme II. Loss of a ligand P (reaction b) to form a 17-electron intermediate CpCo(P)H appears not completely unreasonable in view of the increasing number of examples that are now documented for cobalt complexes CpCoPX[6,18] but is unlikely in the case of diphos complexes **4**–**6**.

Alternatively, MH may decompose with formation of hydrogen in a second-order process (reaction d) or may react with additional protons and uptake of one further electron as shown in reaction c in Scheme II.

Among the complexes $[MH]^+$ studied, only the diphos compounds $[4H]^+$ and $[5H]^+$ in the solvent propylene carbonate have been found to exhibit increasing reversibility at scan rates >1 V/s at Pt, vitreous-carbon, and Hg electrodes (Figure 4). Peak current

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(17) The proportionality of the peak current at E_2 with the concentration of $[MH]^+$ is disturbed as a consequence of the follow-up decomposition of MH. Nevertheless, this disturbance is small as long as the parameter $\lambda = kET/nFv$ (k being the follow-up rate constant, v being the scan rate) is not exceedingly large. With $k \simeq 10^{-3}$ s^{-1}, $\lambda = 200$, which means that the peak height at E_2 is still a reasonable measure for the bulk concentration of $[MH]^+$.

(18) (a) Koelle, U.; Khouzami, F.; Fuss, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 131; *Angew. Chem. Suppl.* **1982**, 230–240. (b) Raabe, E.; Koelle, U. *J. Organomet. Chem.* **1985**, *279*, C29. (c) Koelle, U.; Fuss, B.; Belting, M.; Raabe, E. *Organometallics* **1986**, *5*, 980.

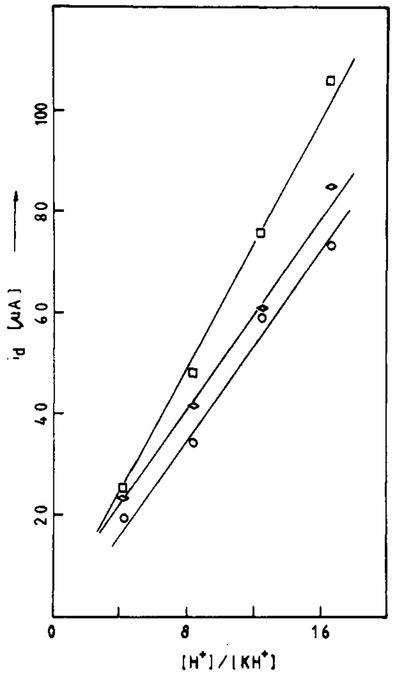

Figure 5. Height of the catalytic wave at the DME for **5**, 6 × 10^{-4} M, in dependence of the concentration of CF_3COOH for three different heights of the mercury reservoir: ○, 31 cm; ◇, 41 cm; □, 51 cm.

ratios are compiled in Table III. As seen from entries 8, 9 and 1, 2 for the complexes $[4H]^+$ and $[5H]^+$ at vitreous carbon, there appears to be a slight decrease in the average of the peak current ratio i_a/i_c when 5 × 10^{-4} M acid (CF_3COOH) is added to the propylene carbonate solution. The effect is more drastic at the Hg electrode, where the anodic peak at E_2 is largest in comparison to the cathodic peak and has completely disappeared at 5 × 10^{-4} M proton concentration. No interpretable effect of added protons on peak current ratios was found in experiments at Pt, where direct proton reduction interferes with reduction of $[MH]^+$ at the necessary acid concentrations.

The feasibility of route d in Scheme II was evaluated by monitoring the peak current ratio with varied concentrations of $[MH]^+$. Results for $[5H]^+$ are given in Table IV. An increase of the peak current ratio with decreasing concentration is clearly indicated, signaling a higher order follow-up reaction of **5**H. Experimental conditions do not allow precise verification of a second-order reaction because the peak current ratios measured are close to the pure kinetic zone where the variation of the peak current ratio with the kinetic parameter $k_2c_0\tau$ (k_2 being the second-order rate constant, c_0 being the bulk concentration of $[MH]^+$, and τ being the time between $E_{1/2}$ and E_λ, the switching potential[19]) is relatively small. Moreover, since it is necessary to employ large values of $E_{1/2} - E_\lambda$ in rapid-scan experiments, the influence of the return potential E_λ on the height of the anodic peak is somewhat uncertain. Introducing experimental parameters into eq 24 of ref 19, which was derived for a second-order follow-up reaction, yields $k_2 = 5 \times 10^3$ L/(mol s) as a lower value for the rate constant of step d in Scheme II.[20] It can thus be concluded that both reaction c and d are contributing to the decomposition of MH depending on the concentration of $[MH]^+$ and that of protons.

Catalyzed Generation of Hydrogen. Polarographic Experiments. Reprotonating M, generated at E_2, closes the catalytic cycle for hydrogen reduction (eq 1b or eq e in Scheme II). The catalytic action of M or $[MH]^+$, respectively, is easily demonstrated when either complex is reduced at the DME and the height of the polarographic wave at E_2 is monitored in dependence of the acid concentration. Results for $[5H]PF_6/CF_3COOH$ in propylene carbonate are given in Figure 5. The increase of i_d with the acid concentration for ratios of H^+:**5** up to 16 clearly demonstrates the catalytic nature of this wave. Note that the increase in current at low to medium proton concentrations follows the proton concentration linearly rather than the familiar $C_{H^+}{}^{1/2}$ dependence expected for a simple catalytic cycle,[21] which implies a higher order dependence from the proton concentration. Under the assumption of a pseudo-second-order reaction the catalytic rate constant $k_2' = 2.4 \times 10^5$ L/s mol, representing reaction paths d and e in Scheme II, is calculated from the experimental parameters. Noteworthy is the fact that no such catalytic current is observed when $[\mathbf{1}]^+$ is reduced at the DME in the presence of acid. In this case the limiting current i_d of the wave at E_2 increases until the ratio $[\mathbf{1}]^+$:H^+ is unity and no further increase occurs at higher acid concentrations. This behavior finds its explanation in the slow protonation of **1** (see below).

Bulk Electrolysis. Catalytic hydrogen evolution in a bulk electrolysis experiment was tested with complex **3** in a closed-cell arrangement (cf. Experimental Section). The neutral complex readily dissolved in an aqueous solution buffered to pH 5 and was electrolyzed at a Hg-pool cathode at −1.15 V over 18 h. Hydrogen evolution was monitored by taking samples from the gas volume and analyzing on a Porapack GC column. A cycle number of about 20/molecule is reached after that time. Electrolysis could have been continued if provision was made for a suitable anode reaction and if protons in the solution were replenished. Extension to an aqueous solution is particularly important if sources other than electrodes for the reducing electrons are envisaged. The experiment, though still running at a rather cathodic potential, demonstrates the feasibility of cyclopentadienylcobalt phosphine complexes to act as catalysts for hydrogen evolution.

Reaction of [CpCo(dppe)H]PF$_6$ ([4H]PF$_6$) with Cobaltocene. It was anticipated that neutral complexes MH should be able to act as a source of hydrogen radicals in the presence of a capable hydrogen acceptor such as cobaltocene (**7**).[22] The hypothesis was tested by reacting $[4H]PF_6$ with cobaltocene in dichloromethane. Analogous to the familiar reaction of cobaltocene with organic electrophiles,[23] a reaction according to eq 3 composed of steps 4 and 5 was expected.

$$2\underset{\mathbf{7}}{Cp_2Co} + [CpCo(dppe)H]PF_6 \rightarrow [Cp_2Co]PF_6 + \underset{\mathbf{8}}{CpCoC_5H_6} + CpCo(dppe) \quad (3)$$

$$Cp_2Co + [CpCo(dppe)H]^+ \rightleftarrows [Cp_2Co]^+ + CpCo(dppe)H \quad (4)$$

$$Cp_2Co + CpCo(dppe)H \xrightarrow{k'} CpCo(dppe) + CpCoC_5H_6 \quad (5)$$

When cobaltocene was reacted with $[4H]PF_6$ in a 2:1 molar ratio in dichloromethane at 0 °C, cobaltocenium salt was formed and the cyclopentadienyl cyclopentadiene complex, **8**, the product of hydrogen transfer to cobaltocene, was isolated in about 80% yield. From the data in Table II and the redox potential of cobaltocene in dichloromethane (−0.85 V vs. SCE) it is obvious that the redox equlibrium 4 is to the left by ~0.7 V, which means a steady-state concentration of $[4H]^+$ of about 2.5 × 10^{-7} M. Such a low concentration is still sufficient to drive reaction 5 if $k' \gtrsim 10^3$ s^{-1}, a figure that seems not unreasonable in view of the unsurpassed radical-scavenging ability of cobaltocene.[22]

Note that complex **8** is not a product or an intermediate in the reaction between cobaltocene and protons.[24] It was also verified

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[19] Olmstead, M. L.; Hamilton, R. G.; Nicholson, R. S. *Anal. Chem.* **1969**, *41*, 260.

[20] The parameter $a\tau = (E - E_{1/2})nF/RT$ is about 37 in the present case as compared to 6, the largest value treated in ref 19. If, at larger values of $E - E_{1/2}$, the influence of $a\tau$ on log ($k_2c_0\tau$), the kinetic parameter, is no longer linear as was assumed in eq 24 of ref 19, log ($k_2c_0\tau$) may in fact be greater up to 1 order of magnitude.

[21] Heyrovski, J.; Kuta, J. *Principles of Polarography*; Academic: London, 1966; p 380 ff.

[22] Herberich, G. E.; Schwarzer, J. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 805.

[23] Kemmit, R. D. W.; Russell, D. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, W., Eds.; Pergamon: Oxford, **1982**; Vol. 5, p 323 ff.

experimentally that cobaltocene does not react with NH_4^+, a stronger Brønstedt acid than [**4**H]$^+$, under comparable conditions. From reaction 3 the intermediacy of neutral MH in the course of the reduction of $[MH]^+$ appears firmly established.

Protonation of $CpCo(PPh_3)_2$ (1) as a Consecutive Reaction. It was noted above that the extent of reoxidation of M, generated at the electrode surface by reduction of either M^+ or $[MH]^+$, is dependent on the proton concentration in solution. With respect to the anodic portion of the wave at E_1 equilibrium 2 is a preceding reaction, and if its establishment was rapid, the relative importance of the anodic wave at E_1 should be independent of the scan rate and solely dependent on the proton concentration. With M^+ initially the bulk solution species the protonation of M is a consecutive reaction and should be easily diagnosed by electroanalytical methods. This type of experiment was performed with **1**, where salts [**1**]X are available, and thus [**1**]$^+$ can be made the bulk solution species.

As with the other phosphine/phosphite complexes, electron transfer $M^{0/+}$ at E_1 was reversible and reasonably rapid for **1**, giving a peak current ratio of unity and a peak potential separation ≤ 100 mV at scan rates up to 1 V/s. In the presence of increasing amounts of acid the anodic/cathodic peak current ratio at E_1 not only drops below 1 but also becomes dependent on the scan rate, signalizing that protonation of **1** in this case occurs at a rate comparable to the electrochemical time window. If one assumes an equilibrium constant K_B of the same order as was determined for **3** and **5**, then the protonation equilibrium (eq 2) also in this case will be far to the right and the protonation can be treated as an irreversible consecutive reaction (EC_i).

Cyclic voltammograms recorded with scan rates $v = 0.05$–0.5 V/s and ratios [**1**]$^+$:H^+ up to 3 qualitatively vary with these two parameters in the expected manner. From a working curve[25] and tables[26] relating the peak current ratio to the kinetic parameter, the pseudo-first-order rate constant $k = 28 \pm 10\ s^{-1}$ is extracted. Even if there is considerable scatter in the individual k values and conditions of a true pseudo-first-order reaction may not be given by a threefold excess of protons over the reacting species, this value nevertheless shows that the protonation of complex **1** is a relatively slow reaction. This in turn explains why compound **1** does not show a catalytic wave at E_2 in the polarogram though it may well be effective in a bulk electrolysis experiment.

Discussion

The principal points that have emerged from the above experiments are summarized as follows:

(i) Cyclopentadienyl(phosphine)cobalt complexes are protonated by ammonium ion in organic solvents. Thus, in a medium containing more than 1 equiv of acid, protonation is virtually complete and complexes $[MH]^+$ are the only species present in solution.

(ii) The electrochemical reduction of the protonated complexes occurs negative from that of the $M^{+/0}$ couple but positive from that of a strong acid in comparable concentration. The primary reduction product is the neutral intermediate MH, which may decay to M and H_2 or may react with more protons in a proton–hydride reaction to form hydrogen, depending on the reaction conditions. In dilute solution the second-order decay of MH can be expected to be slow enough to make the hydride–proton reaction prevail, and the same holds for strongly acidic media. Moreover, in homogeneous solution, where no catalysis by a metal surface is possible, decay of MH may be even slower and the proton–hydride reaction may dominate over a wide concentration range.

Considering the catalytic effect of **5** for the evolution of hydrogen at potential E_2, it is evident from Figure 5 that instead of the simple reaction sequence for a catalytic current where a species Z reacts with the primary reduction product to regenerate the oxidized form,[21] a concentration dependence of the catalytic current on the proton concentration is observed, which points to a process pseudo second order in protons. When the catalytic cycle is written in the form of eq 6 and 7, rate law 8 obtains, which seems to be compatible with the experimental observation.

$$M + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [MH]^+ \qquad K_B = k_1/k_{-1} \tag{6}$$

$$[MH]^+ + H^+ + 2e^- \xrightarrow{k_2} M + H_2 \tag{7}$$

$$dc_{[MH]^+}/dt = c_M[(-k_2/K_B)c_{H^+}{}^2 + k_1] \tag{8}$$

The validity of this assumption in detail depends on a number of concentrations and rate constants. We are presently studying the exact solution of catalytic Scheme I with the variation of parameters in steps a–e to see which set of parameters produces a response similar to the one observed experimentally. Results of this study will be forwarded.

In conclusion, a few remarks in conjunction with the energy balance of the reaction scheme presented seem appropriate and are presented in the terminology of eq 9–13.

$$M + H^+ \rightarrow [MH]^+ \qquad \Delta G_{prot} \tag{9}$$

$$[MH]^+ - e^- \underset{E_2}{\longrightarrow} MH \qquad \Delta G^1 = -E_2F \tag{10}$$

$$MH + H^+ \rightarrow M^+ + H_2 \qquad \Delta G^2 \tag{11}$$

$$2MH \rightarrow 2M + H_2 \qquad \Delta G^3 \tag{12}$$

$$M^+ + e^- \underset{E_1}{\longrightarrow} M \qquad \Delta G^4 = -E_1F \tag{13}$$

The potential E_2 must in all cases be negative of the proton/hydrogen potential at Pt. ΔG_{prot} is negative, and the extra stabilization lent to the proton when it is bound to a basic metal complex M is reflected in a higher endothermic redox energy ΔG^1 ($E_2 < 0$). In redox step 10 a species of high energy is generated; i.e., reaction 10 provides the driving force for (11) or (12), whichever is operative. In case hydrogen evolution is via (11), a further reduction step, eq 13, is involved, which is more energy consuming the more negative E_1 (i.e. species M^+ is highly stabilized). On the other hand, a highly negative value of E_1 can be considered as an extra driving force for reaction 11. Since the enthalpy released in exothermic steps 9 and 11 or 12 is wasted, the overall redox energy necessary for proton reduction via the above cycle is at a minimum in a system where ΔG_{prot} as well as ΔG^2 and ΔG^3 are small, i.e. a metal complex of moderate Brønstedt basicity and with a mildly oxidizing cation M^+, ideally a system where $E_1 \simeq E_2$ and both are in a potential range accessible by optically excited electrons.

From Table II there is no obvious relation between E_1 and E_2 nor is there an apparent dependence of E_2 from the measured (**3**, **5**) or extrapolated (cf. **2** as the strongest basic complex within the series) basicity of the metal complexes. Steric factors appear to be of great importance in protonation equilibria, too. This makes difficult a prediction of E_2 on the basis of the chemical composition of the complexes. On the other hand, it opens a chance to find systems where both redox potentials E_1 and E_2 fulfill the requirements necessary to drive a catalytic hydrogen cycle.

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Registry No. **1**, 32993-07-0; **2**, 79639-49-9; [**2**H]PF_6, 79639-64-8; **3**, 32677-72-8; [**3**H]PF_6, 102588-51-2; **4**, 86365-01-7; [**4**H]PF_6, 102575-82-6; **5**, 33520-47-7; [**5**H]PF_6, 102575-84-8; **6**, 102575-80-4; [**6**H]PF_6, 102575-86-0; $CpCo(C_2H_4)_2$, 69393-67-5; Cp_2Co, 1277-43-6; $CpCo(C_5H_6)$, 33032-03-0; H_2, 1333-74-0.

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(24) The reaction of **7** with protons under suitable conditions gives [**7**]$^+$ and H_2 as the only products. Though **8** also is known to be acid-sensitive, its reaction with protons has been found to be much slower than that of **7** (Koelle, U., to be submitted for publication), which rules out **8** as an intermediate in the overall reaction of **7** with protons.

(25) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

(26) Speiser, B. *Anal. Chem.* **1985**, *57*, 1390.