

Palladium and cobalt complexes of substituted quinoline, bipyridine and phenanthroline as catalysts for electrochemical reduction of carbon dioxide

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Abstract—The complexes of $[M(PPh_3)_2L]X$ (M = Pd, Co; L = substituted quinoline, bipyridine and phenanthroline, and X = Cl, Br or ClO₄) have been found to be an electrocatalyst for the reduction of CO₂ in acetonitrile (AN) and AN-water (8% for volume) solutions containing 0.1 M tetraethylammonium perchlorate (TEAP) at a glassy carbon or Pt electrode. The complexes working as the catalyst were $[M(PPh_3)_2L]X$ [L = 2-methyl-8-hydroxyquinoline (2-m-8-Hq), 2-quinoxalinol (2-Qui.), 1-hydroxyisoquinoline (1-Hiq), 3-hydroxyisoquinoline (3-Hiq), 4,4'-Dimethyl-2,2'-bipyridine (4,4'-dim-2,2'-Bipy) and 4-methyl-1,10phenanthroline (4-m-1, 10-Phen)] at the applied potential of -1.30 V vs Ag/10 mM Ag⁺. Under anhydrous conditions, CO was a dominant product with the current efficiency of 83% and the amount was independent of the kind of the catalysts. In the AN-water solution, however, the reduction products were CO and HCOOH in addition to H₂. © 1997 Elsevier Science Ltd

Key words: Palladium and cobalt complexes, electrochemical reduction, carbon dioxide, substituted quinoline, bipyridine and phenanthroline ligands.

INTRODUCTION

There are currently considerable interests in the chemistry of carbon dioxide due to its role in the greenhouse effect and in the possibility of using CO_2 as a chemical feedstock. The electrochemical reduction of CO₂ is expedited by a variety of homogeneous and heterogeneous catalysis [1]. The most extensively studied homogeneous catalysts are transition-metal complexes containing either macrocyclic or bipyridine ligands [2]. Only a few reports have appeared describing the electrochemical reduction of CO₂ using transition-metal phosphine complexes [3-5]. The electrochemical reduction of CO₂ to CO in acidic acetonitrile or dimethylformamide solutions is catalyzed by [Pd (triphosphine) (solvent)] (BF₄)₂ complexes [3, 6]. Depending on the nature of the triphosphine ligand, these complexes show high catalytic rates and selectivities at relatively positive potentials. On the other hand, the following metal complexes are known as the catalysts for the

reduction of CO_2 to HCOOH: rhodium phosphine [3], phthalocyanine complexes and macrocycles of Co and Ni [7], and ruthenium bipyridine [8]. Thus, the electrochemical reduction of CO_2 can be controlled by changing the central metal and/or the ligand of metal complexes. Although a variety of metal ions has been examined, there are only a few reports concerning the effect of ligands on the catalytic activity of transition-metal complexes [9].

Polypyridyl ligands such as 2,2'-bipyridine or 1,10-phenanthroline have been found to operate in homogeneous catalysis either as electron "reservoirs" in metal complexes [10] or as promoters of catalytic reactions [11]. Certain polypyridyl complexes of the second- and third-row transition metals have been reported to exhibit catalytic activities for the electrochemical reduction of CO₂. In some cases, mechanistic studies have gained an insight into how these reactions occur and into the factors that determine the selectivities and efficiencies of product formation [10].

Recently, we have reported that $[PdCl_2L_2]$ complexes [L = pyrazole (Pyra), 4-methylpyridine (4-

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Mpy) and 3-methylpyrazole (3-Mpyra)] catalyze the electrochemical reduction of CO₂ to afford HCO_2^- in aqueous solutions. The reaction mechanisms were explained as: $[Pd(Pyra)_2]^{2+}$ is first electroreducted to give $[Pd(Pyra)_2]$, and which reacts with CO₂ to form $[Pd(Pyra)_2 (CO_2)]$; the latter complex is protonated to afford $[Pd(Pyra)_2CO_2H]^+$ and finally dissociates to HCOOH and $[Pd(Pyra)_2]^{2+}$ [12]:

$$[Pd(Pyra)_2]^{2+} + 2e^{-} \rightarrow [Pd(Pyra)_2]$$
(1)

$$[Pd(Pyra)_2] + CO_2 \rightarrow [Pd(Pyra)_2(CO_2)]$$
(2)

 $[Pd(Pyra)_2(CO_2)] + H_2O$

$$\rightarrow [Pd(Pyra)_2CO_2H]^+ + OH^- \quad (3)$$

$$[Pd(Pyra)_2CO_2H]^+ + H_2O$$

$$\rightarrow [Pd(Pyra)_2]^{2+} + HCOOH + OH^{-} \quad (4)$$

In order to extend such catalytic process, palladium and cobalt complexes of substituted quinoline, bipyridine and phenanthroline were here used as homogeneous catalysts for the electroreduction of CO_2 , and CO and formate were confirmed to be the reduction products.

EXPERIMENTAL

Spectroscopic measurements

IR spectra were taken for samples in Nujol mulls between NaCl plates on a Shimadzu FT IR-8100M spectrometer. ¹H NMR spectra were recorded at 270.05 MHz on a JEOL EX-270 FT NMR spectrometer, with deutero-dimethyl sulfoxide as solvent and tetramethylsilane as internal standard. UV and visible spectra were recorded with a Shimadzu UV-2200 spectrophotometer in the range 300–900 nm at room temperature.

Electrochemical measurements

Glassy carbon electrodes (Tokai, grade GC-20) of diameter 3 mm were used in most voltammetric experiments unless otherwise stated. The cyclic voltammetric (CV) experiments were carried out in the same way as described before [12]. The electrode potential was measured against Ag/10 mM AgNO₃ + 0.1 M TEAP in AN. Potentiostatic electrolyses were performed by using a H-type two-compartment gastight cell.

Quantitative flow electrolysis experiments were carried out in a simple two-compartment cell reported elsewhere [13]. The working electrode was a bundle of glassy carbon fibers (grade GC-20, Tokai) tied with a Au wire that was served as a lead. The sample solution was flowed into the cell to be electrolyzed before it reached the outlet. Flow rates were regulated with an Atto model SJ-1211 pump. By examining the reduction of ferricyanide, the electrolysis at flow rates up to 4 cm³ min⁻¹ was confirmed to

be quantitative (>98% efficiency) and the number of electrons transferred was directly evaluated from the limiting current.

Gaseous products were analysed with a Shimadzu GC-8A gas chromatograph and the amount of HCOOH produced in the solution was determined with a Hitachi M 655 HPLC.

Chemicals

Reagent-grade AN (Wako Pure Chemicals Co.) used was allowed to stand overnight on CaH₂ distilled over **P**₂**O**₅. Bis(triphenylphosand phine)palladium(II)chloride, 4,4'-dimethyl-2,2'-4-methyl-1,10bipyridine, isocarbostyril and phenanthroline were Aldrich reagent grade. 2-Quinoxalinol, anhydrous sodium perchlorate, dibromobis(triphenylphosphine)cobalt, 2-methyl-8hydroxyquinoline and 3-hydroxyisoquinoline used were Wako reagent grade. Tetraethylammonium perchlorate (TEAP) was dried in vacuum immediately before use. All of these chemicals were used without further purification.

The complexes $[Pd(PPh_3)_2(2-m-8-Hq)]Cl$ (1), $[Pd(PPh_3)_2(3-Hiq)]Cl$ (3), $[Pd(PPh_3)_2(1-Hiq)]Cl$ (4) and $[Co(PPh_3)_2(2-m-8-Hq)Br$ (9) were prepared according to the literature [14-16].

Preparation of [Pd(PPh₃)₂(2-Qui.)]Cl

[Pd(PPh₃)₂Cl₂] (0.20 g, 0.28 mmol) and 2-quinoxalinol (0.30 g, 2.06 mmol) were dissolved in chloroform (35 ml). The mixture was stirred at room temperature for more than 24 h under nitrogen atmosphere and the filtrate was refluxed for *ca*. 3 h. After cooling to room temperature, the brown solid **2** was separated out, washed with chloroform and dried *in vacuo*. This complex was recrystallized from a mixture of chloroform and hexane. Yield 0.38 g (76%), m. pt. 195–196°C (decomp.). Anal: Calc. for C₄₄H₃₆N₂OClP₂Pd: C, 65.03; H, 4.43; N, 3.45; P, 7.64; Pd, 13.11. Found: C, 64.78; H, 4.20; N, 4.00; P, 7.31; Pd, 14.00%. IR (cm⁻¹, Nujol): ν (O—H) 3420, ν (P—Ph) 1460. ¹H NMR [(CD₃)₂SO]: δ 7.31–7.40 (m, PPh₃), 12.5 (s, N=CH).

Reaction between [Pd(PPh₃)₂Cl₂] and 4-methyl-1,10-phenanthroline

[Pd(PPh₃)₂Cl₂] (0.20 g, 0.28 mmol) was dissolved in chloroform (50 ml) and a solution of 4-methyl-1,10phenanthroline (0.10 g, 0.55 mmol) and sodium perchlorate (0.10 g, 0.81 mmol) dissolved in the same solvent (10 ml) was then added. The color was gradually changed from yellow to orange. The mixture was stirred for *ca*. 8 h at room temperature. The orange solid **5** was separated out, washed with methanol and dried *in vacuo*. The thin layer chromatographic examination of the orange solid on silica plate (eluent: petroleum ether:diethyl ether, 1:1, v/v) was made and the purity of the complex was identified by a single spot. Yield 0.25 g (62%), m. pt. 188°C. Anal: Calc. for C₄₉H₄₀N₂O₈Cl₂P₂Pd: C, 57.46;

Table 1.								
UV-VIS	data	for	relevant	complexes	of	palladium	and	cobalt ^a

		$\lambda_{\rm max}$, nm (ε , M ⁻¹) ^b	
No.	Complex	N_2 -Sat.	CO ₂ -Sat.
1	[Pd(PPh ₃) ₂ (2-m-8-Hq)]Cl	375 (1780), 315 (1550)	300 (3300)
2	[Pd(PPh ₃) ₂ (2-Qui.)]Cl	340 (2000), ^c 278 (2300)	360 (1250) ^c
3	[Pd(PPh ₃) ₂ (3-Hiq)]Cl	355 (4700), 300 (3800)	400 (700)
4	[Pd(PPh ₃) ₂ (1-Hiq)]Cl	360 (2200), 295 (3600)	430 (1750)
5	[Pd(PPh ₃) ₂ (4-m-1,10-Phen)](ClO ₄) ₂	480 (800), ^d 355 (6600)	420 (2700), 350 (3700)
6	[Pd(PPh ₃) ₂ (4,4'-dim-2,2'-Bipy)](ClO ₄) ₂	530 (900), 490 (800)	340 (500)
7	$[Co(PPh_3)_2(4-m-1,10-Phen)](ClO_4)_2$	690 (1250), ^d 630 (1000), ^d 350 (1350)	700 (1600), ^d 425 (1800)
8	[Co(PPh ₃) ₂ (4,4'-dim-2,2'-Bipy)](ClO ₄) ₂	520 (1000), 470 (1250)	460 (1050),°
9	[Co(PPh ₃) ₂ (2-m-8-Hq)]Br	380 (1650), 312 (1600)	400 (2300)

^aIn acetonitrile.

^bMolar extinction coefficient at band maximum ($\varepsilon = A/lc$) and values in parentheses.

°Shoulder.

^dBroad.

Key: 2-m-8-Hq = 2-methyl-8-hydroxyquinoline, 2-Qui. = 2-quinoxalinol, 1- and 3-Hiq = hydroxyisoquinoline, 4-m-1,10-Phen = 4-methyl-1,10-phenanthroline, 4,4'-dim-2,2'-Bipy = 4,4'-dimethyl-2,2'-bipyridyl and PPh₃ = bipyridyl and PPh₃ = triphenylphosphine.

H, 3.91; N, 2.74; P, 6.06; Pd, 10.40. Found: C, 58.00; H, 4.00; N, 2.61; P, 6.96; Pd, 11.00%. IR (cm⁻¹, Nujol): v (P—Ph) 1470, v (Cl—O) 1070. ¹H NMR [(CD₃)₂SO]: δ 2.58 (s, 3H), 2.86 (s, 3H), 7.56–7.62 (m, PPh₃), 9.02 (s, N=CH), 9.15 (N=CH).

Reactions between $[Pd(PPh_3)_2Cl_2]$ and 4,4'dimethyl-2,2'-bipyridine, $[Co(PPh_3)_2Br_2]$ and 4methyl-1,10-phenanthroline, and $[Co(PPh_3)_2Br_2]$ and 4,4'-dimethyl-2,2'-bipyridine were performed in a similar way as described above.

RESULTS AND DISCUSSION

Synthesis and characterization of metal complexes

Reaction of bis(triphenylphosphine)palladium(II) with 2-methyl-8-hydroxyquinoline chloride in dichloromethane under N2 atmosphere gave a pale yellow solid [Pd(PPh₃)₂(2-m-8-Hq)]Cl (1). The IR spectrum of the solid showed ring breathing vibrations at 1635, 1590, 1575 cm⁻¹ and C-H out-of-plane deformations at 782, 745, 720 cm⁻¹, characteristic of the quinolate ligand [17]; a sharp band for v (P-Ph) occurred at 1460 cm⁻¹ (triphenylphosphine [17]). The v (O-H) band at 3405 cm^{-1} , observed in the free ligand, was absent in the complex, suggesting the deprotonation of the ligand and the coordination at the oxygen site. Also, the ring breathing band due to v (C=N) at 1610 cm⁻¹ in the free ligand shifted to 1580 cm⁻¹ in the complex [decrease in v (C=N) by 30 cm^{-1}], indicating the coordination through the heterocyclic nitrogen atom [18-20]. In addition, the ¹H NMR spectrum of complex 1 showed low field peaks in the δ 6.85 \pm 0.09 range for the quinolinol 5 and/or 7 hydrogen(s), intimating the presence of N, O-Pd bonds. The ¹H NMR spectra of the complexes 5 and 7 in DMSO showed two sets of methyl signals at δ 2.58 (d, 3H) and 2.88 (d, 3H), phosphine signals at δ 7.51–7.63 (m, PPh₃), ring proton signals at δ 7.65 (d), 7.75 (d), 8.10 (d) and 8.22 (d), and another two signals due to the N=CH protons at δ 9.00 (d) and 9.17 (d). These signals can be assigned in the comparison with palladium and platinum complexes of phenanthroline [21, 22].

The UV-VIS spectra of the parent complexes of $[M(PPh_3)_2L]X$ (M = Pd, Co; L = 2-m-8-Hq, 2-Qui., 4-m-1,10-Phen and 4,4'-dim-2,2'-Bipy; X = Cl, Br or ClO₄) exhibited two main absorption bands under a N₂ atmosphere, except complex 7 (Table 1). The highest absorption at approximately 690 nm for the complex 7 is associated with a $\pi \rightarrow \pi^*$ transition of the coordinated 4-m-1,10-Phen ligand (Fig. 1). There are also intense bands around 350 nm assignable to



Fig. 1. UV-VIS absorption spectra of $[Co(PPh_3)_2(4-m-1,10-Phen)](ClO_4)_2$ in the absence (solid line) and presence (dashed line) of CO₂.

MLCT transitions [23]. These MLCT transition bands are dependent upon the LUMO energy of coordinated ligands, occurring at a lower band for 2 and 9 compared with that for 7. However, the observed MLCT band for 7 appears to be very wide, showing a vibrational structure. Since the 4-m-1,10-Phen system is characterized by two low-lying unoccupied molecular orbitals of comparable energies [24], the visible MLCT absorption of 7 should contain two types of very closely located MLCT transitions, $d \rightarrow \pi$ (8) and $d \rightarrow \pi$ (9), and the order of these in the complex relative to the free ligand is a matter of some interest [25]. The shift of MLCT band to lower frequency for 8 compared with that for 7 is attributed to the lower LUMO energy of the 4,4'-dim-2,2'-Bipy ligand. A moderately strong $(\varepsilon = 9.0 \times 10^2 \,\mathrm{M^{-1} \, cm^{-1}})$ absorption around 530 nm is assigned to a $d \rightarrow d$ transition [26] of the central metal ion.

Complexes 1-9 exhibited one absorption under a CO_2 atmosphere, except complex 5 and 7 (Table 1). The $\pi \rightarrow \pi^*$ absorptions disappear and one new band appear for each of the complexes due to the MLCT (Table 1). The most significant trend in the absorption data of each group is the progressive hypsochromic shift in the MLCT absorption maximum as methyl groups are introdcued. In detail, the effects of methyl substituents on the MLCT transitions of bis(1,10-phenanthroline)copper(I) complexes in terms of inductive and hyperconjugative perturbations of the ligand π orbitals as well as ligand-dependent shifts in the metal 3d orbital energies [27]. The charge-transfer transition can be viewed as an oxidation of the central metal with a concomitant reduction of the (NN) ligand, the observed shifts in absorption maximum are in accord with the prediction based on the acceptor properties of ligands. The spectra of the reduced Pd^{II} and Co^{II} complexes exhibit interligand $\pi \rightarrow \pi^*$ and $\pi^* \rightarrow \pi^*$ transitions in the UV-vis regions [28], the added electrons being localized on separated ligands.

Electrochemical studies of [M(PPh₃)₂L]X complexes under N₂

The cyclic voltammogram of $[Pd(PPh_3)_2(2-m-8-Hq)]Cl$ under N₂ is shown in Fig. 2. CV data obtained for the Pd and Co complexes in 0.1 M TEAP-AN on a glassy carbon electrode are summarized in Table 2. Complexes 1-9 show two successive quasi-reversible, two-electron reductions at potentials between -0.40and -1.25 V vs Ag/10 mM Ag⁺ in AN. The two-electron nature of the reductions for the complexes is supported by two observations. A plot of i_p of the first cathodic current vs the square root of the scan rate ($v^{1/2}$) was linear in the range between 10 and 200 mV s⁻¹, indicating that the charge-transfer reaction is diffusion-controlled. The number of electrons involved in the cathodic waves is the



Fig. 2. Cyclic voltammograms of $0.9 \text{ mM} [Pd(PPh_3)_2(2-m-8-Hq)Cl in AN containing 0.1 M TEAP under a N₂ atmosphere using a glassy carbon electrode.$

difference between the peak potential and the potential at half-height, $E_p - E_{p/2}$. The first cathodic wave also has an $E_p - E_{p/2}$ value of 29 mV at a scan rate of 50 mV s⁻¹. This value agrees well with the 25 mV value expected for a reversible two-electron reduction followed by a fast chemical reaction [29]. Column electrolysis for all of these complexes 1–9 result in the passage of approximately 2.0 electrons per molecule (Fig. 3 and Table 2). Exhaustive electrolysis of all these complexes 1–9 were performed and the *n* values were estimated by equation (5) and the results are given in Table 2.

$$n = it(=Q)/Fcv \tag{5}$$

In equation (5), n is the number of electrons involved in catalyst reduction, *i* is the current, *t* is the time, c is the concentration of substrate, v is the volume of the solution and F is the Faraday constant (*ie* 96,485 C mol⁻¹). The complex $[Pd(PPh_3)_2(4,4'$ dim-2,2'-Bipy)](ClO₄)₂ has been shown to undergo a reversible two-electron reduction and should have a diffusion coefficient almost identical with that of $[Co(PPh_3)_2(4-m-1,10-Phen)](ClO_4)_2$. All of the complexes examined are roughly the same in size and shape, resulting in the similar value of diffusion coefficients. The ratios of the peak current for each triphenylphosphine palladium complex to the analogous cobalt complexes range from 0.90 to 0.78 for solutions of the same concentration. These results indicate that the number of electrons transferred during the reduction of these two complexes is the same and, consequently, the reduction wave at -1.20 V for 7 involves two electrons.

Although the cathodic wave for the triphenylphosphine complex shows a two-electron reduction with relatively fast electron-transfer kinetics, the reoxidation of the reduced species is quite variable. For the $[Pd(PPh_3)_2(4-m-1,10-Phen)](ClO_4)_2$ complex shown in Fig. 4, the reoxidation is facile at low scan rate $(\sim 10 \text{ mV s}^{-1})$ with a ΔE_p of 38 mV and i_{pc}/i_{pa} ratio of 0.89. At a scan rate of 4 V s⁻¹, however, these values were 70 mV and 0.42, respectively.

								$i_{\rm pc}$ (CO ₂)/		
No.	Complex	$E_{ m pa}^{ m l}$	$E_{\rm pc}$	$E_{ m pa}^2$	$E_{ m pc}^2$	$i_{\rm pc}$ (N ₂)	$i_{\rm pc}$ (CO ₂)	$i_{\rm pc}$ (N ₂)	пь	n ^c
_	[Pd(PPh ₃)b(2-m-8-Ha)]Cl ^d	-1.05 (-0.48)	-1.21 (-0.50)	-1.60 (-0.95)	-1.85 (-1.05)	3.2	4.5	1.40	1.96	2.17
. 6	Pd(PPh ₁) ₅ (2-Oui.) Cl ^d	-1.08(-0.40)	-1.18 (-1.25)	-1.60(-1.50)	-1.80 (-1.78)	3.0	3.5	1.17	1.94	2.11
	Pd(PPh ₁) ₆ (3-Hia) Cl ^d	-1.00(-0.50)	-1.15 (-1.05)	-1.55 (-0.95)	-1.70 (-1.45)	3.7	4.8	1.29	2.01	1.90
4	[Pd(PPh ₃) ₂ (1-Hia)]C ⁶	-1.15(-0.55)	-1.25(-0.60)	-1.70(-1.05)	-1.80 (-1.15)	4.5	6.2	1.37	2.01	1.93
ŝ	[Pd(PPh ₁) ₅ (4-m-1,10-Phen)](ClO ₄) ₂	-1.05 (-0.85)	-1.25 (-1.15)	-1.75 (-0.90)	-1.80 (-1.70)	5.5	6.4	1.16	1.98	2.08
9	[Pd(PPh ₁) ₂ (4,4'-dim-2,2'-Bipy)](ClO ₄) ₂	-1.03(-0.90)	-1.20 (-0.98)	-1.75 (-1.35)	-1.79 (-1.50)	3.3	4.8	1.45	1.97	2.17
1	[Co(PPh ₁) _b (4-m-1,10-Phen)](ClO ₄) ₂	-0.95(-0.80)	-1.00 (-0.95)	-1.40 (-1.45)	-1.50 (-1.55)	2.8	3.2	1.14	1.98	2.13
	[Co(PPh ₁) ₅ (4,4'-dim-2,2'-Bipy)](ClO ₄) ₂	-0.90(-0.55)	-1.00 (-1.15)	-1.60(-1.22)	-1.80(-1.38)	6.0	8.5	1.41	1.90	2.12
•	[Co(PPh ₃) ₂ (2-m-8-Hq)]Br ^d	-0.35 (-0.62)	-0.85 (-0.95)	-1.05 (-1.25)	-1.20 (-1.35)	6.0	6.5	1.08	1.95	2.05
1										
^a The	sweep rate was 0.05 V s ⁻¹ .									
ہ - 1	number of electrons transferred (in column ele	otrolweic)								

Cyclic voltammetric data for the $[M(PPh_3)_2L]X$ complexes in 0.1 M TEAP-AN^a Table 2.

 $v_n =$ number of electrons transferred (in column electrolysis). $v_n =$ number of electrons transferred (in exhaustive electrolysis).

^d0.9 mM.

°0.8 mM.

dimethyl-2,2'-bipyridyl and $PPh_3 = triphenylphosphine$.

 E_{μ}^{n} and $E_{\mu}^{n} =$ first anodic and cathodic peak potentials *vs* Ag/Ag⁺ electrode, E_{μ}^{2} and E_{μ}^{2} = second anodic and cathodic peak potentials. i_{μ} (CO₂)/ i_{μ} (N₂) is the ratio of the cathodic peak current in CO₂-sat. to that in N₂-sat. for the first cathodic wave. Parenthese value are under CO₂-sat. Key: 2-m-8-Hq = 2-methyl-8-hydroxyquinoline, 2-Qui: = 2-quinoxalinol, 1- and 3-Hiq = hydroxyisoquinoline, 4-m-1,10-Phen = 4-methyl-1,10-phenanthroline, 4.4'-dim-2,2'-Bipy = 4.4'-

Electrochemical reduction of carbon dioxide



Fig. 3. Relationship between the number of electrons transferred with respect to the potential in 0.1 M TEAP-AN solutions of 1.0 mM $[Pd(PPh_3)_2(4,4'-dim-2,2'-Bipy)](ClO_4)_2$ in column electrolysis.

Electrochemical reduction of CO₂ catalyzed by palladium and cobalt complexes of [M(PPh₃)₂L]X in AN solution

The cyclic voltammogram of $[Pd(PPh_3)_2(2-m-8-Hq)]Cl$ in the presence of CO₂ gives a large cathodic current around -1.05 V vs Ag/Ag⁺, as shown in Fig. 5. This large current is attributed to the electrochemical reduction of CO₂ catalyzed by $[Pd(PPh_3)_2(2-m-8-Hq)]Cl$. The complex $[Pd(PPh_3)_2(2-Qui.)]Cl$ in AN under carbon dioxide atmosphere displays a strong cathode peak around -1.78 V vs Ag/Ag⁺ (Fig. 6), which is more negative than that of $[Pd(PPh_3)_2(2-m-8-Hq)]Cl$. In view of this result, the activation of CO₂ by $[Pd(PPh_3)_2(2-Qui.)]Cl$ may be less effective than that by $[Pd(PPh_3)_2(2-m-8-Hq)]Cl$. The catalytic current in CO₂-saturated AN was observed for all of the complexes examined in the region -0.40 to -1.78 V.

Potentiostatic electrolyses of CO_2 were performed in a H-type cell in AN solutions containing 0.1 M tetraethylammonium perchlorate at -1.30 V. In the solution saturated with CO_2 , the concentration of CO_2 was 0.2–0.24 M [30], being considerably in excess of the catalyst (1 mM in [M(PPh₃)₂L]X). The



Fig. 5. Cyclic voltammograms of $1.0 \text{ mM} [Pd(PPh_3)_2(2-m-8-Hq)Cl in the absence (solid line) and presence (dashed line) of CO₂ in AN with 0.1 M TEAP at a glassy carbon electrode.$

electrolysis experiments were normally conducted for 50-180 min, and after the initial high current levels for reduction the electrocatalytic current level remained fairly constant throughout the remainder of the experiment. Product analyses (Table 3) showed that carbon monoxide was a predominate reduction product. In all cases, control experiments were performed to demonstrate that the product was, in fact, derived from CO_2 and that the reduction of CO_2 was catalyzed by the metal complex; the AN solution in the presence of the metal complex under N_2 and AN solution without the metal complex but with added CO₂ did not produce HCOOH. An increase in the cathodic current is observed in the presence of CO₂ compared with nitrogen. The experiments described here establish that the complex $[M(PPh_3)_2L]X$ is relatively stable and effective as the catalyst for the electroreduction of CO₂ to CO with a current efficiency of 83%. A turnover number of 8 was calculated based on the moles of CO produced per mole of catalyst. There was no formate formation observed in the electrolysis of AN solution with CO₂. The current densities in the electrolysis were almost



Fig. 4. Cyclic voltammograms of 1.0 mM [Pd(PPh₃)₂(4-m-1,10-Phen)](ClO₄)₂ in AN containing 0.1 M TEAP under a N₂ atmosphere using a glassy carbon electrode.



Fig. 6. Cyclic voltammograms of 0.8 mM [Pd(PPh₃)₂(2-Qui.)]Cl in the absence (solid line) and presence (dashed line) of CO₂ in AN with 0.1 M TEAP at a glassy carbon working electrode.

Experiment no	o. Catalyst	Amount of product ^b (CO/µmol dm ⁻³)
1	[Pd(PPh ₃) ₂ (2-m-8-Hq)]Cl	203 (60.2)
2	[Pd(PPh ₃) ₂ (2-Oui.)]Cl	191 (56.7)
3	[Pd(PPh ₃) ₂ (3-Hiq)]Cl	246 (73.0)
4	[Pd(PPh ₃) ₂ (1-Hig)]Cl	251 (74.5)
5	$[Pd(PPh_3)_2(4-m-1,10-Phen)](ClO_4)_2$	205 (60.9)
6	$[Pd(PPh_3)_2(4,4'-dim-2,2'-Bipy)](ClO_4)_2$	273 (81.0)
7	$[Co(PPh_3)_2(4-m-1,10-Phen)](ClO_4)_2$	211 (62.6)
8	$[Co(PPh_3)_2(4,4'-dim-2,2'-Bipy)](ClO_4)_2$	281 (83.4)
9	[Co(PPh ₃) ₂ (2-m-8-Hq)]Br	207 (61.4)

Table 3. Electrochemical reduction of CO_2 catalyzed by palladium and cobalt complexes in acetonitrile⁴

^a-1.30 V vs Ag/Ag+ at a platinum working electrode.

^bCurrent efficiency (%) in parentheses.

Key: 2-m-8-Hq = 2-methyl-8-hydroxyquinoline, 2-Qui. = 2-quinoxalinol, 1- and 3-Hiq = Hydroxyisoquinoline, 4-m-1,10-Phen = 4-methyl-1,10-phenanthroline, 4,4'-dim-2,2'-Bipy = 4,4'-dimethyl-2,2'-bipyridyl and PPh₃ = triphenylphosphine.

same $(2-3 \text{ mA cm}^{-2})$ for the palladium and cobalt complexes with 2-methyl-8-hydroxyquinoline and 4,4'-dimethyl-2,2'-bipyridine, while the rate of CO₂ reduction was somewhat slow when the palladium and cobalt complexes with 4-methyl-1,10-phenan-throline were used as catalysts.

Electrochemical reduction of CO_2 catalyzed by palladium and cobalt complexes of $[M(PPh_3)_2L]X$ in $AN + H_2O$ solution

The reduction of CO_2 was performed in AN-water (8% by volume) solution containing several palladium and cobalt complexes by potentiostatic electrolysis and the results are also shown in Table 4. Addition of H₂O to the electrolytic solution results in a significant amount of formate in addition to CO, indicating that H₂O acts as the proton source as expected. Exhaustive analyses of the electrolytic solution and the gas phase in the test electrode compartment revealed that carbon monoxide and formate was the reduction product of CO₂. In these experiments, the catalytic solutions were exhaustively electrolyzed and the amount of HCOOH, CO and H_2 formed were analyzed by HPLC and gas chromatography. In 1 h, 65 C passed and the product analysis gave carbon monoxide (0.085 mM) and formate (0.15 mM) respectively (Table 4, experiment 1). The initial applied potential was -1.30 V and the next was decreased and reduced gradually to -1.25 V; the current was remarkably stable at that stage. When we corrected for the equivalents needed for the initial two-electron reduction of the complex and noted that two electrons were required for the production of HCOOH, CO and H₂. The current efficiencies of the CO and formate formation are tabulated in Table 4. It can be seen that the total charge passed can be

Table 4.
Electrochemical reduction of CO2 catalyzed by palladium and cobalt complexes in water (8%
by volume)-acetonitrile ^a

		Amount of product ^b		
Experiment no.	Catalyst	CO	$\frac{\text{HCO}_2}{(\mu \text{mol } \text{dm}^{-3})}$	
1	[Pd(PPh ₃) ₂ (2-m-8-Hq)]Cl	85 (25.2)	151 (44.8)	
2	[Pd(PPh ₃) ₂ (2-Qui.)]Cl	81 (24.0)	127 (37.7)	
3	[Pd(PPh ₃) ₂ (3-Hiq)]Cl	107 (31.7)	85 (25.2)	
4	[Pd(PPh ₃) ₂ (1-Hiq)]Cl	105 (31.1)	87 (25.8)	
5	[Pd(PPh ₃) ₂ (4-m-1,10-Phen)](ClO ₄) ₂	106 (31.5)	133 (39.5)	
6	[Pd(PPh ₃) ₂ (4,4'-dim-2,2'-Bipy)](ClO ₄) ₂	149 (44.2)	101 (30.0)	
7	$[Co(PPh_3)_2(4-m-1,10-Phen)](ClO_4)_2$	110 (32.6)	138 (41.0)	
8	[Co(PPh ₃) ₂ (4,4'-dim-2,2'-Bipy)](ClO ₄) ₂	151 (44.8)	98 (29.1)	
9	[Co(PPh ₃) ₂ (2-m-8-Hq)]Br	87 (25.8)	148 (43.9)	

a - 1.30 V vs Ag/Ag + at a platinum working electrode.

^bCurrent efficiency (%) in parentheses.

Key: $2\text{-m-8-Hq} = 2\text{-methyl-8-hydroxyquinoline}, 2\text{-Qui} = 2\text{-quinoxalinol}, 1\text{- and 3-Hiq} = Hydroxyisoquinoline, 4-m-1,10-Phen = 4-methyl-1,10-phenanthroline, 4,4'-dim-2,2'-Bipy = 4,4'-dimethyl-2,2'-bipyridyl and PPh_3 = triphenylphosphine.$



Fig. 7. Cyclic voltammograms of $1.0 \text{ mM} [Pd(PPh_3)_2(2-m-8-Hq)Cl in AN (solid line) and AN-water (dashed line) containing 0.1 M TEAP under CO₂ at a glassy carbon working electrode.$

accounted for by the formation of HCOOH, CO and H_2 . The combined error in the current efficiencies is estimated to be $\pm 10\%$. The total current efficiency for the appearance of the reduction products never approaches 100%. A possible reason for this is the formation of undetected reduction product. Upon addition of H₂O, a current increased in the potential region more negative than -1.0 V due to the generation of hydrogen (Fig. 7). The magnitude of the current enhancement was the same within experimental error at either Pt or glassy carbon electrodes. The current increase was in proportion to the amount of water added. The only reduction product was carbon monoxide in each of two cases and the amount was independent of the kind of the catalyst (Table 4). No formate was detected when complexes 1-9 were electrolyzed in dry AN in the presence of CO_2 .

Coulometric experiments under N₂ are relatively uncomplicated, there is no sign of electrocatalytic behavior and H_2 is not produced as a product. However, it is especially noteworthy that the electrocatalyzed production of H₂ only appears as a pathway in the presence of added CO2. The IR spectrum of the crude product obtained by evaporation of the solution under reduced pressure displayed a v (C==O) band at 1997 cm⁻¹ assignable to $[M(PPh_3)_2L(CO)]^{2+}$. The identification of $[M(PPh_3)_2L(CO)]^{2+}$ and CO_3^{2-} species in the reaction mixture suggests that the reaction of [M(PPh₃)₂L]^o with CO_2 initially produces [M(PPh_3)_2L(COO)], which then undergoes the oxide transfer by another CO₂. The absence of differing reactivity between catalysts in AN-water may be explained by that water is a strong acid in AN and the equilibrium concentration of $[M(PPh_3)_2L(COOH)]^+$ is very small.

The amounts of carbon monoxide increased and formic acid decreased with the increasing donor property of the ligand. For instance, the amount of carbon monoxide generated increased in the order: $[Pd(PPh_3)_2(2 - m - 8 - Hq)]Cl \sim [Co(PPh_3)_2(2 - m - 8 - 4q)]Cl \sim [Co(PPh_3)_2($

Hq)]Br < $[Pd(PPh_3)_2(4 - m - 1,10 - Phen)](ClO_4)_2$ ~ $[Co(PPh_3)_2(4 - m - 1,10 - Phen)](ClO_4)_2$ < $[Pd(PPh_3)_2(4,4' - dim - 2,2' - Bipy)](ClO_4)_2$, whereas that of formic acid decreased in the same order. The amount of carbon monoxide also increased in the order; $[Pd(PPh_3)_2(2-Qui.)]Cl < [Pd(PPh_3)_2(3-Hiq)Cl ~ [Pd(PPh_3)_2(1-Hiq)]Cl.$

Mechanisms

The results of the potentiostatic electrolysis as a function of added H_2O gave an insight into the mechanism. On the addition of water, the HCO_2^-/CO product ratio increased, whereas in dry acetonitrile, the product was only CO. By the analogy with the stoichiometric chemistry of palladium, platinum and nickel triphosphines with CO_2 [3–5] and iron(0) porphyrins complex [31, 32], reasonable mechanistic possibilities may be proposed for the catalytic chemistry. The electrochemical results showed that a two-electron reaction is involved in the initial stage of CO_2 reduction and the proton required in the formation of HCOOH is derived from the added H_2O .

A probable set of reactions are shown in equations (6–11).

$$[\mathbf{M}(\mathbf{PPh}_3)_2\mathbf{L}]^{2+} + 2\mathbf{e}^{-} \rightarrow [\mathbf{M}(\mathbf{PPh}_3)_2\mathbf{L}]^{\circ}$$
 (6)

$$[M(PPh_3)_2L]^\circ + 2CO_2$$

 $\rightarrow [M(PPh_3)_2L(CO)]^{2+} + CO_3^{2-}$

 $[M(PPh_3)_2L(CO)]^{2+} + 2CO_2 + 2e^{-1}$

 $\rightarrow 2CO + CO_3^{2-} + [M(PPh_3)_2L]^{2+}$ (8)

(7)

 $[\mathbf{M}(\mathbf{PPh}_3)_2 \mathbf{L}]^{\circ} + \mathbf{CO}_2 \rightarrow [\mathbf{M}(\mathbf{PPh}_3)_2 \mathbf{L}(\mathbf{COO})] \quad (9)$

 $[M(PPh_3)_2L(COO)] + H_2O$

$$\rightarrow [M(PPh_3)_2 L(COOH)]^+ + OH^- \quad (10)$$

 $[M(PPh_3)_2L(COOH)]^+ + H_2O$

 $\rightarrow [M(PPh_3)_2L]^{2+} + HCOOH + OH^{-} \quad (11)$

The reaction of [M(PPh₃)₂ L]° with CO₂ affording $[M(PPh_3)_2 \ L \ (CO)]^{2+}$ and CO_3^{2-} [equation (7)] possibly proceeds via $[M(PPh_3)_2L(COO)]$ and the subsequent oxide abstraction by CO₂ [5b]. The reductive disproportionation of CO2 affording CO and CO_3^{2-} [equation (8)] in the electrochemical CO_2 reduction by $[M(PPh_3)_2L(CO)]^{2+}$ in the presence of LiBF₄ also could be ascribed to the participation of $[M(PPh_3)_2L]^\circ$ and $[M(PPh_3)_2L(COO)]$ in the catalytic cycle. The electrochemical reduction of CO₂ by $[M(PPh_3)_2L(CO)]^{2+}$ affords CO and CO_3^{2-} [equation (8)]. $[M(PPh_3)_2L(CO)]^{2+}$ is electrochemically reduced by two electrons to give $[M(PPh_3)_2 L]^{2+}$ with CO elimination and $[M(PPh_3)_2L]^{2+}$ reacts with CO₂ to give the σ -CO₂ complex [M(PPh_3)₂L(COO) [equation (9)]. From the fact that both CO and HCO_2^- were generated as products, it can be inferred that the capture of $[M(PPh_3)_2L(COOH)]^+$ by H₂O leads to second intermediates which take part in different ways to give either CO or HCO_2^- . The formation of a doubly hydrogen-bonded complex-opens the route to the cleavage of one of the two C86O binds giving CO within the iron coordination sphere [31].

CONCLUSION

The electrocatalytic reduction of CO_2 was triggered by an initial two-electron reduction of the complex. The catalyst remained intact through a number of redox cycles under conditions where CO or formate were the ultimate products. The appearance of formate anion in the product distribution is favored by added H₂O and there was an element of product selectivity in the catalysis based on water content.

The amounts of products were dependent on the nature of the metal complex operating as the catalyst; carbon monoxide increased and formic acid decreased with increasing the donor property of the ligand. Marked substituent effects were observed upon the electrochemical properties of complexes of the type $[Co(PPh_3)_2(NN)]^+$, especially with respect to substitution at the 4- and 4'-positions of the bipy moiety.

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REFERENCES

- B. P. Sullivan, K. Krist and H. E. Guard, *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide*, Elsevier, New York (1993).
- J. P. Collin and J. P. Sauvage, Coord. Chem. Rev. 93, 245 (1989).
- B. D. Steffey, A. Miedaner, M. L. Maciejewski-Farmer, P. R. Bernatis, A. M. Herring, V. S. Allered, V. Carperos and D. L. DuBois, *Organometallics* 13, 4844 (1994), and references therein.
- P. R. Bernatis, A. Miedaner, R. C. Haltiwanger and D. L. DuBois, Organometallics 13, 4835 (1994).
- (a) A. M. Herring, B. D. Steffey, A. Miedaner, S. A. Wander and D. L. DuBois, *Inorg. Chem.* 34, 1100 (1995); (b) H. Nakajima, Y. Kushi, H. Nagao and K. Tanaka, *Organometallics* 14, 5093 (1995).
- D. L. DuBois and A. Miedaner, *Inorg. Chem.* 25, 4642 (1986); 27, 2479 (1988); A. Miedaner, D. L. DuBois and C. Curtis, *J. Organomet.* 12, 299 (1993).

- (a) S. Kapusta and N. Hackerman, J. Electrochem. Soc. 131, 1511 (1984); (b) K. Takahashi, K. Hiratsuka, H. Sasaki and S. Toshima, Chem. Lett. 305 (1979).
- 8. H. Ishida, H. Tanaka, K. Tanaka and T. Tanaka, J. Chem. Soc., Chem. Commun. 131 (1987).
- 9. B. P. Sullivan and T. J. Meyer, Organometallics 5, 1500 (1986).
- J. R. Pugh, M. R. M. Bruce, B. P. Sullivan and T. J. Meyer, *Inorg. Chem.* 30, 86 (1991), and references therein.
- (a) E. Alessio, G. Zassinovich and G. Mestroni, J. Mol. Catal. 18, 113 (1983); see also: E. Alessio, G. Clauti and G. Mestroni, J. Mol. Catal. 29, 77 (1985); (b) A. Hamnett and P. Christensen, J. Electroanal. Chem. 395, 195 (1995); (c) P. Christensen, A. Hamnett, A. V. G. Muir and J. A. Timney, J. Chem. Soc., Dalton Trans. 1455 (1992).
- A. G. M. Mostafa Hossain, T. Nagaoka and K. Ogura, Electrochim. Acta 41(17), 2773 (1996).
- T. Nagaoka, T. Sasaki, K. Ogura and T. Yoshino, J. Chem. Soc., Faraday Trans. 1 83, 1823 (1987).
- 14. S. Cimini, R. Vgo and G. La Monica, J. Chem. Soc. A 416 (1971).
- Y. S. Sohn and A. L. Balch, J. Am. Chem. Soc. 93, 1290 (1971).
- J. S. Valentine and D. Valentine, J. Am. Chem. Soc. 92, 5795 (1970).
- 17. L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, 3rd ed., Chapman and Hall, London (1975).
- M. T. H. Tarafder and M. A. L. Miah, *Inorg. Chem.* 25, 2265 (1986).
- S. E. Jacobson, R. Tang and F. Mares, *Inorg. Chem.* 17, 3055 (1978).
- H. Mimoun, M. Postel, F. Casabianaca, J. Fischer and A. Mitschler, *Inorg. Chem.* 21, 1303 (1982).
- 21. K. J. Cavell, D. J. Stufkens and K. Vrieze, *Inorg. Chim.* Acta 17, 67 (1980).
- F. P. Fanizzi, F. P. Intini, L. Maresca, G. Natile, M. Lanfranchi and A. Tiripicchio, J. Chem. Soc., Dalton Trans. 1007 (1991).
- 23. R. A. Palmer and T. S. Piper, *Inorg. Chem.* 5, 864 (1966).
- 24. (a) E. M. Kober and T. J. Meyer, *Inorg. Chem.* 24, 106 (1985); (b) W. Kaim, *J. Am. Chem. Soc.* 104, 3833 (1982).
- (a) T. Ito, N. Tanaka, I. Hanazaki and S. Nakakura, Bull. Chem. Soc. Jpn 42, 702 (1969); (b) N. Saunders, J. Chem. Soc., Dalton Trans. 345 (1972); (c) B. Mayoh and P. Day, Theor. Chim. Acta 49, 259 (1978).
- R. R. Ruminski and J. D. Petersen, *Inorg. Chim. Acta* 97, 129 (1985).
- A. A. D. Paggio and D. R. McMillin, *Inorg. Chim.* 22, 691 (1983), and references therein.
- P. S. Braterman and J.-I. Song, J. Org. Chem. 56, 4678 (1991).
- C. P. Andrieux and J. M. Saveant, in *Investigation of Rate and Mechanisms of Reactions* (Edited by C. F. Bernasconi), Vol. 6, 41E, Part 2, p. 331. Wiley, New York (1986).
- T. Nagaoka, N. Nishii, K. Fujii and K. Ogura, J. Electroanal. Chem. 322, 383 (1992).
- I. Bhugun, D. Lexa and J.-L. Saveant, J. Am. Chem. Soc. 118(7), 1769 (1996).
- I. Bhugun, D. Lexa and J.-L. Saveant, J. Am. Chem. Soc. 118(16), 3982 (1996).