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ELECTROCATALYTIC REDUCTION OF CARBON DIOXIDE BY SUBSTITUTED PYRIDINE AND PYRAZOLE COMPLEXES OF PALLADIUM

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Abstract—A series of $[PdCl_2L_2]$ complexes (L = substituted pyridine and pyrazole) has been tried as an electrocatalyst for the reduction of CO₂ in acetonitrile (AN) containing 0.1 M tetraethylammonium perchlorate (TEAP) at glassy carbon or Pt electrodes. The complexes working as the catalyst were $[PdCl_2L_2]$ (L = Pyrazole (Pyra), 4-Methylpyridine (4-Mpy) and 3-methylpyrazole (3-Mpyra)) at an applied potential of -1.10 V vs Ag/10 mM Ag⁺ and the reduction products were formic acid and H₂ with no CO. The current efficiency for the formation of formic acid were 10, 20 and 10.2% for Pd complexes of Pyra, 4-Mpy and 3-Mpyra, respectively. The current efficiency for the hydrogen evolution were 31-54%, and the source of the formate proton and hydrogen was from the added water (4% by volume). Copyright © 1996 Elsevier Science Ltd

Key words: palladium complexes, electrochemical reduction, carbon dioxide, substituted pyridine and pyrazole ligands.

INTRODUCTION

The electrochemical reduction of carbon dioxide has attracted considerable attention as a possible source of carbon for the synthesis of organic molecules and as a possible means of energy storage. Electrochemical reduction of CO_2 has been noted as one practical method, however for selective reduction of CO₂ without evolution of H₂ effective electrocatalysts are required. There have been many reports concerning electrochemical reduction of CO₂ catalysed by transition-metal complexes[1-15], and the products obtained shown to depend on the nature not only of the central metal ions but also of ligands attached. For instance, complexes of Ni and Co with macrocycles[1], palladium phosphine complexes[2] and pyridine complexes of Re[3], Ru[4] and Rh[5] as catalysts are known to generate CO in the electrochemical reduction of CO_2 . On the other hand, catalysts for formation of HCO_2^- are reported for rhodium phosphine complexes[6], phthalocyanine complexes and macrocycles of Co and Ni[7], a palladium-based electrode[8], ruthenium bipyridine complexes[9] and iron-sulphur clusters[10]. Other the reduction are HCHO[11], products in MeOH[12] and CH₄[13], all of which are produced by solid metal catalysts, except for K₂Fe[Fe(CN)₆] which affords MeOH[12a]. Thus, the electrochemical reduction of CO_2 can be controlled by changing the metal ion and/or the ligand of transition-metal catalysts. While a variety of transition-metal ions has been examined there are only a few reports concerning the effect of ligands on the catalytic activity of transition-metal complexes[14].

Electrochemical reduction of carbon dioxide has been fairly intensively studied. The reduction of carbon dioxide at metal electrodes in aqueous solutions usually yields formate and/or carbon monoxide, depending on the kind of metals used, except for a copper electrode where methane and ethylene are produced under appropriate electrolysis conditions[16]. As far as we know no studies have been reported on the monodentate ligand like substituted pyridine and pyrazole complexes of palladium on the reduction of carbon dioxide.

Here we present the synthesis and electrochemical reduction of CO_2 catalyses by palladium complexes of substituted pyridine and pyrazole ligands namely, pyrazole (Pyra), 4-Methylpyridine (4-Mpy) and 3-Methylpyrazole (3-Mpyra) in aqueous solutions to afford HCO_2^- and H_2 as CO_2 reduction product. No CO was detected as a reduction product.

EXPERIMENTAL

Measurements

Infrared 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. Ultraviolet and visible spectra were recorded with a Shimadzu UV-2200 spectrophotometer in the range 300-900 nm at room temperature.

Electrochemical measurements

Cyclic voltammetric (cv) experiments in 0.1 M TEAP-AN (1 mM in metal complex) were done with a Hokuto-Denko HAB-151 potentiostat/scanner.

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The working electrode was a glassy carbon electrode polished immediately before use with $1 \mu m Al_2O_3$, the auxiliary electrode was a platinum wire and the reference electrode was an Ag/10 mM Ag⁺ electrode. All solutions were initially purged for a minimum of 20 min with N₂ or CO₂ gas that were presaturated with AN. Controlled-potential electrolysis (coulometry) experiments 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[17]. The working electrode was a bundle of glassy carbon fibres (grade GC-20, Tokai) tied with a Au wire, a lead of the working electrode. Sample solution flowed into the cell from an inlet and was electrolysed completely before it reached the outlet. Flow rates were regulated with an Atto model SJ-1211 pump. By examining ferrocyanide reduction with the column electrolysis, we found electrolysis to be quantitative (>97% efficiency) at flow rates up to $4 \text{ cm}^3 \text{ min}^{-1}$, and the number of electrons transferred could be evaluated directly from the limiting current up to this flow rate.

Gaseous products were analysed on a Shimadzu GC-8A gas chromatograph equipped with a 2-m column filled with Unibeads 1S and using Ar as a carrier gas for the determination of H_2 . The amount of HCOOH produced in the solution was determined with a Hitachi M 655 HPLC Processor.

Materials

Palladium(II) chloride, anhydrous acetonitrile, vinylpyridines, methylpyridines and pyrazole were used Wako reagent grade and 3-methylpyrazole were Aldrich reagent grade. All of the chemicals were used without further purification in the present studies. Acetonitrile used in the electrochemical experiments was allowed to stand overnight on CaH₂ and distilled over P_2O_5 .

Synthesis

Preparation of bis(acetonitrile)dichloropalladium (II). [PdCl₂(CH₃CN)₂] (No. 1) was prepared by refluxing PdCl₂ in acetonitrile (40 ml) under continuous stirring in nitrogen atmosphere for about 2h. The colour of the solution was red. After 2h refluxing the hot, red solution was filtered and poured into a large volume of petroleum ether (b.p. 40-60°C) with constant stirring until a yellow crystal of complex (No. 1) was separated out. The solid was filtered and washed with petroleum ether, and the last traces of the solvent were removed in vacuo. The thin layer chromatographic examination of the yellow solid on silica plate (eluent: petroleum etherdiethyl ether, 1:1, v/v) was made, and the purity of the complex was identified by a spot exhibited. This complex was recrystallized from a mixture of dichloromethane and ether containing acetonitrile (approximately 5% by volume). Yield 0.51 g (51%), $m.p. = 128 - 129^{\circ}C.$ Elemental analysis: $C_4H_6N_2Cl_2Pd$ (% Calc. C: 18.50, H: 2.31, N: 10.79, Pd: 41.02; % Found C: 18.28, H: 2.32, N: 10.74, Pd: 41.90). Ir (cm⁻¹, Nujol): $v_{(C \equiv N)} = 2305$. ¹H-NMR [(CD₃)₂SO]: δ (ppm): 2.15 (s, CH₃). Uv/Vis spectrum (λ_{max} , nm): 340, 375.

Reaction between $[PdCl_2(CH_3CN)_2]$ and 2-(1.34 mmol) of vinylpyridine. 0.35 g [PdCl₂ (CH₃CN)₂] and 2-vinylpyridine (0.28 g, 2.66 mmol) were dissolved in warm benzene (25 ml). The mixture was stirred at room temperature for about 15h. A pale yellow solid separated out, it was filtered, washed with benzene, and dried in vacuo. TLC examination showed high purity of the complex (No. 3). Yield 0.27 g (77%), m.p. = $198-199^{\circ}C$ (dec.). Elemental analysis: C₁₄H₁₄N₂Cl₂Pd (% Calc. C: 43.37, H: 3.61, N: 7.22, Pd: 27.47; % Found C: 43.82, H: 3.60, N: 7.14, Pd: 28.30). Ir (cm⁻¹, Nujol): $v_{(C=C)} = 1620, 1560, v_{(C-N)} = 1250, 1130, 1110, v_{(C=C-H)} = 990, 975, 935. ¹H-NMR [(CD₃)₂SO]: <math>\delta$ (ppm): 5.75 (d, NCC) = 0.000 (cm) - 0.0 $HC=CH_2$), 6.10 (m, $HC=CH_2$), 9.41 (d, N=CH), 6.92, 7.44 (d, Ar-H). Uv/Vis spectrum (λ_{max} , nm): 480, 820.

Reaction between $[PdCl_2(CH_3CN)_2]$ and pyrazole. 0.35 g (1.34 mmol) of $[PdCl_2(CH_3CN)_2]$ and pyrazole (0.18 g, 2.64 mmol) were dissolved in warm benzene (25 ml). The mixture was stirred at room temperature for about 6 h. A deep yellow solid separated out, was filtered, washed with benzene and dried in vacuo. TLC examination of this solid showed the high purity of the complex (No. 4) and this complex recrystallized from a mixture of dichloromethane and hexane. Yield 0.38 g (79%), m.p. = 217°C. Elemental analysis: $C_6H_8N_4Cl_2Pd$ (% Calc. C: 22.97, H: 2.55, N: 17.87, Pd: 33.95; % Found C: 22.41, H: 3.30, N: 17.89, Pd: 34.80). Ir ́¹H- $(cm^{-1}, Nujol): v_{(N-H)} = 2750, 970, 950.$ NMR[(CD₃)₂SO]: δ (ppm): 7.56 (CH=N), 7.86 (N=CH). Uv/Vis spectrum (λ_{max} , nm): 450, 725.

Reaction between [PdCl₂(CH₃CN)₂] and 4-, 2- and 3-methylpyridine. A solution of [PdCl₂(CH₃CN)₂] (0.35 g, 1.34 mmol) and 4-, 2- or 3-methylpyridine (0.25 g, 2.68 mmol) were dissolved in warm benzene (25 ml). The solution mixture was stirred at room temperature for about 10h, in case of 3- and 4methylpyridines and about 15h in case of 2methylpyridine. A yellow solid (Nos. 5, 6) and pale yellow (No. 7) separated out, were filtered, washed with benzene and dried in vacuo. TLC examination of these solids showed the high purity of the complexes (Nos 5-7). All of these complexes were recrystallized from a mixture of dichloromethane and hexane. Yield 0.26 g (85%), m.p. = $214-215^{\circ}C$ (dec.) (No. 5); 0.18 g (61%), m.p. = 220-222°C (dec.) (No. 6); 0.19 g (63%), m.p. = 210° C (No. 7), was identified different spectroscopic method. Elemental by analysis: C₁₂H₁₄N₂Cl₂Pd (% Calc. C: 39.62, H: 3.85, N: 7.70, Pd: 29.28; % Found C: 39.57, H: 3.73, N: 7.71, Pd: 29.70). Ir (cm⁻¹, Nujol): v (CH₂) = 1450, 1375. ¹H-NMR [(CD₃)₂SO]: δ (ppm): 2.59 (d, CH₃), 3.44 (s, CH₃), 8.64, 8.98 (CH=N), 7.30, 7.46, 7.85 (d, Ar-H). Uv/Vis spectrum (λ_{max} , nm): 380, 740.

Reaction of $[PdCl_2(CH_3CN)_2]$ with 3-methylpyrazole. 3-methylpyrazole (0.20 g, 2.43 mmol) and $[PdCl_2(CH_3CN)_2]$ (0.20 g, 0.77 mmol) were dissolved in warm benzene (30 ml). This solution was stirred at room temperature for about 12 h. During this time no precipitate was formed, but a clear deep yellow solution was observed. After 12 h, this solution was filtered and the filtrate was concentrated to a small volume (5 ml) and the solid precipitated as a yellow crystal separated out by addition of hexane (30 ml). The precipitated product was filtered, washed with hexane and dried *in vacuo* at room temperature. TLC examination showed high purity of the complex (No. 8). Yield 0.33 g (82%), m.p. = 138°C. An analytically pure sample was obtained by recrystallization from dichloromethane and hexane. Elemental analysis: $C_8H_{12}N_4Cl_2Pd$ (% Calc. C: 28.12, H: 3.51, N: 16.40, Pd: 31.17; % Found C; 28.60, H: 3.67, N: 17.20, Pd: 31.70). *Ir* (cm⁻¹, Nujol): $v_{(N-H)} = 2750$, 970, 950. ¹H-NMR [(CD₃)₂SO]: δ (ppm): 2.18 (s, CH₃), 2.65 (s, CH₃), 12.99 (CH=N), 13.66 (CH=N). *uv*/Vis spectrum (λ_{max} , nm): 460, 800.

RESULTS AND DISCUSSION

Synthesis and characterization of metal complexes

Reaction of palladium(II) chloride with anhydrous acetonitrile under N_2 atmosphere in the refluxing condition results in the formation of [PdCl₂(CH₃CN)₂] complex (No. 1). The presence of coordinated acetonitrile in this complex is indicated by the observation of infrared band $2305 \,\mathrm{cm}^{-1}$. The complex (No. 1) 2305 cm⁻¹, showed the increase in $v_{(C=N)}$: the band was 51 cm^{-1} higher than that (2254 cm^{-1}) found for the free ligand. Hence, the complex (No. 1) is confirmed to be coordinated through the lone pair of electrons on the nitrogen atom. The wave numbers 1155 cm^{-1} and 410 cm^{-1} in CH₃CN belong to the degenerate vibrations of the linear system $(H_3) - C - C \equiv N$, the former being mainly due to a CH₃ rocking vibration, and the latter to a C-C=N bending. Two $v_{(CN)}$ bands are expected: higher wave number band is possibly the combination band arising from the symmetric CH₃ deformation and symmetric C-C stretching modes which appear as weak bands in the range of 1350- 1370 cm^{-1} and $930-950 \text{ cm}^{-1}$, respectively. In addition, the ¹H NMR spectrum of complex (No. 1) exhibits a single resonance at δ 2.15 ppm that is

assigned to the methyl protons of coordinated acetonitrile, while free acetonitrile protons show the signal at δ 2.00 ppm. The chemical shifts of the methyl protons shifted from δ 2.00 ppm in uncoordinated acetonitrile to δ 2.15 ppm in complex (No. 1). Elemental analysis indicates the presence of two acetonitrile ligands per palladium atom. These spectral results are consistent with the formulation of the compound (No. 1) as a square-planar complex.

The acetonitrile ligand is easily displaced from complex (No. 1) by addition of substituted pyridine and pyrazole ligands, equations (1 and 2). Complexes (Nos. 2–8) have been characterized by ¹H NMR

$$PdCl_2 + 2CH_3CN \xrightarrow{reflux}$$

$$[PdCl_2(CH_3CN)_2] \quad (1)$$

$$[PdCl_2(CH_3CN)_2] + 2L \xrightarrow{r \cdot t}$$

$$[PdCl_2L_2] + 2CH_3CN \quad (2)$$

$$(L = 2-, and 4-Vpy, Pyra, 4-, 2-,$$

and 3-Mpy or 3-Mpyra)

spectra, infrared spectra, uv-visible spectrum and elemental analysis. Also described in the Experimental Section the spectroscopic data, all of which are consistent of these complexes. Our spectroscopic measurements are in good agreement with the results reported for some palladium, zinc and copper complexes of various substituted pyridine and pyrazole ligands[18-25].

Electrochemical studies of $[PdCl_2L_2]$ complexes under N_2

The cyclic voltammogram of $[PdCl_2(Pyra)_2]$ under N₂ is shown in Fig. 1. Cyclic voltammetric data obtained for the Pd complexes in 0.1 M



Fig. 1. Cyclic voltammograms of 1.0 mM [PdCl₂(Pyra)₂] in AN containing 0.1 M TEAP under N₂ atmosphere using glassy carbon electrode.

| No. | Complex | E_{pa}^{b} , V | E_{pc}^{c}, V | i _{pc} (N ₂) | i _{pc} (CO ₂) | $\frac{i_{\rm pc}(\rm CO_2)}{i_{\rm pc}(\rm N_2)}$ | n |
|-----|---|------------------|-----------------|-----------------------------------|------------------------------------|--|------|
| 3 | $[PdCl_2(2-Vpy)_2]$ | -0.61 | -1.22 | 4.5 | 5.8 | 1.29 | |
| 4 | [PdCl ₂ (Pyra)] | -0.85 | -1.12 | 4.5 | 5.5 | 1.22 | 1.96 |
| 5 | [PdCl ₂ (4-Mpy) ₂] | -0.91 | -1.15 | 3.9 | 4.4 | 1.13 | 2.01 |
| 6 | [PdCl ₂ (2-Mpy) ₂] | -0.35 | -1.25 | 2.1 | 2.5 | 1.20 | |
| 7 | [PdCl ₂ (3-Mpy) ₂] | -0.40 | -1.20 | 2.5 | 2.8 | 1.12 | |
| 8 | [PdCl ₂ (3-Mpyra) ₂] | -0.84 | -1.15 | 4.5 | 4.9 | 1.08 | 1.98 |

Table 1. Cyclic voltammetric data for the [PdCl₂L₂] complexes in 0.1 M TEAP-AN vs the Ag/Ag⁺ electrode^a

* The sweep rate was 50 mV s^{-1} . * Anodic peak potential. Cathodic peak potential. Key: Vpy = vinylpyridine, Mpy = methylpyridine, Pyra = pyrazole and Mpyra = methylpyrazole.

TEAP-AN at a glassy carbon working electrode are summarized in Table 1. Complexes (Nos. 3-8) show in cyclicvoltammograms a quasi-reversible, twoelectron reductions at potentials between -0.35 and -1.20 V vs Ag/10 mM Ag⁺ in AN. The two-electron nature of the reductions for the complexes is supported by two observations. First, column electrolyses of these complexes (Nos. 4, 5 and 8), result in the passage of approximately 2.0 electrons per molecule (Fig. 2 and Table 1). Second, the cathodic wave at -1.12 V is diffusion-controlled as shown by a linear plot of the peak current (i_n) vs the square root of the scan rate $(v^{1/2})$ between 20 and 200 mV s^{-1} [26]. The number of electrons involved in the cathodic waves is the difference between the peak potential and the potential at half-height, $E_p - E_{p/2}$. $E_{\rm p} - E_{\rm p/2}$ should be 28 mV for a two-electron process and 57 mV for a one-electron process[27]. The 26 mV value observed for $[PdCl_2(Pyra)_2]$ at 50 mV s⁻¹ implies a two-electron reduction. The other complexes listed in Table 1 have $E_p - E_{p/2}$ values ranging from 31-47 mV at 50 mV s⁻¹. These values are less than the 57 mV required for oneelectron processes and are more consistent with a two-electron reduction slightly broadened by slow

electron-transfer processes or uncompensated resistance.

The ratio of the anodic peak current to the cathodic peak current in cyclic voltammogram was approximately 0.7. A ratio of less than 1.0 suggests a chemical reaction following the initial reduction. This reaction is not loss of ligand, because the addition of excess ligand does not increase this ratio[26]. The complex $[Pd(etp)(PEt_3)](BF_4)_2$ has been shown to undergo a reversible two-electron reduction[28] and should have a diffusion coefficient nearly identical with that of [PdCl₂(3-Mpyra)₂]. The ratio of the peak current of the cathodic wave at -1.15 V of No. 8 to the peak current of the two-electron reduction wave of [PdCl₂(Pyra)₂] is 0.82 for the solutions of the same concentration. This result indicates that the number of electrons transferred during the reduction of these two compounds is the same, and consequently the reduction wave at -1.15 V for No. 8 involves two electrons.

Cyclic voltammograms for complex of $[PdCl_2(Pyra)_2]$ in AN with 0.1 M TEAP show that an initial 2e reduction occurs at potentials that are similar for the 4-methylpyridine and 3-methylpyrazole complexes (Table 1). The reduction peak is



Fig. 2. Relationship between number of electrons transferred with respect to potential in 0.1 M TEAP-AN solutions of 1.0 mM [PdCl₂(4-Mpy)₂] in column electrolysis.

around -1.20 V for each complex (Nos. 4, 5 and 8). The quasi-reversible, two-electron reductions of these complexes are expected to involve structural changes from square-planar to pseudo-tetrahedral geometries[29].

Electrocatalytic reduction of CO_2

The cyclic voltammogram of $[PdCl_2(Pyra)_2]$ in the presence of CO₂ gives a large cathodic current around -1.30 V vs Ag/Ag⁺ as shown in Fig. 3. This large current is attributed to the electrochemical reduction of CO₂ catalyzed by $[PdCl_2(Pyra)_2]$. The complex $[PdCl_2(3-Mpyra)_2]$ in AN under carbon dioxide atmosphere displays a strong cathode peak around -1.70 V vs Ag/Ag⁺, (Fig. 4) which is more negative than that of $[PdCl_2(Pyra)_2]$. In view of this result, the activation of CO₂ by $[PdCl_2(3-Mpyra)_2]$ may be less effective than that by $[PdCl_2(Pyra)_2]$. The cyclic voltammogram in acetonitrile-water under a carbon dioxide atmosphere, however, shows a large cathodic current around -1.20 V vs Ag/Ag⁺, which may correspond to reduction of CO₂. Thus, $[PdCl_2(3-Mpyra)_2]$ may function as a catalyst for the electrochemical reduction of CO₂, in particular being efficient in acetonitrile-water.

Current enhancement is observed in cyclic voltammograms of solutions saturated in CO_2 , but only for the reversible pyra-based reductions of $[PdCl_2(Pyra)_2]$ (Fig. 3). Current enhancements in CO_2 -saturated AN, which are indicative of the electrocatalyzed reduction of CO_2 , are observed for all



Fig. 3. Cyclic voltammograms of 1.0 mM [PdCl₂(Pyra)₂] in the absence (----) and presence (----) of CO₂ in AN with 0.1 M TEAP at a glassy carbon electrode.



Fig. 4. Cyclic voltammograms of 1.0 mM [PdCl₂(3-Mpyra)₂] in the absence (----) and presence (----) of CO₂ in AN with 0.1 M TEAP at a glassy carbon working electrode.

of the complexes except $[PdCl_2(2-Vpy)_2]$, $[PdCl_2(2-Mpy)_2]$ and $[PdCl_2(3-Mpy)_2]$ in the region -1.0 to -1.6 V.

Controlled-potential electrolyses were performed in a H-type two-compartment gastight cell by using electrolyte solutions that were 0.1 M in tetraethylammonium perchlorate (TEAP) in AN at -1.10 V. They were purged with CO₂ for a minimum of 20 min prior to the electrolysis. With the solutions saturated in CO₂, [CO₂] = 0.2-0.24 M[30], the concentration of CO₂ is considerably in excess of the catalyst (1 mM in [PdCl₂L₂] (L = Pyra, 4-Mpy, 3-Mpyra)). The electrolysis experiments were normally conducted for 40-100 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 2) showed that formate and H_2 were the predominate reduction products. Gas chromatography was used to determine the composition of the gases above the solution after electrolysis. No HCOOH was detected in control experiments in which no catalyst was present. In all cases control experiments were performed to demonstrate that the products were, 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 CO_2 did not produce HCOOH. No formate was detected when complexes 4, 5, or 8 were electrolyzed in dry AN in the presence of CO_2 . However, when water (4%) was added to the closed cell containing one of the complexes generated under these conditions, both HCOOH and H₂ were formed, and catalytic activity under electrolysis began.

The experiments described here establish that the complex $[PdCl_2L_2]$ is relatively stable, facile electrocatalyst for the reduction of CO₂ to formate forming. The reduction is initiated following an initial twoelectron reduction of the complexes. Before no addition of water there was no formate formation observed. But the appearance of formate anion in the product distribution is favored by added H₂O, and there is an element product selectivity in the catalysis based on water content. Large amount of H₂ was evolved which is a good source for the production of formate.

Experiment 1 in added water (4% by volume) (Table 2) is a representative CO_2 electrocatalysis experiment. In 1 h, 60 C passed and product analysis gave formate (0.03 mM) and H₂ (0.095 mM) respectively. 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 both HCO_2^- and H_2 , the current efficiencies were 10% and 31%, respectively for $HCO_2^$ and H_2 . Results obtained in experiments 1 to 3 in Table 2 show that the protons required for the reduction products are derived from the addition of water. In all experiments in Table 2, addition of H_2O to the electrolysis solution results in a significant amount of formate and hydrogen is produced. Apparently, H_2O acts as the proton source for this case, as expected.

The current efficiencies obtained were also 10-22% for HCO₂ and 31-54% for H₂ as shown in Table 2. Exhaustive analyses of the electrolyte solution and the gas phase in the test electrode compartment revealed that formate and H₂ were the sole product of carbon dioxide reduction. Then the fate of the rest of the charges is a matter of discussion; in our experiment, no CO was detected as a reduction product. The effect of added water was studied by cv glassy-carbon Pt electrodes and (scan at rate = $0.2 V s^{-1}$; [PdCl₂(Pyra)₂] = 1.5 mM). At the glassy carbon electrode, there was an initial decrease in the current ratio, i_d/i_{CO_2} as the water concentration was increased. At a Pt electrode under identical conditions, the current ratio, i_d/i_{CO_2} showed a similar dependence on [H₂O] with a slight decrease in i_d/i_{CO_2} , presumably due to hydrogen evolution. The results of the controlled-potential electrolysis experiments as a function of added [H₂O] gave further insight into the mechanism. With added water, the HCO_{2}^{-}/H_{2} product ratio increased, whereas in dry AN, no reduction product was observed.

The influence of the monodentate ligand was also investigated by controlled potential electrolysis. In these experiments, the catalytic solutions were exhaustively electrolyzed, and the amount of HCO₂ and H_2 formed were analyzed by HPLC and gas chromatography. These results were used to calculate the current efficiencies for these products as shown in Table 2. It can be seen that the total charge passed can be accounted for by the formation of H_2 and HCO_2^- . The combined error in the current efficiencies is estimated to be $\pm 20\%$. The electrolysis experiments also provide information on the selectivity and current efficiencies of the various catalysts. Although 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. Such an irrecoverable

 Table 2. Electrochemical reduction of CO₂ catalyzed by palladium complexes in water (4% by volume) acetonitrile^a

| | | Amount of product ^b | | | |
|-----------|---|--------------------------------|---------------------------|--|--|
| Expt. no. | Catalyst | HCO ₂ | $H_2 (\mu mol dm^{-3})$ | | |
| 1 | [PdCl ₂ (Pyra) ₂] | 30.0 (10.0) | 95 (31.0) | | |
| 2 | [PdCl ₂ (4-Mpy) ₂] | 60.0 (20.0) | 138 (41.0) | | |
| 3 | [PdCl ₂ (3-Mpyra) ₂] | 32.0 (10.2) | 166 (54.0) | | |

 * - 1.10 V vs Ag/Ag⁺ at a platinum working electrode. ^b Current efficiency (%) in parentheses. Key: Pyra = pyrazole. Mpy = methyl-pyridine and Mpyra = methylpyrazole.

chemical change in the catalyst could explain why the system gradually moves from the reduction of CO_2 toward H_2 production. However, it is especially noteworthy that the electrocatalyzed production of H_2 only appears as a pathway in the presence of added CO_2 .

Coulometric experiments under N_2 are relatively uncomplicated, there is no sign of electrocatalytic behavior, and H_2 is not produced as a product. The apparent deactivation of the catalytic capabilities of the system may be tied to the appearance of a black strip, insoluble material (experiment 3) that appears as a suspension during catalytic reduction. This material is completely insoluble in common organic solvents. Wet chemical tests, *ie*, complete dissolution in aqua regia, show that the material is not palladium metal. This material may be responsible for ~20% of the reducing equivalents that are not accounted for as H_2 or HCO_2^- .

Possible reduction mechanisms

The low solubility of the complexes and HCOOH product makes the mechanistic experiments difficult. We can, by analogy to the known stoichiometric chemistry of palladium, platinum and nickel triphosphines with $CO_2[2]$, propose reasonable mechanistic possibilities for the catalytic chemistry.

The electrochemical results show that the initial CO_2 reduction chemistry originates in the twoelectron-reduction product $[PdL_2]^0$ and that the proton requirement in the reduction products is derived from the added H₂O. Since $[Pd(Pyra)_2]^{+2}$ must be reduced by 2e before catalysis occurs, and the reduction takes place at the pyra ligands, the pyra (π^*) levels act as electron reservoirs for the net two-electron reduction of CO_2 .

An appealing set of reactions that may play a role are shown in equations 3-5.

$$[Pd(Pyra)_2]^{+2} + 2e \rightarrow [Pd(Pyra)_2]$$
(3)

$$[Pd(Pyra)_2] + CO_2 \rightarrow [Pd(Pyra)_2(CO_2)]$$
 (4)

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

$$\rightarrow [Pd(Pyra)_2CO_2H]^+ + OH^-. \quad (5)$$

The first step involves binding to the highly reduced, electron-rich complex. Although the nature of the presumed complex between $[Pd(Pyra)_2]^{+2}$ and CO₂ and the mode of CO₂ binding are not known, it is tempting to speculate that CO₂ is carbon-bound[31]. Following protonation, a bound formate anion in $[Pd(Pyra)_2CO_2H]^+$ should behave chemically in a fashion analogous to that of bound Cl⁻ in $[Pd(Pyra)_2Cl_2]$, *ie*, rapid dissociation to give $[Pd(Pyra)_2]^{+2}$ for re-entry into the reduction cycle *via* equation (6).

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

$$\rightarrow [Pd(Pyra)_2]^{+2} + HCOOH + OH^-. \quad (6)$$

Finally, the structure of the monodentate ligand appears to exert a major influence over the selectivity of the catalysts, but a clear understanding of this relationship is not yet available.

CONCLUSION

Our results have some important implications about the monodentate palladium complexes for the reduction of CO_2 . These are:

(i) Upon reduction the complexes lose a halide or *pseudo*-halide ligand providing a potential binding site for CO_2 ; (ii) selection of either H_2 or formate as the reduction product is possible depending on the nature of the catalyst; (iii) the pyridine and pyrazole ligands can act as electron acceptor sites at accessible potentials which undoubtedly plays a major role in the chemistry; (iv) the appearance of H_2 as a competitive product; and (v) the appearance of the black strip (expt. 3) during the electrolysis period.

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