

# Hydrogen production using cobalt-based molecular catalysts containing a proton relay in the second coordination sphere†

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Received 31st March 2008, Accepted 19th May 2008

First published as an Advance Article on the web 11th June 2008

DOI: 10.1039/b805309j

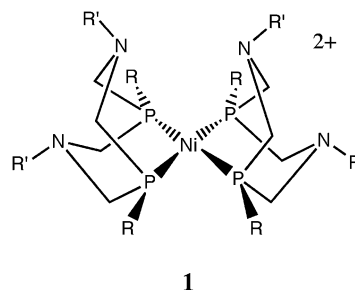
The cobalt analogue of a highly active nickel electrocatalyst for hydrogen production has been synthesized and characterized as  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$ . In the presence of triflic acid in acetonitrile solution, the complex loses one cyclic diphosphine ligand to form  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ , which has been synthesized independently and structurally characterized. The latter complex serves as an electrocatalyst for hydrogen formation with a turnover frequency of  $90 \text{ s}^{-1}$  and an overpotential of 285 mV using bromoanilinium tetrafluoroborate as the acid. A similar cobalt complex with a related diphosphine ligand that does not contain a pendant base is not catalytically active, confirming an important role for the pendant amine in the catalytic reaction.

## Introduction

The development of highly efficient catalysts for the interconversion of electrical energy and fuels could have a significant impact on the feasibility of future energy distribution systems. The simplest fuel is hydrogen, and its production from electricity requires the reduction of two protons by two electrons to form  $\text{H}_2$ . Both platinum metal and hydrogenase enzymes efficiently catalyze this reaction. Because the hydrogenase enzymes use either iron or a combination of iron and nickel in their active sites, these enzymes demonstrate that expensive precious metals such as platinum are not required for this reaction. X-ray diffraction studies have provided information on the structures of the active sites of [FeFe] and [NiFe] hydrogenase enzymes,<sup>1–5</sup> and this has led to efforts to develop simple structural analogs of these active sites with the goal of developing synthetic catalysts and probing mechanistic features.<sup>6–14</sup> Other molecular electrocatalysts for hydrogen production based on first row transition metal complexes have also been reported.<sup>15</sup>

For the [FeFe] hydrogenase enzyme it has been suggested that a pendant base in the second coordination sphere facilitates the heterolytic cleavage of  $\text{H}_2$  and the transfer of the resulting proton to a proton-conduction channel leading to the exterior of the protein.<sup>2</sup> These considerations led us to synthesize nickel and iron complexes containing diphosphine ligands with pendant nitrogen bases that could play a similar role in simple functional models of the active site. These pendant bases can facilitate  $\text{H}_2$  binding, heterolytic cleavage of  $\text{H}_2$ , proton exchange with bases in solution, and proton coupled electron transfer events. These results have been summarized in a recent review.<sup>16</sup>

The facile reversibility of the heterolytic cleavage of hydrogen in the proposed active site implies that the hydride acceptor ability of the iron center and the proton acceptor ability of the base are carefully balanced so that the free energy of this reaction is close to  $0 \text{ kcal mol}^{-1}$ . Studies of those features controlling the hydride acceptor abilities of metal complexes containing diphosphine ligands have also been carried out in our laboratories.<sup>17,18</sup> Efforts to match the hydride acceptor ability of the metal center, controlled largely by features of the first coordination sphere, with the proton acceptor ability of a pendant base in the second coordination sphere, led to the development of nickel-based catalysts for  $\text{H}_2$  production and oxidation having the general features shown in structure **1**. When  $\text{R} = \text{R}' = \text{Ph}$ , the complex  $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2](\text{BF}_4)_2$  serves as a catalyst for the electrochemical reduction of protons to produce  $\text{H}_2$ . When  $\text{R} = \text{cyclohexyl}$  and  $\text{R}' = \text{benzyl}$ , an electrocatalyst for  $\text{H}_2$  oxidation is obtained.<sup>19</sup> Further studies of these catalysts have shown that they are not inhibited by CO concentrations of several percent.<sup>20</sup> In contrast, derivatives of iron(II) that contain two cyclic diphosphine ligands are six coordinate octahedral complexes that do not show catalytic activity.<sup>21</sup>



In an effort to extend this work to other first row transition metals, we report the preparation of new cobalt complexes containing either the cyclic  $\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2$  ligand or other related acyclic diphosphines. Only the derivatives with diphosphine ligands containing pendant amines demonstrated the ability to catalyze the electrochemical reduction of protons to  $\text{H}_2$ . In

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† CCDC reference numbers 683301 and 683302. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b805309j

contrast to nickel complexes, for which optimal catalytic activity is obtained when two cyclic ligands with pendant bases are coordinated to nickel, the catalytic activity for proton reduction observed for  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$  was found to result from loss of a diphosphine ligand to form  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  in the presence of strong acid. The latter complex has been isolated and characterized and shown to be the true electrocatalyst for hydrogen production.

## Results

### Synthesis and characterization of cobalt complexes

The addition of two equivalents of the cyclic diphosphine ligand 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane,  $\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2$ , to an acetonitrile solution of  $[\text{Co}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$  followed by workup provides a convenient synthesis of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$ . Elemental analysis of the product is consistent with this formulation, and a dichloromethane solution of this complex exhibited a broad EPR signal at room temperature with a  $g$  value of 2.11. This value is similar to the values observed previously for  $[\text{Co}(\text{PP}_3)(\text{CH}_3\text{CN})](\text{BF}_4)_2$  ( $g = 2.11$ , where  $\text{PP}_3 = (\text{Ph}_2\text{PCH}_2\text{CH}_2)_3\text{P}$ ) and  $[\text{Co}(\text{dppe})_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$  ( $g = 2.20$ , where  $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) in dichloromethane.<sup>22</sup>

Recrystallization of the new complex from dichloromethane/ethanol solutions at room temperature under a slow stream of nitrogen over a period of two days resulted in the formation of the chloride adduct,  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{Cl})](\text{BF}_4)$ . A mass spectrum obtained using electrospray ionization from acetonitrile solutions showed evidence for a parent cation and a fragment corresponding to the loss of chloride. An X-ray diffraction study was performed on the crystals obtained by slow room-temperature recrystallization from methylene chloride to confirm the nature of this complex. The crystal consists of discrete cations and  $\text{BF}_4^-$  anions. A drawing of the cation is shown in Fig. 1, and a list of selected bond lengths and angles are given in Table 1. The cation is best described as a trigonal bipyramid with the chloride ligand occupying an equatorial position. The relatively small bite angles observed for the two diphosphine ligands ( $81.02^\circ$  and

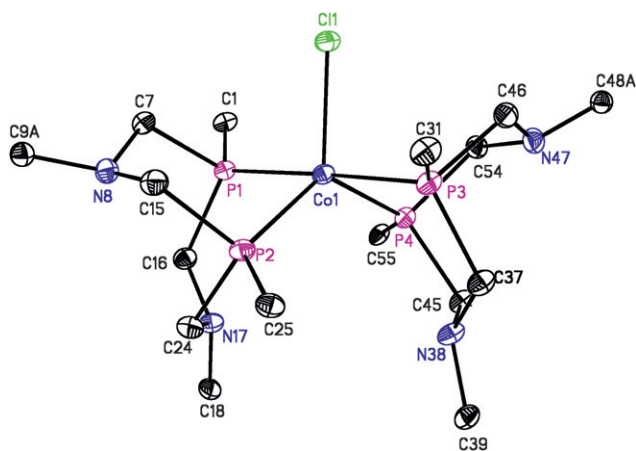
**Table 1** Selected bond distances (Å) and bond angles ( $^\circ$ ) for  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{Cl})](\text{BF}_4)$

Bond distances			
Co(1)–P(1)	2.2133(8)	Co(1)–P(4)	2.2303(8)
Co(1)–P(2)	2.2368(8)	Co(1)–Cl(1)	2.2870(8)
Co(1)–P(3)	2.2014(9)		
Bond angles			
P(1)–Co(1)–P(2)	82.15(3)	P(2)–Co(1)–P(4)	125.04(3)
P(3)–Co(1)–P(4)	81.02(3)	P(1)–Co(1)–Cl(1)	90.30(3)
P(1)–Co(1)–P(4)	100.09(3)	P(2)–Co(1)–Cl(1)	124.55(3)
P(2)–Co(1)–P(3)	95.23(3)	P(3)–Co(1)–Cl(1)	91.57(3)
P(1)–Co(1)–P(3)	177.34(4)	P(4)–Co(1)–Cl(1)	110.40(3)

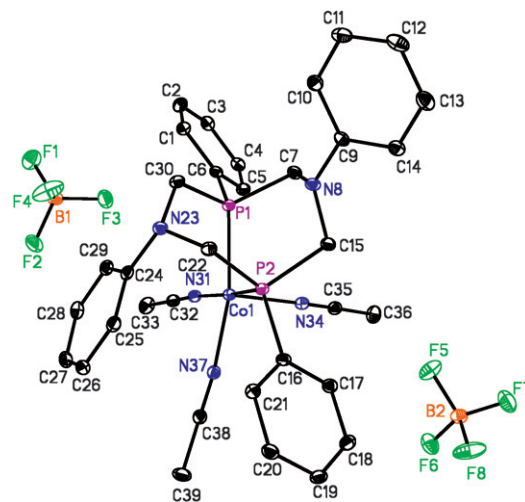
$82.15^\circ$ ) of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{Cl})]^+$  result in a structure that is distorted somewhat from an ideal trigonal bipyramid, but the P1–Co–P3 bond angle of  $177.34^\circ$  formed by the two axial phosphine ligands is close to the ideal  $180^\circ$ .

The addition of one equivalent of either  $\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2$  or 1,3-(diphenylphosphino)propane (dppp) to an acetonitrile solution of  $[\text{Co}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$  followed by workup provides a convenient synthesis of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  and  $[\text{Co}(\text{dppp})(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ , respectively. Structural studies of crystals isolated from these preparations are consistent with their formulations. A perspective drawing and numbering scheme for the structure of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  are shown in Fig. 2, and selected bond distances and angles are given in Table 2. The geometry of the cation is best described as a square pyramid with two acetonitrile ligands and the two phosphorus atoms of the diphosphine ligand forming the basal plane, and the third acetonitrile ligand occupying the axial position.

The Co–N bond length for the axial acetonitrile is  $0.13 \text{ \AA}$  longer than those of the equatorial acetonitrile ligands. The six-membered ring adjacent to the axial acetonitrile ligand adopts a chair conformation to minimize steric interactions. The second six-membered ring of the diphosphine ligand has a boat conformation, and the phenyl ring is folded over the cobalt atom resulting in Co(1)–C(24) and Co(1)–C(25) distances of 3.03 and 3.09 Å, respectively. A similar structure of lower quality has been



**Fig. 1** Drawing of the  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{Cl})]^+$  cation showing atom numbering scheme. Only the *ipso*-carbon atoms of the phenyl rings are shown and the hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 30% probability.



**Fig. 2** Perspective drawing and numbering scheme for  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ . Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at 30% probability.

**Table 2** Selected bond distances (Å) and bond angles (°) for [Co(P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)(CH<sub>3</sub>CN)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub>

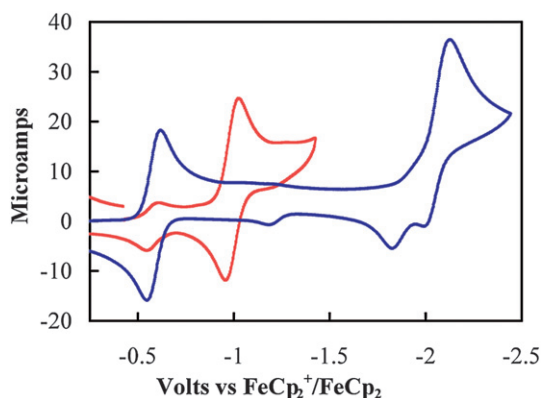
Bond distances			
Co(1)–P(1)	2.1918(5)	Co(1)–N(34)	2.0776(15)
Co(1)–P(2)	2.1978(5)	Co(1)–N(37)	1.9427(15)
Co(1)–N(31)	1.9516(15)		
Bond angles			
P(1)–Co(1)–P(2)	82.450(17)	N(34)–Co(1)–P(1)	98.58(4)
N(31)–Co(1)–N(37)	88.69(6)	N(37)–Co(1)–P(2)	91.91(4)
N(34)–Co(1)–N(37)	96.53(6)	N(31)–Co(1)–P(2)	172.61(4)
N(31)–Co(1)–N(34)	90.15(6)	N(34)–Co(1)–P(2)	97.09(4)
N(37)–Co(1)–P(1)	164.41(5)	N(31)–Co(1)–P(1)	95.08(4)

determined previously for a complex without a pendant amine in the diphosphine ligand, [Co(dppp)(CH<sub>3</sub>CN)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub>.<sup>23</sup> The greatest structural differences are the larger P–Co–P angle of 92.99° for the dppp ligand compared to 82.45° for the P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub> ligand and the absence of the N-phenyl ring in the ligand backbone of the dppp ligand.

A similar reaction of [Co(CH<sub>3</sub>CN)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> with one equivalent of bis(diethylphosphinomethyl)methyl amine (Et<sub>2</sub>PCH<sub>2</sub>N(Me)CH<sub>2</sub>PEt<sub>2</sub>, PNP) was carried out to form [Co(PNP)(CH<sub>3</sub>CN)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub>. The product was not structurally characterized, but is presumed to have a structure similar to those of the other mono(diphosphine) derivatives. The PNP ligand, which forms a 6-membered chelate ring upon coordination, is assumed to be in the more stable chair conformation, as observed for the nickel and iron complexes with this ligand.<sup>24,25</sup>

### Electrochemical studies

The cyclic voltammogram of [Co(P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> consists of a single reversible wave at  $E_{1/2} = -0.58$  V ( $\Delta E_p = 71$  mV) followed by a quasi-reversible reduction wave at  $E_{1/2} = -2.04$  V ( $\Delta E_p = 100$  mV), as seen in Fig. 3 (blue trace). The reversible reduction at  $-0.58$  V is a diffusion-controlled one-electron wave assigned to the Co(II/I) couple. Based on the peak height (1.8 times that of the wave at  $-0.58$ ), the quasi-reversible reduction wave at  $-2.04$  V appears to involve two electrons



**Fig. 3** Cyclic voltammogram of  $3 \times 10^{-3}$  M solutions of [Co(P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> (blue trace) and [Co(P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)(CH<sub>3</sub>CN)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub> (red trace). Conditions: scan rate = 200 mV s<sup>-1</sup>, 0.3 M NBu<sub>4</sub>BF<sub>4</sub> (supporting electrolyte) acetonitrile solution, glassy carbon working electrode.

**Table 3** Cyclic voltammetry parameters for the Co(II/I) couples of [Co(diphosphine)<sub>x</sub>(CH<sub>3</sub>CN)<sub>y</sub>](BF<sub>4</sub>)<sub>2</sub> complexes

Complex	<sup>a</sup> $E_{1/2}/V$	<sup>b</sup> $\Delta E_p/mV$	<sup>c</sup> $i_a/i_c$
[Co(P <sup>Ph</sup> <sub>2</sub> N <sup>Ph</sup> <sub>2</sub> )(CH <sub>3</sub> CN)](BF <sub>4</sub> ) <sub>2</sub>	-0.58	71	1.0
[Co(P <sup>Ph</sup> <sub>2</sub> N <sup>Ph</sup> <sub>2</sub> )(CH <sub>3</sub> CN) <sub>3</sub> ](BF <sub>4</sub> ) <sub>2</sub>	-0.99	70	1.0
[Co(PNP)(CH <sub>3</sub> CN) <sub>3</sub> ](BF <sub>4</sub> ) <sub>2</sub>	-1.15	150	0.9
[Co(dppp)(CH <sub>3</sub> CN) <sub>3</sub> ](BF <sub>4</sub> ) <sub>2</sub>	-0.91	72	0.9
[Co(CH <sub>3</sub> CN) <sub>6</sub> ](BF <sub>4</sub> ) <sub>2</sub>	-1.21	95	0.9

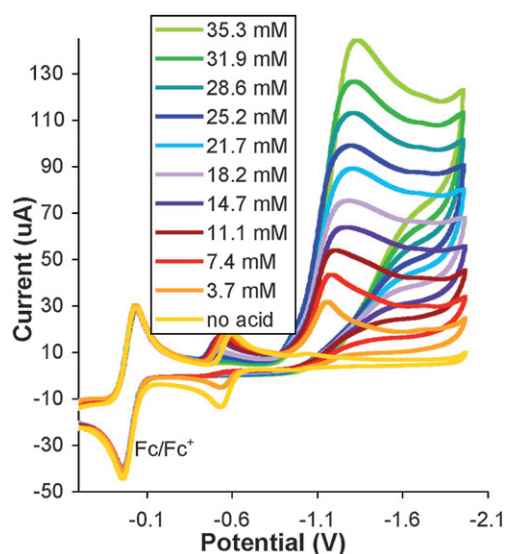
<sup>a</sup> Volts *versus* the FeCp<sub>2</sub><sup>+</sup>/FeCp<sub>2</sub> couple in 0.2 M NEt<sub>4</sub>BF<sub>4</sub>/CH<sub>3</sub>CN solutions. <sup>b</sup> Separation of cathodic and anodic peak potentials at a scan rate of 100 mV s<sup>-1</sup>. Under these conditions ferrocene exhibited  $\Delta E_p$  values of  $70 \pm 5$  mV. <sup>c</sup> Ratio of anodic and cathodic peak currents at 100 mV s<sup>-1</sup>.

corresponding to an overall Co(II/I) reduction process. A second oxidation wave with  $E_p = -1.81$  V is associated with the reduction wave at  $E_{1/2} = -2.04$  V. The Co(I) species is a highly strained tetrahedral complex that could relax by forming bimetallic complexes with bridging diphosphine ligands (tentatively assigned to the peak at  $-1.81$  V) as observed for nickel and palladium complexes containing bis(diphenylphosphino)methane, a diphosphine ligand with a small bite angle.<sup>26</sup>

The cyclic voltammograms of the complexes containing a single diphosphine ligand have also been studied, and these also exhibit a well defined, reversible or quasi-reversible, one-electron reduction in acetonitrile solution assigned to the Co(II/I) couple. Parameters associated with this couple are included in Table 3. All of the complexes exhibit other poorly defined and irreversible waves at more negative potentials, but the Co(II/I) couple is the most relevant couple for the catalytic reactions described below. The red trace in Fig. 3 is a cyclic voltammogram of [Co(P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)(CH<sub>3</sub>CN)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub>. The potential for this derivative ( $-0.99$  V) is significantly more negative than that observed for the bis(diphosphine) analogue discussed above ( $-0.58$  V). The CVs of [Co(P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)(CH<sub>3</sub>CN)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub> obtained from different syntheses consistently show that a small amount (*ca.* 15%) of the bis(diphosphine) complex is present. This may be due to a ligand redistribution equilibrium in this solvent, but analogous contaminants are not observed in the CVs of the other mono(diphosphine) complexes. The Co(II/I) potentials for the other [Co(diphosphine)(CH<sub>3</sub>CN)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub> complexes in this series are also more negative than  $-0.9$  V, as shown in Table 3, and the range in these potentials reflects the electronic differences in the diphosphine ligands in the series. The most negative Co(II/I) potential in the complexes studied was observed for [Co(CH<sub>3</sub>CN)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> ( $E_{1/2} = -1.21$  V,  $\Delta E_p = 95$  mV).

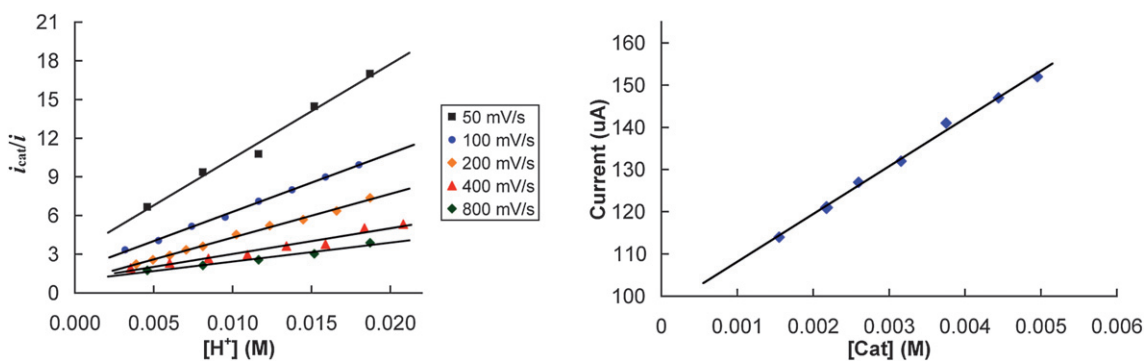
### Studies of catalytic hydrogen production

Fig. 4 shows successive cyclic voltammograms of [Co(P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> recorded in acetonitrile with increasing concentrations of triflic acid. In the presence of triflic acid, the cyclic voltammogram of [Co(P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> exhibits a catalytic wave for the reduction of protons at a half peak potential of  $-1.00 \pm 0.05$  V. This potential does not correspond to the Co(II/I) or Co(I) couples of the parent complex. The height of the Co(II/I) wave associated with [Co(P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> at  $-0.58$  V decreases with



**Fig. 4** Successive cyclic voltammograms of a  $1.2 \times 10^{-3}$  M solution of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$  in acetonitrile at increasing concentrations of triflic acid. Conditions: scan rate =  $200 \text{ mV s}^{-1}$ ,  $0.3 \text{ M NBU}_4\text{BF}_4$  (supporting electrolyte), glassy carbon working electrode. Potentials are referenced to the ferrocenium/ferrocene couple shown at  $0.0 \text{ V}$ .

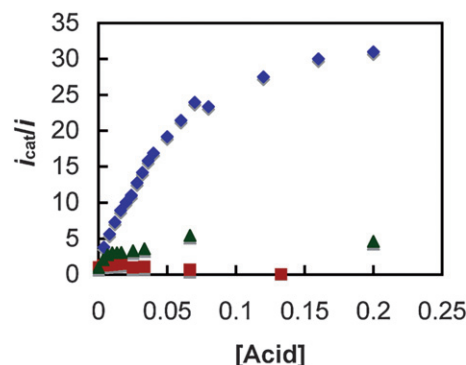
increasing acid concentration while the height of the catalytic wave at  $-0.99 \text{ V}$  increases several fold. The potential of the catalytic wave matches that of the  $\text{Co}(\text{II/I})$  couple of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ , which is proposed to be the active catalyst. The left graph in Fig. 5 shows plots of  $i_{\text{cat}}/i$  (where  $i_{\text{cat}}$  is the peak current in the presence of acid and  $i$  is the peak current in the absence of acid) versus triflic acid concentration over several different scan rates for this catalytic formation of hydrogen. Linear plots are observed over the range of acid concentration ( $0$ – $0.025 \text{ M}$ ) and scan rates ( $50$ – $800 \text{ mV s}^{-1}$ ), which indicates a second-order dependence on  $[\text{H}^+]$  for the catalytic reaction.<sup>27</sup> A first order dependence of the catalytic current on the concentration of catalyst is demonstrated by the linear dependence of the catalytic current on catalyst precursor concentration at constant acid concentration ( $0.022 \text{ M}$ , right graph in Fig. 5). This gives an overall rate law for the production of hydrogen of rate  $= k [\text{H}^+]^2[\text{catalyst}]$ .



**Fig. 5** Plots of  $i_{\text{cat}}/i$  vs. triflic acid concentration for a  $1.2 \times 10^{-3}$  M solution of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$  at several different scan rates (left graph). (b) Plot of catalytic current vs. concentrations of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$  demonstrating first order kinetic behavior (right graph). Conditions:  $0.3 \text{ M NBU}_4\text{BF}_4$  (supporting electrolyte) acetonitrile solution, glassy carbon working electrode.

The catalytic activity of the proposed catalyst,  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ , was studied using *p*-bromoanilinium tetrafluoroborate ( $[\text{BrC}_6\text{H}_4\text{NH}_3][\text{BF}_4]$ ) as the acid. In the presence of this acid (or tetrafluoroboric acid), the cyclic voltammogram of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  exhibits a catalytic wave for the reduction of protons with a half peak potential ( $-0.99 \text{ V}$ ) that corresponds to the  $\text{Co}(\text{II/I})$  couple of this complex. A plot of  $i_{\text{cat}}/i$  versus acid concentration is shown in Fig. 6 (blue diamonds). The linear region of this plot is again consistent with a second order dependence of the overall catalytic rate on acid at low acid concentrations. At higher concentrations of acid, no acid dependence is observed, and this is interpreted in terms of a rate-limiting elimination of  $\text{H}_2$  under these conditions. Using the limiting current in this acid-independent region, a turnover frequency of  $90 \text{ s}^{-1}$  can be calculated for this catalyst.<sup>27</sup> A controlled potential electrolysis experiment was performed on the complex at  $-1.1 \text{ V}$  in the presence of tetrafluoroboric acid, and the evolution of  $\text{H}_2$  was confirmed by gas chromatography (current efficiency =  $101 \pm 5\%$ ).

The catalytic activities of related cobalt diphosphine complexes with bromoanilinium tetrafluoroborate have also been investigated by cyclic voltammetry. During the stepwise addition of this acid to  $[\text{Co}(\text{dppp})(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  only a small



**Fig. 6** Plots of the  $i_{\text{cat}}/i$  ratio as a function of the concentration (M) of *p*-bromoanilinium tetrafluoroborate for  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  (blue diamonds),  $[\text{Co}(\text{dppp})(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  (solid red squares) and  $[\text{Co}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$  (green triangles). The scan rate was  $0.05 \text{ V s}^{-1}$  for all data. The  $E_{1/2}$  values for the respective catalysts are given in Table 3.

current enhancement is observed for the Co(*ii*/*i*) couple at  $-0.91$  V, which is consistent with a reversible electron transfer followed by an irreversible protonation reaction. However, the current enhancement is not sufficiently large to indicate catalysis. Fig. 6 shows a plot of the ratio of the current observed in the presence of acid to the peak current observed in the absence of acid for different acid concentrations of this complex (solid red squares).

The addition of bromoanilinium tetrafluoroborate to acetonitrile solutions of  $[\text{Co}(\text{PNP})(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  results in the loss of the diphosphine ligand as indicated by a bleaching of the solution. However, in the presence of the weaker acid anisidinium tetrafluoroborate, no bleaching is observed and ratios of  $i_{\text{cat}}/i$  exceeding 15 ( $-1.15$  V and a scan rate of  $0.05$  V  $\text{s}^{-1}$ ) indicate an active catalyst for  $\text{H}_2$  production. As a final control, the addition of bromoanilinium tetrafluoroborate to acetonitrile solutions of  $[\text{Co}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$  results in  $i_{\text{cat}}/i$  ratios of 3–5 at  $-1.21$  V (green triangles in Fig. 6) that are clearly much smaller than those observed for  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ .

## Discussion

The complex  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$  provides for a direct comparison of structural features, redox properties and catalytic activity with the highly active nickel catalyst for hydrogen production,  $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$ . In an effort to grow crystals of the cobalt complex in dichloromethane, crystals of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{Cl})]^+$  were obtained instead. The source of the chloride ligand is presumed to be a trace HCl contaminant in the solvent. The structure of this cation confirmed the presence of two coordinated cyclic diphosphine ligands with the fifth ligand in an equatorial position of a trigonal bipyramidal geometry. Two of the chelate rings of the diphosphine ligands are in boat conformations with  $\text{Co}\cdots\text{N}$  distances of 3.50 and 3.52 Å, while the two chelate rings adjacent to the coordinated fifth ligand assume chair conformations to minimize steric interactions. The structure is very similar both in geometry and bond parameters to that observed previously for the nickel acetonitrile analogue.<sup>19</sup>

The cyclic voltammogram of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})]^{2+}$  can be compared with those observed for other  $\text{M}(\text{diphosphine})_2$  complexes of the first row metal ions. Because both the seventeen-electron Co(*ii*) cation, of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})]^{2+}$ , and the corresponding eighteen-electron Co(*i*) cation are five-coordinate, the observed reversibility of the Co(*ii*/*i*) couple at  $-0.58$  V is expected. Only one additional, quasi-reversible reduction wave is observed at  $-2.04$  V. In contrast, a related diphosphine complex  $[\text{Co}(\text{dppe})_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$  has three reversible one-electron reduction waves at  $-0.70$ ,  $-1.56$ , and  $-2.03$  V.<sup>18</sup> It is known from studies of nickel(*ii*) and palladium(*ii*) bis(diphosphine) complexes that smaller chelate bite sizes result in large negative shifts in the potential of the  $d^8/d^9$  couples and a decrease in the separation between the  $d^8/d^9$  and  $d^9/d^{10}$  couples.<sup>28</sup> The small chelate bite of the heterocyclic diphosphine ligand  $\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2$  apparently results in similar shifts in potentials for the cobalt complex to give a two-electron reduction for the Co(*ii*/*i*) couple. The current amplitude of the wave at  $-2.04$  V is consistent with this assignment.

The onset potential of approximately  $-1.0$  V for the production of hydrogen in the presence of triflic acid in acetonitrile

solutions of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$  does not correspond to the Co(*ii*/*i*) potential, nor does it correspond to the more negative potentials associated with the Co(*i*/*i*–1) couple of this complex. The decrease in the peak height of the Co(*ii*/*i*) wave of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$  as the acid concentration increased indicated that this complex was decomposing in the presence of triflic acid and suggested that one or more of the diphosphine ligands was being removed by protonation of the ligand at high acid concentrations. This type of acid-induced ligand loss was not observed in the previously studied nickel complex  $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$ , and this reveals a significant difference in the chemistry of the two five-coordinate metal complexes. The trend is consistent with the generally observed greater lability of Co(*ii*) vs. Ni(*ii*) derivatives.

The complex  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  is readily synthesized by addition of one equivalent of the cyclic ligand to  $[\text{Co}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ . In contrast, the addition of one equivalent of ligand to  $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$  under similar conditions led only to the formation of a mixture of  $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$  and the starting solvated complex. An X-ray diffraction study of the cobalt product confirmed that the square pyramidal dication contains only one cyclic ligand with one chelate ring in the chair form and the second in a boat. The  $\text{Co}\cdots\text{N}$  distance to the proximal amine is 3.24 Å, and in addition, the phenyl ring of that amine is oriented over the top of the cobalt ion with  $\text{Co}\cdots\text{C}(24)$  and  $\text{Co}\cdots\text{C}(25)$  distances of 3.03 and 3.09 Å, respectively. The structural data alone are not definitive of a bonding interaction between the Co and a C=C bond of the Ph ring. At these long distances, any interaction would be quite weak, though a weak bonding interaction was found at similar distances ( $\text{W}\cdots\text{C}$  distances 2.901(13) and 3.072(13) Å) in  $\text{CpW}(\text{CO})_2(\text{IMes})^+$  (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) where one C=C of a mesityl ring had an interaction with the metal.<sup>29</sup>

The  $E_{1/2}$  of the Co(*ii*/*i*) couple of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ ,  $-0.99$  V, corresponds to the potential observed for the catalytic wave of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$  in acetonitrile in the presence of triflic acid. This confirms that the actual catalytic species for hydrogen formation is  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ . The negative shift in the half-wave potential of the Co(*ii*/*i*) couple from  $-0.58$  V for the bis(diphosphine) complex to  $-0.99$  V for the mono(diphosphine) derivative suggests that the hard nitrogen donors of the acetonitrile ligands are more electron-donating than the softer diphosphine ligand in this system. Because a strong acid such as triflic acid is no longer required to remove one of the diphosphine ligands, catalytic activity can now be observed using weaker acids, and this allows the catalysis to proceed with a lower overpotential. For example, a catalytic wave is observed at  $-0.99$  V in the presence of *p*-bromoanilinium tetrafluoroborate ( $\text{p}K_{\text{a}} = 9.4$  in acetonitrile<sup>30</sup>) and anisidinium tetrafluoroborate ( $\text{p}K_{\text{a}} = 11.8$  in acetonitrile<sup>30</sup>). Because of the lower acidity of anisidinium tetrafluoroborate, the catalytic currents are much smaller than for *p*-bromoanilinium tetrafluoroborate. At high concentrations of the *p*-bromoanilinium salt, the catalytic current observed for the production of  $\text{H}_2$  is independent of acid concentrations and a limiting turnover frequency of  $90$   $\text{s}^{-1}$  at  $22$  °C was determined. From the operating potential of this catalyst and the  $\text{p}K_{\text{a}}$  value of *p*-bromoanilinium tetrafluoroborate (9.4), the overpotential for

hydrogen production can be calculated to be 285 mV using the standard NHE potential in acetonitrile suggested by Evans *et al.*<sup>31</sup>

The cobalt derivative  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  shows a slower rate for proton reduction than that reported for  $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$  ( $350 \text{ s}^{-1}$ ), while the overpotential is somewhat reduced compared to that estimated for the nickel system (*ca.* 350 mV). Mechanistic studies have established the same rate law for both systems:  $\text{rate} = k'[\text{H}^+][\text{catalyst}]$  at low acid concentrations and  $\text{rate} = k[\text{catalyst}]$  at high acid concentrations. Theoretical and experimental studies of the nickel catalysts have suggested that the positioning of two amines near the nickel ion is critical for high catalytic activity because interaction with *both* amines stabilizes the formation of a dihydrogen ligand on the Ni(II) ion.<sup>19</sup> A similar effect cannot be achieved for the cobalt catalyst, which contains only one positioned amine base. However, the complex  $[\text{Co}(\text{dppp})(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ , which contains no pendant base in the ligand backbone of the diphosphine ligand, exhibits no significant catalytic activity for hydrogen production under the same conditions that  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  exhibits relatively high catalytic rates. This suggests that the positioned amine in the cyclic ligand plays an important role in the catalytic activity of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ . Previous NMR studies of diamagnetic iron diphosphine complexes containing a single pendant amine have shown that the base facilitates both intermolecular proton exchange between the protonated complex and protons in solution as well as intramolecular Fe–H⋯H–N exchange.<sup>32</sup> Similar exchange processes appear likely for this cobalt system. In addition, a mechanistic step may be proposed in which an intramolecular interaction of a cobalt-hydride with the adjacent protonated amine promotes formation of a H–H bond. Similar M–H⋯H–N interactions have been proposed previously in our studies of the electrocatalysis of hydrogen oxidation promoted by  $[\text{Ni}(\text{PNP})_2]^{2+}$ .<sup>24</sup>

The complex  $[\text{Co}(\text{PNP})(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  was prepared in an attempt to further probe the role of the pendant base in the catalytic activity of this system. The PNP complex incorporates a more basic amine as a result of more electron donating substituents than those in  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  (methyl and ethyl *versus* phenyl). As a result of the increased basicity, the weaker acid, anisidinium tetrafluoroborate ( $\text{p}K_{\text{a}} = 11.8$  in acetonitrile), can be used, and catalytic hydrogen production is observed. These observations further support the postulate that a base in the second coordination sphere plays an important role in hydrogen formation. Additional studies on the cobalt systems with PNP ligands will be reported in a subsequent publication.

It is interesting that catalytic waves for hydrogen production are observed by cyclic voltammetry when tetrafluoroboric acid is added to the simple solvated complex  $[\text{Co}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ . The onset potential for the catalytic wave corresponds to the potential of the Co(II/I) couple for this complex at  $-1.21 \text{ V}$ . However as shown in Fig. 6, the complex is nearly inactive when the weaker *p*-bromoanilinium acid is used. The negative potential and strong acid required for this catalytic reaction indicate that it proceeds with a large overpotential and does not significantly contribute to the observed catalytic activity of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  or  $[\text{Co}(\text{PNP})(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ .

## Summary and conclusions

This work has extended studies on the electrocatalytic production of  $\text{H}_2$  using first row transition metal complexes containing diphosphine ligands with pendant nitrogen bases.  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  has a catalytic turnover frequency of  $90 \text{ s}^{-1}$  with an estimated overpotential of 285 mV. In contrast to previously studied nickel complexes, two cyclic diphosphine ligands with positioned nitrogen bases are not required for high activity. A comparison of the catalytic behavior of  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$  with that of  $[\text{Co}(\text{dppp})(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ , for which no catalytic activity is observable by cyclic voltammetry, indicates that the pendant amine is playing an important role in the catalysis of  $\text{H}_2$  production. This is supported by the observation that the complex containing the flexible acyclic diphosphine incorporating an amine base,  $[\text{Co}(\text{PNP})(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ , is also a catalyst in the presence of a weak acid.

An important conclusion from this work is that cobalt complexes containing diphosphine ligands with pendant bases can exhibit catalytic rates for hydrogen production comparable to those of previously reported nickel complexes. The amine base in the second coordination sphere plays a crucial role in these catalytic processes, but for cobalt complexes this high catalytic activity is obtained with only *one* positioned pendant base rather than *two* as required in the nickel complexes.

## Experimental

### Materials and instrumentation

The syntheses of  $[\text{Co}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ ,<sup>33</sup>  $\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2$ ,<sup>19</sup> and  $\text{PNP}^{24}$  have been reported elsewhere. Synthetic reactions were carried out under nitrogen. Electrochemical measurements were performed at room temperature under a nitrogen atmosphere in acetonitrile solutions containing either 0.30 M tetrabutylammonium tetrafluoroborate ( $\text{Bu}_4\text{NBF}_4$ ) or 0.20 M tetraethylammonium tetrafluoroborate. Cyclic voltammetry data were collected using a Cypress Systems model CS-1200 computer aided potentiostat with a three-electrode system. The working electrode was a 2 mm diameter glassy carbon disk and the counter electrode was an uncoated glassy carbon rod with a 3 mm diameter. The reference electrode was a silver wire coated with silver chloride and immersed in a 0.20 M electrolyte solution of tetraethylammonium tetrafluoroborate in  $\text{CH}_3\text{CN}$  and separated from the sample solution by a Vycor tip. However, all potentials are referenced to the ferrocenium/ferrocene couple ( $\text{FeCp}_2^+/\text{FeCp}_2$ ), using ferrocene as an internal standard.

### Synthesis of $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$

A mixture of  $\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2$  (0.306 g, 0.672 mmol) and  $[\text{Co}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$  (0.160 g, 0.336 mmol) in acetonitrile was stirred at room temperature for 6 h. The brownish solution was reduced to approximately 1 mL, and 5 mL of methylene chloride was added. Fifteen mL of methanol was added with stirring, and the volume of the solution reduced until a precipitate began to appear. Additional precipitate formed upon cooling to  $-15 \text{ }^\circ\text{C}$  overnight, which was isolated by filtration. This process was repeated a second time to yield an orange-brown microcrystalline product. Yield: 0.171 g, 43%. Elemental analyses calcd. for

$C_{58}H_{59}B_2CoF_8N_5P_4$ : C, 58.91; H, 5.03; N, 5.92. Found: C, 58.28; H, 4.79; N, 5.69. ESI<sup>+</sup> MS, *m/z* ( $CH_3CN$ ): 1002  $\{[Co(P^{Ph}_2N^{Ph}_2)_2Cl]^+\}$ , 483  $\{[Co(P^{Ph}_2N^{Ph}_2)_2]^{2+}\}$ .

### $[Co(P^{Ph}_2N^{Ph}_2)(CH_3CN)_3](BF_4)_2$

$[Co(CH_3CN)_6](BF_4)_2$  (0.20 g, 0.42 mmol) was dissolved in 5 mL acetonitrile and  $P^{Ph}_2N^{Ph}_2$  (0.19 g, 0.42 mmol) was added. The brown solution was stirred at room temperature overnight, and then solvent was removed *in vacuo*. The resulting brown solid was recrystallized from acetonitrile/ether and identified by an X-ray diffraction study. Yield: 70%. Elemental analyses calcd. for  $C_{34}H_{37}B_2CoF_8N_5P_2$ : C, 50.40; H, 4.60; N, 8.65. Found: C, 50.16; H, 4.87; N, 8.65. Electrochemical data are reported in Table 3. The procedure described here was followed for all the  $[Co(diphosphine)(CH_3CN)_3](BF_4)_2$  derivatives reported.

### X-Ray diffraction studies

A suitable crystal of  $[Co(P^{Ph}_2N^{Ph}_2)_2Cl]BF_4$  or  $[Co(P^{Ph}_2N^{Ph}_2)(CH_3CN)_3](BF_4)_2$  was selected, attached to a glass fiber and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ) equipped with a Cryocool NeverIce low temperature device. For each structure, data were measured using omega scans  $0.3^\circ$  per frame for 20 s, and a full sphere of data was collected. A total of 2400 frames were collected in each case with a final resolution of  $0.83 \text{ \AA}$  for  $[Co(P^{Ph}_2N^{Ph}_2)_2Cl]BF_4$  and  $0.77 \text{ \AA}$  for  $[Co(P^{Ph}_2N^{Ph}_2)(CH_3CN)_3](BF_4)_2$ . Cell parameters were retrieved using SMART<sup>34</sup> software and refined using SAINTPlus<sup>35</sup> on all observed reflections. Data reduction and correction for

Lorentzian polarization and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.<sup>36</sup> Each structure was solved by direct methods and refined by least squares method on  $F^2$  using the SHELXTL program package.<sup>37</sup> No decomposition was observed during data collection.

The structure of  $[Co(P^{Ph}_2N^{Ph}_2)_2Cl]BF_4$  was solved in the space group  $C2/c$  (#15) by analysis of systematic absences. Aryl rings C9–C14 and C48–C53 were disordered and modeled in two positions with occupancies 65 : 35%. One of the half occupied  $BF_4$  groups was also disordered over an inversion center. The diffraction contribution from disordered solvent molecules was removed using the subroutine SQUEEZE in the PLATON software suite.<sup>38</sup> All other non-hydrogen atoms were refined anisotropically. The structure of  $[Co(P^{Ph}_2N^{Ph}_2)(CH_3CN)_3](BF_4)_2$  was solved in the space group  $P2(1)/n$  (#14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. Details of the data collections and refinements are given in Table 4. Complete structural data are provided in the ESI.†

### Acknowledgements

This work was supported by the Chemical Sciences program of the Office of Basic Energy Sciences of the Department of Energy. The Pacific Northwest National Laboratory is operated by Battelle for the US Department of Energy.

The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

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**Table 4** Crystal data for  $[Co(P^{Ph}_2N^{Ph}_2)_2Cl](BF_4)$  and  $[Co(P^{Ph}_2N^{Ph}_2)(CH_3CN)_3](BF_4)_2$

Formula	$C_{56}H_{56}BClCoF_4N_4P_4$	$C_{34}H_{37}B_2CoF_8N_5P_2$
Formula weight	1090.12	810.18
Temperature	90(2) K	90(2) K
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2(1)/n$
Unit cell dimensions	$a = 34.2939(13) \text{ \AA}$ $\alpha = 90^\circ$ $b = 12.9425(5) \text{ \AA}$ $\beta = 121.872(1)^\circ$ $c = 28.6361(11) \text{ \AA}$ $\gamma = 90^\circ$	$a = 10.0584(4) \text{ \AA}$ $\alpha = 90^\circ$ $b = 20.1715(7) \text{ \AA}$ $\beta = 93.1020(10)^\circ$ $c = 17.6050(6) \text{ \AA}$ $\gamma = 90^\circ$
Volume	10793.8(7) $\text{ \AA}^3$	3566.7(2) $\text{ \AA}^3$
Z	8	4
Density(calc)	1.342 $\text{ Mg m}^{-3}$	1.509 $\text{ Mg m}^{-3}$
Absorption coefficient	0.541 $\text{ mm}^{-1}$	0.647 $\text{ mm}^{-1}$
$F(000)$	4520	1660
Crystal size, mm	$0.47 \times 0.20 \times 0.09$	$0.29 \times 0.16 \times 0.10$
Theta range for data collection	$1.40$ to $25.25^\circ$	$1.54$ to $27.50^\circ$
Reflections collected	62971	52775
Independent reflections	9775 [ $R(\text{int}) = 0.0446$ ]	8183 [ $R(\text{int}) = 0.0384$ ]
Absorption correction	Semi-empirical	Semi-empirical
Goodness-of-fit on $F^2$	1.065	1.034
Final R indices	$R1 = 0.0514$ , $wR2 = 0.1372$	$wR1 = 0.0345$ , $wR2 = 0.0838$
R indices (all data)	$R1 = 0.0634$ , $wR2 = 0.1446$	$R1 = 0.0449$ , $wR2 = 0.0899$
Largest diff. peak and hole	1.597 and $-0.816 \text{ e \AA}^{-3}$	0.466 and $-0.266 \text{ e \AA}^{-3}$

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