Bridgehead isomer effects in bis(phosphido)-bridged diiron hexacarbonyl proton reduction electrocatalysts

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Electronic Supporting Information (ESI)
**Additional $^1\text{H}$ and $^{31}\text{P}[^1\text{H}]$ NMR spectra and simulations**

**Experimental.** Spectra were simulated using the NUMMRIT module in the SpinWorks (v4.2) program. Note: swapping the shifts of the two P atoms and the sign of the JHH at the same time gives the same results.

2. *SpinWorks 4.2.0*, Copyright © 2015, Kirk Marat, University of Manitoba

*a,e-[Fe$_2$(CO)$_6$(μ$_2$-P(PhH)$_2$)], 1a(Ph).*

![Figure 1S](attachment:image1.png)

**Figure 1S.** Experimental (bottom trace) and simulated (top trace) for the P–H region of the 500 MHz $^1\text{H}$ NMR spectrum.

![Figure 2S](attachment:image2.png)

**Figure 2S.** Experimental $^{31}\text{P}[^1\text{H}]$ spectrum (bottom trace) and its simulation (top trace).
Simulation data.

Groups and chemical shifts:

<table>
<thead>
<tr>
<th>#</th>
<th>name</th>
<th>shift (Hz)</th>
<th>spins</th>
<th>species</th>
<th>spin</th>
<th>sym</th>
<th>shift (ppm)</th>
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<tr>
<td>4</td>
<td>Pb</td>
<td>15643.431</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>77.319</td>
</tr>
</tbody>
</table>

Scalar coupling constants: (round up to 1 dec pl)

\[
\begin{align*}
    j[1, 2] &= j[Ha, Hb] = -1.000000 \\
    j[1, 3] &= j[Ha, Pa] = 373.487870 \\
    j[1, 4] &= j[Ha, Pb] = 17.018000 \\
    j[2, 3] &= j[Hb, Pa] = 24.834120 \\
    j[2, 4] &= j[Hb, Pb] = 380.817250 \\
\end{align*}
\]

Linewidth: 3.5 Hz

\[a,e-[\text{Fe}_2(\text{CO})_6\{\mu_2-\text{PH}(R-2'-\text{methoxy-1,1'-'binaphthyl})\}_2], \text{1a(bn')}.\]

**Figure 3S.** Experimental (bottom trace) and simulated (top trace) for the P–H region of the 500 MHz \(^1\text{H} \text{NMR} \) spectrum.
Figure 4S. Experimental $^{31}$P($^1$H) spectrum (bottom trace) and its simulation (top trace).

Simulation data.

Groups and chemical shifts:

<table>
<thead>
<tr>
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<th>name</th>
<th>shift (Hz)</th>
<th>spins</th>
<th>species</th>
<th>spin</th>
<th>sym</th>
<th>shift (ppm)</th>
</tr>
</thead>
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<td>1</td>
<td>1</td>
<td>59.992</td>
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</table>

Scalar coupling constants: (round up to 1 dec pl)

\[ j[1, 2] = j[H_a, H_b] = -0.750000 \]
\[ j[1, 3] = j[H_a, P_a] = 388.164760 \]
\[ j[1, 4] = j[H_a, P_b] = 18.885710 \]
\[ j[2, 3] = j[H_b, P_a] = 26.704100 \]
\[ j[2, 4] = j[H_b, P_b] = 396.675760 \]
\[ j[3, 4] = j[P_a, P_b] = -167.793220 \]

Linewidth: 3.5 Hz
e.e-[Fe₂(CO)₆(µ₂-PHPh)]₂, 1b(Ph).

The \(^1\text{H}\) NMR spectrum was modelled as a AA'XX' system for the two P-H groups with coupling to \textit{ortho} protons of the phenyl substituent; \textit{i.e.}, overall as a AA'(MM')2XX' spin system. There will be some extra small couplings to the \textit{meta} and \textit{para} protons that may broaden the multiplets, but will not change the larger evaluated couplings. The \(^{31}\text{P}(^1\text{H})\) spectrum shows a singlet at 86.4 ppm.

**Figure 5S.** Experimental (bottom trace) and simulated (top trace) for the P–H region of the 500 MHz \(^1\text{H}\) spectrum.

**Simulation data**

Groups and chemical shifts:

<table>
<thead>
<tr>
<th>#</th>
<th>name</th>
<th>shift (Hz)</th>
<th>spins</th>
<th>species</th>
<th>spin sym</th>
<th>Shift (ppm)</th>
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<tr>
<td>1</td>
<td>Ha</td>
<td>1738.943</td>
<td>1</td>
<td>1</td>
<td>1 2</td>
<td>3.480 (P-H)</td>
</tr>
<tr>
<td>2</td>
<td>Ho1</td>
<td>3817.990</td>
<td>1</td>
<td>1</td>
<td>1 2</td>
<td>ortho protons</td>
</tr>
<tr>
<td>3</td>
<td>Ho2</td>
<td>3817.990</td>
<td>1</td>
<td>1</td>
<td>1 2</td>
<td>ortho protons</td>
</tr>
<tr>
<td>4</td>
<td>Pb</td>
<td>15643.431</td>
<td>1</td>
<td>2</td>
<td>1 2</td>
<td>86.4 (31P)</td>
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</tbody>
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Scalar coupling constants:

- \(j[1,1] = j[\text{Ha,Ha}] = 1.500000\) (approx.; < 2Hz)
- \(j[1,2] = j[\text{Ha,Ho1}] = 0.000000\) (4 bonds not fitted)
- \(j[1,3] = j[\text{Ha,Ho2}] = 0.000000\)
- \(j[1,4] = j[\text{Ha,Pb}] = 371.050000\)
- \(j[2,1] = j[\text{Ho1,Ha}] = 0.000000\)
- \(j[2,2] = j[\text{Ho1,Ho1}] = -1.500000\) (4 bonds, not fitted, and makes no difference)
- \(j[2,3] = j[\text{Ho1,Ho2}] = 0.000000\)
- \(j[2,4] = j[\text{Ho1,Pb}] = 0.000000\)
- \(j[3,1] = j[\text{Ho2,Ha}] = 0.000000\)
- \(j[3,2] = j[\text{Ho2,Ho1}] = 0.000000\)
- \(j[3,3] = j[\text{Ho2,Ho2}] = -1.500000\)
- \(j[3,4] = j[\text{Ho2,Pb}] = 14.000000\)
$j[4, 1] = j[\text{Pb, Ha}] = 31.580000$

$j[4, 2] = j[\text{Pb, Ho1}] = 14.000000$

$j[4, 3] = j[\text{Pb, Ho2}] = 0.000000$

$j[4, 4] = j[\text{Pb, Pb}] = -129.750000$

$e,e$-[Fe$_2$(CO)$_6$($\mu_2$-PH(R-2′-methoxy-1,1′-binaphthyl))$_2$], 1b(bn′).

The methoxybinaphthyl group was modelled as a substituted phenyl group with one ortho proton (Ho, 7.83 ppm) and one meta proton (Hm, 7.94 ppm)

**Figure 6S.** Experimental (bottom trace) and simulated (top trace) of the 500 MHz $^1$H spectrum of $e,e$-[Fe$_2$(CO)$_6$($\mu_2$-PHPh)$_2$], 1b(bn′): (a) the P–H region, (b) part of aryl region (the peak at 7.88 ppm was not required for the simulation in the P–H region).
Simulation data

Groups and chemical shifts:

<table>
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<tr>
<th></th>
<th>name</th>
<th>shift (Hz)</th>
<th>spins</th>
<th>species spin</th>
<th>sym</th>
<th>atom type, shift</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Ha</td>
<td>1250.756</td>
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<td>1</td>
<td>1</td>
<td>P-Ha, 2.0841 ppm</td>
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<tr>
<td>2</td>
<td>Ho</td>
<td>4699.200</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>ortho protons, 7.8303 ppm</td>
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<tr>
<td>3</td>
<td>Hm</td>
<td>4762.418</td>
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<td>1</td>
<td>1</td>
<td>meta protons, 7.9356 ppm</td>
</tr>
<tr>
<td>4</td>
<td>P</td>
<td>46510.331</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>$^{31}$P, 77.5 ppm</td>
</tr>
</tbody>
</table>

Scalar coupling constants (Hz):

- $j[1, 1] = j[Ha,Ha] = 0.500000$ (approx. Say < 2Hz)
- $j[1, 2] = j[Ha,Ho] = 0.500000$ (approx. Say < 2Hz)
- $j[1, 3] = j[Ha,Hm] = 0.000000$
- $j[1, 4] = j[Ha,P] = 391.280000$ 1J P-Ha
- $j[2, 1] = j[Ho,Ha] = 0.000000$
- $j[2, 2] = j[Ho,Ho] = 0.000000$
- $j[2, 3] = j[Ho,Hm] = 8.680000$ (3J Ho-Hm))
- $j[2, 4] = j[Ho,P] = 11.820000$ 3J P-Ho
- $j[3, 1] = j[Hm,Ha] = 0.000000$
- $j[3, 2] = j[Hm,Ho] = 0.000000$
- $j[3, 3] = j[Hm,Hm] = 0.000000$
- $j[3, 4] = j[Hm,P] = 1.700000$ 4J P-Hm
- $j[4, 2] = j[P,Ho] = 0.000000$
- $j[4, 3] = j[P,Hm] = 0.000000$

**additional Figures From Electrochemical Studies**

**Figure 7S.** CV of dimer $a_e-[Fe_2(CO)_6(\mu_2-\text{PHPh})_2], \text{1a(Ph)},$ with extended potential range recorded at $v = 100 \text{ mV s}^{-1}.$ All other conditions are identical to those listed in the caption to Figure 7 in the paper.
Figure 8S. CVs of $e,e-[\text{Fe}_2(\text{CO})_6(\mu_2-\text{PHPh})_2]$, 1b(Ph), at different scan rates: $v = 100, 200, 400, 800, 1600$ mVs$^{-1}$ with other conditions as in Figure 7 in paper. The inset shows a plot of $i_p$ versus $v^{1/2}$ for peak R1.

Figure 9S. Electrocatalysis of proton reduction: CVs of $e,e-[\text{Fe}_2(\text{CO})_6(\mu_2-\text{PHPh})_2]$, 1b(Ph), (1.0 mM) and added TsOH. Inset: Current data for the catalytic wave C2 versus equiv. of acid.
**Figure 10.** Electrocatalysis of proton reduction: CVs of $a_i-[Fe_2(CO)_6(μ_2-P(bn')H)]_2 \ 1a(bn')$ (1.0 mM) and added TsOH. Inset: Catalytic current ratio data for the catalytic wave $C_2$ versus equiv. of added acid.

**Figure 11.** Electrocatalysis of proton reduction: CVs of $e,e-[Fe_2(CO)_6(μ_2-P(bn')H)]_2, \ 1b(bn')$, (1.0 mM) and added TsOH. Inset: Catalytic current ratio data for the catalytic wave $C_2$ versus equiv. of added acid.
Further spectra from studies of $[\text{Fe}_2(\text{CO})_6(\mu-1,2-\{\text{FcCH}_2\text{PCH}_2\}_2\text{C}_6\text{H}_4)]$ (4)

Figure 12S. Spectra from a variable temperature 400 MHz $^1$H NMR study of 4 in benzene-$d_6$.

Figure 13S. CVs of 4 (1.3 mM) in THF$-[(n-$Bu)$_4$N][PF$_6$] (0.4 M) showing the effect of switching before the second reduction process ($R2^*$); all other conditions as for Fig 7 in the paper.
Figure 14S. a) $^1$H NMR spectrum of 4 (bottom trace) and product(s) generated upon reduction of 4 with a Na mirror (top trace) in THF-$d_8$ (400 MHz, 298 K); b) $^{31}$P($^1$H) NMR spectrum of products generated after reduction of 4 with a Na mirror in THF-$d_8$ (161.9 MHz, 298 K).
Figure 15S. a) Simulated CV of 4 using DigiElch 6.F software and the following input parameters: [4] = 2.6 mM, D = 10^{-5} cm^2 s^{-1}; 100 mV s^{-1}; A(electrode planar) = 0.0078 cm^2; E (4/4\textsuperscript{-}) = -2.00 V, α = 0.45, k_s = 3.5x10^{-4} cm s^{-1}; K_{eq}^1 = 5 \times 10^4 and k_f = 1; E ([4\textsuperscript{-}]'/4\textsuperscript{2-}) = -1.52 V, α = 0.86, k_s = 4x10^{-5} cm s^{-1}; K_{eq}^2 = 2.59 \times 10^3 and k_f = 10^3; E (4\textsuperscript{2+}/4) = 0.03 V, α = 0.5, k_s = 10^{-1} cm s^{-1}; b) Mechanism used in simulation of the electrochemistry of 4.
Figure 165. (a) CVs of 4 (1.3 mM) with added TsOH in tetrahydrofuran–0.4 M [Bu₄N][PF₆]; \( \nu = 100 \text{ mV s}^{-1} \), other conditions as in Figure 7. The black diamonds indicate the peaks \( C1 \) and the red asterisks indicate peaks \( C2 \). (b) CVs TsOH in tetrahydrofuran–0.4 M [Bu₄N][PF₆] in the absence and presence of 4.
**Electrocatalysis using** [Fe₂(CO)₆(μ-P(CH₂Fc)H)₂] **and** [Fe₂(CO)₆(μ-P(CH₂Fc)Me)₂]

**Figure 175.** Plots of catalytic current ratio against equiv. of added acid for [Fe₂(CO)₆(μ-P(CH₂Fc)H)₂] (top) and [Fe₂(CO)₆(μ-P(CH₂Fc)Me)₂] (bottom) using data taken from Figure 7 in Gimbert-Suriñach *et al.* *Organometallics* 2012, 31, 3480-3491.