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Edgar, Mark, Mark Elsegood, Pingchuan Liu, Christopher R Miles, Martin Smith, and Shimeng Wu. 2022.
"Supplementary Information Files for Dinuclear Palladium(ii) and Platinum(ii) Complexes of a Readily Accessible Bicyclic Diphosphane". Loughborough University. https://doi.org/10.17028/rd.Iboro.20080034.v1.

# European Journal of Inorganic Chemistry 

Supporting Information

## Dinuclear Palladium(II) and Platinum(II) Complexes of a Readily Accessible Bicyclic Diphosphane

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## Supporting Information

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Molecular structure of $\mathbf{3 a} \cdot 12 \mathrm{CD}_{3} \mathrm{CN}$ in the solid state. All hydrogen atoms and some solvents have been omitted for clarity. Selected bond lengths $[\AA]$ and angles [ ${ }^{\circ}$ ]: $\operatorname{Pd}(1)-P(1) 2.2220(17)$, $\mathrm{Pd}(1)-\mathrm{P}(2 \mathrm{~A}) 2.2337(17), \mathrm{Pd}(1)-\mathrm{Cl}(1) 2.3410(18), \mathrm{Pd}(1)-\mathrm{Cl}(2) 2.3501(17), \mathrm{P}(1)-\mathrm{P}(2) 2.187(2)$; $\mathrm{Cl}(1)-\mathrm{Pd}(1)-\mathrm{Cl}(2) 94.72(7), \mathrm{P}(1)-\mathrm{Pd}(2)-\mathrm{P}(2 \mathrm{~A}) 98.56(6)$.
Figure S32 Molecular structure of $\mathbf{4 a} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$ in the solid state. All hydrogen atoms and solvents have been omitted for clarity. Selected bond lengths [ $\AA$ ] and angles [ ${ }^{\circ}$ ]: $\mathrm{Pd}(1)-\mathrm{P}(1)$ 2.254(3), $\mathrm{Pd}(1)-\mathrm{P}(2) 2.239(3), \mathrm{Pd}(1)-\mathrm{Cl}(1) 2.365(3), \mathrm{Pd}(1)-\mathrm{Cl}(2) 2.342(3) ; \mathrm{P}(1)-\mathrm{Pd}(2)-\mathrm{P}(2) 93.82(10)$, $\mathrm{Cl}(1)-\mathrm{Pd}(1)-\mathrm{Cl}(2) 90.88(10)$.

## Experimental for dichloropalladium(II) complexes 4a and 4b

Synthesis of 4a: To $\left[\mathrm{PdCl}_{2}\left(\eta^{4}-\mathrm{C}_{8} \mathrm{H}_{12}\right)\right](0.027 \mathrm{~g}, 0.098 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ was added $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{~N}\left\{\mathrm{C}_{6} \mathrm{H}_{4}\left(4-\mathrm{NMe}_{2}\right)\right\} \mathrm{CH}_{2} \mathrm{PPh}_{2}(0.052 \mathrm{~g}, 0.098 \mathrm{mmol})$, preformed from 2 equiv. of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ and $\mathrm{H}_{2} \mathrm{NC}_{6} \mathrm{H}_{4}\left(4-\mathrm{NMe}_{2}\right)$, and the solution stirred for 1 h . The volume of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ was reduced in vacuo to approx. $1-2 \mathrm{~mL}$. Addition of diethyl ether ( 20 mL ) and hexanes ( 20 mL ) afforded solid $4 \mathbf{a}$ which was collected by suction filtration and dried. Yield 0.058 g , $83 \%$. Selected data for $4 \mathrm{a}:{ }^{1} \mathrm{H}(500 \mathrm{MHz})$ : $\delta 7.86-7.82\left(8 \mathrm{H}, \mathrm{m}\right.$, arom. $H$ ), $7.46\left(4 \mathrm{H}, \mathrm{dd}, J_{\mathrm{HH}}\right.$ $8.2,6.7 \mathrm{~Hz}$, arom. $H$ ), $7.37\left(8 \mathrm{H}, \mathrm{dt}, J_{\mathrm{HH}} 7.6,2.2 \mathrm{~Hz}\right.$, arom. $\left.H\right), 6.67\left(4 \mathrm{H}, \mathrm{d}, J_{\mathrm{HH}} 8.2 \mathrm{~Hz}\right.$, arom. H), $3.84\left(4 \mathrm{H}, \mathrm{t},{ }^{2} \mathrm{~J}_{\mathrm{PH}} 3.1 \mathrm{~Hz}, \mathrm{CH}_{2}\right), 2.88\left(6 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}(202 \mathrm{MHz}): \delta 10.1 \mathrm{ppm}$. FT-IR $(\mathrm{KBr}): v_{\text {PdCl }} 310,293 \mathrm{~cm}^{-1}$. Anal. Calcd for $\mathrm{C}_{34} \mathrm{H}_{34} \mathrm{Cl}_{2} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{Pd} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$ (\%): C, $52.89 ; \mathrm{H}, 4.57$; N, 3.52. Found: C, 53.04; H, 4.55; N, 3.50.

Synthesis of 4b: To $\left[\mathrm{PtCl}_{2}\left(\eta^{4}-\mathrm{C}_{8} \mathrm{H}_{12}\right)\right](0.035 \mathrm{~g}, 0.094 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ was added $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{~N}\left\{\mathrm{C}_{6} \mathrm{H}_{4}\left(4-\mathrm{NMe}_{2}\right)\right\} \mathrm{CH}_{2} \mathrm{PPh}_{2}(0.050 \mathrm{~g}, 0.094 \mathrm{mmol})$, preformed from 2 equiv. of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ and $\mathrm{H}_{2} \mathrm{NC}_{6} \mathrm{H}_{4}\left(4-\mathrm{NMe}_{2}\right)$, and the solution stirred for 1 h . The volume of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ was reduced in vacuo to approx. $1-2 \mathrm{~mL}$. Addition of diethyl ether ( 20 mL ) and hexanes ( 20 mL ) afforded a yellow solid $\mathbf{4 b}$ which was collected by suction filtration and dried. Yield $0.045 \mathrm{~g}, 65 \%$. Selected data for $\mathbf{4 b}:{ }^{1} \mathrm{H}(500 \mathrm{MHz}): \delta 7.85-7.80(8 \mathrm{H}, \mathrm{m}$, arom. H$), 7.46(4 \mathrm{H}$, t, $J_{\mathrm{HH}} 7.0 \mathrm{~Hz}$, arom. $H$ ), $7.38\left(8 \mathrm{H}, \mathrm{t}, J_{\mathrm{HH}} 6.8 \mathrm{~Hz}\right.$, arom. $\left.H\right), 6.68-6.65(2 \mathrm{H}$, m, arom. $H), 6.57$ $\left(2 \mathrm{H}, \mathrm{d}, J_{\mathrm{HH}} 9.1 \mathrm{~Hz}\right.$, arom. $H$ ), $3.88\left(4 \mathrm{H}\right.$, dd, $\left.{ }^{3} J_{\mathrm{PtH}} 50.0 .{ }^{2} J_{\mathrm{PH}} 5.0 \mathrm{~Hz}, \mathrm{CH} 2\right), 2.87(6 \mathrm{H}, \mathrm{s}, \mathrm{CH} 3)$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}(202 \mathrm{MHz}): \delta-6.1 \mathrm{ppm},{ }^{1} \mathrm{JPtP}^{2} 3400 \mathrm{~Hz} . \mathrm{FT}-\mathrm{IR}(\mathrm{KBr}): v \mathrm{PtCl} 317,290 \mathrm{~cm}^{-1}$. Anal. Calcd for $\mathrm{C}_{34} \mathrm{H}_{34} \mathrm{Cl}_{2} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{Pd} \cdot 0.5 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ (\%): C, 49.26; H, 4.20; N, 3.33. Found: C, 49.27; H, 4.32; N, 3.13.

## NMR data

Figure S1 $\quad{ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{P}-\mathbf{P}\left(\mathbf{N M e}_{\mathbf{2}}\right)\left(\right.$ recorded in $\left.\mathrm{CDCl}_{3}\right)$.


Figure S2 $\quad{ }^{13} \mathbf{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound $\mathbf{P}-\mathbf{P}\left(\mathbf{N M e}_{2}\right)$ (recorded in $\left.\mathrm{CDCl}_{3}\right)$.


Figure S3 $\quad{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound $\mathbf{P}-\mathbf{P}\left(\mathbf{N M e}_{2}\right)$ (recorded in $\left.\mathrm{CDCl}_{3}\right)$.


Figure S4 ${ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{1 a}$ (recorded in $\mathrm{CDCl}_{3}$ ).


Figure S5 $\quad{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound 1a (recorded in $\left.\mathrm{CDCl}_{3}\right)$.


Figure S6 $\quad{ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{1 b}$ (recorded in $\mathrm{CDCl}_{3}$ ).


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${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound $\mathbf{1 b}$ (recorded in $\mathrm{CDCl}_{3}$ ).


Figure S8 $\quad{ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{1 c}$ (recorded in $\mathrm{CDCl}_{3}$ ).


Figure S9 $\quad{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound $\mathbf{1 c}$ (recorded in $\mathrm{CDCl}_{3}$ ).


Figure S10 ${ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{2 b}$ (recorded in $\mathrm{CDCl}_{3}$ ).


Figure S11 ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound $\mathbf{2 b}$ (recorded in $\mathrm{CDCl}_{3}$ ).


Figure S12 ${ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{2 c}$ (recorded in $\mathrm{CDCl}_{3}$ ).


Figure S13 ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound $\mathbf{2 c}$ (recorded in $\mathrm{CDCl}_{3}$ ).


Figure S14 ${ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{2 d}$ (recorded in $\mathrm{CDCl}_{3}$ ).


Figure S15 $\quad{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound $\mathbf{2 d}$ (recorded in $\mathrm{CDCl}_{3}$ ).


Figure S16 ${ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{2 e}$ (recorded in $\mathrm{CDCl}_{3}$ ).


Figure S17 ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound $\mathbf{2 e}$ (recorded in $\mathrm{CDCl}_{3}$ ).


Figure S18 ${ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{3 a}$ (recorded in $\mathrm{CD}_{3} \mathrm{CN}$ ).


Figure S19 $\quad{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound $\mathbf{3 a}$ (recorded in $\mathrm{CD}_{3} \mathrm{CN}$ ).


Figure S20 ${ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{3 b}$ (recorded in $\mathrm{CD}_{3} \mathrm{CN}$ ).


Figure S21 $\quad{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound $\mathbf{3 b}$ (recorded in $\mathrm{CD}_{3} \mathrm{CN}$ ).


Figure S22 ${ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{3 c}$ (recorded in $\mathrm{CD}_{3} \mathrm{CN}$ ).


Figure S23 $\quad{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound $\mathbf{3 c}$ (recorded in $\mathrm{CD}_{3} \mathrm{CN}$ ).


Figure S24 ${ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{3 d}$ (recorded in $\mathrm{CD}_{3} \mathrm{CN}$ ).


Figure S25 $\quad{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound $\mathbf{3 d}$ (recorded in $\mathrm{CD}_{3} \mathrm{CN}$ ).


Figure S26 ${ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{4 a}$ (recorded in $\mathrm{CDCl}_{3}$ ).


Figure S27 ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound $\mathbf{4 a}$ (recorded in $\mathrm{CDCl}_{3}$ ).


Figure S28 ${ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{4 b}$ (recorded in $\mathrm{CDCl}_{3}$ ).


Figure S29 ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound $\mathbf{4 b}$ (recorded in $\mathrm{CDCl}_{3}$ ).


## X-ray figures

Figure S30 Molecular structure of $\mathbf{3 a} \cdot 12 \mathrm{CD}_{3} \mathrm{CN}$ in the solid state. All hydrogen atoms and some solvents have been omitted for clarity. Selected bond lengths $[\AA \AA]$ and angles $\left[{ }^{\circ}\right]$ : $\mathrm{Pd}(1)-\mathrm{P}(1) 2.2220(17), \mathrm{Pd}(1)-\mathrm{P}(2 \mathrm{~A}) 2.2337(17), \mathrm{Pd}(1)-\mathrm{Cl}(1) 2.3410(18), \mathrm{Pd}(1)-\mathrm{Cl}(2)$
2.3501(17), $\mathrm{P}(1)-\mathrm{P}(2)$ 2.187(2); $\mathrm{Cl}(1)-\mathrm{Pd}(1)-\mathrm{Cl}(2) 94.72(7), \mathrm{P}(1)-\mathrm{Pd}(2)-\mathrm{P}(2 \mathrm{~A}) 98.56(6)$.


Figure S31 Packing plot of $\mathbf{3 a} \cdot 12 \mathrm{CD}_{3} \mathrm{CN}$ in the solid state showing packing arrangement.


## Single crystal X-ray data for $\mathbf{4 a} \cdot \mathbf{C H}_{\mathbf{2}} \mathbf{C l}_{\mathbf{2}}$

Suitable crystals of $\mathbf{4 a} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$ were obtained by slow diffusion of hexanes onto a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of $\mathbf{4 a}$. Crystal data for $\mathbf{4 a} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}: \mathrm{C}_{34} \mathrm{H}_{34} \mathrm{Cl}_{2} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{Pd} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}: M_{\mathrm{r}}=794.80$, yellow plate, $0.53 \times 0.28 \times 0.06 \mathrm{~mm}^{3}$, monoclinic, space group $P 2_{1} / c, a=9.852(2), b=12.814(3), c$ $=27.315(6) \AA, \beta=98.547(4)^{\circ}, V=3410.0(13) \AA^{3}, T=150(2) \mathrm{K}, Z=4, \lambda=0.71073 \AA$, $\mu\left(\mathrm{Mo}_{\mathrm{K}} \mathrm{K}_{\alpha}\right)=0.98 \mathrm{~mm}^{-1}, \theta$ range for data collection $=1.8-25.0^{\circ}, 5951$ independent reflections measured, $R_{\text {int }}=0.042, d_{\text {calc }}=1.548 \mathrm{~g} \mathrm{~cm}^{-3}, R 1=0.099$ (for 5114 data with $I>$ $2 \sigma(I)), w R 2=0.246$ (for all data), and 399 refined parameters, largest difference map features between 3.05 and $-2.85 \mathrm{e} / \mathrm{A}^{3}$.

Figure S32 Molecular structure of $\mathbf{4 a} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$ in the solid state. All hydrogen atoms and solvents have been omitted for clarity. Selected bond lengths [ $\AA$ ] and angles [ ${ }^{\circ}$ ]: $\operatorname{Pd}(1)-\mathrm{P}(1)$ 2.254(3), $\mathrm{Pd}(1)-\mathrm{P}(2) 2.239(3), \mathrm{Pd}(1)-\mathrm{Cl}(1) 2.365(3), \mathrm{Pd}(1)-\mathrm{Cl}(2) 2.342(3) ; \mathrm{P}(1)-\mathrm{Pd}(2)-\mathrm{P}(2)$ 93.82(10), $\mathrm{Cl}(1)-\mathrm{Pd}(1)-\mathrm{Cl}(2) 90.88(10)$.


