Noncovalent CH–π and π–π Interactions in Phosphoramidite Palladium(II) Complexes with Strong Conformational Preference

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Supporting Information
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1 General Information

Chemicals were purchased from Sigma Aldrich (Merck) and used without any further purification. Deuterated solvents were purchased from Deutero or Sigma Aldrich (Merck). CD$_2$Cl$_2$ was freshly distilled over CaH$_2$ under argon atmosphere; PhMe-$d_8$ was distilled over Na under argon atmosphere. PCl$_3$ was distilled under reduced pressure. The samples were stored at room temperature between the measurements.

Ligands labelled X’ are labelled with an asterisk (X*) in the Figures.

Abbreviations:
- acac: acetylacetonate
- cod: cycloocta-1,5-diene
- eth: ethylene

2 NMR Spectrometer Data

NMR experiments were performed on a Bruker Avance III HD 600 MHz spectrometer, equipped with a 5 mm BB-1H/19F TBI-F probe equipped with a z-gradient (53.5 gauss.cm$^{-1}$). The spectrometer was operating at 600 MHz for $^1$H, 565 MHz for $^{19}$F, 243 MHz for $^{31}$P, and 151 MHz for $^{13}$C. The temperature was controlled in the VT-experiments by BVT 3000 and BVTE 3900. All spectra were recorded in anhydrous CD$_2$Cl$_2$ at 300.0 K if not stated otherwise. Additional NMR spectra were acquired on Bruker Avance III HD 400 MHz spectrometer operating at 400, 376, 162, and 101 MHz, for $^1$H, $^{19}$F, $^{31}$P and $^{13}$C, respectively. For NMR measurements employing standard NMR solvents, 5 mm NMR tubes were used. NMR data were processed, evaluated, and plotted with TopSpin 4.0.8 software. 1D stacked plots were processed and plotted in Mestrenova 14.0. Further plotting of the spectra was performed with Corel Draw 2020 software. $^1$H and $^{13}$C chemical shifts were referenced to the respective solvent signals (5.32 ppm for $^1$H and 54.0 ppm for $^{13}$C in CD$_2$Cl$_2$ at 300 K). The heteronuclear $^{31}$P and $^{19}$F spectra were referenced, employing Ξ (X) according to Harris et al.$^{[1]}$

3 Pulse Sequences and Parameters

Standard Bruker pulse sequences with the following parameters were used throughout the work.

- $^1$H-NMR: zg30; Relaxation delay = 2 s, Acquisition time = 1.27 s, SW = 22.0 ppm, TD = 64k, NS = 8 – 64.
- $^{13}$C($^1$H)-NMR: Pulse program: zgpg30; Relaxation delay = 2.00 s, Acquisition time = 0.80 s, SW = 270.0 ppm, TD = 64k, NS = 8k – 12k.
- $^{19}$F($^1$H)-NMR: Pulse program: zgfhigqn.2; Relaxation delay = 1.00 s, Acquisition time = 2.30 s, SW = 10.0 ppm, TD = 128k, NS = 32 – 64.
- $^{31}$P-NMR: Pulse program: zg; Relaxation delay = 2.00 s, Acquisition time = 4.50 s, SW = 100 ppm, TD = 212k, NS = 64 – 128.
- $^{31}$P($^1$H)-NMR: Pulse program: zgpg; Relaxation delay = 2.00 s, Acquisition time = 1.24 s, SW = 100 ppm, TD = 64k, NS = 256.
1D selective NOESY: Pulse program: selnogp with 180° Gaussian shaped pulse; Relaxation delay = 2.0 s, Acquisition time = 2.53 s, \( SW = 22.0 \text{ ppm} \), \( TD = 64k \), \( NS = 128 - 256 \), mixing time \( D8 = 25 - 400 \text{ ms} \).

1D selective ROESY: Pulse program: selrogp with 180° Gaussian shaped pulse; Relaxation delay = 2.0 s, Acquisition time = 3.20 s, \( SW = 17.0 \text{ ppm} \), \( TD = 64k \), \( NS = 256 \), spinlock time \( P15 = 200 \text{ ms} \).

1D selective TOCSY: pulse program: selmgp with 180° Gaussian shaped pulse; Relaxation delay = 2.0 s, Acquisition time = 2.53 s, \( SW = 21.5 \text{ ppm} \), \( TD = 64k \), \( NS = 32 \), spinlock time \( D9 = 120 \text{ ms} \).

\( ^1\text{H},^1\text{H} - \text{COSY} \): pulse program: cosygpqf; Relaxation delay = 2 s, Acquisition time = 0.34 s (F2), \( SW = 10.0 \text{ ppm} (F2), 10.0 \text{ ppm} (F1) \); \( TD = 4k (F2), 256 (F1) \), \( NS = 4 \).

\( ^3\text{P},^3\text{P} - \text{COSY} \): pulse program: cosyetgp; Relaxation delay = 3 s, Acquisition time = 0.46 s (F2), \( SW = 10.0 \text{ ppm} (F2), 10.0 \text{ ppm} (F1) \); \( TD = 4k (F2), 256 (F1) \), \( NS = 4 \).

\( ^1\text{H},^1\text{H} - \text{TOCSY} \): pulse program: mlevphpp or mlevesgpph; Relaxation delay = 2 s, Acquisition time = 0.85 s (F2), \( SW = 2.0 \text{ ppm} (F2), 2.0 \text{ ppm} (F1) \); \( O1P = 7.5, TD = 2k (F2), 256 (F1) \), \( NS = 16 \), spinlock time \( D9 = 80 - 120 \text{ ms} \).

\( ^1\text{H},^1\text{H} - \text{HSQC} \): pulse program: hsqcetgpsi2; Relaxation delay = 2.0 s, Acquisition time = 0.17 s (F2), \( SW = 10.0 \text{ ppm} (F2), 160 \text{ ppm} (F1) \); \( TD = 2k (F2), 256 (F1) \), \( NS = 8 \), \( \text{cnst2} = 145 \text{ Hz} \).

\( ^1\text{H},^1\text{H} - \text{HSQC-TOCSY} \): pulse program: hsqcdietgpsisp.2; Relaxation delay = 2.0 s, Acquisition time = 0.17 s (F2), \( SW = 10.0 \text{ ppm} (F2), 160 \text{ ppm} (F1) \); \( TD = 2k (F2), 256 (F1) \), \( DS = 32 \), \( NS = 24 \), \( \text{cnst2} = 145 \text{ Hz} \), \( D9 = 80 \text{ ms} \).

\( ^1\text{H},^{13}\text{C} - \text{HMBC} \): Pulse program: hmbcgplpndqf; Relaxation delay = 2.0 s, Acquisition time = 0.22 s, \( SW = 15.0 \text{ ppm} (F2), 220 \text{ ppm} (F1) \); \( TD = 4k (F2), 256 (F1) \), \( NS = 12 \), \( \text{cnst13} = 10 \text{ Hz} \).

\( ^1\text{H},^{31}\text{P} - \text{HMBC} \): Pulse program: inv4gplrndqf; Relaxation delay = 2.0 s, Acquisition time = 0.28 s, \( SW = 12.0 \text{ ppm} (F2), 100 \text{ ppm} (F1) \); \( TD = 4k (F2), 256 (F1) \), \( NS = 4 - 8 \); delay for the evolution of long-range couplings \( D6 = 60 \text{ ms} \).

\( ^1\text{H},^1\text{H} - \text{NOESY} \): Pulse program: noesygpph; Relaxation delay = 4.0 s, Acquisition time = 0.31 s, \( SW = 16 \text{ ppm} (F2), 16 \text{ ppm} (F1) \); \( TD = 6k (F2), 256 (F1) \), \( NS = 24 \), mixing time \( D8 = 300 - 400 \text{ ms} \).

\( ^1\text{H},^1\text{H} - \text{ROESY} \): Pulse program: roesyphpp.2; Relaxation delay = 5.0 s, Acquisition time = 0.29 s, \( SW = 17 \text{ ppm} (F2), 17 \text{ ppm} (F1) \); \( TD = 6k (F2), 256 (F1) \), \( NS = 36 \), spinlock time = 200 ms.

\( ^1\text{H},^{19}\text{F} - \text{HOESY} \): Pulse program: hoesyph or hoesygpph; Relaxation delay = 3.0 s, Acquisition time = 1.82 s, \( SW = 2 \text{ ppm} (F2), 16 \text{ ppm} (F1) \); \( TD = 512 (F1) \), \( NS = 16 \), mixing time \( D8 = 300 - 350 \text{ ms} \).

\( ^1\text{H} \text{ Inversion recovery} \): pulse program: t1ir; Relaxation delay = 15 s, Acquisition time = 1.27 s, \( SW = 21.55 \text{ ppm} \), 10 experiments with variable delay 0.01 s – 15 s, \( NS = 8 \).
4 Structures of Ligands

**Amide Group Variation**

- B
- B' (R)
- B (S)
- C
- D
- D' (R)
- D (S)
- E
- E' (R)
- E (S)
- G
- G' (R)
- G (S)
- H
- H' (R)
- H (S)

**Aryl Group Variations**

- E2
- E2' (R)
- E2 (S)
- E3
- E3' (R)
- E3 (S)
- E4
- E4' (R)
- E4 (S)
- E5
- E5' (R)
- E5 (S)
- E6
- E6' (R)
- E6 (S)

**Symmetric Ligands**

- A1
- A1' (R)
- A1 (S)
- A2
- A2' (R)
- A2 (S)
- F
- F' (R)
- F (S)

(S)
5 Supramolecular Balance

The supramolecular balance using cis-Pd(II) bis(phosphoramidite complexes was proposed earlier by our group.\textsuperscript{[2,3]}

\[
K_{eq}(A/F) = \frac{[\text{Pd}(A)(F)\text{Cl}_2]^2}{[\text{Pd}(A)_2\text{Cl}_2][\text{Pd}(F)_2\text{Cl}_2]}
\]

where the concentrations of the complexes were taken from $^{31}$P NMR spectra.

\[
\Delta G_{(A/F)} = -RT \ln K_{eq(A/F)}
\]
6 Additional Results

6.1 Diastereomer of Ligand F

Using ligand F’, an (S,S,S)-diastereomer of ligand F, the hetero- to homocomplex ratios of cis-PdL₂Cl₂ were nearly statistical. This result shows that the configuration and axial chirality of ligand F is essential in the supramolecular balance.

Figure S2. Hetero- to homocomplex ratios of mixtures of ligands E/E’ and ligand F’.

6.2 Symmetric Di(isopropyl) Biphenol Ligand

Ligand I is an achiral and symmetric alternative of ligands E/E’, containing two isopropyl groups. The hetero- to homocomplex ratio 16:1:1 is between the ratios for the ligands E and E’. There is free rotation about C-N and P-N bonds. The complex cis-Pd(I)(F)Cl₂ showed two doublets for methyl groups at 300 K due to this rotation. However, at 190 K, the rotation was slowed down. Methyl groups “1” and “2”; and “3” and “4” are connected within isopropyl groups as shown by COSY experiment. Methyl groups “1” and “3”; and “2” and “4” are in mutual exchange. Because at these experimental conditions the NOE crosspeaks had the same phase as the exchange peaks, additional ROESY experiment was performed that clearly distinguished between these two. NOE/ROE crosspeaks to the naphthyl backbone were detected only for the “2” and “4” methyl groups, confirming the synchronized rotation in the complex, i.e. the isopropyl groups pointing outside and inside of the complex can exchange, but without any further C-N bond rotation.
Figure S3. Slowed rotation of di(isopropyl) group in the complex cis-Pd(I)(F)Cl₂, corroborated by NOESY and ROESY experiments at 190 K.

6.3 Isomerization Process

The trans-cis isomerization proceeds most probably via associative substitution and Berry pseudorotation of the pentacoordinate system, which is a typical process for square planar d⁶-metal complexes such as Pd(II) (see J. Hartwig, Organotransition Metal Chemistry, University Science Books, Sausalitos, 2010). In our system, no intermediate complexes were detected by NMR.
7 NMR Features of the Supramolecular Balance

7.1 Trans- to Cis- Isomerization

Figure S4. $^{31}$P/$^1$H NMR (243 MHz, CD$_2$Cl$_2$) spectra of trans-complexes with ligands H and F (top), and cis-complexes with ligands E' and F (bottom). The small outer peaks of the AB system in the trans-complexes are often hidden in the noise.

Figure S5. $^{31}$P/$^{31}$P $^1$H-COSY (243 MHz, CD$_2$Cl$_2$) spectrum of cis-complexes with ligands E' and F, showing correlation between the two different ligands in the heterocomplex. The E' ligand in the heterocomplex is colored in blue, while the F ligand is colored in green.
Figure S6. $^{1}H,^{31}P$-HMBC (600 MHz, CD$_2$Cl$_2$) spectrum of cis-complexes with ligands E’ and F, showing correlation between protons and phosphorus nuclei in the complexes. The E’ ligand in the heterocomplex is colored in blue, while the F ligand is colored in green.

Figure S7. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra of trans- and cis-complexes with ligands E/E’ and F, showing upfield chemical shift of the methyl signals upon isomerization.
Figure S8. $^{31}$P($^1$H) NMR (243 MHz, CD$_2$Cl$_2$) spectra of trans-complexes with ligands H and F (bottom), and the isomerization process to the cis-complexes (top).

Table 1. $^1$H chemical shift differences upon trans- to cis-complex isomerization are larger in the heterocomplexes compared to the homocomplexes, indicating stronger interactions in the heterocomplexes.

| Complex       | Proton (E) | trans/ cis | $\Delta \delta$ | Complex       | Proton (H) | trans/ cis | $\Delta \delta$ |
|---------------|-----------|------------|-----------------|---------------|-----------|------------|-----------------|
| Pd(E)(F)Cl$_2$| Ph(CH)$_3$| 5.66       | 4.23            | -1.43         | Pd(H)(F)Cl$_2$| Ph(CH)$_3$| 5.68       | 4.23            | -1.45         |
|               | CH(CH$_3$)$_2$| 3.47  | 2.82            | -0.65         | CH(CH$_3$)$_2$| Ph(CH)$_3$| 3.02       | 2.40            | -0.62         |
| Pd(E)$_2$Cl$_2$| Ph(CH)$_3$| 5.71       | 4.77            | -0.94         | Pd(H)$_2$Cl$_2$| Ph(CH)$_3$| 5.68       | 4.78            | -0.90         |
|               | CH(CH$_3$)$_2$| 3.47  | 3.16            | -0.31         | CH(CH$_3$)$_2$| Ph(CH)$_3$| 3.01       | 2.78            | -0.23         |
7.2 NOE Interactions

7.2.1 Complex cis-Pd(E)(F)Cl$_2$

Figure S9. 1D NOESY (600 MHz, CD$_2$Cl$_2$, 300 K, mixing time 300 ms) spectra of cis-Pd(E)(F)Cl$_2$, showing interligand NOEs between the Ph(Me)CH group of ligand E and naphthyl ring of ligand F.
Figure S10. 2D NOESY (600 MHz, CD$_2$Cl$_2$, 300 K) spectra of cis-Pd(E)(F)Cl$_2$, showing interligand NOEs between the Ph(Me)CH group of ligand E and naphthyl ring of ligand F.

Figure S11. 2D NOESY (600 MHz, CD$_2$Cl$_2$, 200 K, mixing time 450 ms) spectra of cis-Pd(E)(F)Cl$_2$, showing interligand NOEs between the Ph(Me)CH group of ligand E and naphthyl ring of ligand F.
7.2.2 Complex \( \text{cis-Pd(E')}\text{(F)Cl}_2 \)

*Figure S12.* 1D NOESY (600 MHz, CD\(_2\)Cl\(_2\), 300 K, mixing time 300 ms) spectra of \( \text{cis-Pd(E')}\text{(F)Cl}_2 \), showing no interligand NOEs between the Ph(Me)CH group of ligand E' and naphthyl ring of ligand F.

*Figure S13.* 2D NOESY (600 MHz, CD\(_2\)Cl\(_2\), 210 K, mixing time 400 ms) spectra of \( \text{cis-Pd(E')}\text{(F)Cl}_2 \), showing no interligand NOEs between the Ph(Me)CH group of ligand E' and naphthyl ring of ligand F.
7.2.3 Complex \textit{cis}-\textrm{Pd}(\text{H})(\text{F})\text{Cl}_2

Figure S14. 1D NOESY (600 MHz, CD$_2$Cl$_2$, 300 K, mixing time 350 ms) spectra of \textit{cis}-\textrm{Pd}(\text{H})(\text{F})\text{Cl}_2, showing interligand NOEs between the Ph(\text{Me})\text{CH} group of ligand \text{H} and naphthyl ring of ligand \text{F}.

Figure S15. 2D NOESY (600 MHz, CD$_2$Cl$_2$, 300 K) spectra of \textit{cis}-\textrm{Pd}(\text{H})(\text{F})\text{Cl}_2, showing interligand NOEs between the Ph(\text{Me})\text{CH} group of ligand \text{H} and naphthyl ring of ligand \text{F}.
7.2.4 Complex \( \text{cis-Pd(H')}\text{(F)Cl}_2 \)

\[ \text{cis-Pd(H')}\text{(F)Cl}_2 \]

Figure S16. 1D NOESY (600 MHz, CD\(_2\)Cl\(_2\), 300 K, mixing time 350 ms) spectra of \( \text{cis-Pd(H')}\text{(F)Cl}_2 \), showing no interligand NOEs between the Ph(Me)CH group of ligand H' and naphthyl ring of ligand F. A weak interaction between the cyclohexyl CH and the naphthyl group was detected, possibly due to competing interactions and conformational restriction of rotation.
Figure S17. 1D NOESY (600 MHz, CD$_2$Cl$_2$, 300 K, mixing time 400 ms) spectra of cis-Pd(E2)(F)Cl$_2$, showing interligand NOEs between the Ph(Me)CH group of ligand E2 and naphthyl ring of ligand F.
Figure S18. 1D NOESY (600 MHz, CD$_2$Cl$_2$, 300 K, mixing time 400 ms) spectra of cis-Pd(E2)(F)Cl$_2$, showing no interligand NOEs between the $i$-Pr group of ligand E2 and naphthyl ring of ligand F.
7.2.6 Complex \( \text{cis-Pd(E2')}(\text{F})\text{Cl}_2 \)

\[ \text{cis-Pd(E2')}(\text{F})\text{Cl}_2 \]
Figure S19. 2D NOESY (600 MHz, CD$_2$Cl$_2$, 300 K) spectra of cis-Pd(E2')(F)Cl$_2$, showing interligand NOEs between the 4-MeOC$_6$H$_4$(Me)CH group of ligand E2' and naphthyl ring of ligand F.
7.3 Variable Temperature NMR

7.3.1 Complex cis-Pd(E)(F)Cl₂

The heterocomplex cis-Pd(E')(F)Cl₂ showed less dependence on the temperature than complex cis-Pd(E)(F)Cl₂. Downfield $^{31}$P doublet (ligand F) of the heterocomplex remained sharp even at very low temperatures in both complexes, while the ligand E phosphorus signal (upfield doublet) reached coalescence at 220 – 230 K, due to slowed-down rotation around the biphenyl axis (atropisomerism). The $^1$H signals of cis-Pd(E')(F)Cl₂ also remained sharp down to 220 K, suggesting a higher stability and/or reduced flexibility of this complex than cis-Pd(E)(F)Cl₂.

Figure S20. Variable temperature $^{31}$P NMR (243 MHz, CD₂Cl₂) of the heterocomplex cis-Pd(E)(F)Cl₂ and the corresponding homocomplexes.
**Figure S21.** Aliphatic portion (0 – 2 ppm) of variable temperature $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra (spectra 1 – 13: 180 – 300 K).

**Figure S22.** Aliphatic portion of variable temperature $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra (spectra 1 – 13: 180 – 300 K).
Figure S23. Aromatic portion of variable temperature $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra (spectra 1 – 13: 180 – 300 K).

7.3.2 Complex cis-Pd(E')(F)Cl$_2$
Figure S24. Variable temperature $^{31}$P NMR (243 MHz, CD$_2$Cl$_2$) spectra (spectra 1 – 9: 180 – 260 K; spectrum 10: 280 K; spectrum 11: 300 K).

Figure S25. Portion of variable temperature $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra (spectra 1 – 9: 180 – 260 K; spectrum 10: 280 K; spectrum 11: 300 K).

Figure S26. Portion of variable temperature $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra (spectra 1 – 9: 180 – 260 K; spectrum 10: 280 K; spectrum 11: 300 K).
Figure S27. Portion of variable temperature $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra (spectra 1 – 9: 180 – 260 K; spectrum 10: 280 K; spectrum 11: 300 K).
7.4 Homocomplexes

Figure S28. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra of free ligand E and trans- and cis-homocomplexes Pd(E)$_2$Cl$_2$. Orange dots mark the free cod signals. The horizontal red arrow represents the signal dispersion present in the cis-complex.

Figure S29. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra of trans- and cis-homocomplexes Pd(E)$_2$Cl$_2$, showing upfield chemical shift changes upon isomerization.
Figure S30. $^{31}$P NMR (243 MHz, CD$_2$Cl$_2$) spectra of the isomerization process of homocomplex trans-Pd(E)$_2$Cl$_2$ to the corresponding homocomplexes.
7.5 Solvent Effects

*Table 2.* Hetero- to homocomplex ratios of cis-Pd(E)(F)Cl$_2$ and cis-Pd(E')(F)Cl$_2$ in different solvents. Additional $^{31}$P peaks were present (marked with asterisk).

| solvent  | cis-Pd(E)(F)Cl$_2$ | cis-Pd(E')(F)Cl$_2$ |
|----------|--------------------|---------------------|
| CD$_2$Cl$_2$ | 8:1:1              | 22:1:1              |
| CDCl$_3$   | 12:1:1             | 64:1:1              |
| PhMe-$d_8$ | *                 | 48:1:1              |
| THF-$d_8$  | 6:1:1              | 63:1:1’             |

*Table 3.* Hetero- to homocomplex ratios of cis-Pd(H)(F)Cl$_2$ and cis-Pd(H')(F)Cl$_2$ in different solvents. Additional $^{31}$P peaks were present in THF-$d_8$ (marked with asterisk).

| solvent  | cis-Pd(H)(F)Cl$_2$ | cis-Pd(H')(F)Cl$_2$ |
|----------|--------------------|---------------------|
| CD$_2$Cl$_2$ | 3:1:1              | 15:1:1              |
| THF-$d_8$  | 7:1:1’             | 9:1:1’              |
8 Structural Assignment

$^1$H NMR; $^{13}$C NMR; $^1$H,$^1$H-COSY; $^1$H,$^1$H-TOCSY; $^1$H,$^1$H-NOESY/ROESY; $^1$H,$^{13}$C-HSQC; $^1$H,$^{13}$C-HSQC-TOCSY; $^1$H,$^{13}$C-HMBC; and $^1$H,$^{31}$P-HMBC spectra were acquired for the structural elucidation. In some cases, the overlap of signals prevented full assignment. Signals of the released COD ($\delta_H$ 2.35 and 5.56 ppm) were present in all spectra.

8.1 Cis-Pd(E)$_2$Cl$_2$

The structure of the cis-homocomplex is symmetric and only one set of signal is observed.

| $^1$H - Ligand E | $^{13}$C - Ligand E |
|------------------|--------------------|
| a                | 130.3              |
| b                | 149.4              |
| c                | 8.14               |
|                  | 125.04             |
| d                | 7.47               |
|                  | 130.35             |
| e                | 7.11               |
|                  | 126.90             |
| f                | 6.80               |
|                  | 130.2              |
| g                | 3.16               |
|                  | 49.60              |
| h                | 0.41               |
|                  | 24.22              |
| i                | 1.11               |
|                  | 24.05              |
| j                | 4.78               |
|                  | 57.20              |
| k                | 1.47               |
|                  | 17.61              |
| l                | 141.71             |
| m                | 7.22               |
|                  | 128.10             |
| n                | 6.89               |
|                  | 127.80             |
| o                | 7.05               |
|                  | 127.47             |
8.2  Cis-Pd(E)(F)Cl₂

| H - Ligand E | C - Ligand E |
|--------------|--------------|
| A            | 122.0        |
| B            | 151.2        |
| C            | 7.28         |
| D            | 7.18         |
| E            | 7.09         |
| F            | 7.39         |
| a            | 130.8        |
| b            | 149.7        |
| c            | 8.17         |
| d            | 7.50         |
| e            | 7.12         |
| f            | 6.76         |
| g            | 2.83         |
| h            | 0.10         |
| i            | 1.06         |
| j            | 4.24         |
| k            | 0.95         |
| l            | 141.0        |
| m            | 6.93         |
| n            | 6.78         |
| o            |              |

| H - Ligand F | C - Ligand F |
|--------------|--------------|
| 1            | 123.4        |
| 2            | 148.0        |
| 3            | 8.56         |
| 4            | 8.12         |
| 5            | 131.1        |
| 6            | 131.9        |
| 7            | 7.85         |
| 8            | 7.26         |
| 9            | 6.62         |
| 10           | -            |
| 11           | 4.52         |
| 12           | 1.54         |
| 13           | 141.3        |
| 14           | 6.71         |
| 15           | 6.48         |
| 16           | 6.66         |
| 1'           | 121.9        |
| 2'           | 148.8        |
| 3'           | 6.85         |
| 4'           | 7.44         |
| 5'           | 131.6        |
| 6'           | 7.79         |
| 7'           | 7.42         |
| 8'           | 7.17         |
| 9'           | 7.10         |
| 10'          | 132.9        |
### 8.3 Cis-Pd(E')(F)Cl₂

|        | ¹H - Ligand E' | ¹³C - Ligand E' | ¹H - Ligand F | ¹³C - Ligand F |
|--------|----------------|----------------|--------------|----------------|
| A      |                |                | 1            | 123.56         |
| B      |                | 150.56         | 2            | 148.15         |
| C      | 7.18           |                | 3            | 8.52           |
| D      | 7.41           |                | 4            | 7.77           |
| E      | 7.37 126.06    |                | 5            | 132.54         |
| F      | 7.05 129.05    |                | 6            |                |
| a      |                | 130.45         | 7            | 7.23           |
| b      |                | 148.99         | 8            |                |
| c      | 8.18 124.95    |                | 9            |                |
| d      | 7.48 130.36    |                | 10           | 132.59         |
| e      | 7.13 126.83    |                | 11           | 4.59 56.46     |
| f      | 6.85 130.14    |                | 12           | 1.53 19.30     |
| g      | 2.81 49.55     |                | 13           | 141.60         |
| h      | 0.62 23.16     |                | 14           | 6.67 128.79    |
| i      | 0.42 24.40     |                | 15           | 6.50 127.69    |
| j      | 4.40 55.27     |                | 16           | 6.71 127.41    |
| k      | 0.85 18.6      |                | 1'           | 122.0          |
| l      |                | 138.8          | 2'           | 148.95         |
| m      |                |                | 3'           | 6.84 119.69    |
| n      | 7.08 128.9     |                | 4'           | 7.40 131.64    |
| o      |                |                | 5'           |                |
|        |                |                | 6'           |                |
|        |                |                | 7'           |                |
|        |                |                | 8'           |                |
|        |                |                | 9'           |                |
|        |                |                | 10'          |                |
### 8.4 Cis-Pd(H)(F)Cl₂

![Diagram of Cis-Pd(H)(F)Cl₂]

|   | ¹H - Ligand H | ¹³C - Ligand H |   | ¹H - Ligand F | ¹³C - Ligand F |
|---|--------------|--------------|---|--------------|--------------|
| A | 130.52       |              | 1 | 123.41       |              |
| B | 150.59       |              | 2 | 148.19       |              |
| C | 7.13         | 121.22       | 3 | 8.54         | 124.03       |
| D | 7.35         | 130.08       | 4 | 8.11         | 131.22       |
| E | 7.25         | 126.24       | 5 |             | 132.26       |
| F | 7.34         | 130.2        | 6 | 7.84         | 128.27       |
| a | 130.45       |              | 7 | 7.25         | 125.82       |
| b | 149.36       |              | 8 | 6.6          | 126.39       |
| c | 8.13         | 125.16       | 9 | 6.29         | 127.17       |
| d | 7.49         | 130.38       | 10|             | 131.79       |
| e | 7.1          | 126.87       | 11| 4.5          | 56.55        |
| f | 6.72         | 130.07       | 12| 1.52         | 19.25        |
| g | 4.23         | 56.37        | 13|             | 141.49       |
| h | 0.94         | 16.36        | 14| 6.64         | 128.87       |
| i | 140.86       |              | 15| 6.48         | 127.7        |
| j | 6.92         | 128.47       | 16| 6.69         | 127.41       |
| k | 6.75         | 127.82       | 1' |             | 122.1        |
| l | 6.88         | 127.45       | 2' |             | 149          |
| m | 2.4          | 57.57        | 3' | 6.86         | 119.74       |
| n | 1.64         | 34.42        | 4' | 7.45         | 131.69       |
| o | 1.44         | 26.87        | 5' |             | 132.31       |
| p | 0.48         | 25.38        | 6' | 7.78         | 128.78       |
| q | 0.89         | 27.2         | 7' | 7.42         | 125.68       |
| r | 0.53         | 34.58        | 8' | 7.17         | 126.61       |
| n' | 1.75        |              | 9' | 7.09         | 127.6        |
| o' | 0.74        |              | 10'|           | 133.02       |
| p' | 1.03        |              |    |              |              |
| q' | 0.39        |              |    |              |              |
| r' | 0.4         |              |    |              |              |
### 8.5 Cis-Pd(H')\((F)Cl_2\)

![Diagram of Cis-Pd(H')(F)Cl₂]

|      | \(^1\text{H} - \text{Ligand H'}\) | \(^{13}\text{C} - \text{Ligand H'}\) | \(^1\text{H} - \text{Ligand F}\) | \(^{13}\text{C} - \text{Ligand F}\) |
|------|----------------------------------|----------------------------------|-------------------------------|----------------------------------|
| **A** |                                  | 130.87                           |                               | 1                                | 123.22                           |
| **B** |                                  | 150.37                           |                               | 2                                | 148.24                           |
| **C** | 7.2                              | 121.44                           |                               | 3                                | 8.54                             | 123.69                           |
| **D** | 7.47                             | 130.15                           |                               | 4                                | 7.77                             | 131.94                           |
| **E** | 7.36                             | 126.51                           |                               | 5                                |                                  | 132.43                           |
| **F** | 7.46                             | 130.51                           |                               | 6                                | 7.34                             | 129.29                           |
| **a** |                                  | 130.88                           |                               | 7                                | 7.15                             | 125.99                           |
| **b** |                                  | 149.08                           |                               | 8                                | 7.16                             | 126.92                           |
| **c** | 8.17                             | 125.16                           |                               | 9                                | 7.08                             | 127.62                           |
| **d** | 7.49                             | 130.43                           |                               | **10**                           |                                  | 132.08                           |
| **e** | 7.12                             | 126.82                           |                               | **11**                           | 4.59                             | 56.4                             |
| **f** | 6.84                             | 130.09                           |                               | **12**                           | 1.52                             | 19.32                           |
| **g** | 4.41                             | 55.5                             |                               | **13**                           |                                  | 141.55                           |
| **h** | 0.79                             | 18.7                             |                               | **14**                           | 6.67                             | 128.77                           |
| **i** |                                  | 138.77                           |                               | **15**                           | 6.5                              | 127.7                            |
| **j** | 7.09                             | 129.15                           |                               | **16**                           | 6.7                              | 127.36                           |
| **k** | 7.09                             | 127.78                           |                               | **1’**                           | 121.94                           |
| **l** | 7.09                             | 126.53                           |                               | **2’**                           | 148.99                           |
| **m** | 2.35                             | 58.27                            |                               | **3’**                           | 6.87                             | 119.79                           |
| **n** | 1.42                             | 33.09                            |                               | **4’**                           | 7.42                             | 131.61                           |
| **o** | 0.29                             | 26.8                             |                               | **5’**                           |                                  | 132.1                            |
| **p** | 0.47                             | 25.28                            |                               | **6’**                           | 7.78                             | 128.84                           |
| **q** | 0.64                             | 27.35                            |                               | **7’**                           | 7.44                             | 125.87                           |
| **r** | 0.73                             | 34.91                            |                               | **8’**                           | 7.25                             | 126.74                           |
| **n’**| 0.96                             |                                  |                               | **9’**                           | 7.23                             | 127.65                           |
| **o’**| 1.18                             |                                  |                               | **10’**                          |                                  | 133.04                           |
| **p’**| 1.01                             |                                  |                               |                                  |                                  |                                  |
| **q’**| 1.06                             |                                  |                               |                                  |                                  |                                  |
| **r’**| 0.9                              |                                  |                               |                                  |                                  |                                  |
Cis-Pd(E2)(F)Cl₂

|   | ¹H - Ligand E2 | ¹³C - Ligand E2 | ¹H - Ligand F | ¹³C - Ligand F |
|---|---------------|----------------|--------------|---------------|
| A |               | 132.29         | 1            | 123.5         |
| B |               | 150.91         | 2            | 148.24        |
| C | 7.12          | 121.19         | 3            | 8.55          |
| D | 7.38          | 130.14         | 4            | 8.12          |
| E | 7.27          | 126.2          | 5            | 132.26        |
| F | 7.34          | 130.33         | 6            | 7.86          |
| a |               | 132.01         | 7            | 7.28          |
| b |               | 149.4          | 8            | 6.7           |
| c | 8.15          | 125.2          | 9            | 6.42          |
| d | 7.49          | 130.44         | 10           | 132.14        |
| e | 7.1           | 126.83         | 11           | 4.5           |
| f | 6.74          | 130.06         | 12           | 1.53          |
| g | 2.84          | 48.58          | 13           | 141.48        |
| h | 1.02          | 23.85          | 14           | 6.65          |
| i | 0.13          | 23.85          | 15           | 6.47          |
| j | 4.21          | 55.61          | 16           | 6.7           |
| k | 0.95          | 16.7           | 1'           | 122           |
| l | 4.22          | 132.9          | 2'           | 149.06        |
| m | 6.83          | 129.54         | 3'           | 6.82          |
| n | 6.29          | 113.1          | 4'           | 7.44          |
| o |               | 158.92         | 5'           | 132.86        |
| p | 3.6           | 55.51          | 6'           | 7.79          |
|   |               |                | 7'           | 7.42          |
|   |               |                | 8'           | 7.2           |
|   |               |                | 9'           | 7.11          |
|   |               |                | 10'          | 133           |
### Cis-Pd(E'2)(F)Cl₂

|       | ¹H - Ligand E₂' | ¹³C - Ligand E₂' | ¹H - Ligand F | ¹³C - Ligand F |
|-------|----------------|-----------------|---------------|---------------|
| A     | 123.29         | 132.47          | 150.66        | 148.27        |
| B     | 130.37         | 126.82          | 149.12        | 148.91        |
| C     | 7.19           | 121.49          | 8.53          | 123.26        |
| D     | 130.93         | 126.56          | 7.81          | 131.81        |
| E     | 7.48           | 130.46          | 7.44          | 132.96        |
| F     | 7.44           | 130.5           | 7.41          | 129.26        |
| a     | 130.37         | 125.14          | 7.2           | 126.06        |
| b     | 149.12         | 130.17          | 7.11          | 126.97        |
| c     | 8.18           | 125.14          | 7.1           | 129.38        |
| d     | 7.48           | 126.82          | 7.11          | 132.15        |
| e     | 7.12           | 130.17          | 4.59          | 56.49         |
| f     | 6.85           | 49.23           | 1.53          | 19.31         |
| g     | 2.79           | 6.84            | 6.67          | 128.79        |
| h     | 0.64           | 23.26           | 6.5           | 127.72        |
| i     | 0.41           | 24.41           | 6.71          | 127.39        |
| j     | 4.37           | 54.9            | 121.87        | 132.96        |
| k     | 0.81           | 18.74           | 148.91        | 132.09        |
| l     | 130.83         | 6.84            | 7.4           | 131.63        |
| m     | 6.96           | 113.19          | 7.2           | 127.66        |
| n     | 6.61           | 159.26          | 7.24          | 127.66        |
| o     | 3.82           | 7.77            | 7.24          | 133.04        |
| p     | 55.74          | 7.77            |               |               |
### 8.8 Cis-Pd(E3)(F)Cl₂

![Chemical Structure of Cis-Pd(E3)(F)Cl₂]

|          | ¹H - Ligand E₃ | ¹³C - Ligand E₃ | ¹H - Ligand F | ¹³C - Ligand F |
|----------|---------------|----------------|--------------|---------------|
| A        | 130.2         | 150.88         | 1            | 123.56        |
| B        | 150.88        | 121.24         | 2            | 148.18        |
| C        | 7.24          | 121.24         | 3            | 8.55          |
| D        | 7.39          | 130.15         | 4            | 8.12          |
| E        | 7.28          | 126.24         | 5            | 132.23        |
| F        | 7.35          | 130.33         | 6            | 7.87          |
| a        | 130.42        | 149.35         | 7            | 7.29          |
| b        | 149.35        | 125.19         | 8            | 6.69          |
| c        | 8.16          | 125.19         | 9            | 6.39          |
| d        | 7.49          | 130.42         | 10           | 127.17        |
| e        | 7.1           | 126.85         | 11           | 132.17        |
| f        | 6.75          | 130.06         | 12           | 4.52          |
| g        | 2.85          | 48.96          | 13           | 19.22         |
| h        | 1.02          | 23.97          | 14           | 141.49        |
| i        | 0.15          | 23.93          | 15           | 6.66          |
| j        | 4.22          | 56.17          | 16           | 128.83        |
| k        | 0.97          | 16.53          | 1'           | 121.95        |
| l        | 142.43        | 127.43         | 2'           | 149.02        |
| m        | 6.38          | 114.91         | 3'           | 119.89        |
| n        | 159.59        | 128.57         | 4'           | 7.4           |
| o        | 6.42          | 112.1          | 5'           | 131.58        |
| p        | 6.66          | 128.57         | 6'           | 7.78          |
| q        | 6.62          | 121.11         | 7'           | 128.73        |
| r        | 3.51          | 55.51          | 8'           | 7.42          |
|          |               |                | 9'           | 125.7         |
|          |               |                | 10'          | 127.51        |
|          |               |                |               | 132.94        |
### SUPPORTING INFORMATION

#### 8.9 Cis-Pd(E3')(F)Cl₂

![Diagram of Cis-Pd(E3')(F)Cl₂]

|      | ¹H - Ligand E3' | ¹³C - Ligand E3' | ¹H - Ligand F | ¹³C - Ligand F |
|------|----------------|-----------------|--------------|----------------|
| A    |                | 130.9           |              | 123.27         |
| B    |                | 150.59          |              | 148.22         |
| C    | 7.24           | 121.44          | 3            | 8.52           |
| D    | 7.45           | 130.48          | 4            | 7.76           |
| E    | 7.18           | 126.57          | 5            |                |
| F    | 7.35           | 130.21          | 6            | 7.38           |
| a    |                | 130.53          | 7            | 7.14           |
| b    |                | 149.05          | 8            | 7.12           |
| c    | 8.13           | 125.02          | 9            | 7.1            |
| d    | 7.48           | 130.34          | 10           | 7.1            |
| e    | 7.16           | 126.82          | 11           | 4.6            |
| f    | 6.92           | 130.1           | 12           | 1.53           |
| g    | 2.79           | 49.67           | 13           | 141.55         |
| h    | 0.7            | 23.34           | 14           | 6.68           |
| i    | 0.42           | 24.49           | 15           | 6.5            |
| j    | 4.35           | 55.21           | 16           | 6.71           |
| k    | 0.83           | 18.69           | 1'           | 121.89         |
| l    |                | 140.28          | 2'           | 148.89         |
| m    | 6.74           | 114.72          | 3'           | 6.85           |
| n    |                | 159.43          | 4'           | 7.4            |
| o    | 6.7            | 113.85          | 5'           |                |
| p    | 6.94           | 128.76          | 6'           | 7.78           |
| q    | 6.47           | 120.82          | 7'           | 7.42           |
| r    | 3.87           | 56.35           | 8'           | 7.25           |
|      |                |                  | 9'           | 7.24           |
|      |                |                  | 10'          | 132.95         |
8.10 Cis-Pd(E4)(F)Cl₂

|   | ¹H - Ligand E₄ | ¹³C - Ligand E₄ |   | ¹H - Ligand F | ¹³C - Ligand F |
|---|----------------|----------------|---|--------------|----------------|
| A |               | 130.51         | 1 |              | 123.48         |
| B |               | 150.82         | 2 |              | 148.23         |
| C | 7.07          | 120.98         | 3 | 8.56         | 124.06         |
| D | 7.39          | 130.21         | 4 | 8.12         | 131.25         |
| E | 7.29          | 126.32         | 5 |             | 132.27         |
| F | 7.35          | 130.42         | 6 | 7.87         | 128.51         |
| a |               | 130.34         | 7 | 7.29         | 125.96         |
| b |               | 149.29         | 8 | 6.75         | 126.35         |
| c | 8.15          | 125.18         | 9 | 6.45         | 127.08         |
| d | 7.49          | 130.46         | 10|             | 132.06         |
| e | 7.11          | 126.92         | 11| 4.5          | 56.56          |
| f | 6.76          | 130.05         | 12| 1.53         | 19.32          |
| g | 2.81          | 48.8           | 13|             | 141.42         |
| h | 1.02          | 23.77          | 14| 6.64         | 128.81         |
| i | 0.14          | 23.82          | 15| 6.47         | 127.73         |
| j | 4.22          | 55.66          | 16| 6.71         | 127.46         |
| k | 1             | 16.71          | 1’|             | 121.96         |
| l |               | 136.86         | 2’|             | 148.91         |
| m | 6.91          | 130.1          | 3’| 6.82         | 119.52         |
| n | 6.47          | 114.6          | 4’| 7.45         | 131.84         |
| o |               | 162.2          | 5’|             | 132.04         |
|   |               |                | 6’| 7.79         | 128.85         |
|   |               |                | 7’| 7.43         | 125.86         |
|   |               |                | 8’| 7.21         | 126.76         |
|   |               |                | 9’| 7.13         | 127.51         |
|   |               |                | 10’|            | 132.98        |
8.11 Cis-Pd(E4')(F)Cl2

|       | 1H - Ligand E4' | 13C - Ligand E4' | 1H - Ligand F | 13C - Ligand F |
|-------|-----------------|------------------|---------------|---------------|
| A     | 130.8           |                  | 1             | 123.22        |
| B     | 150.62          |                  | 2             | 148.2         |
| C     | 7.19            | 121.39           | 3             | 8.51          | 123.71        |
| D     | 7.49            | 130.56           | 4             | 7.6           | 131.72        |
| E     | 7.36            | 126.61           | 5             | 132.32        |
| F     | 7.43            | 130.51           | 6             | 6.72          | 128.75        |
| a     | 130.23          |                  | 7             | 6.72          | 125.79        |
| b     | 148.99          |                  | 8             | 7.04          | 126.4         |
| c     | 8.17            | 125.12           | 9             | 7.09          | 126.83        |
| d     | 7.48            | 130.33           | 10            | 131.87        |
| e     | 7.14            | 126.89           | 11            | 4.62          | 56.48         |
| f     | 6.86            | 130.11           | 12            | 1.55          | 19.31         |
| g     | 2.73            | 49.43            | 13            | 141.56        |
| h     | 0.65            | 23.2             | 14            | 6.72          | 128.8         |
| i     | 0.43            | 24.42            | 15            | 6.51          | 127.75        |
| j     | 4.37            | 54.6             | 16            | 6.7           | 127.43        |
| k     | 0.83            | 18.69            | 1'            | 121.86        |
| l     | 134.69          |                  | 2'            | 148.93        |
| m     | 7.05            | 130.86           | 3'            | 6.86          | 119.72        |
| n     | 6.78            | 114.5            | 4'            | 7.42          | 131.69        |
| o     | 162.52          |                  | 5'            | 132.09        |
|       |                 |                  | 6'            | 7.78          | 128.75        |
|       |                 |                  | 7'            | 7.44          | 125.87        |
|       |                 |                  | 8'            | 7.22          | 126.76        |
|       |                 |                  | 9'            | 7.19          | 127.63        |
|       |                 |                  | 10'           | 133.02        |
### 8.12 Cis-Pd(E5)(F)Cl₂

![CIS-Pd(E5)(F)Cl2](image)

| 1H - Ligand E5 | 13C - Ligand E5 | 1H - Ligand F | 13C - Ligand F |
|----------------|-----------------|---------------|---------------|
| A              | 130.36          | 1              | 123.47        |
| B              | 150.95          | 2              | 148.18        |
| C              | 7.25            | 3              | 8.56          |
| D              | 7.34            | 4              | 8.1           |
| E              | 7.24            | 5              | 132.04        |
| F              | 7.35            | 6              | 7.78          |
| a              | 130.47          | 7              | 7.03          |
| b              | 149.43          | 8              | 5.73          |
| c              | 8.19            | 9              | 5.94          |
| d              | 7.51            | 10             | 131.87        |
| e              | 7.11            | 11             | 4.54          |
| f              | 6.76            | 12             | 1.54          |
| g              | 2.85            | 13             | 141.52        |
| h              | 1.1             | 14             | 6.68          |
| i              | 0.1             | 15             | 6.5           |
| j              | 4.37            | 16             | 6.72          |
| k              | 1.16            | 1'             | 122.12        |
| l              | 138.34          | 2'             | 149.01        |
| m              | 7.07            | 3'             | 6.92          |
| n              | 133.47          | 4'             | 7.49          |
| o              | 132.96          | 5'             | 132.02        |
| p              | 7.17            | 6'             | 7.79          |
| q              | 7.29            | 7'             | 7.39          |
| r              | 7.33            | 8'             | 7.13          |
| s              | 7.33            | 9'             | 7.02          |
| t              | 7.33            | 10'            | 132.94        |
| u              | 7.56            |                |               |
### 8.13 Cis-Pd(E5')(F)Cl₂

|       | ¹H - Ligand E5' | ¹³C - Ligand E5' | ¹H - Ligand F | ¹³C - Ligand F |
|-------|----------------|------------------|--------------|--------------|
| A     |                | 130.93           | 1            | 123.22       |
| B     |                | 150.69           | 2            | 148.2        |
| C     | 7.26           | 121.45           | 3            | 8.51 123.71  |
| D     | 7.51           | 130.52           | 4            | 7.6 131.72   |
| E     | 7.38           | 126.64           | 5            | 132.32       |
| F     | 7.48           | 130.58           | 6            | 6.72 128.75  |
| a     |                | 130.37           | 7            | 6.72 125.79  |
| b     |                | 149.07           | 8            | 7.04 126.4   |
| c     | 8.23           | 125.23           | 9            | 7.09 126.83  |
| d     | 7.51           | 130.23           | 10           | 131.87       |
| e     | 7.16           | 126.89           | 11           | 4.62 56.48   |
| f     | 6.89           | 130.1            | 12           | 5.55 19.31   |
| g     | 2.81           | 49.59            | 13           | 141.56       |
| h     | 0.65           | 23.3             | 14           | 6.72 128.8   |
| i     | 0.44           | 24.51            | 15           | 6.51 127.75  |
| j     | 4.49           | 55.21            | 16           | 6.7 127.43   |
| k     | 0.99           | 18.5             | 1             | 121.86       |
| l     |                | 136.6            | 2             | 148.93       |
| m     | 6.98           | 126.62           | 3             | 6.86 119.72  |
| n     |                | 133.25           | 4             | 7.42 131.69  |
| o     |                | 133.31           | 5             | 132.09       |
| p     | 7.66           | 127.31           | 6             | 7.78 128.75  |
| q     | 7.71           | 128.57           | 7             | 7.44 125.87  |
| r     | 7.6            | 128.66           | 8             | 7.22 126.76  |
| s     | 7.46           | 126.05           | 9             | 7.19 127.63  |
| t     | 7.46           | 126.3            | 10            | 133.02       |
| u     | 7.84           | 127.94           |               |              |
### 8.14 Cis-Pd(E6)(F)Cl₂

![Chemical structures](image)

|       | **¹H - Ligand E6** | **¹C - Ligand E6** |       | **¹H - Ligand F** | **¹C - Ligand F** |
|-------|--------------------|--------------------|-------|-------------------|-------------------|
| **A** |                    | 130.75             | **1** |                   | 123.35            |
| **B** |                    | 151.11             | **2** |                   | 148.08            |
| **C** | 7.27               | 121.09             | **3** | 8.5               | 123.95            |
| **D** | 7.42               | 130.26             | **4** | 7.9               | 131.48            |
| **E** | 7.33               | 126.53             | **5** |                   | 132.34            |
| **F** | 7.37               | 130.67             | **6** | 7.55              | 128.41            |
| **a** |                    | 130.37             | **7** | 7.04              | 125.81            |
| **b** |                    | 149.48             | **8** | 6.7               | 126.32            |
| **c** | 8.28               | 125.39             | **9** | 6.74              | 126.95            |
| **d** | 7.52               | 130.61             | **10**|                   | 132.34            |
| **e** | 7.14               | 126.88             | **11**| 4.55              | 56.53             |
| **f** | 6.77               | 130.11             | **12**| 1.55              | 19.26             |
| **g** | 3.65               | 57.68              | **13**|                   | 141.45            |
| **h** | 0.59               | 22.01              | **14**| 6.65              | 128.85            |
| **i** | 0.06               | 21.62              | **15**| 6.48              | 127.68            |
| **j** | 4.91               | 52.28              | **16**| 6.7               | 127.39            |
| **k** | 1.07               | 23.24              |       | 1.07              | 121.94            |
| **l** |                    | 140.16             | **1′**|                   | 121.94            |
| **m** |                    | 129.96             | **2′**|                   | 149.05            |
| **n** |                    | 134.1              | **3′**| 6.87              | 119.8             |
| **o** | 7.54               | 127.91             | **4′**| 7.44              | 131.72            |
| **p** | 7.05               | 125.45             |       | 6′                | 132.09            |
| **q** | 8.05               | 125.84             | **5′**|                   | 128.78            |
| **r** | 7.7                | 123.12             | **7′**| 7.45              | 125.81            |
| **s** | 7.31               | 126.63             | **8′**| 7.22              | 126.72            |
| **t** | 7.37               | 125.65             | **9′**| 7.16              | 127.55            |
| **u** | 7.72               | 129.12             | **10′**|                  | 133.04            |
### 8.15 Cis-Pd(I)(F)Cl₂

![Diagram](image)

| \(^1\)H - Ligand I | \(^{13}\)C - Ligand I | \(^1\)H - Ligand F | \(^{13}\)C - Ligand F |
|-------------------|----------------------|------------------|---------------------|
| A                 | 130.98               | 1                | 123.66              |
| B                 | 150.41               | 2                | 148.41              |
| C                 | 7.06 121.57          | 3                | 8.61 124.5          |
| D                 | 7.45 130.25          | 4                | 8.2 131.34          |
| E                 | 7.34 126.5           | 5                |                    |
| F                 | 7.43 130.12          | 6                | 8.04 129.22         |
| a                 | 130.75               | 7                | 7.51 126.4          |
| b                 | 149.14               | 8                | 7.25 127.62         |
| c                 | 8.02 124.71          | 9                | 7.24 127.66         |
| d                 | 7.43 130.4           | 10               |                    |
| e                 | 7.07 126.74          | 11               | 4.52 56.38          |
| f                 | 6.79 130.09          | 12               | 1.52 19.31          |
| g                 | 3.2 48.53            | 13               |                    |
| h                 | 0.73 21.94           | 14               | 6.63 128.79         |
| i                 | 0.36 22.8            | 15               | 6.48 127.69         |
|                   |                      | 16               | 6.69 127.36         |
|                   |                      | 1’               | 6.69 127.36         |
|                   |                      | 2’               | 121.65              |
|                   |                      | 3’               | 149.04              |
|                   |                      | 4’               | 6.77 119.78         |
|                   |                      | 5’               | 7.38 131.65         |
|                   |                      | 6’               | 132.08              |
|                   |                      | 7’               | 7.77 128.89         |
|                   |                      | 8’               | 7.46 125.84         |
|                   |                      | 9’               | 7.27 126.79         |
|                   |                      | 10’              | 7.28 127.65         |
|                   |                      |                  | 133.04              |
9 Synthetic Procedures

The secondary amines required for the synthesis of phosphoramidites were synthesized from commercial enantiopure α-methylbenzylamines by reductive amination using NaBH(OAc)$_3$ and related procedures,[4–6] or acylation/LiAlH$_4$ reduction[7] according to reported literature procedures.

9.1 Synthesis of Phosphoramidite Ligands

Phosphoramidite ligands were synthesized according to the reported procedure of Fletcher et al.[4,8] Typical yields for biphenyl ligands were 40 – 60 %, for naphthyl-substituted ligands 90 – 99 %.

*Representative Procedure A:* To a solution of PCl$_3$ (210 μL, 2.38 mmol) in DCM (17 mL), cooled to 0 °C, was added Et$_3$N (1.7 mL, 12 mmol, 5 eq.) and the mixture was stirred under argon at 0 °C for 15 min. A solution of (S)-N-(1-phenylethyl)propan-2-amine (390 mg, 2.38 mmol, 1 eq.) in DCM (4 mL) was then added and the mixture warmed to room temperature. After stirring for 4 h, solid biphenyl-2,2'-diol (445 mg, 2.38 mmol, 1 eq.) was added and the mixture stirred overnight. The reaction was then quenched by the addition of sat. aq. NaCl and the mixture was extracted with DCM (2 x 50 mL). The organic layer was dried over MgSO$_4$, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent petroleum ether/DCM/Et$_3$N 80:20:1) to give the product (ligand E', 557 mg, 62 %) as a white foam.
Ligand B: (R)-N-methyl-N-(1-phenylethyl)dibenzo[d,f][1,3,2]dioxaphosphepin-6-amine

\[
\text{Ph} \quad \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \quad \begin{array}{c}
\text{Me} \\
\text{Me}
\end{array} \quad \text{P-N-Me}
\]

\(^{1}H\) NMR (600 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 7.50 – 7.45 (m, 4H), 7.43 – 7.18 (m, 8H), 7.12 – 7.07 (m, 1H), 4.86 (dq, \(J = 10.8, 7.0\) Hz, 1H), 2.20 (d, \(J = 4.7\) Hz, 3H), 1.67 (d, \(J = 7.0\) Hz, 3H).

\(^{31}P\)\(^{1}H\) NMR (243 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 148.66.

\(^{13}C\) NMR (151 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 152.08 (d, \(J = 5.0\) Hz), 142.46 (d, \(J = 5.1\) Hz), 131.48 (d, \(J = 3.1\) Hz), 131.36 (d, \(J = 3.0\) Hz), 130.24 – 129.98 (m), 129.64 (dd, \(J = 7.4, 1.1\) Hz), 128.66, 127.78 (d, \(J = 1.4\) Hz), 127.45, 124.87 (dd, \(J = 11.8, 1.1\) Hz), 122.28 (dd, \(J = 7.8, 1.2\) Hz), 55.93 (d, \(J = 40.7\) Hz), 27.22 (d, \(J = 1.2\) Hz), 18.78 (d, \(J = 8.2\) Hz).

HRMS (ESI\(^{+}\)): calcd. for [C\(_{21}\)H\(_{20}\)NO\(_2\)P+H]\(^{+}\) ([M+H]\(^{+}\): \(m/z\) 350.1310; found 350.1304.

HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min\(^{-1}\), 254 nm. (R)-B: 5.85 min; \(er >99:1\).

Ligand B': (S)-N-methyl-N-(1-phenylethyl)dibenzo[d,f][1,3,2]dioxaphosphepin-6-amine

\[
\text{Ph} \quad \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \quad \begin{array}{c}
\text{Me} \\
\text{Me}
\end{array} \quad \text{P-N-Me}
\]

Identical NMR data to B.

HRMS (ESI\(^{+}\)): calcd. for [C\(_{21}\)H\(_{20}\)NO\(_2\)P+H]\(^{+}\) ([M+H]\(^{+}\): \(m/z\) 350.1310; found 350.1305.

HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min\(^{-1}\), 254 nm. (S)-B: 6.16 min; \(er\) 99:1.
Ligand C: \((R)-N\text{-ethyl-}N\text{-}(1\text{-phenylethyl})\text{dibenzo[d,f][1,3,2]dioxaphosphepin-6-amine}\)

\[
\text{Ph} \quad \text{O} \quad \text{P} \quad \text{N} \quad \text{Me}
\]

\(^1\text{H NMR (400 MHz, CD}_2\text{Cl}_2\):} \delta 7.54 – 7.44 (m, 4H), 7.44 – 7.20 (m, 7H), 7.17 (dt, \(J = 8.0, 1.2\) Hz, 1H), 7.12 (dt, \(J = 8.0, 1.2\) Hz, 1H), 4.69 (dq, \(J = 11.2, 7.1\) Hz, 1H), 2.87 (dp, \(J = 14.3, 7.2\) Hz, 1H), 2.70 (dq, \(J = 14.2, 7.1, 5.4\) Hz, 1H), 1.71 (dd, \(J = 7.1, 1.7\) Hz, 3H), 0.87 (t, \(J = 7.1\) Hz, 3H).

\(^{31}\text{P}\{^1\text{H}\} \text{ NMR (162 MHz, CD}_2\text{Cl}_2\):} \delta 150.00.

\(^{13}\text{C NMR (101 MHz, CD}_2\text{Cl}_2\):} \delta 152.16 (d, \(J = 4.8\) Hz), 152.04 (d, \(J = 5.1\) Hz), 144.04 (d, \(J = 3.4\) Hz), 131.26 (d, \(J = 3.1\) Hz), 130.06 (d, \(J = 1.9\) Hz), 129.55 (d, \(J = 4.6\) Hz), 128.64, 127.74 (d, \(J = 1.7\) Hz), 127.40, 124.78 (d, \(J = 3.5\) Hz), 122.35, 55.74 (d, \(J = 28.4\) Hz), 38.50 (d, \(J = 4.7\) Hz), 21.85 (d, \(J = 16.4\) Hz), 16.79 (d, \(J = 2.7\) Hz).

\text{HRMS (ESI^+):} \text{ calcd. for } [C_{22}H_{22}NO_2P+H]^+ ([M+H]^+): m/z 364.1466; \text{ found 364.1462.}

\text{HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min}^{-1}, 254 nm. \((R)-C\): 5.85 min; \text{ er >99:1.}
Ligand D: \((R)-N\)-benzyl-\(N\)-(1-phenylethyl)dibenzo[d,f][1,3,2]dioxaphosphepin-6-amine

\[
\begin{align*}
\text{Ph} & \quad \text{O} \quad \text{P} \quad \text{N} \quad \text{Me} \quad \text{Ph} \\
\text{Ph} & \quad \text{O} \quad \text{P} \quad \text{N} \quad \text{Me} 
\end{align*}
\]

\(^1\)H NMR (600 MHz, CD\(_2\)Cl\(_2\)): \(\delta 7.50 – 7.40\) (m, 6H), \(7.40 – 7.15\) (m, 10H), \(7.08 – 7.04\) (m, 1H), \(4.36\) (dq, \(J = 14.2, 7.2\) Hz, 1H), \(4.05\) (dd, \(J = 15.5, 4.4\) Hz, 1H), \(3.57\) (dd, \(J = 15.4, 3.4\) Hz, 1H), \(1.59\) (dd, \(J = 7.2, 2.7\) Hz, 3H).

\(^31\)P\(_{\text{H}}\) NMR (243 MHz, CD\(_2\)Cl\(_2\)): \(\delta 144.01\) (d, \(J = 13.1\) Hz).

\(^{13}\)C NMR (151 MHz, CD\(_2\)Cl\(_2\)): \(\delta 152.20\) (d, \(J = 5.4\) Hz), \(151.73\) (d, \(J = 3.8\) Hz), \(143.58\), \(139.85\), \(131.50\) (d, \(J = 3.3\) Hz), \(131.15\) (d, \(J = 2.8\) Hz), \(130.39 – 129.84\) (m), \(129.68\) (d, \(J = 13.7\) Hz), \(128.81\), \(128.60\), \(128.56\), \(127.91\) (d, \(J = 1.8\) Hz), \(127.66\), \(127.24\), \(125.93 – 124.15\) (m), \(123.20 – 121.21\) (m), \(57.11\) (d, \(J = 25.2\) Hz), \(48.24\), \(22.69\) (d, \(J = 23.7\) Hz).

HRMS (ESI\(^+\)): calcd. for [C\(_{27}\)H\(_{44}\)NO\(_2\)P+H\]^+: \(m/z\) 426.1623; found 426.1619.

HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min\(^{-1}\), 254 nm. \((R)-\text{D}: 5.15\) min; \(\text{er} >99:1\).

Ligand D\(^\prime\): \((S)-N\)-benzyl-\(N\)-(1-phenylethyl)dibenzo[d,f][1,3,2]dioxaphosphepin-6-amine

\[
\begin{align*}
\text{Ph} & \quad \text{O} \quad \text{P} \quad \text{N} \quad \text{Me} \quad \text{Ph} \\
\text{Ph} & \quad \text{O} \quad \text{P} \quad \text{N} \quad \text{Me} 
\end{align*}
\]

Identical NMR data to D.

HRMS (ESI\(^+\)): calcd. for [C\(_{27}\)H\(_{44}\)NO\(_2\)P+H\]^+: \(m/z\) 426.1623; found 426.1616.

HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min\(^{-1}\), 254 nm. \((S)-\text{D}: 5.73\) min; \(\text{er} >99:1\).
Ligand E: *(R)-N-isopropyl-N-(1phenylethyl)dibenzo[d,f][1,3,2] dioxaphosphepin-6-amine

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (600 MHz, CD}_2\text{Cl}_2): } & \delta 7.56 - 7.47 \text{ (m, 4H), 7.41 - 7.32 \text{ (m, 4H), 7.28 - 7.18 \text{ (m, 5H), 4.64 \text{ (dq, } J = 10.6, 7.1 \text{ Hz, 1H), 3.44 \text{ (dp, } J = 10.4, 6.8 \text{ Hz, 1H), 1.66 (d, } J = 6.8 \text{ Hz, 3H), 1.30 (d, } J = 6.8 \text{ Hz, 3H), 0.98 (d, } J = 6.8 \text{ Hz, 3H). }} \\
\text{\textsuperscript{31}P\text{\textsuperscript{1}H} NMR (243 MHz, CD}_2\text{Cl}_2): } & \delta 149.46. \\
\text{\textsuperscript{13}C NMR (151 MHz, CD}_2\text{Cl}_2): } & \delta 152.25 (d, J = 6.7 \text{ Hz}), 151.99 (d, J = 4.3 \text{ Hz}), 145.04, 131.34 (d, J = 3.3 \text{ Hz}), 130.89 (d, J = 3.1 \text{ Hz}), 130.17 (dd, J = 4.3, 1.4 \text{ Hz}), 129.49 (dd, J = 6.6, 1.3 \text{ Hz}), 128.45, 127.85 (d, J = 2.1 \text{ Hz}), 126.98, 124.86 (d, J = 1.3 \text{ Hz}), 124.62 (d, J = 1.3 \text{ Hz}), 122.55 (d, J = 1.5 \text{ Hz}), 122.47, 52.34 (d, J = 11.9 \text{ Hz}), 46.51 (d, J = 12.0 \text{ Hz}), 24.97 (d, J = 8.5 \text{ Hz}), 24.09 (d, J = 8.2 \text{ Hz}), 22.70. \\
\text{HRMS (ESI\textsuperscript{+}): } & \text{calcd. for [C}_{23}\text{H}_{24}\text{NO}_2\text{P}+\text{H}]^+ (\text{[M+H]}^+): m/z 378.1623; \text{found 378.1624.} \\
\text{HPLC: } & \text{Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min}^{-1}, 254 \text{ nm. (R)-E: 4.98 min; er >99:1.}
\end{align*}
\]

Ligand E': *(S)-N-isopropyl-N-(1phenylethyl)dibenzo[d,f][1,3,2] dioxaphosphepin-6-amine

\[
\begin{align*}
\text{Identical NMR data to E.} \\
\text{HRMS (ESI\textsuperscript{+}): } & \text{calcd. for [C}_{23}\text{H}_{24}\text{NO}_2\text{P}+\text{H}]^+ (\text{[M+H]}^+): m/z 378.1623; \text{found 378.1622.} \\
\text{HPLC: } & \text{Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min}^{-1}, 254 \text{ nm. (S)-E: 5.15 min; er 98.5:1.5.}
\end{align*}
\]
Ligand G: \((R)-N-(\text{pentafluorophenyl})\text{methyl}-N-(1\text{phenylethyl})\text{dibenzo}[d,f][1,3,2]dioxaphosphepin-6-\text{amine}\)

\[\text{Ph} \quad \text{Me} \quad \text{Ph} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F}\]

\(^1H\) NMR (600 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 7.50 (dd, \(J = 7.8, 1.7\) Hz, 2H), 7.42 – 7.36 (m, 4H), 7.30 – 7.19 (m, 6H), 7.18 – 7.13 (m, 1H), 4.71 (p, \(J = 7.3\) Hz, 1H), 4.35 – 4.28 (m, 1H), 4.11 (dd, \(J = 15.1, 6.4\) Hz, 1H), 1.72 (dd, \(J = 7.1, 1.0\) Hz, 3H).

\(^{31}\text{P}\)\(^{\text{[1]H}}\) NMR (243 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 145.74 (t, \(J = 17.7\) Hz).

\(^{19}\text{F}\)\(^{\text{[1]H}}\) NMR (565 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) -141.50 – -142.11 (m, ortho-2F), -157.03 (t, \(J = 20.7\) Hz, para-1F), -164.01 – -164.33 (m, meta-2F).

\(^{13}\text{C}\) NMR (151 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 153.26 – 149.30 (m), 146.02 (d, \(J = 11.8\) Hz), 144.41 (t, \(J = 9.9\) Hz), 141.67 (d, \(J = 3.4\) Hz), 141.04, 139.37, 137.85 (t, \(J = 15.0\) Hz), 136.19 (t, \(J = 11.8\) Hz), 130.89 (d, \(J = 3.2\) Hz), 130.57 (d, \(J = 3.2\) Hz), 129.84 (dd, \(J = 3.8, 1.3\) Hz), 129.44 (d, \(J = 1.2\) Hz), 129.31 (d, \(J = 1.2\) Hz), 127.82, 127.22 (d, \(J = 1.3\) Hz), 127.02, 124.81 (d, \(J = 1.2\) Hz), 124.69 (d, \(J = 1.3\) Hz), 121.91, 112.80 (t, \(J = 16.7\) Hz), 54.03 (d, \(J = 16.7\) Hz), 35.09 (d, \(J = 22.4\) Hz), 18.96 (d, \(J = 10.2\) Hz).

HRMS (ESI\(^{+}\)): calcd. for [C\(_{27}\)H\(_{19}\)F\(_5\)NO\(_2\)P+H]\(^+\) ([M+H]\(^+\)) : \(m/z\) 516.1152; found 516.1148.

HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min\(^{-1}\), 254 nm. (R)-G: 5.44 min; er >99:1.

Ligand G': \((S)-N-(\text{pentafluorophenyl})\text{methyl}-N-(1\text{phenylethyl})\text{dibenzo}[d,f][1,3,2]dioxaphosphepin-6-\text{amine}\)

\[\text{Ph} \quad \text{Me} \quad \text{Ph} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F}\]

Identical NMR data to G.

HRMS (ESI\(^{+}\)): calcd. for [C\(_{27}\)H\(_{19}\)F\(_5\)NO\(_2\)P+H]\(^+\) ([M+H]\(^+\)) : \(m/z\) 516.1152; found 516.1152.

HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min\(^{-1}\), 254 nm. (S)-G: 5.05 min; er >99:1.
Ligand H: (R)-N-cyclohexyl-N-(1-phenylethyl)dibenzo[d,f][1,3,2]dioxaphosphepin-6-amine

\[
\begin{align*}
\text{H NMR (600 MHz, CD}_2\text{Cl}_2):} & \quad \delta 7.60 - 7.46 (m, 4H), 7.44 - 7.30 (m, 4H), 7.28 - 7.18 (m, 5H), \\
& \quad 4.66 (dq, J = 10.0, 7.2 Hz, 1H), 2.89 (tdd, J = 14.9, 10.3, 3.9 Hz, 1H), 1.99 (d, J = 11.5 Hz, 1H), \\
& \quad 1.78 - 1.41 (m, 9H), 1.10 - 0.96 (m, 2H), 0.88 - 0.76 (m, 1H).
\end{align*}
\]

\[
\begin{align*}
\text{P\{H\} NMR (243 MHz, CD}_2\text{Cl}_2):} & \quad \delta 149.65.
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (151 MHz, CD}_2\text{Cl}_2):} & \quad \delta 152.27 (d, J = 6.7 Hz), 151.97 (d, J = 4.1 Hz), 144.90, 131.45 \\
& \quad (d, J = 3.4 Hz), 130.91 (d, J = 3.0 Hz), 130.66 - 129.88 (m), 130.05 - 129.13 (m), 128.37, \\
& \quad 127.92 (d, J = 1.9 Hz), 126.96, 124.85 (d, J = 1.3 Hz), 124.57 (d, J = 1.3 Hz), 122.49 (d, J = \\
& \quad 1.4 Hz), 122.39, 55.14 (d, J = 11.4 Hz), 52.69 (d, J = 10.2 Hz), 35.17 (d, J = 8.4 Hz), 26.93 (d, \\
& \quad J = 1.9 Hz), 25.88, 22.43.
\end{align*}
\]

HRMS (ESI\(^{+}\)): calcd. for \([C_{26}H_{28}NO_2P+H]^+\) ([M+H]\(^+\)): \(m/z\) 418.1936; found 418.1933.

HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min\(^{-1}\), 254 nm. (R)-H: 5.03 min; er >99:1.

Ligand H': (S)-N-cyclohexyl N-(1-phenylethyl)dibenzo[d,f][1,3,2]dioxaphosphepin-6-amine

\[
\begin{align*}
\text{HRMS (ESI\(^{+}\)):} & \quad \text{calcd. for } [C_{26}H_{28}NO_2P+H]^+ ([M+H]^+) : m/z 418.1936; \text{found 418.1934.}
\end{align*}
\]

HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min\(^{-1}\), 254 nm. (S)-H: 5.69 min; er 98:2.
Ligand F: \((S)_n-N,N\text{-bis((R)-1-phenylethyl})\text{dinaphtho}[2,1-d:1’,2’-f][1,3,2]dioxaphosphepin-4-amine\) (Feringa ligand)

Ligand F was prepared according to a literature procedure\(^4\). NMR spectra matched those reported.

**HRMS (ESI\(^+\))**: calcd. for \([C_{36}H_{30}NO_2P+H]^+\) (\([M+H]^+\)): \(m/z\) 540.2092; found 540.2085.
Ligand A2: \(N,N\)-bis((R)-1-(naphthalen-2-yl)ethyl)dibenzo[d,f][1,3,2]dioxaphosphepin-6-amine

Ligands A2 and A2' were prepared according to a literature procedure.\cite{6,9} NMR spectra matched those reported.

HRMS (ESI\(^+\)): calcd. for \([C_{36}H_{30}NO_2P+H]^+\) ([M+H]\(^+\)): \(m/z\ 540.2092\); found 540.2088.

HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min\(^{-1}\), 254 nm. (R,R)-A2: 6.59 min; \(er>99:1\).

Ligand A2': \(N,N\)-bis((S)-1-(naphthalen-2-yl)ethyl)dibenzo[d,f][1,3,2]dioxaphosphepin-6-amine

HRMS (ESI\(^+\)): calcd. for \([C_{36}H_{30}NO_2P+H]^+\) ([M+H]\(^+\)): \(m/z\ 540.2092\); found 540.2094.

HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min\(^{-1}\), 254 nm. (S,S)-A2: 7.53 min; \(er>99:1\).
Ligand I: N,N-diisopropylbifenzo[d,f][1,3,2]dioxaphosphepin-6-amine

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{): } & \delta 7.49 \text{ (dd, } J = 7.6, 1.7 \text{ Hz, } 2\text{H}), 7.36 \text{ (td, } J = 7.7, 1.7 \text{ Hz, } 2\text{H}), 7.29 - 7.18 \text{ (m, } 4\text{H}), 3.54 \text{ (dh, } J = 10.6, 6.8 \text{ Hz, } 2\text{H}), 1.26 \text{ (d, } J = 6.8 \text{ Hz, } 12\text{H}). \\
\text{31P\{H\} NMR (162 MHz, CDCl}_3\text{): } & \delta 152.64. \\
\text{13C NMR (101 MHz, CDCl}_3\text{): } & \delta 152.05 \text{ (d, } J = 5.5 \text{ Hz), 131.04 \text{ (d, } J = 3.2 \text{ Hz), 129.83, 129.05, 124.29, 122.26, 44.73 \text{ (d, } J = 12.7 \text{ Hz), 24.59 \text{ (d, } J = 8.2 \text{ Hz).} \\
\text{HRMS (ESI\textsuperscript{+}): } & \text{calcd. for } [C_{18}H_{22}NO_2P+H]^+ \text{ (}[M+H]^+) : m/z 316.1466; \text{ found } 316.1463.
\end{align*}
\]
Ligand E2: \((R)-N\text{-isopropyl-}\(N\text{-}(1-(4\text{-methoxyphenyl})\text{ethyl})\text{dibenzo}[d,f][1,3,2]\text{dioxaphosphepin}\)-6-amine\)

\[\text{\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{N} \text{Me} \\
\text{O} \\
\text{Ph}
\end{array}}\]

\(^1\text{H NMR (400 MHz, CDCl}^3\): \(\delta 7.51 - 7.17 \text{ (m, 10H), 6.91 - 6.80 \text{ (m, 2H), 4.62 (dq, } J = 9.7, 7.1 \text{ Hz, 1H), 3.81 (s, 3H), 3.39 (dp, } J = 11.5, 6.8 \text{ Hz, 1H), 1.61 (d, } J = 7.1 \text{ Hz, 3H), 1.32 (d, } J = 6.8 \text{ Hz, 3H), 1.01 (d, } J = 6.8 \text{ Hz, 3H).}\)

\(^{31}\text{P\{\text{^1H}\}} \text{ NMR (162 MHz, CDCl}^3\): \(\delta 149.88.\)

\(^{13}\text{C NMR (101 MHz, CDCl}^3\): \(\delta 158.40, 152.02 \text{ (d, } J = 7.0 \text{ Hz), 151.72 \text{ (d, } J = 4.2 \text{ Hz), 136.40, 131.16, 130.65, 129.95, 129.16, 129.06, 128.81 \text{ (d, } J = 1.8 \text{ Hz), 124.51, 124.23, 122.41, 122.25, 113.47, 55.37, 51.39 \text{ (d, } J = 9.6 \text{ Hz), 46.03 \text{ (d, } J = 14.4 \text{ Hz), 25.33, 24.38 \text{ (d, } J = 9.4 \text{ Hz), 22.20.}\)

HRMS (ESI\(^+\)): calcd. for \([C_{24}H_{26}NO_3P]+H\)\(^+\) ([M+H]\(^+\): m/z 408.1729; found 408.1727.

HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min\(^{-1}\), 254 nm. \((R)-E2\) 6.86 min; \(er >99:1.\)

Ligand E2': \((S)-N\text{-isopropyl-}\(N\text{-}(1-(4\text{-methoxyphenyl})\text{ethyl})\text{dibenzo}[d,f][1,3,2]\text{dioxaphosphepin}\)-6-amine\)

\[\text{\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{N} \text{Me} \\
\text{O} \\
\text{Ph}
\end{array}}\]

Identical NMR data to E2.

HRMS (ESI\(^+\)): calcd. for \([C_{24}H_{26}NO_3P]+H\)\(^+\) ([M+H]\(^+\): m/z 408.1729; found 408.1724.

HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min\(^{-1}\), 254 nm. \((S)-E2\) 8.11 min; \(er >99:1.\)
Ligand E3: \((R)-N\text{-isopropyl}-N-(1-(3\text{-methoxyphenyl})ethyl)\text{dibenzo}[d,f][1,3,2]\text{dioxaphosphepin-6-amine}\)

\[
\begin{align*}
\text{H NMR (400 MHz, CD}_2\text{Cl}_2) & : \delta 7.49 (dd, J = 7.6, 1.7 \text{ Hz}, 2\text{H}), 7.41 - 7.30 (m, 2\text{H}), 7.30 - 7.15 (m, 6\text{H}), 7.10 (ddt, J = 7.7, 1.6, 0.8 \text{ Hz}, 1\text{H}), 6.83 - 6.76 (m, 1\text{H}), 4.63 (dq, J = 10.1, 7.1 \text{ Hz}, 1\text{H}), 3.84 (s, 3\text{H}), 3.45 (dp, J = 10.8, 6.8 \text{ Hz}, 1\text{H}), 1.66 (d, J = 7.1 \text{ Hz}, 3\text{H}), 1.32 (d, J = 6.8 \text{ Hz}, 3\text{H}), 1.03 (d, J = 6.8 \text{ Hz}, 3\text{H}). \\
\text{31P\{H\} NMR (162 MHz, CD}_2\text{Cl}_2) & : \delta 149.55.
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (101 MHz, CD}_2\text{Cl}_2) & : \delta 159.63, 151.95 (d, J = 6.8 \text{ Hz}), 151.72 (d, J = 4.4 \text{ Hz}), 146.45, 131.09 (d, J = 3.5 \text{ Hz}), 130.66 (d, J = 3.1 \text{ Hz}), 129.95 (d, J = 3.7 \text{ Hz}), 129.20, 129.10 (d, J = 2.5 \text{ Hz}), 124.53, 124.29, 122.26 (d, J = 4.8 \text{ Hz}), 119.88 (d, J = 2.1 \text{ Hz}), 113.47 (d, J = 2.3 \text{ Hz}), 112.19, 55.31, 52.10 (d, J = 11.0 \text{ Hz}), 46.26 (d, J = 13.0 \text{ Hz}), 25.04, 24.18 (d, J = 9.0 \text{ Hz}), 22.58.
\end{align*}
\]

\[
\text{HRMS (ESI\textsuperscript{+})}: \text{calcd. for } [C_{24}H_{26}NO_3P+H]^{+}: m/z \ 408.1729; \text{ found } 408.1725.
\]

\[
\text{HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min}^{-1}, 254 \text{ nm. (R)-E3}: 6.69 \text{ min}; \text{ er } >99:1.
\]

Ligand E3': \((S)-N\text{-isopropyl}-N-(1-(3\text{-methoxyphenyl})ethyl)\text{dibenzo}[d,f][1,3,2]\text{dioxaphosphepin-6-amine}\)

\[
\begin{align*}
\text{Identical NMR data to E3.}
\end{align*}
\]

\[
\begin{align*}
\text{HRMS (ESI\textsuperscript{+})}: \text{calcd. for } [C_{24}H_{26}NO_3P+H]^{+}: m/z \ 408.1729; \text{ found } 408.1725.
\end{align*}
\]

\[
\begin{align*}
\text{HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min}^{-1}, 254 \text{ nm. (S)-E3}: 6.46 \text{ min}; \text{ er } >99:1.
\end{align*}
\]
Ligand E4: \((R)-N\text{-isopropyl-}N\text{-}(1\text{-}(4\text{-fluorophenyl})\text{ethyl})\text{dibenzo}[d,f][1,3,2]\text{dioxaphosphepin\-6-amine}\)

\[
\text{\textsuperscript{1}H NMR (400 MHz, CD}_2\text{Cl}_2): \delta 7.55 – 7.45 (m, 4H), 7.43 – 7.32 (m, 2H), 7.31 – 7.16 (m, 4H), 7.08 – 6.97 (m, 2H), 4.69 – 4.56 (m, 1H), 3.38 (dhept, \(J = 11.2, 6.8\) Hz, 1H), 1.66 – 1.59 (m, 3H), 1.31 (d, \(J = 6.8\) Hz, 3H), 0.99 (d, \(J = 6.8\) Hz, 3H).
\]

\[
\text{\textsuperscript{31}P\{\textsuperscript{1}H\} NMR (162 MHz, CD}_2\text{Cl}_2): \delta 149.60.
\]

\[
\text{\textsuperscript{19}F NMR (376 MHz, CD}_2\text{Cl}_2): \delta -117.32.
\]

\[
\text{\textsuperscript{13}C NMR (101 MHz, CD}_2\text{Cl}_2): \delta 163.25, 160.83, 152.18 (d, \(J = 6.9\) Hz), 151.84 (d, \(J = 4.0\) Hz), 140.63, 131.37 (d, \(J = 3.5\) Hz), 130.78 (d, \(J = 3.0\) Hz), 130.19 (t, \(J = 1.9\) Hz), 129.64 (d, \(J = 2.0\) Hz), 129.57, 129.55, 129.48, 124.96, 124.64, 122.53 (d, \(J = 1.5\) Hz), 122.43, 115.13, 114.92, 51.63 (d, \(J = 10.3\) Hz), 46.44 (d, \(J = 13.7\) Hz), 25.22 (d, \(J = 8.1\) Hz), 24.25 (d, \(J = 9.1\) Hz), 22.40 (d, \(J = 11.2\) Hz).
\]

HRMS (ESI\textsuperscript{+}): calcd. for \([C_{23}H_{23}FNO_2P+H]^+ ([M+H]^+): m/z 396.1529; found 396.1526.

HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min\textsuperscript{-1}, 254 nm. (\(R\)-E4): 5.02 min; \textit{er} 99:1.

Ligand E4\': \((S)-N\text{-isopropyl-}N\text{-}(1\text{-}(4\text{-fluorophenyl})\text{ethyl})\text{dibenzo}[d,f][1,3,2]\text{dioxaphosphepin\-6-amine}\)

Identical NMR data to E4.

HRMS (ESI\textsuperscript{+}): calcd. for \([C_{23}H_{23}FNO_2P+H]^+ ([M+H]^+): m/z 396.1529; found 396.1525.

HPLC: Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min\textsuperscript{-1}, 254 nm. (\(S\)-E4): 5.16 min; \textit{er} >99:1.
Ligand E5: (R)-N-isopropyl-N-(1-(naphthalen-2-yl)ethyl)dibenzo[d,f][1,3,2]dioxaphosphepin-6-amine

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{):} & \delta 7.90 – 7.73 (m, 5H), 7.54 – 7.20 (m, 10H), 4.82 (dq, J = 9.3, 7.0 Hz, 1H), 3.45 (dp, J = 11.2, 6.8 Hz, 1H), 1.75 (d, J = 7.0 Hz, 3H), 1.36 (d, J = 6.8 Hz, 3H), 1.00 (d, J = 6.8 Hz, 3H). \\
\text{31P{\text{1H}}} \text{ NMR (162 MHz, CDCl}_3\text{):} & \delta 149.54.
\end{align*}
\]

\[
\begin{align*}
\text{13C NMR (101 MHz, CDCl}_3\text{):} & \delta 133.33, 132.56, 131.11, 130.72, 129.98 (d, J = 3.8 Hz), 129.17 (d, J = 10.7 Hz), 128.11, 128.83, 126.91, 126.07, 125.79, 125.58, 124.56, 124.32, 122.40, 122.29, 52.23 (d, J = 10.0 Hz), 46.23 (d, J = 14.1 Hz), 25.30, 24.34 (d, J = 9.1 Hz), 22.16. \\
\text{HRMS (ESI\textsuperscript{+}):} & \text{ calcd. for [C}_{27}\text{H}_{26}\text{NO}_2\text{P}+\text{H}]^+: m/z 428.1779; \text{ found 428.1776.} \\
\text{HPLC:} & \text{ Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min}^{-1}, 254 \text{ nm. (R)-E5: 6.05 min; er >99:1.}
\end{align*}
\]

Ligand E5': (S)-N-isopropyl-N-(1-(naphthalen-2-yl)ethyl)dibenzo[d,f][1,3,2]dioxaphosphepin-6-amine

\[
\begin{align*}
\text{Identical NMR data to E5.} \\
\text{HRMS (ESI\textsuperscript{+}):} & \text{ calcd. for [C}_{27}\text{H}_{26}\text{NO}_2\text{P}+\text{H}]^+: m/z 428.1779; \text{ found 428.1777.} \\
\text{HPLC:} & \text{ Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min}^{-1}, 254 \text{ nm. (S)-E5: 5.92 min; er >99:1.}
\end{align*}
\]
Ligand E6: (R)-N-isopropyl-N-(1-(naphthalen-1-yl)ethyl)dibenzo[d,f][1,3,2]dioxaphosphepin-6-amine

**1H NMR (400 MHz, CD2Cl2):** δ 7.54 – 7.44 (m, 4H), 7.44 – 7.20 (m, 7H), 7.17 (dt, J = 8.0, 1.2 Hz, 1H), 7.12 (dt, J = 8.0, 1.2 Hz, 1H), 4.69 (dq, J = 11.2, 7.1 Hz, 1H), 2.87 (dp, J = 14.3, 7.2 Hz, 1H), 2.70 (ddq, J = 14.2, 7.1, 5.4 Hz, 1H), 1.71 (dd, J = 7.1, 1.7 Hz, 3H), 0.87 (t, J = 7.1 Hz, 3H).

**31P{1H} NMR (162 MHz, CD2Cl2):** δ 150.85.

**13C NMR (101 MHz, CD2Cl2):** δ 152.32, 143.22, 134.35, 131.28, 131.00, 130.49, 130.20, 130.15, 129.56, 129.50, 129.36, 127.63, 126.50, 125.96, 125.81, 124.84, 124.71, 124.12, 124.05, 122.98, 122.59, 122.30, 49.66 (d, J = 21.7 Hz), 46.77, 25.19 (d, J = 28.5 Hz), 22.74 (d, J = 33.5 Hz).

**HRMS (ESI+):** calcd. for [C27H26NO2P+H]+ ([M+H]+): m/z 428.1779; found 428.1774.

**HPLC:** Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min⁻¹, 254 nm. (R)-E6: 5.13 min; er >99:1.

Ligand E6’: (S)-N-isopropyl-N-(1-(naphthalen-1-yl)ethyl)dibenzo[d,f][1,3,2]dioxaphosphepin-6-amine

Identical NMR data to E6.

**HRMS (ESI+):** calcd. for [C27H26NO2P+H]+ ([M+H]+): m/z 428.1779; found 428.1775.

**HPLC:** Chiralpak IC, eluent hexane:i-PrOH 99:1, 0.9 mL.min⁻¹, 254 nm. (S)-E6: 5.28 min; er >99:1.
9.2 Supramolecular Balance Sample Preparation

Representative Procedure B: An oven-dried Schlenk flask was charged with ligand (R)-E (15.10 mg, 0.040 mmol, 1 eq.), ligand (S,R,R)-F (21.58 mg, 0.040 mmol, 1 eq.) and Pd(cod)Cl$_2$ (11.42 mg, 0.040 mmol, 1 eq.). The flask was evacuated under vacuum and back-filled with argon (3x). Freshly distilled CD$_2$Cl$_2$ (2 mL) was then added and the mixture stirred at rt for 15 min. A sample (0.6 mL, 20 mM) was taken into NMR tube for analysis. The remaining solution was stored in a glass vial.

The samples are stable at room temperature and are not air sensitive. Upon equilibration from trans- to cis-complexes, which took hours to months depending on the ligands, the color of the solution turned from orange to pale yellow.
9.3 Rhodium Complexes

**Representative Procedure C:** An oven-dried Schlenk flask was charged with ligand \((R)-E\) (15.10 mg, 0.040 mmol, 1 eq.), ligand \((S,R,R)-F\) (21.58 mg, 0.040 mmol, 1 eq.) and \(\text{Rh(acac}(\text{eth})_2\) (10.32 mg, 0.040 mmol, 1 eq.). The flask was evacuated under vacuum and back-filled with argon (3x). Freshly distilled \(\text{CD}_2\text{Cl}_2\) (2 mL) was then added and the mixture stirred at rt for 15 min with evolution of gas (ethylene). A sample (0.6 mL) was taken into NMR tube for analysis. The remaining red solution was stored in a glass vial. The samples decomposed slowly.

In total, four distinct homocomplexes and one heterocomplex are formed. No isomerization was observed for the heterocomplex, suggesting that tetrahedral geometry might be preferred to square-planar arrangement or the complexes are more flexible than their Pd(II) counterparts. \(^{103}\)Rh is an NMR-active nucleus (100 % abundance) that splits the phosphorus signals by \(^1J_{\text{Rh-P}}\).

![Diagram of Rhodium Complexes](image)

**Figure S31.** Synthesis of Rh(I) bis(phosphoramidite) complexes.

**\(^{31}\)P\(^1\)H NMR**

- **Rh(E)(F)(acac)**
  - 4 homocomplex structures
  - 1 heterocomplex

- **Rh(E)\(_2\)(acac)**
  - \(^1J_{\text{Rh-P}}\) 300 Hz
  - \(^2J_{\text{P-P}}\) 82 Hz

- **Rh(F)\(_2\)(acac)**

![31P NMR Spectrum](image)

**Figure S32.** \(^{31}\)P NMR (243 MHz, \(\text{CD}_2\text{Cl}_2\)) spectrum.
Figure S33. Comparison of $^{31}$P NMR (243 MHz, CD$_2$Cl$_2$) spectra of Rh(I) complexes.
Platinum(II) complexes were prepared using ligands E/E' and F from Pt(cod)Cl₂ analogously to the Pd(II) complexes. The Pt compounds contain 33 % of NMR-active $^{195}$Pt that gave rise to the satellite peaks. The $^1J_{Pt,P}$ coupling was 2910 Hz, while the $^2J_{P-P}$ couplings were relatively small, about 4 – 5 Hz. Additional peaks were observed in the $^{31}$P NMR spectrum. However, the compounds were not stable and decomposed, which prevented further analysis.

![Comparison of $^{31}$P NMR spectra of Pt(II) complexes.](image)

**Figure S34.** Comparison of $^{31}$P NMR (243 MHz, CD₂Cl₂) spectra of Pt(II) complexes.
Ligands B/B'
Ligand C

(R)-enantiomer
Ligands D/D'

**R/S mixture**

**(_R_)-enantiomer**

**(_S_)-enantiomer**
Ligand E/E’

R/S mixture

(R)-enantiomer

(S)-enantiomer
Ligands G/G'

R/S mixture

(R)-enantiomer

(S)-enantiomer
Ligands H/H'

**R/S mixture**

**(R)-enantiomer**

**(S)-enantiomer**
Ligands A2/A2’
Ligands E2/E2’

$R/S$ mixture

$(R)$-enantiomer

$(S)$-enantiomer
Ligands E3/E3'

**R/S mixture**

**(+)-enantiomer**

**(-)-enantiomer**
Ligands E5/E5′

**R/S mixture**

**(<R>-enantiomer**

**(<S>-enantiomer**
Ligands E6/E6'
11 NMR Spectra

11.1 Synthesized Ligands

11.1.1 Ligand B

Figure S35. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum.
Figure S36. $^{13}$C NMR (151 MHz, CD$_2$Cl$_2$) spectrum.

Figure S37. $^{31}$P($^1$H) NMR (243 MHz, CD$_2$Cl$_2$) spectrum.
11.1.2 Ligand C

Figure S38. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectrum.

Figure S39. $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) spectrum.
11.1.3 Ligand D

Figure S40. $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$) spectrum.

Figure S41. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum.
**Figure S42.** $^{13}$C NMR (151 MHz, CD$_2$Cl$_2$) spectrum.

**Figure S43.** $^{31}$P{H} NMR (243 MHz, CD$_2$Cl$_2$) spectrum.
11.1.4 Ligand E

Figure S44. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum.

Figure S45. $^{13}$C NMR (151 MHz, CD$_2$Cl$_2$) spectrum.
Figure S46. $^{31}$P($^1$H) NMR (243 MHz, CD$_2$Cl$_2$) spectrum.

11.1.5 Ligand G

Figure S47. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum.
Figure S48. $^{13}$C NMR (151 MHz, CD$_2$Cl$_2$) spectrum.

Figure S49. $^{31}$P($^1$H) NMR (243 MHz, CD$_2$Cl$_2$) spectrum.
Figure S50. $^{19}$F NMR (565 MHz, CD$_2$Cl$_2$) spectrum.

11.1.6 Ligand H

Figure S51. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum.
Figure S52. $^{13}$C NMR (151 MHz, CD$_2$Cl$_2$) spectrum.

Figure S53. $^{31}$P[$^1$H] NMR (243 MHz, CD$_2$Cl$_2$) spectrum.
11.1.7  Ligand I

**Figure S54.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum.

**Figure S55.** $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum.
Figure S56. $^{31}$P($^1$H) NMR (162 MHz, CDCl$_3$) spectrum.

11.1.8 Ligand E2

Figure S57. $^1$H NMR (400 MHz, CDCl$_3$) spectrum.
Figure S58. $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum.

Figure S59. $^{31}$P{$_1^1$H} NMR (162 MHz, CDCl$_3$) spectrum.
Figure S60. $^1$H NMR (400 MHz, CDCl$_3$) spectrum.

Figure S61. $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum.
Figure S62. $^{31}$P($^1$H) NMR (162 MHz, CDCl$_3$) spectrum.

11.1.10 Ligand E4

Figure S63. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectrum.
Figure S64. $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) spectrum.

Figure S65. $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$) spectrum.
Figure S66. $^{19}$F($^1$H) NMR (376 MHz, CD$_2$Cl$_2$) spectrum.

11.1.11 Ligand E5

Figure S67. $^1$H NMR (400 MHz, CDCl$_3$) spectrum.
Figure S68. $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum.

Figure S69. $^{31}$P{$^1$H} NMR (162 MHz, CDCl$_3$) spectrum.
Figure S70. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectrum.

Figure S71. $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) spectrum.
Figure S72. $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$) spectrum.
11.2 Bis(phosphoramidite) Pd Complexes

In this section, the $^1$H (600 MHz, CD$_2$Cl$_2$, 300K), $^{13}$C (151 MHz), and $^{31}$P($^1$H) (243 MHz) NMR spectra are provided. $^{19}$F($^1$H) NMR (565 MHz) and 1D TOCSY spectra are shown in some cases.

11.2.1 Trans-Pd(E)$_2$Cl$_2$
11.2.2 Cis-Pd(E)$_2$Cl$_2$
11.2.3  *Cis*-Pd(E)(F)Cl$_2$
11.2.4  \textit{Cis}-Pd(E')(F)Cl₂
11.2.6 Cis-Pd(H)(F)Cl₂

IR: M2089 heterocomplexes of M2080 and S,R,R-Peringa, stored in vial, prep: 14.

FTI-F
$^{13}$C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
TBI-F

13C{($^1$H)}: MZ089 R-Cy-heterocomplexes of MZ080 and G,R,R-Peringa, prep: 14.08.19.
11.2.7 *Cis-Pd(H)(F)Cl₂*

**NMR Spectra:**

**1H NMR:**
- M2081 heterocomplexes of M2081 and S,B,R-Ferina prep: 09.18, meas: 12.10.

**TDI-T**
11.2.8 *Cis*-Pd(E2)(F)Cl₂

1H: MZi13 heterocomplexes of (R)-MeO i-Pr and S,R,2-Ferings. prep: 14.12.18, in TBI-F
13C(1H): MZ138 hetero complexes of (R)-MeO i-Pr and S,R,R-Perings, prep: 14.12.)
TBZ-P
11.2.9 \textit{Cis-Pd(E2')}(F)Cl$_2$

IR: M2147 heterocomplexes of (S)-4-MeO i-Pr phosphoramidite and S,R,R-Peringa, TB5-F

\begin{figure}
\centering
\includegraphics[width=\textwidth]{spectrum.png}
\caption{Spectrum of \textit{Cis-Pd(E2')}(F)Cl$_2$}
\end{figure}
$^{13}$C([R]: ME147 heterocomplexes of (S)-4-MeO i-Pt phosphoramidite and S,R,R-Feri TBI-P
11.2.10  *Cis*-Pd(E3)(F)Cl$_2$
11.2.11  *Cis-Pd(E3')(F)Cl₂*

1H: M212 hetero complexes of (S)-3-MeO i-Pr phosphoramidite and S,S,R-feringa, TDI-F
11.2.12  *Cis-Pd(E4)(F)Cl₂*

IR: MZ148 heterocomplexes of (R)-4-F i-Pr phosphoramidite and S,R,R-Terleng, p;
TBI-F
$^{19}$F($^1$H): MIL48 heterocomplexes of (S)-$^4$-F i-Fr phosphoramidite and S,R,R-Pitzer, prep: 09.01.19, T25-T
11.2.13  Cis-Pd(E4')(F)Cl₂

JH: 

[Chemical structure and spectra image]

SUPPORTING INFORMATION
13C(1H): MD176 heterocomplexes of (S)-4-F phosphoramidite and S,R,R-Feringa, pTBI-F
$^{19}$F NMR spectra of $\text{E4}^*$ and F; $\text{E4}^*$ is assigned by comparison to literature values.
11.2.14  Cis-Pd(E5)(F)Cl₂

NMR spectra of (R)-2-Naphthyl i-Fr and S,R,R-ferins, prep: 09.01

TBI-F
SUPPORTING INFORMATION

13C(1H) NMR heterocomplexes of (S)-2-Naphth phosphoramidite and S,R,R-Feing

TRI-F
11.2.16  Cis-Pd(E6)(F)Cl₂

IR: M2T24 heterocomplexes of (R)-1-Naphth phosphoramidite and S,R,R-feringa, p;
TB1-F
11.2.17  Cis-Pd(I)(F)Cl₂

IR: M168 heterocomplexes of (i-Pr)₂ phosphoramidite and S,R,R-feringa, prep: IBI-F

SUPPORTING INFORMATION
11.2.18  

*Cis*-Pd(B)₂Cl₂
11.2.19  
*Cis-Pd(B)(F)Cl₂*
11.2.20  Cis-Pd(D)₂Cl₂
12 Computational Details

12.1 Geometry optimizations

Density functional theory (DFT) calculations were performed with ORCA 4.1.1. The geometries were optimized using the GGA PBE functional\[^{[10]}\] with D3(BJ) dispersion correction\[^{[11]}\] and the split-valence plus polarization def2-SVP basis set.\[^{[12]}\] For the Pd atom, def2-ECP was used. For the structures optimized in the solvent model, CPCM or SMD implicit solvation model for dichloromethane was used.\[^{[13]}\] Frequency calculations were performed at the same level of theory as for geometry optimizations to verify the stationary points as minima (no imaginary frequencies) on the potential energy surface, as well as to obtain thermal Gibbs free energy corrections at 298 K with Grimme’s entropy corrections using quasi-rigid rotor harmonic approximation (qRRHO) applied to all frequencies below 100 cm\(^{-1}\).\[^{[14]}\]

GFN-XTB2 metadynamics\[^{[15]}\] was used to generate the possible conformers of the complexes with CH2Cl2 metaopt vtight option.

Visualizations of all computed structures were created using the CYLview.

Noncovalent interaction (NCI) plot was generated by NCIPlot\[^{[16–18]}\] and visualized by VMD 1.9.3.\[^{[19]}\]

12.2 Single-point calculations

To refine the computed energy, single point calculations were performed in ORCA 4.1.1 software package\[^{[20,21]}\] using the following methods: spin component scaled MP2,\[^{[22]}\] and double hybrid B2PLYP\[^{[23]}\] extrapolated to the complete basis set limit (CBS) with VeryTightSCF convergence criteria. CBS(DT) represents the def2-SVP/def2-TZVP extrapolation with matching auxiliary basis sets, while CBS(TQ) represents the def2-TZVPP/def2-QZVPP extrapolation. Rijcosx approximation was employed for the calculations, as well as RI-MP2 approximation for the double hybrid with matching auxiliary basis sets.\[^{[24,25]}\]

\[ E_{\text{SCF}}(X) = E_{\text{SCF}}(\infty) + A \exp(-\alpha \sqrt{X}) \]

The correlation (MP2) energy was extrapolated as follows:

\[ E_{\text{corr}}^{(\infty)} = \frac{X^\beta E_{\text{corr}}^{(X)} - Y^\beta E_{\text{corr}}^{(Y)}}{X^\beta - Y^\beta} \]

\(X, Y\) are the basis set cardinal numbers (def2-SVP: 2, def2-TZVP/TZVPP: 3, def2-QZVPP: 4). \(A\) is a constant, and \(\alpha, \beta\) are basis set specific constant \(\alpha_{23} = 10.39; \alpha_{34} = 7.88; \beta_{23} = 2.40; \beta_{34} = 2.97.\)

DLPNO-CCSD(T) Calculations

The DLPNO-CCSD(T) single-point energy calculations\[^{[26,27]}\] were conducted in Orca 4.1.1 with def2-TZVP basis set, Rijcosx approximation, and NormalPNO (\(T_{\text{CutPNO}} 3.3 \times 10^{-7}\)) settings. \(T_{\text{CutPairs}}\) was set to \(10^{-5}\).
The T1 diagnostics value was <0.02 in all cases. Local energy decomposition of total and interaction energy was performed according to Bistoni et al.\cite{28,29} Triples corrections were added to the dispersive and non-dispersive components of the correlation energy. The corresponding dispersion interaction density (DID) plots were visualized with Paraview 5.9.0.\cite{30}

12.3 NMR Chemical Shift Calculations

GIAO NMR chemical shifts were calculated in Orca 4.1.1 using TPSS-D3(BJ) functional and IGLO-III basis set.\cite{31} Def2-TZVP and def2-ECP basis sets were assigned to Pd atom. Rijcosx approximation was used with def2/JK auxiliary basis set.\cite{32} Solvent effects were mimicked by SMD solvation model (dichloromethane). From the methods screened, TPSS/IGLO-III was the most appropriate method. TMS was used as the standard.

*Orca input example:*

```
! TPSS IGLO-III Def2/J Def2/JK Rijcosx GridX6 NoFinalGridX Grid7 VeryTightSCF NMR CPCM(CH2Cl2)
%cpcm smd true
SMDsolvent "dichloromethane"
end
```

12.4 Gibbs free energies

Unless specified otherwise, Gibbs free energy values, \( \Delta G_{DCM,T} \), are used throughout the text. The \( \Delta G \) value is obtained by adding the SMD solvation correction and the corresponding free energy corrections at temperature \( T \) calculated at the PBE/def2-SVP level, to \( \Delta E \) calculated at the single-point calculation level (Equation 2).

The SMD solvation energy (PCPM dielectric + SMD CDS free energy correction) calculated at PBE-D3(BJ)/def2-SVP level of theory was used.

\[
\Delta G^{\text{sol,298K}} = \Delta E_{\text{tot}} + SMD \text{ solvation correction}_{\text{DCM}} + \Delta G_{\text{corr}}^{q\text{RRHO};\ 298\ K} + D3(BJ) \text{ correction (optional)}
\]

*Equation 2.* Calculation of Gibbs free energy for species in DCM at 298 K.
12.5 Conformations & Energetics of Complexes

12.5.1 *Cis*-Pd(E)(F)Cl₂

Table 4. 547 conformers generated by GFN-xTB2 were optimized by DFT. The lowest energy conformers based on PBE-D3(BJ)/def2-SVP energies were evaluated further with B2PLYP-D3(BJ) single-point energies as shown in the table.

| Conf | Energy | Delta E | Gcorr | B2PLYP/DT | D3(BJ) | Gsolv | kJ·mol⁻¹ |
|------|--------|---------|-------|-----------|--------|--------|---------|
| 423  | -4416.33283 | -0.06506 | 0.881568 | -4421.089362 | -0.215777 | -4420.488636 | 0.00 |
| 407  | -4416.32971 | -0.06511 | 0.881223 | -4421.086676 | -0.215077 | -4420.485643 | 7.86 |
| 590  | -4416.32786 | -0.06996 | 0.881953 | -4421.080083 | -0.212044 | -4420.480137 | 22.31 |
| 59   | -4416.32535 | -0.07041 | 0.881396 | -4421.077981 | -0.205324 | -4420.472322 | 42.83 |
| 398  | -4416.32366 | -0.06814 | 0.881940 | -4421.078723 | -0.211883 | -4420.476803 | 31.07 |
| 918  | -4416.32534 | -0.06874 | 0.881544 | -4421.077373 | -0.215597 | -4420.480164 | 22.24 |
| 330  | -4416.32401 | -0.06984 | 0.882107 | -4421.076439 | -0.210760 | -4420.474928 | 35.99 |

Overlaid DFT optimized conformers:

Conf_423 (most stable)
Conf_407 ($i$-Pr rotation)

Conf_590 (T-shape interaction)
Conf_59 (i-Pr inside)

Conf_918 (T-shape in the main interaction area)
12.5.2 *Cis-Pd(E')(F)Cl₂*

Table 5. 515 conformers generated by GFN-xTB2 were optimized by DFT. The lowest energy conformers based on PBE-D3(BJ)/def2-SVP energies were evaluated further with B2PLYP-D3(BJ) single-point energies as shown in the table.

|        | PBE/SMD    | solvation | Gcorr  | B2PLYP/DT      | D3(BJ)  | Gsolv       | kJ·mol⁻¹ |
|--------|------------|-----------|--------|----------------|---------|-------------|---------|
| conf_180 | -4416.329889  | -0.06599  | 0.8806904 | -4421.086275  | -0.215047 | -4420.486623  | 0.00 |
| conf_490 | -4416.327083  | -0.06779  | 0.8808007 | -4421.083374  | -0.211738 | -4420.482099  | 11.88 |
| conf_155 | -4416.328048  | -0.06813  | 0.8819172 | -4421.085405  | -0.209109 | -4420.480723  | 15.49 |
| conf_10  | -4416.323122  | -0.06746  | 0.8806918 | -4421.079608  | -0.213952 | -4420.480324  | 16.54 |
| conf_485 | -4416.326753  | -0.06660  | 0.8815821 | -4421.080593  | -0.214303 | -4420.479917  | 17.61 |
| conf_49  | -4416.325801  | -0.06541  | 0.8817674 | -4421.078543  | -0.217644 | -4420.479832  | 17.83 |
| conf_981 | -4416.327014  | -0.07048  | 0.8818211 | -4421.079694  | -0.211046 | -4420.479401  | 18.96 |
| conf_45  | -4416.323615  | -0.06575  | 0.8820223 | -4421.077490  | -0.216850 | -4420.478070  | 22.46 |
| conf_751 | -4416.324676  | -0.06983  | 0.8813510 | -4421.081167  | -0.206593 | -4420.476236  | 27.27 |
| conf_556 | -4416.324085  | -0.06919  | 0.8816359 | -4421.077980  | -0.208555 | -4420.474086  | 32.92 |

Conf_180

![Image of Cis-Pd(E')(F)Cl₂ molecule]
Table 6. 165 conformers generated by GFN-xTB2 were optimized by DFT. The lowest energy conformers based on PBE-D3(BJ)/def2-SVP energies were evaluated further with B2PLYP-D3(BJ) single-point energies as shown in the table.

|        | PBE/SMD  | solvation | Gcorr   | B2PLYP/DT | D3(BJ)  | Gsolv  | kJ·mol⁻¹ |
|--------|----------|-----------|---------|-----------|---------|--------|----------|
| conf_72| -3918.231155 | -0.05484 | 0.7450828 | -3922.249156 | -0.176637 | -3921.735556 | 0.00     |
| conf_80| -3918.228344 | -0.05964 | 0.7446802 | -3922.245858 | -0.170625 | -3921.731443 | 10.80    |
| conf_222| -3918.226150 | -0.06028 | 0.7440678 | -3922.244844 | -0.170373 | -3921.731427 | 10.84    |
| conf_217| -3918.226110 | -0.05922 | 0.7450542 | -3922.242871 | -0.172701 | -3921.729740 | 15.27    |

Conf_72
Table 7. 175 conformers generated by GFN-xTB2 were optimized by DFT. The lowest energy conformers based on PBE-D3(BJ)/def2-SVP energies corresponded to the same structure. The energetics was evaluated further with B2PLYP-D3(BJ) single-point energy as shown in the table.

|       | PBE/SMD | solvation | Gcorr  | B2PLYP/DT | D3(BJ) | Gsolv     |
|-------|---------|-----------|--------|-----------|--------|-----------|
| conf_100 | -4914.434524 | -0.07324  | 1.018544 | -4919.927884 | -0.258393 | -4919.240968 |

Conf_100
12.5.5 Cis-Pd(A1)(F)Cl₂

Table 8. 417 conformers generated by GFN-xTB2 were optimized by DFT. The lowest energy conformers based on PBE-D3(BJ)/def2-SVP energies were evaluated further with B2PLYP single-point energies as shown in the table.

|        | PBE/SMD | solvation | Gcorr  | B2PLYP/DT | D3(BJ)  | Gsolv  | kJ·mol⁻¹ |
|--------|---------|-----------|--------|-----------|---------|--------|----------|
| conf_8 | 4607.716263 | -0.06806 | 0.93075318 | -4612.756297 | -0.23359 | -4612.12719 | 0.00     |
| conf_58| 4607.712993 | -0.06945 | 0.93042605 | -4612.753800 | -0.22853 | -4612.12136 | 15.31    |
| conf_347| 4607.713543 | -0.06969 | 0.93151045 | -4612.753962 | -0.22875 | -4612.12089 | 16.54    |
| conf_57 | 4607.709610 | -0.07098 | 0.93103169 | -4612.747928 | -0.23067 | -4612.11854 | 22.71    |
| conf_224| 4607.710377 | -0.07338 | 0.93146931 | -4612.746200 | -0.22968 | -4612.11780 | 24.67    |
| conf_210| 4607.688961 | -0.07297 | 0.93117998 | -4612.727705 | -0.22466 | -4612.09398 | 87.19    |

Table 9. Gibbs free energies based on SCS-MP2/def2-TZVP/PCM(DCM) single-point energies.

|        | Gcorr  | SCS-MP2 | Gsolv  | kJ·mol⁻¹ |
|--------|--------|---------|--------|----------|
| conf_8 | 0.93075318 | -4605.602950 | -4604.672197 | 0.00     |
| conf_58| 0.93042605 | -4605.594664 | -4604.664238 | 20.90    |
| conf_347| 0.93151045 | -4605.594735 | -4604.663225 | 23.56    |
| conf_57 | 0.93103169 | -4605.591178 | -4604.660147 | 31.64    |
| conf_224| 0.93146931 | -4605.589055 | -4604.657586 | 38.36    |
| conf_210| 0.93117998 | -4605.562407 | -4604.631227 | 107.57   |

Conf_8
**Table 10.** 281 conformers generated by GFN-xTB2 were optimized by DFT. The lowest energy conformers based on PBE-D3(BJ)/def2-SVP energies were evaluated further with B2PLYP single-point energies as shown in the table. The energies show that at least 4 conformers of this complex would be present in the equilibrium mixture due to conformational exchange.

|        | PBE/SMD | solvation | Gcorr  | B2PLYP/DT | D3(BJ)  | Gsolv  | kJ·mol⁻¹ |
|--------|---------|-----------|--------|-----------|----------|--------|----------|
| conf_3 | -4607.710136 | -0.070163 | 0.929682 | -4612.751066 | -0.229727 | -4612.121274 | 0.00      |
| conf_80| -4607.711803 | -0.069571 | 0.930819 | -4612.750381 | -0.231554 | -4612.120687 | 1.54      |
| conf_150| -4607.709931 | -0.069632 | 0.930308 | -4612.751494 | -0.228614 | -4612.119433 | 4.83      |
| conf_177| -4607.709945 | -0.068431 | 0.931624 | -4612.750488 | -0.230836 | -4612.118131 | 8.25      |
| conf_281| -4607.707012 | -0.065971 | 0.931238 | -4612.746306 | -0.232839 | -4612.116710 | 11.98     |
| conf_87 | -4607.707411 | -0.068765 | 0.932039 | -4612.747403 | -0.234219 | -4612.116548 | 14.77     |
| conf_121| -4607.708608 | -0.074796 | 0.930182 | -4612.748573 | -0.223201 | -4612.116388 | 12.83     |
| conf_120| -4607.708309 | -0.072783 | 0.930206 | -4612.749751 | -0.223974 | -4612.116301 | 13.06     |

**Table 11.** Gibbs free energies based on SCS-MP2/def2-TZVP/CPCM(DCM) single-point energies. The relative Gibbs energies computed by this method are the same as those using B2PLYP-D3(BJ) method.

|        | Gcorr  | SCS-MP2 | Gsolv  | kJ·mol⁻¹ |
|--------|--------|---------|--------|----------|
| conf_3 | 0.929682 | -4605.593735 | -4604.66405 | 0.00      |
| conf_80| 0.930819 | -4605.594425 | -4604.66361 | 1.17      |
| conf_150| 0.930308 | -4605.592416 | -4604.66211 | 5.10      |
| conf_177| 0.931624 | -4605.592714 | -4604.66109 | 7.78      |
| conf_281| 0.931238 | -4605.590937 | -4604.65970 | 11.43     |
| conf_87 | 0.932039 | -4605.591308 | -4604.65927 | 12.56     |
| conf_121| 0.930182 | -4605.584761 | -4604.65458 | 24.87     |
| conf_120| 0.930206 | -4605.585553 | -4604.65535 | 22.86     |

Conf_3
## 12.5.7 *Cis*-Pd(A1)$_2$Cl$_2$

*Table 12.* Energy of homocomplex *cis*-Pd(A1)$_2$Cl$_2$ optimized at PBE-D3(BJ)/def2-SVP level of theory.

|         | PBE/SMD       | Gcorr | Gsolv       |
|---------|---------------|-------|-------------|
| conf_1  | -4300.967266  | 0.843210 | -4300.124056 |
### 12.6 Equilibrium Thermochemistry

Table 13. Gibbs free energies of the most stable conformers participating in the matched and mismatched equilibria.

|                        | $E_{\text{tot}}$ (B2PLYP/CBS-TQ) | $G_{298}$ | SMD solvation | $E_{\text{tot}} + G_{298}$ + solvation |
|------------------------|----------------------------------|-----------|---------------|----------------------------------------|
| EF heterocomplex       | -4421.296467                     | 0.88156784 | -0.0650647    | -4420.479964                           |
| (conf_423)             |                                  |           |               |                                        |
| E’F heterocomplex      | -4421.293563                     | 0.88069041 | -0.0659924    | -4420.478865                           |
| (conf_180)             |                                  |           |               |                                        |
| E_homocomplex          | -3922.446167                     | 0.74508278 | -0.0548446    | -3921.755929                           |
| (conf_72)              |                                  |           |               |                                        |
| F_homocomplex          | -4920.144809                     | 1.01854422 | -0.0732357    | -4919.199500                           |
| (conf_100)             |                                  |           |               |                                        |

$$\Delta G_{\text{solv}} = 2\Delta G(\text{EF heterocomplex}) - \Delta G(\text{E homocomplex}) - \Delta G(\text{F homocomplex})$$
Table 14. Single-point energies at DLPNO-CCSD(T)/def2-TZVP level of theory for different conformers of \textit{cis-Pd(E)(F)Cl}_2 and \textit{cis-Pd(E')(F)Cl}_2.

| Conformer       | DLPNO-CCSD(T) energy | PNO Settings   |
|-----------------|----------------------|----------------|
| conf_423        | -4415.341123         | Normal/TCutPairs 1e-5 |
|                 | -4415.291832         | Loose/TCutPairs 1e-5  |
|                 | -4415.365659         | Loose/TCutPairs 1e-3  |
| conf_59         | -4415.274757         | Loose/TCutPairs 1e-5  |
|                 | -4415.344305         | Loose/TCutPairs 1e-3  |
| conf_180 (E')   | -4415.288229         | Loose/TCutPairs 1e-5  |
|                 | -4415.361067         | Loose/TCutPairs 1e-3  |

Table 15. Local energy decomposition of DLPNO-CCSD(T)/def2-TZVP energies for different conformers of \textit{cis-Pd(E)(F)Cl}_2 and \textit{cis-Pd(E')(F)Cl}_2. The fragments included ligands \( E \) or \( E' \), ligand \( F \), and \textit{PdCl}_2.

| Conformer       | Dispersion interaction | Electrostatic interaction | Exchange interaction |
|-----------------|------------------------|---------------------------|----------------------|
|                 | E/F        | Pd/E       | Pd/F       | E/F        | Pd/E       | Pd/F       | E/F        | Pd/E       | Pd/F       | PNO Settings |
| conf_423        | -129.4     | -80.6      | -79.8      | -95.0      | -3151.2    | -3191.1    | -105.3     | -564.0     | -571.3     | Normal/TCutPairs 1e-5  |
|                 | -123.6     | -79.6      | -82.7      | -104.8     | -3191.1    | -105.3     | -564.0     | -571.3     |            | Loose/TCutPairs 1e-5  |
|                 | -143.6     | -100.7     | -104.8     |            |            |            |            |            |            | Loose/TCutPairs 1e-3  |
| conf_59         | -100.7     | -79.2      | -83.4      | -93.4      | -3074.5    | -2998.5    | -557.1     | -545.5     |            | Loose/TCutPairs 1e-5  |
|                 | -119.1     | -100.3     | -105.9     |            |            |            |            |            |            | Loose/TCutPairs 1e-3  |
| conf_180 (E')   | -124.1     | -78.5      | -79.7      | -107.3     | -3185.6    | -579.8     | -569.7     |            |            | Loose/TCutPairs 1e-5  |
|                 | -143.4     | -101.5     | -102.1     |            |            |            |            |            |            | Loose/TCutPairs 1e-3  |

The dispersion interaction between two ligands in \textit{cis-Pd(E)(F)Cl}_2 (conf_423) is the same as in the diastereomeric complex \textit{cis-Pd(E')(F)Cl}_2 (conf_180). However, slightly more favourable electrostatic and exchange interactions suggest that the difference in the complex stabilities is due to the dipole-dipole interactions and steric interactions, but only slightly due to dispersion. Nevertheless, the dispersion interactions aid in stabilizing the complexes.

For \textit{cis-Pd(E)(F)Cl}_2, if the isopropyl group is oriented inside the complex and the Ph(Me)CH interaction area is oriented outside (conf_59), the dispersion and other interactions are diminished. This point to the fact that the proper orientation within the complex is required to achieve full stabilization.
12.8 Computed NMR Chemical Shifts

Table 16. Computed isotropic chemical shieldings for TMS (\(^1\)H and \(^{13}\)C).

| Shielding | TPSS/IGLO-III |
|-----------|---------------|
| \(\sigma C\) | 188.0145      |
| \(\sigma H\) | 31.8643       |

12.8.1 Cis-Pd(E)(F)Cl2

\(^{13}\)C NMR computed chemical shifts for conf_423 correlate extremely well with the experimental values (\(R^2 0.9945\)). Other conformers showed worse correlations (\(R^2 < 0.96\)). \(^1\)H NMR chemical shifts were more challenging to reproduce using computational methods (see below).

Table 17. Computed isotropic chemical shieldings for \(^{13}\)C nuclei and chemical shifts relative to TMS at TPSS/IGLO-III level of theory for conf_423. Computed values were averaged where necessary (colored bars) and scaled using linear equation \(y = 0.9891x - 8.0042\). All values are in ppm.

| atom # | \(\delta\) exp. | \(\sigma\) calc. | calc. \(\delta\) | averaged | abs. error | scaled \(\delta\) | abs. error |
|--------|-----------------|------------------|------------------|----------|------------|-----------------|------------|
| 2'     | 151.2           | 24.991           | 163.0            | 163.0    | 11.82      | 153.2           | 2.04       |
| 3'     | 126.3           | 56.049           | 132.0            | 132.0    | 5.67       | 122.5           | 3.78       |
| 4'     | 126.7           | 50.193           | 137.8            | 137.8    | 11.12      | 128.3           | 1.62       |
| 5'     | 121.1           | 55.79            | 132.2            | 132.2    | 11.12      | 122.8           | 1.68       |
| 6'     | 130.3           | 49.388           | 138.6            | 138.6    | 8.33       | 129.1           | 1.19       |
| 1'     | 122             | 45.868           | 142.1            | 142.1    | 20.15      | 132.6           | 10.59      |
| 1      | 130.8           | 46.778           | 141.2            | 141.2    | 10.44      | 131.7           | 0.89       |
| 6      | 130.1           | 48.005           | 140.0            | 140.0    | 9.91       | 130.5           | 0.38       |
| 5      | 126.9           | 53.122           | 134.9            | 134.9    | 7.99       | 125.4           | 1.48       |
| 4      | 130.5           | 49.87            | 138.1            | 138.1    | 7.64       | 128.6           | 1.87       |
| 3      | 125.2           | 57.907           | 130.1            | 130.1    | 4.91       | 120.7           | 4.51       |
| 2      | 149.7           | 26.045           | 162.0            | 162.0    | 12.27      | 152.2           | 2.50       |
| g      | 48.4            | 126.708          | 61.3             | 61.3     | 12.91      | 52.6            | 4.23       |
| h      | 23.5            | 159.154          | 28.9             | 28.9     | 5.36       | 20.5            | 2.96       |
| atom # | δC exp. | δ calc | calc. δ | averaged | abs. error | scaled δ | abs. error |
|-------|---------|--------|---------|----------|------------|----------|------------|
| i     | 23.6    | 156.809| 31.2    | 31.2     | 7.61       | 22.9     | 0.74       |
| a     | 56.3    | 118.207| 69.8    | 69.8     | 13.51      | 61.0     | 4.74       |
| b     | 16.2    | 163.703| 24.3    | 24.3     | 8.11       | 16.0     | 0.16       |
| c     | 141     | 38.449 | 149.6   | 149.6    | 8.57       | 139.9    | 1.07       |
| d     | 128.2   | 46.042 | 142.0   | 138.3    | 10.14      | 128.8    | 0.63       |
| e     | 127.5   | 52.51  | 135.5   | 135.6    | 8.14       | 126.2    | 1.34       |
| f     | 126.3   | 53.307 | 134.7   |          |            |          |            |
| g     | 52.902  |        |         |          |            |          |            |
| h     | 56.4    | 120.035| 68.0    | 69.5     | 13.07      | 60.7     | 4.30       |
| i     | 19      | 161.066| 26.9    | 26.2     | 7.23       | 17.9     | 1.06       |
| j     | 141.3   | 36.995 | 151.0   | 151.0    | 9.68       | 141.3    | 0.03       |
| k     | 128.3   | 50.121 | 137.9   | 138.5    | 10.15      | 128.9    | 0.64       |
| l     | 52.147  |        | 135.9   | 135.9    |            |          |            |
| m     | 52.095  |        |         |          |            |          |            |
| n     | 53.449  |        | 134.6   |          |            |          |            |
| o     | 128.3   | 49.691 | 138.3   |          |            |          |            |
| p     | 56.3    | 117.063| 71.0    |          |            |          |            |
| q     | 16.2    | 162.506| 25.5    |          |            |          |            |
| r     | 141     | 37.08  | 150.9   |          |            |          |            |
| s     | 128.2   | 45.096 | 142.9   |          |            |          |            |
| t     | 127.5   | 52.154 | 135.9   |          |            |          |            |
| u     | 52.14   |        | 135.9   |          |            |          |            |
| v     | 127.5   | 52.2   | 135.8   |          |            |          |            |
| w     | 128.2   | 53.345 | 134.7   |          |            |          |            |

MAE: 9.36  1.96
Figure S73. Correlation of calculated vs. experimental $^{13}$C chemical shifts.

Table 18. Computed isotropic chemical shieldings for $^1$H nuclei and chemical shifts relative to TMS at TPSS/IGLO-III level of theory for conf_423. Computed values were averaged where necessary and scaled using linear equation $y = 0.9476x - 0.206$. All values are in ppm.

| atom # | $\delta_H$ exp. | $\sigma_{calc}$ | calc. $\delta$ | averaged $\delta$ | abs. error | scaled $\delta$ | abs. error |
|--------|-----------------|-----------------|----------------|-------------------|------------|----------------|------------|
| 3'     | 7.28            | 23.704          | 8.16           | 8.16              | 0.88       | 7.53           | 0.25       |
| 4'     | 7.18            | 23.818          | 8.05           | 8.05              | 0.87       | 7.42           | 0.24       |
| 4      | 7.50            | 23.855          | 8.01           | 8.01              | 0.51       | 7.38           | 0.12       |
| 3      | 7.20            | 22.759          | 9.11           | 9.11              | 1.91       | 8.42           | 1.22       |
| g      | 2.83            | 28.655          | 3.21           | 3.21              | 0.38       | 2.84           | 0.01       |
| i      | 1.06            | 29.924          | 1.94           | 1.63              | 0.57       | 1.34           | 0.28       |
| i      | 1.06            | 30.675          | 1.19           |                   |            |                |            |
| a      | 4.24            | 28.396          | 3.47           | 3.47              | 0.77       | 3.08           | 1.16       |
| b      | 0.95            | 31.108          | 0.76           | 1.79              | 0.84       | 1.49           | 0.54       |
| b      | 0.95            | 29.272          | 2.59           |                   |            |                |            |
| d      | 6.93            | 22.906          | 8.96           | 7.98              | 1.05       | 7.36           | 0.43       |
| e      | 6.78            | 24.563          | 7.30           | 7.41              | 0.63       | 6.81           | 0.03       |
| f      | 24.389          | 7.48            |               |                   |            |                |            |
| e      | 6.78            | 24.352          | 7.51           |                   |            |                |            |
| d      | 6.93            | 24.853          | 7.01           |                   |            |                |            |
| 3'     | 6.85            | 24.368          | 7.50           | 7.50              | 0.65       | 6.90           | 0.05       |
| 4'     | 7.44            | 23.76           | 8.10           | 8.10              | 0.66       | 7.47           | 0.03       |
| e      | 26.474          | 5.39            |               |                   |            |                |            |
| f      | 24.726          | 7.14            |               |                   |            |                |            |
| e      | 24.726          | 7.14            |               |                   |            |                |            |
| d      | 7.80            | 26.626          | 5.24           | 7.38              | 0.42       | 6.78           | 1.02       |
| d      | 7.80            | 24.538          | 7.33           |                   |            |                |            |
| atom # | δ_H exp. | δ_{calc} | calc. δ | averaged | abs. error | scaled δ | abs. error |
|-------|----------|----------|---------|----------|------------|----------|------------|
| f     | 24.039   |          | 7.83    |          |            |          |            |
| e     | 24.52    |          | 7.34    |          |            |          |            |
| d     | 7.80     | 22.908   | 8.96    |          |            |          |            |
| e     | 23.917   |          | 7.95    |          |            |          |            |
| d     | 7.80     | 23.881   | 7.98    |          |            |          |            |
| 3     | 8.56     | 22.321   | 9.54    | 9.54     | 0.98       | 8.84     | 0.28       |
| 4     | 8.12     | 23.229   | 8.64    | 8.64     | 0.52       | 7.98     | 0.14       |
| b     | 1.54     | 28.82    | 3.04    | 2.30     | 0.76       | 1.97     | 0.43       |
| b     | 1.54     | 29.282   | 2.58    |          |            |          |            |
| b     | 1.54     | 30.22    | 1.64    |          |            |          |            |
| a     | 4.52     | 27.678   | 4.19    | 4.33     | 0.19       | 3.90     | 0.62       |
| b     | 1.54     | 28.852   | 3.01    |          |            |          |            |
| b     | 1.54     | 30.472   | 1.39    |          |            |          |            |
| b     | 1.54     | 29.768   | 2.10    |          |            |          |            |
| a     | 4.52     | 27.387   | 4.48    |          |            |          |            |
| 8'    | 7.17     | 24.065   | 7.80    | 7.80     | 0.63       | 7.18     | 0.01       |
| 7'    | 7.42     | 23.835   | 8.03    | 8.03     | 0.61       | 7.40     | 0.02       |
| 9'    | 7.10     | 24.152   | 7.71    | 7.71     | 0.61       | 7.10     | 0.00       |
| 6'    | 7.79     | 23.343   | 8.52    | 8.52     | 0.73       | 7.87     | 0.08       |
| 8     | 6.62     | 24.844   | 7.02    | 7.02     | 0.40       | 6.45     | 0.17       |
| 9     | 6.30     | 25.292   | 6.57    | 6.57     | 0.27       | 6.02     | 0.28       |
| 7     | 7.26     | 24.094   | 7.77    | 7.77     | 0.51       | 7.16     | 0.10       |
| 6     | 7.85     | 23.43    | 8.43    | 8.43     | 0.58       | 7.79     | 0.06       |
| 5     | 7.12     | 24.202   | 7.66    | 7.66     | 0.54       | 7.05     | 0.07       |
| 6     | 6.76     | 24.94    | 6.92    | 6.92     | 0.16       | 6.36     | 0.40       |
| 6'    | 7.39     | 24.103   | 7.76    | 7.76     | 0.37       | 7.15     | 0.24       |
| 5'    | 7.09     | 24.112   | 7.75    | 7.75     | 0.66       | 7.14     | 0.05       |
| h     | 0.10     | 30.997   | 0.87    | 0.82     | 0.72       | 0.57     | 0.47       |
| h     | 0.10     | 30.867   | 1.00    |          |            |          |            |
| h     | 0.10     | 31.274   | 0.59    |          |            |          |            |

MAE 0.65 0.29
Figure S74. Correlation of calculated vs. experimental $^1$H chemical shifts.
12.9 Noncovalent Interaction Plots

*Cis*-Pd(E)(F)Cl$_2$

**strong, repulsive interactions**

**weak, attractive noncovalent interactions**
Cis-Pd(E)(F)Cl₂ (Independent Gradient Model)\textsuperscript{33}
$Cis$-$Pd(E')(F)Cl_2$

$Cis$-$Pd(E2)(F)Cl_2$
**Supporting Information**

\[ \text{Cis-Pd(E4)(F)Cl}_2 \]

\[ \text{Cis-Pd(E)}_2\text{Cl}_2 \]
$\text{Cis-Pd(F)}_2\text{Cl}_2$
Cis-Pd(E)(F)Cl₂ (Dispersion interaction plot) – conf_59 (iPr inside the complex)
Figure S75. Polarization of the C-H bond in the Ph(Me)CH groups of cis-Pd(E)(F)Cl₂ is shown by molecular electrostatic potential map calculated at B3LYP-D3(BJ)/def2-TZVP/SMD(DCM) level of theory.
12.11 Computed Geometry vs. X-ray Crystal Structure

Figure S76. Overlay of the crystal structure of cis-Pd(A1')₂Cl₂ by Alexakis (blue; S,S-stereochemistry was inverted to R,R- to give a mirror image)\[34]\ and a computed structure at PBE/def2-SVP/PCM(DCM) level of theory (red) shows a close match between the structures.

12.12 Potential Pyramidalization of Nitrogen

We did not observe any pyramidalization at the nitrogen in the computed structures of the phosphoramidite complexes. The planar geometry around nitrogen is in line with the $n_N \rightarrow \sigma^{*}_{P-O}$ delocalization and P=N double bond character. The P-O bond antiperiplanar to the nitrogen lone pair is longer (1.683 Å) than the other P-O bond (1.661 Å) for ligand E (similarly for ligand F) in cis-Pd(E)(F)Cl₂.

We also optimized geometry of free ligand E by PBE-D3(BJ)/def2-SVP and B3LYP-D3(BJ)/def2-TZVP methods and no pyramidalization was apparent, in accordance with the work of Corminboeuf et al.\[35\]
**SUPPORTING INFORMATION**

12.13  Coordinates of Computed Structures

_Cis-Pd(E)(F)Cl_2_

Conf_423

Pd 1.6427140000 2.5369630000 1.7293450000
Cl 1.4010040000 3.5941510000 3.8447050000
Cl 3.3821880000 4.0436700000 1.1209420000
P 0.1926680000 1.0185880000 2.5347960000
O 0.2496930000 -0.3762160000 1.5943760000
O 0.6487110000 0.3549210000 3.9873710000
N -1.3561120000 1.5375850000 2.8105460000
C 0.0147820000 -1.6757080000 2.0067570000
C -1.0326470000 -2.3803860000 1.3930260000
C -1.2180300000 -3.7393570000 1.6815810000
C -0.3546530000 -4.3890250000 2.5812710000
C 0.6927060000 -3.6783410000 3.1817410000
C 0.9022850000 -2.3072270000 2.9114360000
C 2.0464800000 -1.5755360000 3.4983550000
C 3.3287110000 -2.1668910000 3.5751490000
C 4.4184060000 -1.4708740000 4.1131820000
C 4.2527880000 -0.1596680000 4.5922220000
C 2.9928380000 0.4523120000 4.5335530000
C 1.9102210000 -0.2579360000 3.9953820000
C -2.2735490000 1.1063710000 3.9024760000
C -1.8656080000 1.6930050000 5.2588740000
C -2.4733270000 -0.4083510000 3.9458530000
C -1.8723100000 2.5503510000 1.8403820000
C -2.1487970000 3.8965860000 2.5032300000
C -3.0318810000 1.9531390000 1.0462530000
C -2.7677010000 0.8660850000 0.1866820000
C -3.7909560000 0.2765330000 -0.5661240000
C -5.1082680000 0.7595480000 -0.4604280000
C -5.3822660000 1.8385340000 0.3929220000
C -4.3495610000 2.4354920000 1.1380970000
P 1.8185480000 1.7759900000 -0.3792880000
O 0.4333700000 0.9089200000 -0.7765510000
O 1.7249500000 2.9520940000 -1.5509410000
N 3.2184910000 0.9605320000 -0.7384020000
C -0.0851850000 0.7726340000 -2.0531880000
C -0.1560870000 -0.5400130000 -2.9825020000
C -0.7475070000 -0.7456660000 -3.8139160000
C -1.2292830000 0.3541400000 -4.5829590000
C -1.1398200000 1.6904320000 -4.0449880000
C -0.6188870000 1.8837280000 -2.7146320000
C -0.6317760000 3.2010290000 -2.0323800000
C -1.8485170000 3.9553950000 -1.8338960000
C -1.7874590000 5.2354030000 -1.1662770000
C -0.5340980000 5.7257690000 -0.6951050000
C 0.6165100000 4.9699720000 -0.8296680000
C 0.5462830000 3.7133840000 -1.4812120000
C 4.0107650000 0.9909520000 -2.0068750000
C 4.6520740000 2.3604970000 -2.2495880000
C 3.2770960000 0.4145820000 -3.2147810000
C 2.5687420000 1.2252960000 -4.1250210000
C 1.9757870000 0.6686280000 -5.2688820000
C 2.0773980000 -0.7088260000 -5.5196280000
C 2.7696670000 -1.5290530000 -4.6140390000
C 3.3636340000 -0.9701280000 -3.4727100000
C 3.7965340000 0.1727350000 0.3958500000
C 5.1304690000 0.7400670000 0.8758390000
C 3.7990950000 -1.3111930000 0.0420600000
C 2.5637920000 -1.9523710000 -0.1842890000
C 2.5050780000 -3.3091710000 -0.5226470000
C 3.6926790000 -4.0508460000 -0.6603500000
C 4.9286840000 -3.4230040000 -0.4413960000

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SUPPORTING INFORMATION

### C 4.9814890000 -2.0623570000 -0.0854620000
H -1.6869970000 -1.8526190000 0.6850930000
H -2.0414610000 -4.2899150000 1.2026130000
H 5.1083020000 0.3936680000 5.0071970000
H 2.8227980000 1.4807560000 4.8814760000
H -3.2466510000 1.5559080000 3.6123630000
H -0.9125650000 1.2532820000 5.6089780000
H -2.6502910000 1.4762980000 6.0114950000
H -1.7302760000 2.7895260000 5.1915690000
H -1.0448350000 2.7129650000 1.1128300000
H -2.4615360000 4.6307440000 1.7353890000
H -1.2217860000 2.4569840000 2.9880850000
H -2.9473070000 3.8348260000 3.2687350000
H -1.7379310000 0.4911900000 0.1073460000
H -3.5567960000 -0.5585990000 -1.2447610000
H -5.9169400000 0.2986390000 -1.0477100000
H -6.4081170000 2.2292030000 0.4763190000
H -4.5799880000 3.2921690000 1.7875420000
H 0.2671610000 -1.3683060000 -1.9996400000
H -0.8130040000 -1.7597330000 -4.2354030000
H 1.4230140000 1.3169030000 -5.9657870000
H 1.6099920000 -1.1425750000 -6.4169820000
H 2.8544700000 -2.6111400000 -4.7990250000
H 3.9167990000 -1.6156890000 -2.7725600000
H 2.4802400000 2.3052050000 -3.9422900000
H 3.6530350000 -5.1157120000 -0.9356040000
H 1.5275670000 -3.7909070000 -0.6781440000
H 1.6382710000 -1.3677690000 -0.0910570000
H 5.8642180000 -3.9937800000 -0.5453780000
H 5.9589420000 -1.5906880000 0.0910170000
H 1.5842750000 5.2925750000 -0.4226430000
H -0.4981770000 6.7040320000 -0.1927800000
H 4.9924630000 1.7983460000 1.1682950000
H 5.9189080000 0.6869350000 0.0983950000
H 5.4785225000 0.1678590000 1.7577950000
H 3.0756540000 0.2944090000 1.2369150000
H 3.8962590000 3.1360870000 -2.4695710000
H 5.3554190000 2.2979740000 -3.1038000000
H 5.2070200000 2.6824510000 -1.3483830000
H 4.8307350000 0.2747050000 -1.7974520000
C -1.5309780000 2.7808860000 -4.8786550000
C -2.0145200000 2.5646150000 -6.1620110000
H -2.2996870000 3.4231420000 -6.7885650000
C -1.7495420000 0.1642150000 -5.8969370000
C -2.1386290000 1.2451090000 -6.6746020000
H -2.5293820000 1.0853420000 -7.6905250000
H -1.4312540000 3.0868160000 -4.4971810000
H -1.8173690000 -0.8621740000 -6.2903470000
C -3.1292630000 3.4537780000 -2.2122483000
C -2.9922630000 5.9705060000 -0.9537710000
C -4.2177070000 5.4612820000 -1.3558020000
C -4.2831860000 4.1863600000 -1.9787430000
H -5.2590700000 3.7668530000 -2.2631640000
H -3.2000430000 2.4572180000 -2.6657120000
H -5.1407530000 6.0334270000 -1.1780790000
H -2.9274100000 6.9477010000 -0.4512650000
H 5.4080740000 -1.9504040000 4.1454400000
C 3.4690010000 -3.1805330000 3.1721720000
H 1.3661150000 -4.1861140000 3.8888990000
H -0.5004760000 -5.4531200000 2.8190320000
H -3.2559320000 -0.6548860000 4.6949930000
H -1.5480860000 -0.9364560000 4.2374940000
H -2.8052280000 -0.7944560000 2.9621070000

Conf_407

Pd 1.5586470000 2.5370670000 1.7768320000
Cl 1.1296730000 3.6322260000 3.8436120000

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Cis-Pd(E')(F)Cl₂

Conf_180

Pd 0.6221440000 -1.5282370000 1.5340510000
Cl -0.4473500000 -3.5207900000 2.2696030000
Cl 2.3191440000 -1.7686510000 3.1921880000
P -0.8544540000 -1.5398730000 -0.1559760000
O -0.2117380000 -0.6134970000 -1.4027840000
O -0.9962540000 -2.9853010000 -0.9543970000
N -2.4235490000 -1.1286790000 0.1890090000
C -0.5352180000 -0.7312050000 -2.7425490000
C -1.1513910000 0.3572170000 -3.3772530000
C -1.3632100000 0.3197690000 -4.7627250000
C -0.9545420000 -0.8026290000 -5.5043460000
C 3.3314700000 -1.8803650000 -4.8609700000
C -0.1103440000 -1.8707060000 -3.4653400000
C 0.6127750000 -2.9669240000 -2.7831150000
C 1.7797800000 -3.5303180000 -3.3485240000
C 2.4871190000 -4.5462910000 -2.6924130000
C 2.0405390000 -5.0278370000 -1.4494660000
C 0.8841580000 -4.4911260000 -0.8645510000
| H                  | C                  | C                  |
|--------------------|--------------------|--------------------|
| 0.4220030000       | 6.2890690000       | 0.1044790000       |
| C                  | -1.6541500000      | 3.6073840000       |
| C                  | -3.0943380000      | 3.7098080000       |
| C                  | -3.8639340000      | 3.5798660000       |
| C                  | -3.1948930000      | 3.3140200000       |
| C                  | -1.8248850000      | 3.1253430000       |
| C                  | -1.0775550000      | 2.2536940000       |
| C                  | 3.2979920000       | 2.8651040000       |
| C                  | 3.1049810000       | 3.5364830000       |
| C                  | 3.2378330000       | 3.8241220000       |
| C                  | 4.1223570000       | 3.6312700000       |
| C                  | 4.1598440000       | 5.3612700000       |
| C                  | 3.3096490000       | 5.6537860000       |
| C                  | 2.4199080000       | 5.8531460000       |
| C                  | 2.3821500000       | 4.9443840000       |
| C                  | 3.1716880000       | 0.3304510000       |
| C                  | 3.8329600000       | 0.0904170000       |
| C                  | 4.0822300000       | 0.1789140000       |
| C                  | 5.4722890000       | -0.0043350000      |
| C                  | 6.2629550000       | -0.1669890000      |
| C                  | 5.6716560000       | -0.1574900000      |
| C                  | 4.2818350000       | 0.0255780000       |
| C                  | 3.5012510000       | 0.2001660000       |
| H                  | -0.3396390000      | -0.5397800000      |
| H                  | 0.4659430000       | -1.7690810000      |
| H                  | 3.8095220000       | -3.8158350000      |
| H                  | 1.3148030000       | -3.4815300000      |
| H                  | -3.9791110000      | -1.3114790000      |
| H                  | -1.6790050000      | -3.9455950000      |
| H                  | 1.5435920000       | 2.0497970000       |
| H                  | 1.3171370000       | 4.0444880000       |
| H                  | 4.8621070000       | 4.3695870000       |
| H                  | 3.3338050000       | 6.3660370000       |
| H                  | 1.7403390000       | 6.7192420000       |
| H                  | 1.6809530000       | 5.1155130000       |
| H                  | 4.7984900000       | 2.7622660000       |
| H                  | 6.2903150000       | -0.2940160000      |
| H                  | 7.3501770000       | -0.3088690000      |
| H                  | 5.9521190000       | -0.2858400000      |
| H                  | 3.8027310000       | 0.0264190000       |
| H                  | 2.4162710000       | 0.3519520000       |
| H                  | -1.2913980000      | 2.8524050000       |
| H                  | -3.7887250000      | 3.2214400000       |
| H                  | 3.0658880000       | 0.1536210000       |
| H                  | 4.6309630000       | 0.8273560000       |
| H                  | 4.2831500000       | -0.9205660000      |
| H                  | 2.3801960000       | -0.4447610000      |
| H                  | 3.2180670000       | 2.7928510000       |
| H                  | 2.1016650000       | 3.9874260000       |
| H                  | 3.8653650000       | 4.3312920000       |
| H                  | 4.3247780000       | 2.4486610000       |
| C                  | -1.5985610000      | 6.1569310000       |
| C                  | -1.6160880000      | 7.3045430000       |
| H                  | -2.1825990000      | 8.1855430000       |
| C                  | -0.1574530000      | 6.2574020000       |
| C                  | -0.9023730000      | 7.3546260000       |
| H                  | -0.9311320000      | 8.2669280000       |
| H                  | -2.1447000000      | 6.1381710000       |
| H                  | 0.4220030000       | 6.2890690000       |
| C                  | -3.8004180000      | 3.8715610000       |
| C                  | -5.2864930000      | 3.6744890000       |
| C                  | -5.9391500000      | 3.8551410000       |
| C                  | -5.1868480000      | 3.9381400000       |
| C                  | -5.7071550000      | 4.0537970000       |
| H                  | -3.2334720000      | 3.9200570000       |
| H                  | -7.0375530000      | 0.9490690000       |
| H                  | -5.8567190000      | 3.5842940000       |
SUPPORTING INFORMATION

Conf_155

Pd 0.7012020000 -0.6877780000 1.9549140000
Cl -0.0299630000 -2.4254050000 3.3964030000
Cl 2.3979250000 -0.0846060000 3.5087510000
P -0.8517070000 -1.4629270000 0.5287030000
O -0.4556260000 -0.9521090000 -1.0173210000
O -0.8307960000 -3.0994620000 0.2840550000
N -2.4346930000 -1.1410150000 0.9056630000
C -0.8530410000 -1.5681790000 -2.1924520000
C -1.6685070000 -0.8446700000 -3.0748840000
C -1.9759030000 -1.3836900000 -4.3320120000
C -1.4650560000 -2.6408080000 -4.6994300000
O -0.6465740000 -3.3518970000 -3.8116910000
C -0.3225920000 -2.8341730000 -2.5382950000
C 0.6057130000 -3.5399330000 -1.6281130000
C 1.7892090000 -4.1371170000 -2.1180570000
C 2.6965210000 -4.7645450000 -1.2553050000
C 2.4360720000 -4.8175590000 0.1251230000
C 1.2628460000 -4.2454810000 0.6391500000
C 0.3645460000 -3.6217350000 -0.2369550000
C -3.6089160000 -2.0493370000 0.7618250000
C -2.6928740000 0.2807010000 1.2859580000
P 1.3608200000 1.0958180000 0.7599340000
O 0.1612620000 1.6100240000 -0.3129070000
O 0.1490845000 2.4983440000 1.6558050000
N 2.8511080000 0.9899160000 0.0283290000
C 0.1194920000 2.9021730000 -0.8156600000
C 0.3801890000 3.0766050000 -2.1990240000
C 0.3439460000 4.3465810000 -2.7462030000
C 0.0794840000 5.4846220000 -1.9279860000
C -0.2045880000 5.3000480000 -0.5231510000
C -0.2330410000 3.9666260000 0.0227260000
C -0.5987950000 3.6750490000 1.4324680000
C -1.8726890000 4.0379250000 2.0044770000
C -2.1508850000 3.6927780000 3.3796900000
C -1.1750720000 2.9852600000 4.1419270000
C 0.0254040000 2.5983840000 3.5729260000
C 0.2869300000 2.9386010000 2.2227900000
C 3.6350450000 2.2112330000 -0.3299430000
SUPPORTING INFORMATION

Conf_10

Pd 0.0634260000 0.1913240000 2.6234140000
Cl -1.4803280000 -0.2132370000 4.4383794000
Cl 1.7081320000 0.9392730000 4.1722930000
P -1.4673150000 -0.7606040000 1.2936100000
O -0.6575320000 -1.2961380000 -0.0797650000
O -2.0663190000 -2.2062870000 1.8274620000
N -2.8357590000 0.1039670000 0.9259390000
C -1.0998840000 -2.3024150000 -0.9210930000
C -1.4147720000 -1.9683950000 -2.2459240000
C -1.7370760000 -2.9825690000 -3.1582090000
C -1.7417360000 -4.3246630000 -2.7399300000
C -1.4209800000 -4.6468610000 -1.4143380000
C -1.0949930000 -3.6451330000 -0.4737370000
C -0.6825790000 -3.9820950000 0.9069840000
C 0.1950980000 -5.0601030000 1.1620290000
C 0.6208230000 -5.3580830000 2.4626840000
C 0.1750530000 -4.5821810000 3.5465860000
C -0.7071910000 -3.5140020000 3.3273530000
C -1.1301270000 -3.2334210000 2.0213730000
C -4.2343600000 -0.4048700000 0.8171860000
C -2.5760910000 1.5208750000 0.5283880000
P 1.4729740000 0.8576130000 1.0039080000
O 0.6681290000 1.0648490000 -0.4821440000
O 1.9775670000 2.4183650000 1.2405200000
N 2.8725390000 -0.0451960000 0.8237650000
C 1.0984050000 1.9555790000 -1.4613820000
C 1.5001210000 1.4038760000 -2.7063890000
C 1.9215050000 2.2399240000 -3.7247730000
C 2.0056430000 3.6491660000 -3.5179460000
C 1.5753130000 4.2065590000 -2.2575060000
C 1.0423110000 3.3563440000 -1.2392540000
C 0.4705410000 3.8520870000 0.0287120000
C -0.6266350000 4.7905310000 0.0621250000
C -1.1114970000 5.2628060000 1.3382730000
C -0.5174460000 4.7794140000 2.5408930000
C 0.4940300000 3.8369840000 2.5038150000
C 0.9622590000 3.3777850000 1.2470620000
C 3.9819260000 0.3573140000 -0.1031410000
C 5.2258940000 -0.5347830000 0.0187790000
C 4.4160400000 1.8016620000 0.1051350000
C 4.8408500000 2.2497360000 1.3719220000
C 5.2832460000 3.5676570000 1.5446140000
C 5.3096850000 4.4542640000 0.4521050000
C 4.8954090000 4.0111810000 -0.8133190000
C 4.4557040000 2.6880810000 -0.9837890000
C 2.7254000000 -1.4560400000 1.3092120000
C 3.5932570000 -1.7614680000 2.5293480000
C 2.7712630000 -2.4817170000 0.1794390000
Conf_485

Pd 0.0564160000 -0.4127280000 2.9400720000
Cl -0.7226820000 -2.1108830000 4.4047510000
Cl 0.6837880000 0.8941700000 4.8252780000
P -0.3548940000 -1.7519550000 1.1706690000
O 0.6023860000 -1.2854000000 -0.1190530000
O 0.2328230000 -3.3167540000 1.3474170000
N -1.8905720000 -1.9456810000 0.5749540000
C 1.2269490000 -2.0609170000 -1.0837790000
C 0.9477550000 -1.7494900000 -2.4255650000
C 1.6557770000 -2.3866210000 -3.4519850000
C 2.6436530000 -3.3348260000 -3.1348750000
C 2.9155440000 -3.6349910000 -1.7950520000
C 2.2189140000 -3.0068920000 -0.7363630000
C 2.5722580000 -3.2947930000 0.6697120000
C 3.9253080000 -3.4599700000 1.0499270000
C 4.2781310000 -3.7703050000 2.3688150000
C 3.2786390000 -3.9270780000 3.3448300000
C 1.9308930000 -3.7594620000 2.9995030000
C 1.5877100000 -3.4431710000 1.6764310000
C -3.1503590000 -1.5323070000 1.2719690000
C -2.0720140000 -2.5779110000 -0.7622600000
O 0.7769610000 1.3734290000 1.7537280000
O -0.0534550000 1.3325100000 0.2345020000
O 0.2627880000 2.8769760000 2.2350950000
N 2.4293600000 1.5583210000 1.7147860000
O -0.1299180000 2.4256660000 -0.5962620000
O 0.5329990000 2.4009620000 -1.8496740000
O 0.3145000000 3.4188910000 -2.7578440000
O -0.5213540000 4.5243200000 -2.4229690000
C -1.1804460000 4.5534070000 -1.1393360000
C -1.0319470000 3.4335560000 -0.2402660000
C -1.7884490000 3.3302700000 1.0324080000
C -3.2311390000 3.4157490000 1.0715850000
C -3.9107500000 3.3745710000 2.3448300000
C -3.1518740000 3.2152930000 3.5417830000
C -1.7805550000 3.0442630000 3.4907790000
C -1.1217730000 3.0846790000 2.2368280000
C 3.2250420000 2.8283310000 1.7663360000
C 3.0770710000 3.5608830000 3.1036030000
C 0.0496080000 3.7189950000 0.5397160000
C 3.8947270000 3.5259800000 -0.5732960000
C 3.7988910000 4.3498460000 -1.7045850000
C 2.8547540000 5.3884990000 -1.7393240000
C 2.0123670000 5.5952490000 -0.6356940000
C 2.1080590000 4.7675160000 0.4935770000
C 3.2140200000 0.2863000000 1.8079520000
C 3.9167840000 0.1297630000 3.1546770000
C 4.1073730000 0.1291760000 0.5812330000
C 5.4970000000 -0.0705640000 0.6726490000
C 6.2719980000 -0.2415210000 -0.4891030000
C 5.6657140000 -0.2236740000 -1.7546570000
C 4.2774310000 -0.0246250000 -1.8545570000
C 3.5134240000 0.1566770000 -0.6963160000
H 0.1809990000 -0.9928870000 -2.6449610000
H 1.4343630000 -2.1381190000 -4.5007660000
H 3.5478830000 -4.1720580000 4.3831000000
H 1.1251800000 -3.8439280000 3.7413290000
H -3.8971050000 -1.5460360000 0.4500110000
Cis-Pd(E)₂Cl₂

Conf_72
SUPPORTING INFORMATION

Conf_80

Pd 1.558562000 2.511797000 1.033616000
Cl 1.506252000 3.792028000 3.038540000
Cl 3.278533000 3.910353000 0.181044000
P 0.133240000 1.111983000 2.074096000
O 0.256520000 0.128778000 1.295500000
N -1.436685000 1.530360000 2.426060000
C -0.116429000 -1.579472000 1.851035000
C -1.196902000 -2.266840000 1.278144000
C -1.518530000 -3.552241000 1.737253000
C -0.756254000 -4.139465000 2.762390000
C 0.327964000 -3.446369000 3.318769000
C 0.673608000 -2.149826000 2.877754000
C 1.187085000 -1.443688000 3.389699000
C 3.092400000 -2.129064000 3.154783000
C 4.242194000 -1.460058000 4.013255000
C 4.198608000 -0.080594000 4.279950000
C 2.999242000 0.626626000 4.111807000
C 1.855363000 -0.057286000 3.677615000
C -2.265119000 2.289704000 1.436713000
C -2.584346000 1.447698000 0.198917000
C -1.674699000 3.654121000 1.069230000
C -2.145281000 1.070728000 3.659942000
C -3.225581000 0.032836000 3.254583000
C -2.628247000 2.291671000 4.444905000
C -1.689670000 3.283288000 4.805473000
C -2.084860000 4.412164000 5.536536000
C -3.428498000 4.573103000 5.921005000
C -4.368907000 3.594315000 5.568929000
C -3.971281000 2.461571000 4.832842000
P 1.722010000 1.433562000 -0.941931000
O 0.310477000 0.576078000 -1.262108000
N 3.093244000 0.513672000 -1.115989000
C -0.214669000 0.232072000 -2.493639000
C 0.406212000 -1.133324000 -2.758527000
C -1.030266000 -1.531699000 -3.948050000
C -1.465713000 -0.562259000 -4.868697000
C -1.289165000 0.798212000 -4.586656000
C -0.664489000 1.230278000 -3.393099000
C -0.548073000 2.670484000 -3.072379000
C -1.618411000 3.560219000 -3.326353000
C -1.523260000 4.921790000 -3.011602000
SUPPORTING INFORMATION

Conf_222
| Atom | x        | y        | z        |
|------|----------|----------|----------|
| H    | -0.861029| 3.715441 | 6.094773 |
| H    | 5.713467  | 1.228767 | 0.533214 |
| H    | 7.019652  | 1.393951 | 2.698140 |
| H    | 0.847304  | 0.137691 | 6.682879 |
| H    | 0.777139  | 0.941944 | 4.443801 |
| H    | 0.030630  | -2.746819| 0.995341 |
| H    | 0.343831  | -5.101659| 1.806199 |
| H    | -0.261661 | -2.176397| 2.549858 |
| H    | 1.146384  | -0.894428| 2.195966 |
| H    | 0.315912  | 0.657532 | 1.464341 |
| Pd   | 2.108689  | 2.262196 | 0.004298 |
| Cl   | 2.290560  | 4.632158 | -0.031116 |
| Cl   | 4.172741  | 2.111130 | -1.170625 |
| P    | 0.074500  | 2.427198 | 0.959727 |
| O    | -0.943079 | 3.535753 | 0.217372 |
| O    | -0.823294 | 1.041529 | 0.652357 |
| N    | -0.070861 | 2.740458 | 2.580630 |
| C    | -1.136563 | 3.367808 | -1.161698 |
| C    | -0.437730 | 4.198820 | -2.049538 |
| C    | -0.639426 | 4.062512 | -3.430110 |
| C    | -1.540575 | 3.101637 | -3.917255 |
| C    | -2.241920 | 2.285763 | -3.022580 |
| C    | -2.054284 | 2.394621 | 1.624210 |
| C    | -2.804808 | 1.525824 | 0.692347 |
| C    | -4.167939 | 1.226084 | -0.924660 |
| C    | -4.882498 | 0.357983 | -0.090176 |
| C    | -4.241030 | -0.242431 | 1.007144 |
| C    | -2.891430 | 0.052644 | 1.261487 |
| C    | -2.184822 | 0.912323 | 0.423022 |
| C    | 1.052168 | 3.125307 | 3.495017 |
| C    | 1.393089 | 4.615994 | 3.423724 |
| Pd   | 2.295272 | 2.245204 | 3.350194 |
| C    | -1.417539 | 2.624924 | 3.207232 |
| C    | -1.963729 | 3.978988 | 3.665076 |
| C    | -1.395296 | 1.533478 | 4.281012 |
| C    | -2.062436 | 1.679597 | 5.512658 |
| C    | -2.050832 | 0.642215 | 6.462220 |
| C    | -1.369912 | -0.555703 | 6.196666 |
| C    | -0.6981000| -0.711248 | 4.971474 |
| C    | -0.711962 | 0.323662 | 4.025710 |
| P    | 2.180183 | 0.010193 | 0.028193 |
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| O    | 3.636188 | -0.699462 | 0.359391 |
| N    | 1.742061 | -0.776870 | -1.369113 |
| C    | 4.218823 | -0.504120 | 1.615664 |
| O    | 5.302998 | 0.378092  | 1.712711 |
| C    | 5.960349 | 0.359391 | 2.942289 |
| C    | 5.372830 | -1.249034 | 2.725408 |
| C    | 2.559399 | -2.159777 | 2.626368 |
| C    | 2.582927 | -3.420361 | 3.264089 |
| C    | 1.463417 | -4.262209 | 3.207289 |
| O    | 0.312233 | -3.856051 | 2.509719 |
| C    | 0.288439 | -2.609122 | 1.869564 |
| C    | 1.417151 | -1.776800 | 1.926911 |
| C    | 2.400128 | -1.962243 | -1.996870 |
| C    | 2.394461 | -3.201536 | -1.098751 |
| C    | 3.786685 | -1.623115 | -2.552383 |
| C    | 0.490216 | -0.277714 | 3.949191 |
| C    | 2.588939 | -2.159777 | 2.626368 |
| C    | 2.582927 | -3.420361 | 3.264089 |
| C    | 1.463417 | -4.262209 | 3.207289 |
| C    | 0.312233 | -3.856051 | 2.509719 |
| C    | 0.288439 | -2.609122 | 1.869564 |
| O    | 0.228772 | -0.504125 | 1.834556 |

**SUPPORTING INFORMATION**
### Cis-Pd(F)\(_2\)Cl\(_2\) 

**Conf_100**

| Atoms | Coordinates |
|-------|-------------|
| Pd    | 0.1706690000, 0.7763390000, 2.5827720000 |
| Cl    | -1.4291490000, 0.9724210000, 4.3337700000 |
| Cl    | 1.9335190000, 1.3578830000, 4.0708890000 |
| P     | -1.5420430000, -0.0164690000, 1.3595450000 |
| O     | -0.9384900000, 0.0167870000, 3.2262260000 |
| N     | -2.7431590000, 0.9796720000, 0.1256660000 |
| C     | -2.8005910000, -0.9583960000, 2.6912310000 |
| C     | -2.4274240000, -4.1600260000, -0.6935700000 |
| C     | -1.7417330000, -3.1081070000, 0.0174450000 |
| C     | 0.2070350000, -4.4554370000, 3.0787040000 |
| C     | 0.2390620000, -3.5283290000, 4.0666240000 |
| C     | 1.0836220000, -2.4858530000, 3.7288490000 |
| C     | -1.5401380000, -2.3710740000, -1.9755900000 |
| C     | -2.7579600000, 2.4650900000, 0.7329610000 |
| C     | -2.7763260000, 3.4353520000, 1.7993470000 |
| C     | -2.5832880000, 2.8551010000, -0.7094610000 |
| C     | -3.5372000000, 3.8309360000, -1.0480790000 |
| C     | -3.8201450000, 4.1137160000, -2.3969570000 |
| C     | -3.1426650000, 3.4345720000, -3.4202940000 |
| C     | -2.1745340000, 2.4693700000, -3.0896450000 |
| C     | -1.9058560000, 2.1815130000, -1.7464890000 |
| C     | -4.2199400000, 0.8312470000, 0.9478040000 |
| C     | -4.7961770000, 0.5802410000, 2.3444870000 |
| C     | -4.6744060000, -0.1684370000, -0.1126430000 |
| C     | -4.9398430000, 0.2924450000, -1.4201020000 |
| C     | -5.4404800000, -0.5750600000, -2.4023050000 |
| C     | -5.6796000000, -1.9239100000, -2.0935560000 |
| C     | -5.4083780000, -2.3968650000, -0.7996100000 |
| C     | -4.9104670000, -1.5264950000, 0.1821580000 |
| P     | 1.7386200000, 0.8896080000, 0.9739880000 |
| O     | 0.9851810000, 1.0136280000, -0.5259900000 |
| O     | 2.5893570000, 2.3166010000, 0.9512690000 |
| N     | 2.9256750000, -0.2690580000, 1.0398400000 |
| C     | 1.5356920000, 1.6274760000, -1.6393140000 |
| C     | 1.7668710000, 0.8132900000, -2.7764060000 |
| C     | 2.2301230000, 1.3897760000, -3.9435390000 |
| C     | 2.5375490000, 2.7811070000, -3.9961080000 |
| C     | 2.3140850000, 3.6023540000, -2.8306800000 |
| C     | 1.7298560000, 3.0130730000, -1.6512530000 |
| C     | 1.3322710000, 3.8162860000, -0.4689600000 |
| C     | 0.4133870000, 4.9275870000, -0.5662290000 |
| C     | 0.0743090000, 5.6719570000, 0.6246500000 |
| C     | 0.6302490000, 5.2856640000, 1.8799570000 |
| C     | 1.4562530000, 4.1805490000, 1.9778870000 |
| C     | 1.7822350000, 3.4555370000, 0.8047870000 |
| C     | 4.3842280000, -0.1088870000, 0.7160780000 |
| C     | 5.0905050000, 0.7476210000, 1.7712520000 |
| C     | 4.6994920000, 0.2777950000, -0.7266820000 |
| C     | 4.8540140000, -0.7413000000, -1.6905590000 |
Cis-Pd(A1)(F)Cl₂

Conf_8
|  | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| C | 1.938790  | 5.812108  | -1.443127 |
| C | 2.415704  | 6.708209  | -2.390786 |
| H | 2.584641  | 7.758926  | -2.110359 |
| C | 2.518393  | 4.945990  | -4.060529 |
| C | 2.695635  | 6.278406  | -3.716242 |
| H | 3.065340  | 6.999570  | -4.460771 |
| H | 1.735612  | 6.155640  | -0.419451 |
| H | 2.756153  | 4.592881  | -5.076004 |
| C | -1.041320 | 5.384478  | -0.406686 |
| C | -1.841935 | 6.103967  | 2.196422  |
| C | -2.495818 | 6.638397  | 1.096592  |
| C | -2.097074 | 6.263093  | -0.213692 |
| H | -2.640363 | 6.657693  | -1.084488 |
| H | -0.765548 | 5.082143  | -1.424904 |
| H | -3.333560 | 7.338526  | 1.237365  |
| H | -2.152972 | 6.369250  | 3.218655  |
| H | 1.433389  | -6.001710 | 2.093012  |
| H | 0.749813  | -5.261727 | -0.187834 |
| H | -1.138110 | -5.350886 | -1.647002 |
| H | -1.704958 | -4.637671 | -3.971592 |
SUPPORTING INFORMATION

Cis-Pd(A1')(F)Cl2

Conf_3

Pd  -0.0093600000 0.0771370000 2.7294280000
Cl  -1.5769840000 -0.3463220000 4.4627340000
Cl  1.6953310000 0.4659710000 4.3496340000
P  -1.5791560000 -0.6445300000 1.2888320000
O  -1.7872620000 -1.1092400000 -0.1202590000
O  -2.2421860000 -2.1046870000 1.7127370000
N  -2.8873470000 0.3279820000 0.9746250000
C  -1.2462140000 -2.0454830000 -1.0294720000
C  -1.5496180000 -1.6169440000 -2.3300250000
C  -1.8844830000 -2.5636660000 -3.3083610000
C  -1.9120820000 -3.9305520000 -2.9801170000
C  -1.6030470000 -4.3461960000 -1.6774810000
C  -1.2667570000 -3.4135790000 -0.6718470000
C  -0.8751870000 -3.8428770000 0.6890410000
C  -0.0060520000 -4.9413280000 0.8813280000
C  0.3850440000 -5.3424850000 2.1651270000
C  -0.0871880000 -4.6515990000 3.2944170000
C  -0.9512300000 -3.5558538000 3.1363950000
C  -1.3364350000 -3.1703890000 1.8461860000
C  -4.3127240000 -0.0114150000 0.6919700000
C  -2.5045850000 1.7636640000 0.7632010000
P  1.5127660000 0.7334650000 1.2092610000
O  0.7402250000 1.1543360000 -0.2297650000
O  2.2205630000 2.1985100000 1.5514040000
N  2.7908680000 -0.3025360000 0.9813400000
C  1.1968040000 2.0983050000 -1.1344200000
C  1.4932900000 1.6449470000 -2.4445980000
C  1.8847880000 2.5530760000 -3.4092860000
C  2.0533950000 3.9316020000 -3.0859090000
C  1.7594660000 4.3869730000 -1.7481410000
C  1.2474080000 3.4510870000 -0.7782090000
C  0.7777130000 3.8686030000 0.5657060000
C  -0.2650660000 4.8534460000 0.7503140000
C  -0.6860320000 5.1947030000 2.0890220000
C  -0.0737960000 4.5536530000 3.2051110000
C  0.8881310000 3.5772320000 3.0217740000
C  1.2842400000 3.2368870000 1.7043790000
C  4.2272100000 0.0409310000 0.7438510000
C  4.8748180000 0.6916880000 1.9712080000
C  4.4822260000 0.7631840000 -0.5644100000
C  4.7095410000 0.0376100000 -1.7406220000
C  5.0261960000 0.6755830000 -2.9493420000
C  5.1198170000 2.0758120000 -3.0002170000
C  4.8874580000 2.8292220000 -1.8386730000
C  4.5694420000 2.1887690000 -0.6308920000
C  2.4729290000 -1.7495250000 1.1895980000
C  3.1578160000 -2.3277790000 2.4258300000
C  2.6787610000 -2.5334810000 -0.1045540000
C  3.4771850000 -3.6904930000 -0.1709180000
C  3.6060730000 -4.4025340000 -1.3776200000
C  2.9305330000 -3.9723090000 -2.5299190000
C  2.1279310000 -2.8190640000 -2.4718750000
C  2.0128690000 -2.1068170000 -1.2724400000
H  -1.5009338000 -0.5430000000 -2.5602890000
H  -2.1235270000 -2.2311770000 -4.3294150000
H  0.2231550000 -4.9573610000 4.3045120000
H  -1.3254920000 -2.9790130000 3.9915120000
H  -4.6478230000 0.7946310000 0.0082570000
H  -1.4798020000 1.8629240000 1.1885280000
H  1.4064050000 0.5718930000 -2.6636060000
H  2.1131430000 2.2131080000 -4.4302670000
H  5.2057470000 0.0750590000 -3.8545310000
H  5.3667410000 2.5819090000 -3.9462030000
Pd  2.0836050000  0.0218120000  1.8700350000
Cl  2.6347100000  0.0454580000  4.1887730000
Cl  4.3891260000  -0.0128610000  1.2809760000
P  -0.0435030000  -0.2433190000  2.5420610000
O  -0.9115860000  -0.9040080000  1.2666570000
O  -0.2608740000  -1.4446950000  3.6651770000
N  -0.84793120000  1.0415310000  3.2284680000
C  -2.0761150000  -1.6424620000  1.3959000000
C  -3.2576700000  -1.1283730000  0.8426530000
C  -4.4174350000  -1.9713130000  0.8368290000
C  -4.3863410000  -3.2139750000  1.3786790000
C  -3.1965850000  -3.7206000000  1.9199720000
C  -2.0158840000  -2.9464600000  1.9422420000
C  -0.7339840000  -3.4941630000  2.4402520000
C  -0.3161990000  -4.7995260000  2.0942700000
C  0.9087900000  -5.3124450000  2.5400980000
C  1.7482010000  -4.5286300000  3.3515940000
C  1.3593050000  -3.2308300000  3.7148880000
C  0.1306930000  -2.7317020000  3.2615120000
C  -1.6401010000  0.9277840000  4.4930970000
C  -0.6834460000  2.3054190000  2.4432600000
P  1.6786300000  0.2027030000  -0.3337760000
O  0.1182760000  0.7991050000  -0.5640230000
O  2.5273390000  1.4033220000  -1.1056030000
N  1.9988140000  -1.1614340000  -1.2264300000
C  -0.3003260000  1.5343210000  -1.6607610000
C  -1.3257680000  0.9722330000  -2.4623350000
C  -1.8251540000  1.6901580000  -3.5316490000
C  -1.2792130000  2.9617870000  -3.8742720000
C  -0.2318400000  3.5265760000  -3.0578000000
C  0.2080580000  2.8191900000  -1.8811490000
C  1.1738580000  3.3985680000  -0.9154190000
C  0.9421390000  4.6640530000  -0.2566400000
C  1.9329780000  5.1768620000  0.6607330000
C  3.1112860000  4.4175830000  0.9209590000
C  3.2990560000  3.1788990000  0.3356350000
C  2.3204190000  2.6823660000  -0.5606610000
C  1.8096820000  -2.4532360000  -0.4953540000
C  3.1291310000  -3.1797690000  -0.2500120000
C  0.7122240000  -3.2805840000  -1.1590690000
C  -0.5625490000  -2.7022800000  -1.3277080000
C  -1.6174610000  -3.4289740000  -1.8911310000
C  -1.4102040000  -4.7531450000  -2.3162670000
C  -0.1428880000  -5.3363240000  -2.1652200000
C  0.9108960000  -4.6064270000  -1.5850220000
C  2.5828560000  -1.2556560000  -2.6010690000
C  4.0437030000  -0.7978290000  -2.6424120000
C  1.7048410000  -0.6513610000  -3.6923980000
C  0.7234590000  -1.4593890000  -4.3049650000
C  -0.0542500000  -0.9697270000  -5.3645940000
C  0.1391950000  0.3407220000  -5.8304130000
C  1.1052610000  1.1975591000  -5.2226260000
C  1.8804950000  0.6666950000  -4.1606790000
H  -3.2498620000  -0.1184990000  0.4107660000
H  -5.3465260000  -1.5163080000  0.4051440000
H  2.7152760000  -4.9223660000  3.6972550000
H  1.9947910000  -2.5781590000  4.3304090000
H  -1.8139300000  -0.1641800000  4.6051470000
H  0.1610680000  2.0728330000  1.7540330000
H  -1.7041760000  -0.0281130000  -2.2165450000
H  1.6237530000  1.2653660000  -4.1580500000
H  -2.6090650000  -2.9613060000  -1.9922980000
H  -2.2362430000  -5.3289330000  -2.7609140000
H  0.0317800000  -6.3717620000  -2.4948980000
H  1.8912400000  -5.0888580000  -1.4618290000
H  -0.7176740000  -1.6646140000  -1.0040290000
H  -0.4676900000  0.7299510000  -6.6623440000
Conf_177
SUPPORTING INFORMATION

Conf_281

Pd -1.6224440000 -1.6444780000 1.2106970000
Cl -3.4138530000 -2.4833840000 2.5347970000
Cl -0.783620000 -3.8433880000 0.8846030000
P -2.7081840000 0.3292770000 1.310940000

WILEY-VCH
SUPPORTING INFORMATION

H -1.7026970000 -2.7591680000 -1.9148150000
H -0.9062160000 -2.5209210000 -3.5067630000
H -2.4787890000 -1.7290180000 -3.1721850000
H -1.5175570000 -0.3810850000 -1.3697690000
H 1.8423640000 -3.5396950000 -0.9509390000
H 2.3563330000 -3.6881350000 -2.6684020000
H 0.6174430000 -3.7049730000 -2.2347290000
H 1.2583520000 -1.5298280000 -3.2183350000
C 5.5088300000 0.6724490000 1.6934400000
C 6.7280270000 1.2989560000 1.4772380000
H 7.6575540000 0.8122220000 1.8098930000
C 5.6203390000 3.1527550000 0.3644090000
H 6.7871590000 2.5559830000 0.8196190000
H 7.7593560000 3.0472730000 0.6601980000
C 5.4774380000 -0.3085250000 2.1874430000
H 5.6523610000 4.1162370000 -0.1667860000
C 3.8664860000 0.7496940000 4.3384950000
C 3.4976270000 -1.4772770000 6.0185740000
C 4.0881370000 -0.3260990000 6.5184580000
C 4.2612370000 0.7994230000 5.6687100000
H 4.7018040000 1.7247680000 6.0700550000
H 3.9883660000 1.6393640000 3.7078360000
H 4.4080970000 -0.2763330000 7.5699010000
C 3.3327560000 -2.3515710000 6.6675860000
H 0.1251460000 6.2589170000 1.9894440000
H 0.1156050000 4.4076480000 3.6453960000
H 1.2279480000 2.5345680000 4.0435340000
H 1.4560000000 0.8029520000 5.8046960000
C -4.4920700000 2.7387590000 0.8907420000
C -4.5002230000 3.4674150000 2.0141620000
C -5.0896780000 3.4230260000 -0.3340120000
C -4.1991880000 4.8345460000 1.9121350000
H -4.3870860000 2.9637290000 2.9838380000
C -4.7894090000 4.7893020000 -0.4395920000
H -5.4594640000 2.8769020000 -1.2151820000
C -4.3400710000 5.5004720000 0.6854800000
H -3.8444070000 5.3793570000 2.7999640000
H -4.9160290000 5.3029420000 -1.4053640000
H -4.0984000000 6.5713060000 0.6046210000
C -6.0146160000 0.8936150000 2.3003400000
H -6.3781300000 -0.1500470000 2.2740880000
H -6.8779410000 1.5643370000 2.4776850000
H -5.3159170000 0.9867790000 3.1522520000
C -5.7059810000 -1.6264600000 0.0277340000
H -5.5526470000 -1.9989330000 1.0561980000
H -5.7656340000 -2.5062700000 -0.6398410000
H -6.6999570000 -1.0838950000 -0.0040782000
C -4.5947020000 -0.1758010000 -1.7870660000
C -3.7971960000 0.9271530000 -2.1564100000
C -5.3889150000 -0.7835350000 -2.7826810000
C -3.7763820000 1.3993740000 -3.4770160000
H -3.1849000000 1.4258290000 -1.3940640000
C -5.3727210000 -0.3105630000 -4.1056550000
H -6.0246230000 -1.6455140000 -2.5357370000
C -4.5644400000 0.7813730000 -4.4601090000
H -3.1282820000 2.2502960000 -3.7373870000
H -5.9985510000 -0.8041510000 -4.8650690000
H -4.5483630000 1.1481590000 -5.4976950000

Conf_87

Pd -0.1143890000 -1.3534770000 2.5886260000
Cl -1.3536240000 -1.9142820000 4.5449200000
Cl 1.6052360000 -2.8717480000 3.2038560000
P -1.9549460000 -0.1759070000 1.9987910000
O -1.8916750000 0.3424500000 0.2575450000
O -3.3076790000 -1.1475090000 2.0038760000
N -2.5077730000 1.1347500000 2.8813130000
SUPPORTING INFORMATION

H -0.5174530000 -2.5437520000 0.2101220000
H 4.1952130000 -2.2137310000 0.4774540000
H 4.5838980000 -3.3074920000 -0.8942670000
H 3.3708600000 -3.7890140000 0.3440270000
H 2.2981280000 -3.1147410000 -1.7816800000
C 4.5418720000 3.7869410000 0.1602610000
C 5.2993120000 4.7027580000 -0.5582490000
H 6.2026110000 5.1370400000 -0.1041370000
C 3.8064590000 4.4996720000 -2.4632120000
C 4.9238570000 5.0759270000 -1.8766310000
H 5.5285760000 5.8075820000 -2.4337900000
H 4.8518150000 3.5008400000 1.1744330000
H 3.5176080000 4.7580080000 -3.4935340000
C 2.4140680000 4.2918670000 2.4774920000
C 3.0956700000 3.6157950000 5.1252430000
C 2.7353220000 4.9182020000 4.8125130000
C 2.3745130000 5.2718620000 3.2393540000
H 2.1051230000 4.5569850000 1.4584050000
H 2.7099840000 5.6897590000 5.5971320000
H 3.3541330000 3.3373440000 6.1587120000
H -3.2779390000 -5.5365270000 -0.9448120000
H -3.6548940000 -3.3221390000 -2.0276390000
H -5.2928970000 -1.6139000000 -2.1640000000
H -5.5786670000 0.5416440000 -3.3883320000
C -4.6830100000 2.0398470000 1.8793460000
C -4.4375780000 3.3896210000 1.5528350000
C -5.6655640000 1.3393680000 1.1496680000
C -5.1513810000 4.0167860000 0.5201640000
H -3.6809600000 3.9616990000 2.1065020000
C -6.3882260000 1.9669820000 0.1235340000
H -5.8644760000 0.2841390000 1.3926830000
C -6.1322790000 3.3096770000 -0.1953100000
H -4.9403700000 5.0695200000 0.2759150000
H -7.1464860000 1.3991490000 -0.4361940000
H -6.6906700000 3.8032870000 -1.0055568000
C -4.3465130000 1.9930080000 4.3836170000
C -3.8680620000 1.4603920000 5.2292820000
H -5.4447000000 1.9296630000 4.5129170000
H -4.0736690000 3.0659390000 4.4278000000
C -0.2574710000 1.5486340000 4.0218790000
H 0.2503120000 2.3376110000 4.6097680000
H 0.4359700000 1.2697360000 3.2045610000
H -0.4314300000 0.6683220000 4.6696070000
C -1.3052960000 3.3529790000 2.6359540000
C -1.4015530000 4.6379340000 3.2038070000
C -0.9021730000 3.2347500000 1.2934590000
C -1.1245950000 5.7831160000 2.4392900000
H -1.7089310000 4.7437620000 4.2567720000
C -0.6242000000 4.3757250000 0.5258470000
H -0.8094840000 2.2399050000 0.8396660000
C -0.7410180000 5.6556400000 1.0943100000
H -1.2122490000 6.7805680000 2.8970490000
H -0.3036030000 4.2611230000 -0.5213510000
H -0.5250700000 6.5515580000 0.4925950000

Conf_121

Pd 0.8694290000 -0.5192990000 1.7752160000
Cl 0.7601700000 -1.1016100000 4.0643180000
Cl 3.0982730000 -1.3394810000 1.6521160000
P -1.3009360000 0.0391750000 1.9672910000
O -1.9436940000 -0.0085430000 0.4185940000
O -2.2882210000 -1.0535470000 2.7091600000
N -1.6671010000 1.4508440000 2.7674580000
C -3.2768390000 -0.1908520000 0.0984240000
C -3.9349260000 0.8341630000 -0.5966630000
C -5.2454360000 0.6318910000 -1.0499750000
H 0.1410120000 -0.2775330000 -3.9097540000
H 2.2462980000 0.3552970000 -2.7639710000
C 2.5811330000 5.1789900000 -2.6325060000
C 2.8009240000 6.0388570000 -3.7002100000
H 0.9299820000 5.0745400000 -4.9150850000
C 1.9634980000 5.9971690000 -1.7549270000
H 0.2873560000 5.0177640000 -5.8078820000
C 1.2633290000 5.7231900000 0.2489730000
C 2.7297540000 5.6623140000 2.6545490000
C 2.8009240000 6.0388570000 -3.7002100000
H 0.8577180000 1.2178510000 5.3560530000
H 2.4570360000 4.0045790000 1.8432220000
C -0.0351140000 3.5677210000 5.1360840000
H -1.4347730000 5.1064400000 3.4842900000
C 1.0066770000 4.5259030000 5.8141160000
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C -4.1753340000 1.7214710000 2.7855630000
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C -2.9198830000 0.7958240000 4.8339020000
C -1.7736860000 0.6860370000 5.6458680000
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Conf_120

Pd 0.7346980000 -0.6853010000 1.7070760000
Cl 0.4947110000 -1.4065150000 3.9541070000
Cl 2.9769010000 -1.4747000000 1.6986900000
P -1.4551780000 -0.1677710000 1.7800810000
O -2.0152400000 -0.1449790000 0.2002770000
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231
| X | Y | Z |
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| 2.2839450000 | 6.0739930000 | -4.5797760000 |
| 2.5302590000 | 6.7886900000 | -5.3796080000 |
| 3.2999370000 | 5.2139960000 | -1.4110380000 |
| 0.7085660000 | 5.1058100000 | -5.7081090000 |
| 1.1521900000 | 5.6609250000 | 0.4242330000 |
| 2.3320770000 | 5.5110310000 | 2.9788770000 |
| 1.6518900000 | 6.6548700000 | 2.5961980000 |
| 1.0504190000 | 6.7246440000 | 1.3115250000 |
| 0.7085660000 | 5.1058100000 | -5.7081090000 |
| 1.5562960000 | 7.6251560000 | 1.0181240000 |
| 0.6671300000 | 5.7243280000 | -0.5590170000 |
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| 1.5837630000 | 0.5936070000 | -1.5789320000 |
| 0.2222200000 | 0.5393790000 | -0.4762370000 |
| 0.3567390000 | 1.2027260000 | 4.1785000000 |
| 0.5218060000 | 4.9218590000 | 5.2139120000 |
| 1.4411250000 | 4.9758950000 | 3.2539860000 |
| 0.1777130000 | 4.1550430000 | 6.5966770000 |
| -0.7733830000 | 5.9713660000 | 5.4301780000 |
| 0.4728800000 | 4.5956950000 | 7.1208140000 |
| -1.5837630000 | 3.2937000000 | 1.3189700000 |
| -1.7408630000 | 2.7345080000 | 0.3793600000 |
| -0.8885520000 | 4.1295650000 | 1.1103950000 |
| -2.5523230000 | 3.7264140000 | 1.6421830000 |
| -4.6714770000 | 0.8156320000 | 2.9160550000 |
| -5.2655790000 | 1.2286070000 | 3.4899420000 |
| -4.3941800000 | -0.2791860000 | 3.0673090000 |
| -5.8320800000 | 1.0264400000 | 1.8424060000 |
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| -2.4199490000 | 0.0476260000 | 5.4102620000 |
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| -2.2244000000 | -0.1248460000 | 6.7886070000 |
| -2.1435790000 | -0.7588590000 | 4.7175960000 |
| -3.0347670000 | 2.1281750000 | 7.1921880000 |
| -3.5960360000 | 3.2620740000 | 5.4250760000 |
| -2.5279700000 | 0.9142670000 | 7.6847370000 |
| -1.8171220000 | -1.0768100000 | 7.1637030000 |
| -3.2679130000 | 2.9305400000 | 7.8830460000 |
| -2.3622860000 | 0.7805240000 | 8.7653710000 |
SUPPORTING INFORMATION

C 1.8041490000 -2.5037420000 -0.5494520000
H -1.7901900000 -0.7085300000 -2.5360550000
H -2.4284240000 -2.7132660000 -3.9122430000
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H 1.9739770000 0.8227920000 -4.9735970000
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