Supplementary Information

Configurational landscapes of chiral iron (II) bis(phosphane) complexes

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TABLE OF CONTENTS

I. Experimental details

Table S1. Details of the reactions done with [FeH(η^2-H_2){(*R,R*)-Me-DUPHOS}$_2$](BF_4) and [FeH(η^2-H_2){(*S,S*)-Me-DUPHOS}$_2$](BF_4) complexes.

II. Tables and figures

Table S2. Simulated ^{1}H and ^{31}P{^{1}H} chemical shifts (ppm) and coupling constants (Hz) for the new species derivatized from [FeH(η^2-H_2){(*R,R*)-Me-DuPhos}$_2$]$^+$.

Figure S1. Simulated (bottom) and experimental (top) ^{1}H NMR spectra (hydride region) of the **[FeH(THF-d_8){(*R,R*)-Me-DuPhos}$_2$]$^+$** compound.

Figure S2. ^{31}P{^{1}H} NMR spectra of the *cis* (*) and *trans* (+) isomers of **[FeHL{(*R,R*)-Me-DuPhos}$_2$]$^+$** (L = Et_2O (top), THF (bottom)).

Figure S3. ^{31}P{^{1}H} NMR spectra of the product obtained from [Fe(H_2O)$_6$](BF_4)$_2$, (*R,R*)-Me-DuPhos and TBAI mixture and registered from -93 to 25 °C in THF-d_8.

Figure S4. ^{31}P{^{1}H} NMR spectrum acquired after addition of KI in a THF-d_8 solution of [FeH(η^2-H_2){(*R,R*)-Me-DuPhos}$_2$](BF_4). The *, ♦, +, and # notations correspond to the characteristic signals of [FeH(η^2-H_2){(*R,R*)-Me-DuPhos}$_2$]$^+$, [FeH(THF-d_8){(*R,R*)-Me-DuPhos}$_2$]$^+$, *trans*-**[FeHI{(*R,R*)-Me-DuPhos}$_2$]** and *cis*-**[FeHI{(*R,R*)-Me-DuPhos}$_2$]** compounds, respectively.

Figure S5. ^{1}H NMR spectra (hydride region) of *trans*-**[FeHCl{(*R,R*)-Me-DuPhos}$_2$]** registered in CD_2Cl_2 (^{1}H{^{31}P} spectrum (top), ^{1}H spectrum (bottom)).

Figure S6. ^{31}P{^{1}H} NMR spectra evolution with time after addition of TBACl in a CD_2Cl_2 solution of [FeH(η^2-H_2){(*R,R*)-Me-DuPhos}$_2$](BF_4).

Table S3. Selected bond distances and angles for compound *trans*-**[FeCl$_2$){(*R,R*)-Me-DuPhos}$_2$]** and comparison with other structurally similar compounds.

Figure S7. X-ray crystal structure of *trans*-**[FeCl$_2$){(*R,R*)-Me-DuPhos}$_2$]**. The hydrogen atoms are omitted for clarity.

Figure S8. X-ray crystal structure of Δ-**[FeI{(*S,S*)-Me-DuPhos}$_2$]$^+$**. The hydrogen atoms are omitted for clarity.

Figure S9. X-ray crystal structure of Λ-**[FeI{(*R,R*)-Me-DuPhos}$_2$]$^+$**. The hydrogen atoms are omitted for clarity.

Figure S10. X-ray crystal structure of **[FeCl{(*R,R*)-Me-DuPhos}$_2$]$^+$.** The hydrogen atoms are omitted for clarity.

Table S4. Selected bond distances and angles for compound **Δ-[FeI{(*S,S*)-Me-DuPhos}$_2$]**(ClO_4), **Λ-[FeI{(*R,R*)-Me-DuPhos}$_2$]**I·H_2O, and [FeI($opdp$)$_2$]I·2CH_2Cl_2 compounds.

Figure S11. Representations of the calculated structures of Λ (left) and Δ (right) isomers of **[FeI{(*R,R*)-Me-DuPhos}$_2$]$^+$**, a) front view, b) lateral view. The hydrogen atoms are omitted for clarity.

Table S5. Main bond distances and angles for Λ- and Δ-**[FeI{(*R,R*)-Me-DuPhos}$_2$]$^+$** isomers, τ parameter, and relative Gibbs free energy for computed geometries.

Figure S12. ^{31}P{^{1}H} NMR spectrum registered after dissolution of crystals of Λ-**[FeI{(*R,R*)-Me-DuPhos}$_2$]**I·H_2O in $(CD_3)_2CO$.

Figure S13. ^{31}P{^{1}H} (top) and ^{35}Cl (bottom) NMR spectra registered after dissolution of crystals of **[FeCl{(*R,R*)-Me-DuPhos}$_2$]**(BF_4) in CD_2Cl_2 and CD_3CN, respectively.

III. Structural description

Details of the structure refinement and X-ray structure determination.

Table S6. Crystal data and structure refinement for Δ-**[FeI{(*S,S*)-Me-DuPhos}$_2$]**(ClO_4) and Λ-**[FeI{(*R,R*)-Me-DuPhos}$_2$]**I·H_2O.

Table S7. Crystal data and structure refinement for **[FeCl{(*R,R*)-Me-DuPhos}$_2$]**(BF_4) and *trans*-**[FeCl$_2$){(*R,R*)-Me-DuPhos}$_2$]**.

IV. Computational data

Optimized Gibbs free energies (in a.u.) and Cartesian atomic coordinates (in Å) of the structures described in Table S5.

V. References

I. Experimental details

Table S1. Details of the reactions done with [FeH(η^2-H_2){(*R*,*R*)-Me-DUPHOS}$_2$](BF_4) and [FeH(η^2-H_2){(*S*,*S*)-Me-DUPHOS}$_2$](BF_4) complexes.

Precursor(s) [a]	Reactor type	Solvent	Temp	Reaction time	Solution color	Solid formed and X-ray identification
[FeH(η^2-H_2){(*R*,*R*)-Me-DuPhos}$_2$](BF_4) (5 mg)	NMR tube	THF-d_8 (750 μL)	Room	Few minutes	Yellow	
[FeH(η^2-H_2){(*R*,*R*)-Me-DuPhos}$_2$](BF_4) (5 mg)	NMR tube	THF-d_8 (750 μL)	Room	Few days	Orange	Orange-red crystals of Λ-**[FeI{(*R*,*R*)-Me-DuPhos}$_2$]**I·H_2O
[FeH(η^2-H_2){(*S*,*S*)-Me-DuPhos}$_2$](BF_4) (5 mg), $KClO_4$ (5 mg); mol ratio 1/5 (Fe/KClO4)	NMR tube	THF-d_8 (750 μL)	Room	Few days	Orange	Orange-red crystals of} Δ-**[FeI{(*S*,*S*)-Me-DuPhos}$_2$]**(ClO_4)
[FeH(η^2-H_2){(*R*,*R*)-Me-DuPhos}$_2$](BF_4) (5 mg), THF-d_8 (50 μL)	NMR tube	CD_2Cl_2 (0.8 mL)	Room	Up to 8 days	Orange	Orange-red crystals
[FeH(η^2-H_2){(*R*,*R*)-Me-DuPhos}$_2$](BF_4) (5 mg), Et_2O (50 μL)	NMR tube	CD_2Cl_2 (0.8 mL)	40 ºC	Up to 30 days	Orange	Orange-red crystals
[FeH(η^2-H_2){(*R*,*R*)-Me-DuPhos}$_2$](BF_4) (5 mg)	NMR tube	$(CD_3)_2CO$ (750 μL)	Room	Few days	Yellow	
[FeH(η^2-H_2){(*R*,*R*)-Me-DuPhos}$_2$](BF_4) (5 mg), KI (8 mg); mol ratio 1/7 (Fe/KI)	NMR tube	THF-d_8 (750 μL)	Room	Up to 7 days	Orange	Orange-red crystals of Λ-**[FeI{(*R*,*R*)-Me-DuPhos}$_2$]**I·H_2O
[Fe(H_2O)$_6$](BF_4)$_2$ (7 mg), (*R*,*R*)-Me-DuPhos (12.5 mg), TBAI (37.5 mg); mol ratio 1/2/5 (Fe/DuPhos/TBAI)	NMR tube	THF-d_8 (750 μL)	50 ºC	1 month	Dark red	
[FeH(η^2-H_2){(*R*,*R*)-Me-DuPhos}$_2$](BF_4) (20 mg), TBAI (49 mg); mol ratio 1/5 (Fe/TBAI)	Schlenk	CH_2Cl_2 (3 mL)	Room	4h	Orange	Orange-red
[FeH(η^2-H_2){(*R*,*R*)-Me-DuPhos}$_2$](BF_4) (5 mg), TBACl (8 mg); mol ratio 1/5 (Fe/TBACl)	NMR tube	CD_2Cl_2 (750 μL)	Room	Up to 5-7 h	Orange	Red crystals of **[FeCl{(*R*,*R*)-Me-DuPhos}$_2$]**(BF_4)
[FeH(η^2-H_2){(*R*,*R*)-Me-DuPhos}$_2$](BF_4) (14 mg), TBACl (24 mg); mol ratio 1/5 (Fe/TBACl)	Schlenk	CH_2Cl_2 (3 mL)	Room	4h	Orange	Red crystals
[FeH(η^2-H_2){(*R*,*R*)-Me-DuPhos}$_2$](BF_4) (5 mg)	Fisher-Porter tube	CH_2Cl_2 (3 mL)	Room	Few days	Yellow	Crystals of *trans*-**[FeCl$_2${(*R*,*R*)-Me-DuPhos}$_2$]**

[a] Reactions done under Ar or N_2, indistinctly.

II. Tables and figures

Table S2. Simulated ^{1}H and $^{31}P\{^{1}H\}$ chemical shifts (ppm) and coupling constants (Hz) for the new species derivatized from $[FeH(\eta^2\text{-}H_2)\{(R,R)\text{-Me-DuPhos}\}_2]^+$.

		Chemical shift (ppm)								
Compound	Stereoisomer	δH	δP_a	δP_b	δP_c	δP_d	$^2J_{HPa}$	$^2J_{HPb}$	$^2J_{HPc}$	$^2J_{HPd}$
$[FeH(THF\text{-}d_8)\{(R,R)\text{-Me-DuPhos}\}_2]^+$	*cis* [a]	-10.3	93.66	110.62	115.31	115.96	36.2	52.3	64.5	62.0
$[FeH(THF\text{-}d_8)\{(R,R)\text{-Me-DuPhos}\}_2]^+$	*trans* [b]		96.0	104.0						
$[FeH(THF\text{-}d_8)\{(R,R)\text{-Me-DuPhos}\}_2]^+$	*cis* [b]	-11.6	89.39	98.70	102.62	110.10	26.9	45.9	58.6	58.6
$[FeHCl\{(R,R)\text{-Me-DuPhos}\}_2]$	*cis* [c]	-9.0	100.56	103.12	122.01	128.70	71.6	63.1	60.1	46.6
$[FeHCl\{(R,R)\text{-Me-DuPhos}\}_2]$	*trans* [c]	-14.8	120.81	124.34						
$[FeHI\{(R,R)\text{-Me-DuPhos}_2]$	*cis* [c]	-10.2	101.08	103.44	122.34	143.60	36.4	52.4	61.2	63.3
$[FeHI\{(R,R)\text{-Me-DuPhos}\}_2]$	*trans* [c]	-14.7	120.46	124.26						

[a] Spectra registered in $THF\text{-}d_8$; [b] in CD_2Cl_2 with *ca.* 6% of THF; [c] in CD_2Cl_2.

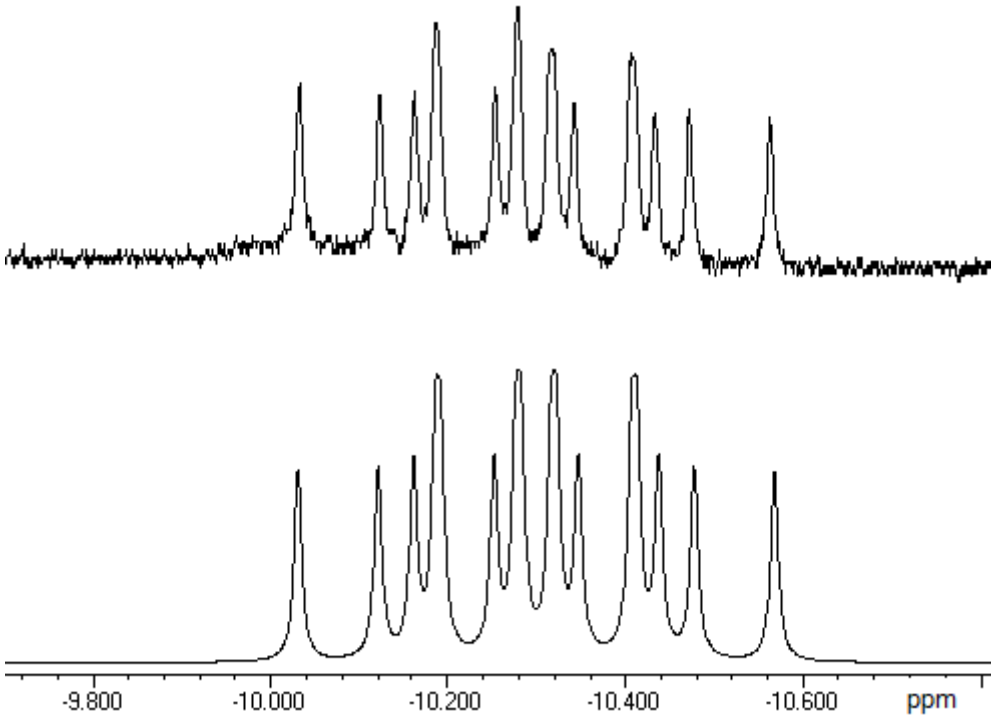

Figure S1. Simulated (bottom) and experimental (top) ^{1}H NMR spectra (hydride region) of the **[FeH(THF-d_8){(*R,R*)-Me-DuPhos}$_2$]$^+$** compound.

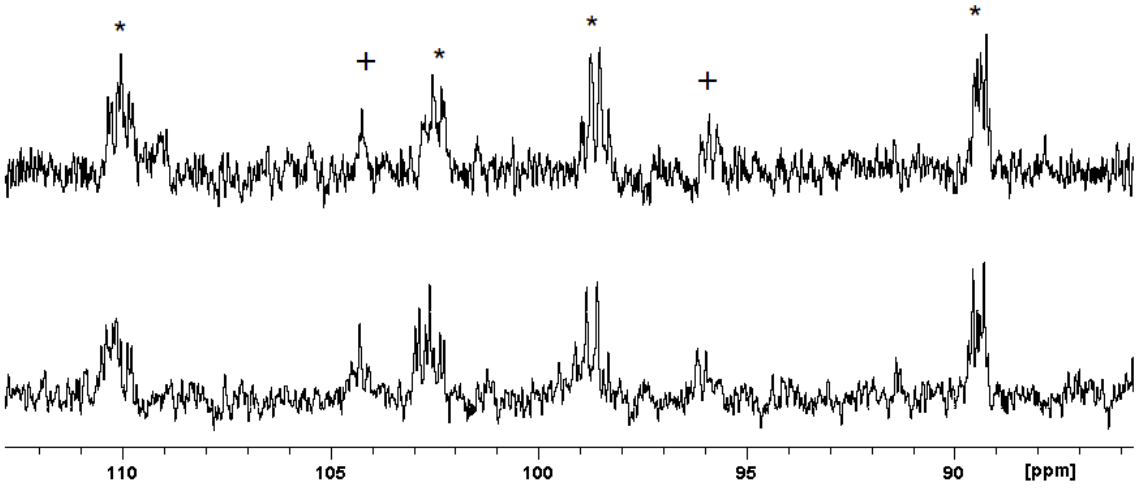

Figure S2. $^{31}P\{^{1}H\}$ NMR spectra of the *cis* (*) and *trans* (+) isomers of **[FeHL{(*R,R*)-Me-DuPhos}$_2$]$^+$** (L = Et_2O (top), THF (bottom)).

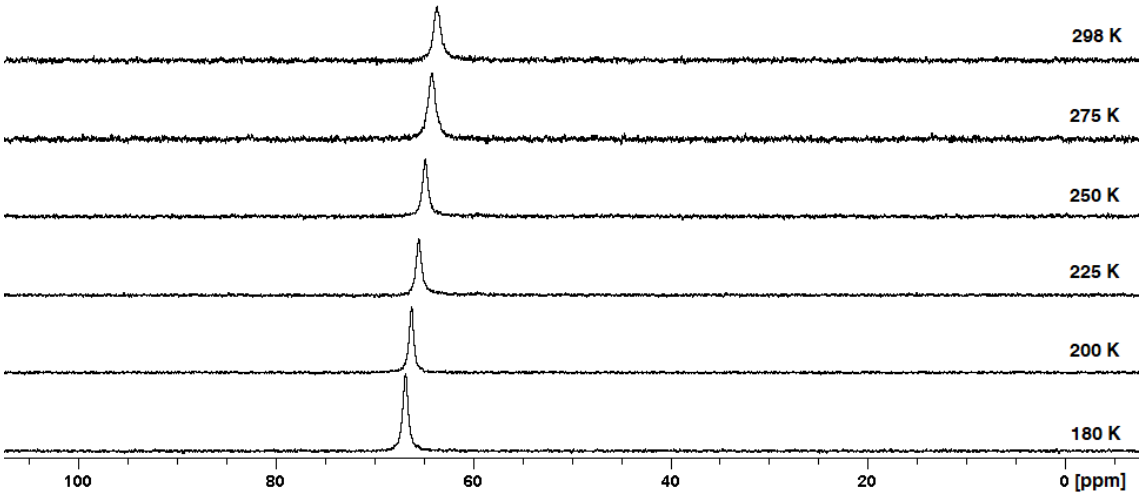

Figure S3. $^{31}P\{^{1}H\}$ NMR spectra of the product obtained from $[Fe(H_2O)_6](BF_4)_2$, (*R*,*R*)-Me-DuPhos and TBAI mixture and registered from -93 to 25 °C in THF-d_8.

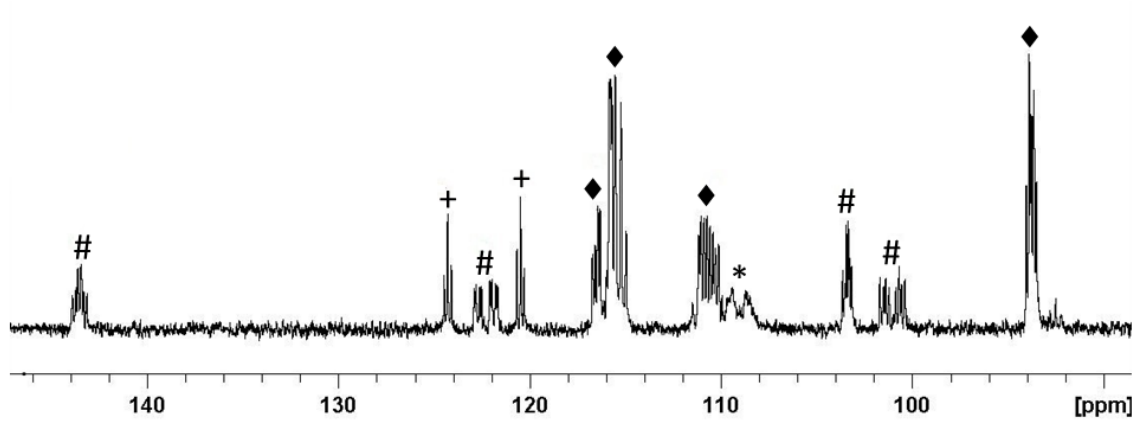

Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum acquired after addition of KI in a THF-d_8 solution of $[FeH(\eta^2\text{-}H_2)\{(R,R)\text{-Me-DuPhos}\}_2](BF_4)$. The *, ♦, +, and # notations correspond to the characteristic signals of $[FeH(\eta^2\text{-}H_2)\{(R,R)\text{-Me-DuPhos}\}_2]^+$, $[FeH(THF\text{-}d_8)\{(R,R)\text{-Me-DuPhos}\}_2]^+$, *trans*-**[FeHI{(*R*,*R*)-Me-DuPhos}$_2$]** and *cis*-**[FeHI{(*R*,*R*)-Me-DuPhos}$_2$]** compounds, respectively.

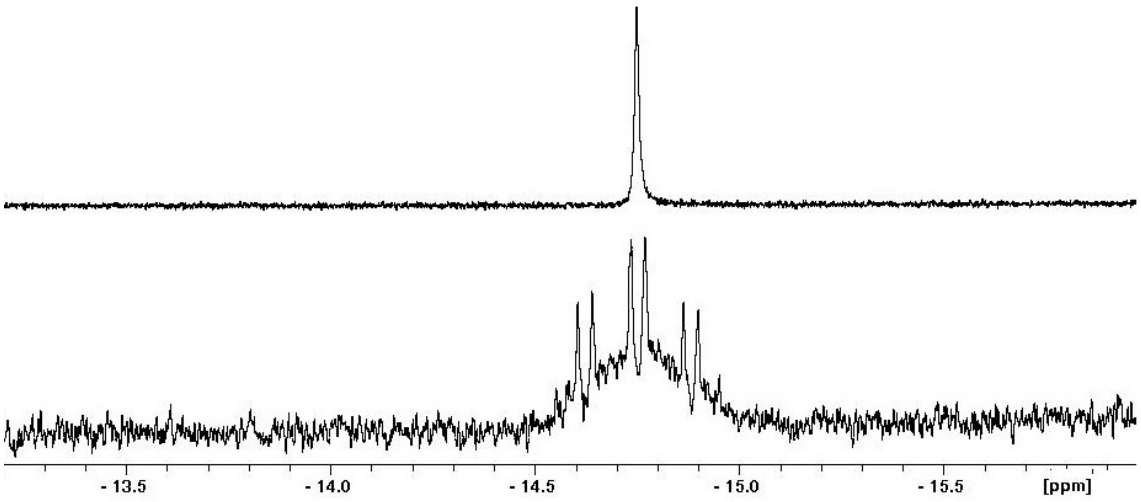

Figure S5. ^{1}H NMR spectra (hydride region) of *trans*-**[FeHCl{(*R*,*R*)-Me-DuPhos}$_2$]** registered in CD_2Cl_2 ($^{1}H\{^{31}P\}$ spectrum (top), ^{1}H spectrum (bottom)).

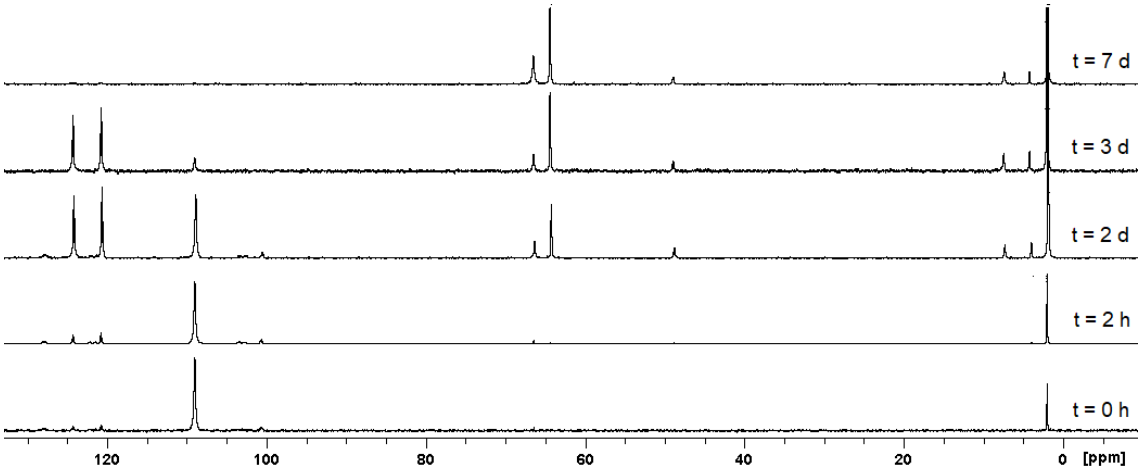

Figure S6. $^{31}P\{^{1}H\}$ NMR spectra evolution with time after addition of TBACl in a CD_2Cl_2 solution of [FeH(η^2-H_2){(*R*,*R*)-Me-DuPhos}$_2$](BF$_4$).

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Table S3. Selected bond distances and angles for compound *trans*-**[FeCl$_2${(*R*,*R*)-Me-DuPhos}$_2$]** and comparison with other structurally similar compounds.

Distances (Å) [a,b]	*trans*-**[FeCl$_2${(*R*,*R*)-Me-DuPhos}$_2$]**	*trans*-**[FeCl$_2$(opdp)$_2$]·THF** [1]	*trans*-[**FeCl$_2$(o-C$_6$H$_4$P(H^{i}Pr$_2$)$_2$]** [c,2]		*trans*-**[FeCl$_2$(dppen)$_2$]** [3]
			A	B	
Fe-P(1)	2.6055(7)	2.612(4)	2.232(2)	2.234(2)	2.675(1)
Fe-P(2)	2.5836(7)	2.623(5)	2.237(2)	2.227(2)	2.532(1)
Fe-Cl	2.3763(6)	2.347(4)	2.333(2)	2.329(2)	2.347(1)
Angles (°) [a]					
P(1)-Fe-P(2)’	174.56(2)	180.00	180.00	180.00	180.00
P(2)-Fe-P(1)’	174.56(2)	180.00	180.00	180.00(8)	180.00
P(1)-Fe-P(2)	77.99(2)	74.38(13)	84.16(7)	84.22(7)	77.96(1)
P(1)’-Fe-P(2)’	77.99(2)	74.38(13)	84.16(7)	84.22(7)	77.96(1)
P(1)-Fe-P(1)’	97.44(3)	105.62(13)	95.84(7)	95.78(7)	102.04(1)
P(2)-Fe-P(2)’	106.73(3)	105.62(13)	95.84(7)	95.78(7)	102.04(1)

[a] Standard deviations of the measurement are given in parenthesis. [b] The remaining phosphorous (P(1)’ and P(2)’) and chlorine (Cl’) atoms are symmetry-related. For all the compounds, the Fe-P(1) bond is *trans* to the Fe-P(2)’ bond, and the Fe-P(2) bond is *trans* to the Fe-P(1)’ bond. [c] A and B refers to each independent molecule in the unit cell.

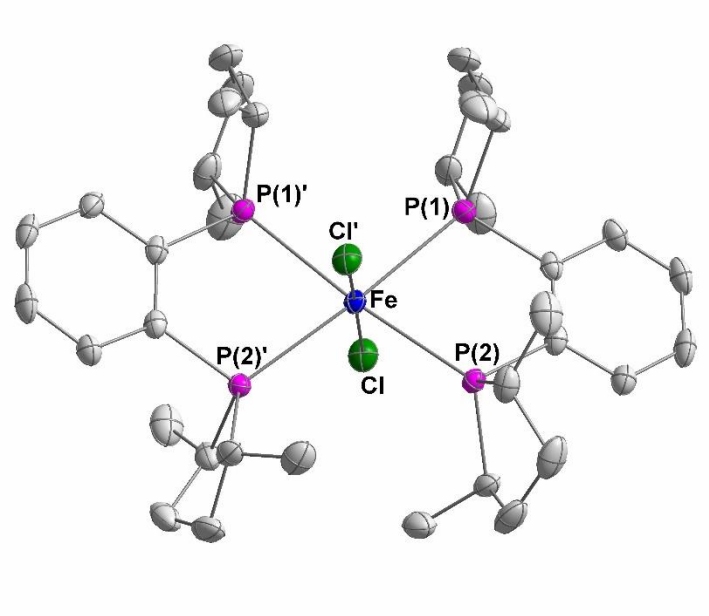


Figure S7. X-ray crystal structure of *trans*-**[FeCl$_2${(*R*,*R*)-Me-DuPhos}$_2$]**. The hydrogen atoms are omitted for clarity.

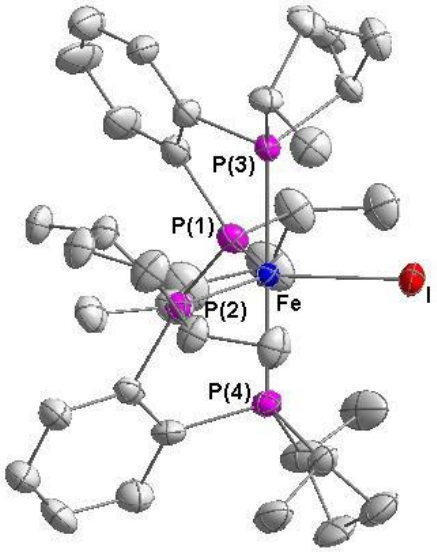


Figure S8. X-ray crystal structure of Δ-**[FeI{(*S*,*S*)-Me-DuPhos}$_2$]$^+$**. The hydrogen atoms are omitted for clarity.

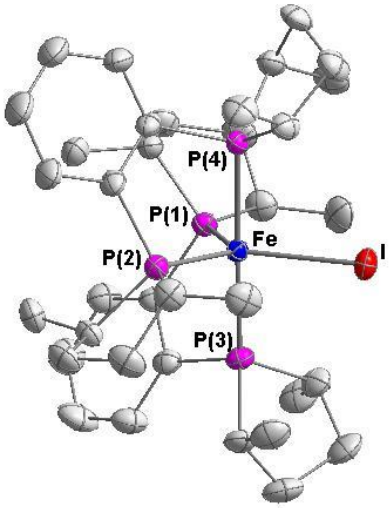


Figure S9. X-ray crystal structure of Λ-**[FeI{(*R*,*R*)-Me-DuPhos}$_2$]$^+$**. The hydrogen atoms are omitted for clarity.

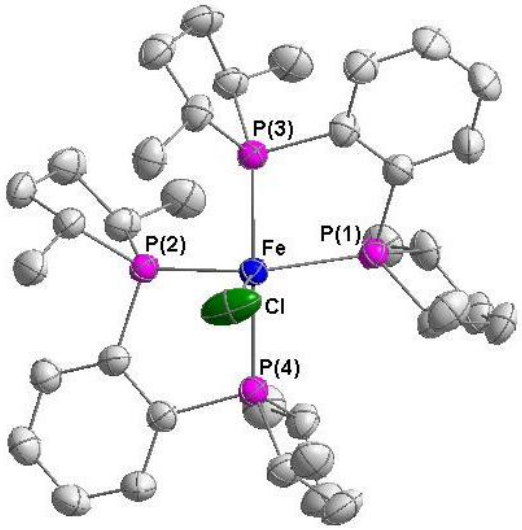


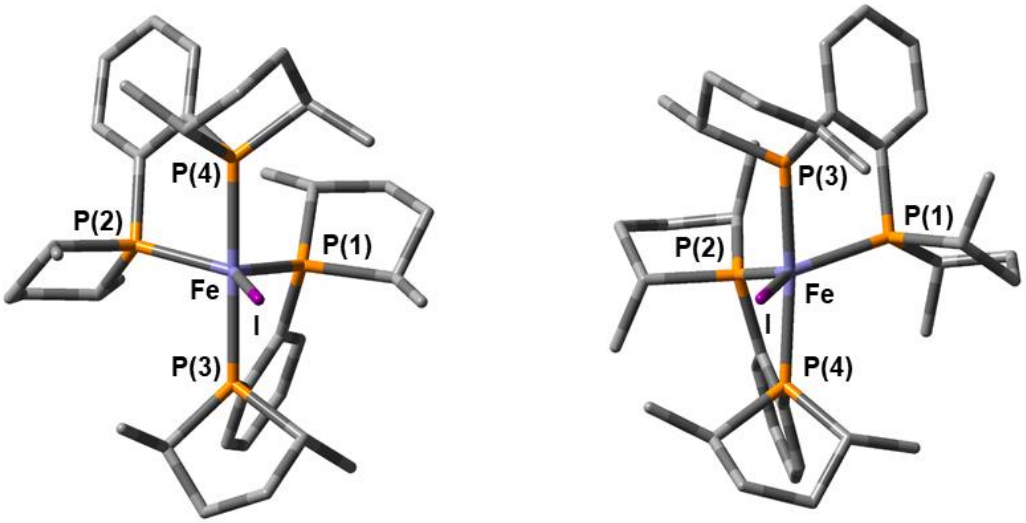
Figure S10. X-ray crystal structure of **[FeCl{(*R*,*R*)-Me-DuPhos}$_2$]$^+$.** The hydrogen atoms are omitted for clarity.

Table S4. Selected bond distances and angles for compound **Δ-[FeI{(*S*,*S*)-Me-DuPhos}$_2$]**(ClO_4), **Λ-[FeI{(*R*,*R*)-Me-DuPhos}$_2$]**I·H_2O, and [FeI(opdp)$_2$]I·2CH_2Cl_2 compounds.

Distances (Å) [a]	**Δ-[FeI{(*S*,*S*)-Me-DuPhos}$_2$]$^+$** [b]		**Λ-[FeI{(*R*,*R*)-Me-DuPhos}$_2$]$^+$** [b]		**[FeI(opdp)$_2$]$^+$** [b],1	
	A	B	A	B	A	B
Fe-P(1)	2.3013(15)	2.2964(15)	2.2909(14)	2.2883(13)	2.378(7)	2.356(5)
Fe-P(2) [c]	2.2892(15)	2.2821(15)	2.2810(14)	2.2859(14)	2.378(7) [d]	2.356(5) [d]
Fe-P(3)	2.2692(14)	2.2694(14)	2.2673(14)	2.2619(14)	2.324(5)	2.315(5)
Fe-P(4)	2.2714(15)	2.2641(15)	2.2648(14)	2.2688(14)	2.324(5) [d]	2.315(5) [d]
Fe-X (X = I, Br)	2.5915(8)	2.5924(7)	2.5760(6)	2.5872(7)	2.646(5)	2.633(5)
Angles (°) [a]						
P(1)-Fe-P(2)	121.71(6)	122.06(6)	120.69(5)	120.76(5)	164.4(2)	167.7(2)
P(3)-Fe-P(4)	179.10(6)	178.85(6)	178.83(5)	178.42(6)	174.5(2)	173.7(2)
P(1)-Fe-P(3)	81.46(5)	81.01(5)	81.39(5)	81.11(5)	80.2(2)	80.6(2)
P(2)-Fe-P(4)	81.39(5)	81.21(5)	81.53(5)	81.61(5)	80.2(2) [d]	80.6(2) [d]
P(1)-Fe-P(4)	97.90(5)	97.94(5)	98.19(5)	99.05(5)	99.0(2)	98.7(2)
P(3)-Fe-P(2)	99.48(6)	99.74(6)	99.63(5)	99.68(5)	99.0(2) [d]	98.7(2) [d]
P(1)-Fe-I	121.62(5)	121.90(5)	121.34(4)	121.33(4)	97.8(1)	93.2(2)
P(2)-Fe-I	116.67(5)	116.04(5)	117.97(4)	117.91(4)	97.8(1) [d]	93.2(2) [d]
P(3)-Fe-I	89.89(4)	89.65(4)	89.19(4)	88.83(4)	92.8(2)	96.2(1)
P(4)-Fe-I	89.92(5)	90.51(4)	90.11(4)		92.8(2) [d]	96.2(1) [d]

[a] Standard deviations of the measurement are given in parenthesis. [b] A and B refers to each independent molecule in the unit cell. [c] For all the compounds, P(2) lies in the plane defined by P(1)-Fe-I. [d] Distances and angles generated by symmetry operations of the space group.

a)



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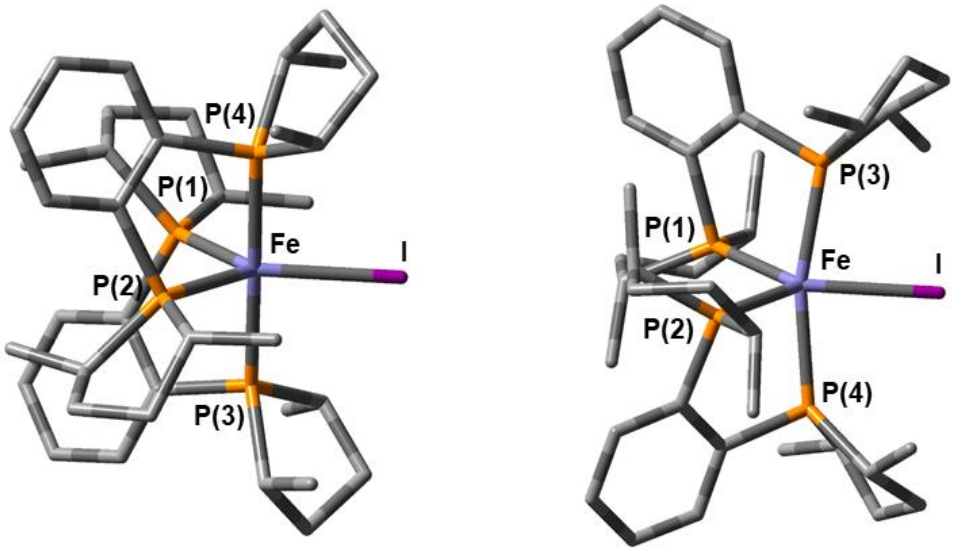

Figure S11. Representations of the calculated structures of Λ (left) and Δ (right) isomers of **[FeI{(*R*,*R*)-Me-DuPhos}$_2$]$^+$**, a) front view, b) lateral view. The hydrogen atoms are omitted for clarity.

Table S5. Main bond distances and angles for Λ- and Δ-**[FeI{(*R*,*R*)-Me-DuPhos}$_2$]$^+$** isomers, τ parameter, and relative Gibbs free energy for computed geometries.

Distances (Å) [a]	**Λ-[FeI{(*R*,*R*)-Me-DuPhos}$_2$]$^+$**		**Δ-[FeI{(*R*,*R*)-Me-DuPhos}$_2$]$^+$**
	Experimental	Calculated	Calculated
Fe-P(1)	2.2896[13]	2.282	2.339
Fe-P(2) [b]	2.2835[24]	2.282	2.318
Fe-P(3)	2.2646[27]	2.317	2.324
Fe-P(4)	2.2668[20]	2.317	2.326
Fe-I	2.5816[56]	2.586	2.617
Angles (deg)			
P(1)-Fe-P(2)	120.73[4]	98.48	94.13
P(3)-Fe-P(4)	178.63[21]	179.35	166.04
P(1)-Fe-P(3)	81.25[14]	82.71	82.33
P(2)-Fe-P(4)	81.57[4]	82.70	82.45
P(1)-Fe-P(4)	98.62[43]	96.87	106.90
P(3)-Fe-P(2)	99.66[3]	96.87	107.76
P(1)-Fe-I	121.34[1]	130.78	137.72
P(2)-Fe-I	117.94[3]	130.74	128.12
P(3)-Fe-I	89.01[18]	90.32	82.91
P(4)-Fe-I	89.93[18]	90.33	83.27
τ [b]	0.96	0.81	0.47
G (kcal/mol) [c]	-	-14.5	0.0

[a] Standard deviations for averaged values are given in brackets. [b] τ corresponds to the Adison parameter. [4] [d] Gibbs free energy relative to the Δ-isomer.

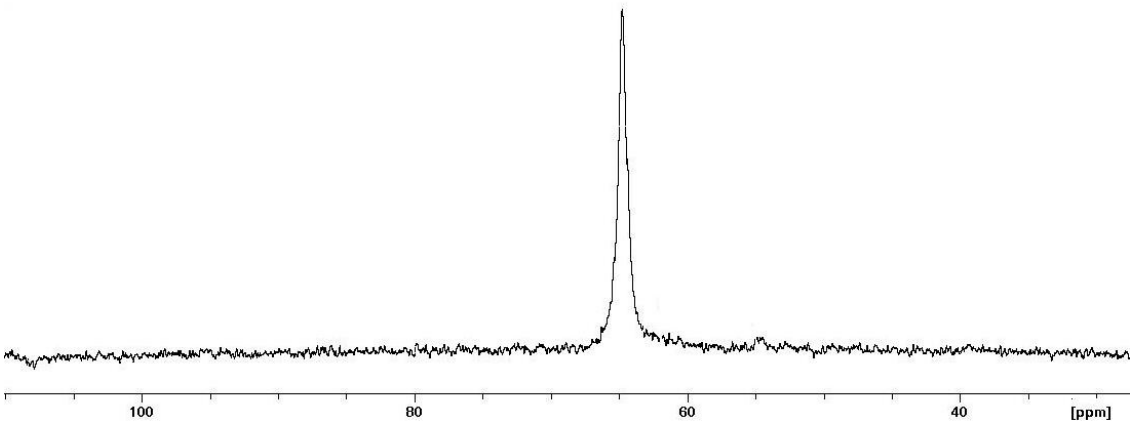

Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum registered after dissolution of crystals of Λ-**[FeI{(*R*,*R*)-Me-DuPhos}$_2$]**I·H_2O in $(CD_3)_2CO$.

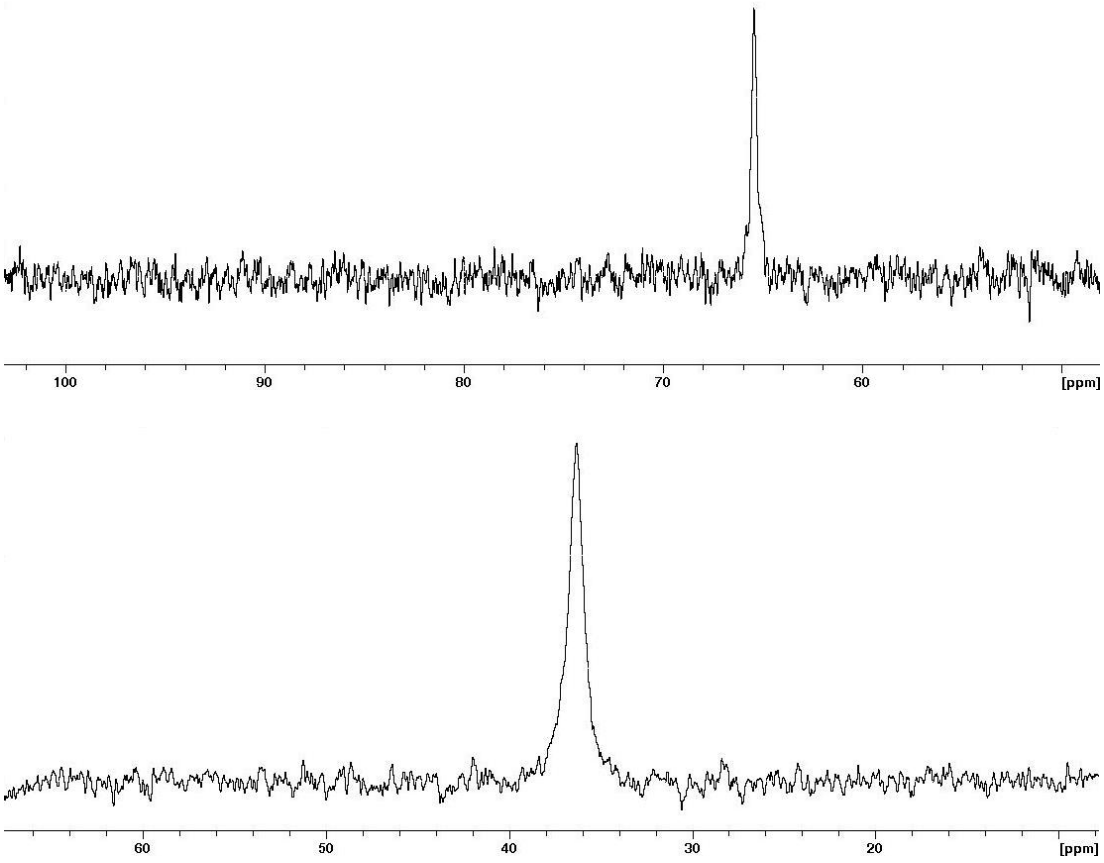

Figure S13. $^{31}P\{^{1}H\}$ (top) and ^{35}Cl (bottom) NMR spectra registered after dissolution of crystals of **[FeCl{(*R*,*R*)-Me-DuPhos}$_2$]**(BF_4) in CD_2Cl_2 and CD_3CN, respectively.

III.Structural description

Details of the structure refinement and X-ray structure determination

Anisotropic displacement parameters were refined for all non-hydrogen atoms of the iron complex cations and of the *trans*-**[FeCl$_2${(*R*,*R*)-Me-DuPhos}$_2$]** compound. The hydrogen atoms were included in calculated positions and refined riding on the respective carbon atoms with isotropic displacement parameters in all compounds. For Δ-**[FeI{(*S*,*S*)-Me-DuPhos}$_2$]**(ClO_4), disorder was observed on two of the four oxygen atoms of each perchlorate counterions. Each pair of oxygen atoms were modeled isotropically over two positions for each oxygen atom, and refined with a constraint to the total occupancy of one. For Λ-**[FeI{(*R*,*R*)-Me-DuPhos}$_2$]**I·H_2O, disorder was observed on the two iodide counterions. Each pair of iodine atoms were modeled isotropically over two positions for each iodine atom, and refined with a constraint to the total occupancy of one. Two peaks were located in the Fourier map and were assigned to two oxygen atoms, which were refined isotropically. These atoms were assigned to two water molecules, and the hydrogen atoms bonded to each oxygen atom were included at their idealized positions. In the case of **[FeCl{(*R*,*R*)-Me-DuPhos}$_2$]**(BF_4), disorder was observed on the four fluorine atoms of the counterion. Each pair of the fluorine atoms were modeled isotropically over two positions for each fluorine atom, and refined with a constraint to the total occupancy of one.

The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 1952455 (Δ-**[FeI{(*S*,*S*)-Me-DuPhos}$_2$]**(ClO_4)), 1952457 (Λ-**[FeI{(*R*,*R*)-Me-DuPhos}$_2$]**I·H_2O), 1952456 (**[FeCl{(*R*,*R*)-Me-DuPhos}$_2$]**(BF_4)), and 1952454 (***trans*-[FeCl$_2${(*R*,*R*)-Me-DuPhos}$_2$]**).

Table S6. Crystal data and structure refinement for **Δ-[FeI{(*S*,*S*)-Me-DuPhos}$_2$]**(ClO_4) and **Λ-[FeI{(*R*,*R*)-Me-DuPhos}$_2$]**I·H_2O

Compound	**Δ-[FeI{(*S*,*S*)-Me-DuPhos}$_2$](ClO$_4$)**	**Λ-[FeI{(*R*,*R*)-Me-DuPhos}$_2$]I·H$_2$O**
Empirical formula	$C_{36}H_{56}ClFeIO_4P_4$	$C_{36}H_{58}FeI_2OP_4$
Formula weight	894.88	940.35
Temperature	293(2) K	200.00(10) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1$
Unit cell dimensions	a = 11.23747(14) Å	11.3411(3) Å
	b = 20.9195(3) Å	20.8867(4) Å
	c = 33.7258(4) Å	17.3185(3) Å
	90°	90°
	90°	103.587(2)°
	90°	90°
Volume	7928.34(18) Å^3	3987.58(14) Å^3
Z	8	4
Density (calculated)	1.499 mg/m^3	1.566 mg/m^3
Absorption coefficient	1.424 mm^{-1}	2.114 mm^{-1}
F(000)	3680.0	1896.0
Crystal size	0.2894 × 0.187 × 0.0625 mm^3	0.241 × 0.162 × 0.064 mm^3
Theta range for data collection	5.844 to 58.206°	5.7 to 48
Index ranges	$-15 \le h \le 15$, $-27 \le k \le 27$, $-40 \le l \le 44$	$-12 \le h \le 12$, $-23 \le k \le 23$, $-19 \le l \le 19$
Reflections collected	93611	70382
Independent reflections	19581 [R(int) = 0.0441]	12484 [R_{int} = 0.0362]
Completeness to theta	(26.32º) 99.71%	(26.32º) 99.80%
Absorption correction	gaussian	gaussian
Data/restraints/parameters	19581 / 0 / 821	12484/1/823
Goodness-of-fit on F^2	1.068	1.024
Final R indexes [I>2sigma(I)]	R_1 = 0.0397, wR_2 = 0.1012	R_1 = 0.0217, wR_2 = 0.0531
Final R indexes (all data)	R_1 = 0.0509, wR_2 = 0.1099	R_1 = 0.0235, wR_2 = 0.0541
Largest diff. peak and hole	0.904 and -1.441 e·Å^{-3}	0.52 and -0.53 e·Å^{-3}
Flack parameter	-0.011(6)	-0.025(5)

Table S7. Crystal data and structure refinement for **[FeCl{(*R*,*R*)-Me-DuPhos}$_2$]**(BF_4) and *trans*-**[$FeCl_2${(*R*,*R*)-Me-DuPhos}$_2$].**

Compound	**[FeCl{(*R*,*R*)-Me-DuPhos}$_2$](BF_4)**	***trans*-[$FeCl_2${(*R*,*R*)-Me-DuPhos}$_2$]**
Empirical formula	$C_{36}H_{56}BClF_4FeP_4$	$C_{36}H_{56}Cl_2FeP_4$
Formula weight	790.79	739.43
Temperature	293(2) K	180.00(10)
Wavelength	0.71073 Å	0.71073 Å
Crystal system	orthorhombic	tetragonal
Space group	$P2_12_12_1$	$P4_12_12$
Unit cell dimensions	14.8107(3) Å	11.05922(16) Å
	16.8676(4) Å	11.05922(16) Å
	15.5365(3) Å	30.7432(7) Å
	90º	90º
	90º	90º
	90º	90º
Volume	3881.34(15) $Å^3$	3760.09(14) $Å^3$
Z	4	4
Density (calculated)	1.353 mg/m^3	1.306 mg/m^3
Absorption coefficient	0.667 mm^{-1}	0.738 mm^{-1}
F(000)	1664.0	1568.0
Crystal size	0.3475 × 0.2515 × 0.1435 mm^3	0.2219 × 0.1503 × 0.0949 mm^3
Theta range for data collection	5.558 to 47.996	5.846 to 55.216
Index ranges	$-16 \le h \le 16$, $-17 \le k \le 19$, $-17 \le l \le 17$	$-14 \le h \le 12$, $-8 \le k \le 14$, $-37 \le l \le 37$
Reflections collected	33898	14568
Independent reflections	6074 [R_{int} = 0.0467]	3945 [R_{int} = 0.0326]
Completeness to theta	(26.32º) 99.75%	(24.66º) 99.44%
Absorption correction	multi-scan	analytical
Data/restraints/parameters	6074/0/423	3945/0/199
Goodness-of-fit on F^2	1.059	1.083
Final R indexes [I>2sigma(I)]	R_1 = 0.0425, wR_2 = 0.1097	R_1 = 0.0266, wR_2 = 0.0576
Final R indexes (all data)	R_1 = 0.0464, wR_2 = 0.1143	R_1 = 0.0323, wR_2 = 0.0604
Largest diff. peak and hole	0.52 and -0.42 e·$Å^{-3}$	0.26 and -0.19 e·$Å^{-3}$
Flack parameter	0.000(8)	-0.001(9)

IV.Computational data

Optimized Gibbs free energies (in a.u.) and Cartesian atomic coordinates (in Å) of the structures described in Table S5:

Λ-[FeI{(*R*,*R*)-Me-DuPhos}$_2$]$^+$

E = -1571.888382 a.u.

Fe	-0.000110556157	-0.555150077035	-0.000392671672
I	-0.000457575025	-3.141187423519	-0.000869630508
P	0.582607410820	0.933607211269	1.627666059841
P	-0.582358363405	0.935507880711	-1.626798840980
P	2.279574611276	-0.542134767805	-0.415916358132
P	-2.279835543981	-0.541955515765	0.414890140065
C	0.598621002636	2.235744316593	-2.353984864307
H	1.568983595282	1.723471697330	-2.270525169164
C	2.881770119442	1.137928939603	0.072440541213
C	2.134408825058	1.784947862648	1.081483767453
C	-0.597913469732	2.233635238493	2.356028314828
H	-1.568547686021	1.722023335441	2.271723691370
C	-3.162799381868	-0.924519401638	2.055455310633
H	-3.370440472097	0.032769018151	2.550200597512
C	0.734016914175	3.592570705422	-1.665710890805
H	-0.201770020088	4.156962342104	-1.666191468808
H	1.478537580793	4.192010723665	-2.202486996457
H	1.073243761388	3.497985010577	-0.633051651852
C	-3.787878530348	3.567750513131	-1.146585795710
H	-4.143724952196	4.498941652326	-1.573288499175
C	-2.881693644421	1.138714198550	-0.071784605602
C	4.056772875659	1.735141004792	-0.405759089488
H	4.641478429482	1.249380533647	-1.179192755588
C	3.384287016256	-1.726269275068	0.604209801701
H	2.690736651021	-2.356561615836	1.169575786214
C	3.789100181436	3.565199155878	1.150263600733
H	4.145435148970	4.495641615248	1.578189125784
C	3.162280829385	-0.923189981710	-2.056975039067
H	3.369780466513	0.034539633424	-2.550918525581
C	-2.133847309501	1.786827107670	-1.079761064884
C	-1.103962936205	0.301712506360	-3.364509106809
H	-2.066802312447	0.809527876709	-3.519118816312
C	-0.732344247099	3.591370684798	1.669330906691
H	0.203902970308	4.154992458505	1.670362780214
H	-1.476296050304	4.190775108576	2.206936808481
H	-1.071823946367	3.498330041055	0.636609541036
C	-4.466118486435	-1.632767499569	1.626896973562
H	-4.893322913292	-2.182829837532	2.473256325878
H	-5.220542280784	-0.904339515381	1.305009103034
C	-2.617763746209	2.983357175643	-1.633015804523
H	-2.086280744283	3.466172029165	-2.444184443163
C	2.344572726362	-1.807087726152	-3.000365857690
H	2.082932804642	-2.765082812558	-2.541976166230
H	2.925772428023	-2.011781857193	-3.906824192932

H	1.414873890820	-1.324645960112	-3.300541558465
C	0.251263564576	2.329489550976	-3.851603123485
H	-0.602757503742	3.003821771479	-4.001405236908
H	1.092083865115	2.763048957980	-4.406026597269
C	-4.056717268680	1.735594774578	0.406775470588
H	-4.641868094632	1.248916608808	1.179295581356
C	-2.345165505321	-1.809159136794	2.998203367439
H	-2.083965374019	-2.767018447700	2.539275137313
H	-2.926185304111	-2.014071983526	3.904723369039
H	-1.415198704357	-1.327188302351	3.298300792096
C	1.103942291743	0.298001974048	3.364753969454
H	2.066836405995	0.805541297724	3.519963405002
C	-1.309906639750	-1.199842591825	-3.559920403191
H	-0.486142911254	-1.797299578727	-3.164370609369
H	-1.401117852339	-1.417414606936	-4.630740020709
H	-2.223971192382	-1.551499817173	-3.080473198522
C	4.373696671654	-1.039417472860	1.552005817522
H	5.136210496907	-0.474482227646	1.006733628369
H	4.887756009893	-1.803127632349	2.147000819661
H	3.892626804404	-0.343228585203	2.244577522159
C	2.618936415387	2.980539173977	1.636253966143
H	2.087902705019	3.462435211504	2.448271009957
C	-0.250846996366	2.325547822383	3.853845063503
H	0.603315854059	2.999493418565	4.004558091039
H	-1.091667135611	2.758712966291	4.408575520142
C	-3.384469213119	-1.725031620585	-0.606545210142
H	-2.690866680465	-2.354728799697	-1.172508196103
C	-4.497642060521	2.953324418933	-0.112909922821
H	-5.402757663632	3.409684050656	0.272328620020
C	-0.093064724828	0.926761685786	-4.345615233753
H	0.815747921886	0.313965412030	-4.397770889757
H	-0.519538487440	0.941724031982	-5.355362271436
C	4.465718625709	-1.631720194686	-1.629246668582
H	4.892885970791	-2.180912097938	-2.476189640179
H	5.220101734719	-0.903525111881	-1.306738723314
C	0.093051376165	0.922203004540	4.346393088074
H	-0.815912030229	0.309583660612	4.397755366406
H	0.519371518811	0.935984818615	5.356221392677
C	4.116721224185	-2.564186259382	-0.464354527527
H	5.012523142266	-3.027955039072	-0.035729171804
H	3.467999846642	-3.375899275086	-0.813473008376
C	4.498262787116	2.952016929371	0.115439544804
H	5.403360014603	3.408645690796	-0.269523517767
C	1.309714514767	-1.203756055696	3.558729049380
H	0.485329293138	-1.800653620151	3.163611245335
H	1.402051758001	-1.422173140535	4.629303633409
H	2.223135447608	-1.555297130007	3.077965035521
C	-4.373891843123	-1.037234945811	-1.553637024544
H	-5.136506187483	-0.473021173981	-1.007757081058
H	-4.887835290759	-1.800334425340	-2.149517538948
H	-3.892881216062	-0.340205651979	-2.245401122933
C	-4.116901331536	-2.564068945495	0.461143838289
H	-5.012604602802	-3.027534109158	0.031984036664
H	-3.468120517605	-3.376044562673	0.809542244791

Δ-[FeI{(*R*,*R*)-Me-DuPhos}$_2$]$^+$

E = -1571.865250 a.u.

Fe	-0.000834087463	0.441861377527	-0.060034214604
I	0.059751083007	3.056597303544	-0.144164830230
P	-0.837329622898	-1.312578295935	-1.361318473443
P	0.815590846732	-0.955621702328	1.599484739434
P	-2.259162640340	0.794717237672	0.358173409603
P	2.258655397163	0.645980307033	-0.572677849545
C	-2.493256795232	-1.775693669169	-0.629385291322
C	3.963456197866	2.776200744764	-1.037067179635
H	3.233200000959	3.580197492242	-1.194735243264
H	4.926572417972	3.252022375772	-0.816954366119
C	3.517859237521	1.915425417402	0.160227316218
C	1.304619996191	-0.077537066737	3.233330437329
C	4.036061291412	1.890363836312	-2.276829375371
H	4.896065697090	1.209392251582	-2.213760835113
H	4.169084547121	2.480907901162	-3.191063717760
C	2.723724461647	1.089112848567	-2.355399411251
C	-1.273178035204	-0.814251861269	-3.163421587974
C	-3.901363816302	3.019996525884	0.248249471269
H	-3.157982743124	3.826263610913	0.282896954116
H	-4.834856513652	3.453200015823	-0.129918469280
C	-2.793021765304	1.631830991773	1.972680017878
C	-3.146172766513	-0.810044859372	0.166672711195
C	-3.401990764031	1.923414652829	-0.713073641027
C	3.088902653285	-0.915647770701	-0.057502113757
C	0.095535635402	-2.486270759589	2.492727101098
C	3.040187473705	-2.797908379853	1.470147898982
H	2.571931888728	-3.366062578031	2.264295363020
C	-0.613766689373	-1.900129845850	-4.042273222097
H	-1.106543395865	-1.940932056339	-5.020486830383
H	0.440518510678	-1.673581657260	-4.230592050714
C	2.434852099324	-1.635183653807	0.965442126319
C	-0.169576152849	-3.033429537256	-1.872256987191
C	-4.414391636654	-1.086421366452	0.698956041793
H	-4.932691479087	-0.338439060686	1.287372332229
C	4.325272199150	-1.365084306187	-0.545402158783
H	4.845716429099	-0.801497737992	-1.311471926884
C	4.900247927052	-2.536110483524	-0.053088326130
H	5.848178721423	-2.883378957320	-0.448894952864
C	4.255592478259	-3.251994873523	0.957147798769
H	4.700802124463	-4.158609959758	1.351815354917
C	0.575909254334	-0.880052882239	4.332255601751
H	1.050237966487	-0.704501468607	5.304710965104
H	-0.467200705061	-0.560704232151	4.428435872415
C	0.630711033406	-2.359036103024	3.937464689192
H	0.035939091218	-2.980990629769	4.616081019954
H	1.665422845624	-2.714316201362	4.008050747525
C	-4.377145282494	-3.283800143028	-0.295203294308
H	-4.844943598568	-4.245867561432	-0.472780190431
C	-3.129286303132	-3.008201825661	-0.855257130114
H	-2.661328798761	-3.771280272740	-1.464224768358
C	-0.728890109690	-3.233426673764	-3.298687215466
H	-0.178215491332	-4.030408481208	-3.811520384957

H	-1.780136640172	-3.541400972678	-3.271463553515
C	-5.023798557987	-2.321403598645	0.481439076644
H	-5.997813459217	-2.529308755150	0.910228374593
C	-4.073648814918	2.420584419144	1.640824539154
H	-4.950983081623	1.760848069938	1.671943357679
H	-4.238460986903	3.197066746123	2.397358642517
C	-2.899964474260	0.776222798593	3.229639877432
H	-1.930084739554	0.363584642971	3.517888708486
H	-3.249446063809	1.396985566365	4.063509963228
H	-3.605824341521	-0.052141862455	3.116232301480
H	-1.983310315220	2.363082727268	2.111667527268
C	-2.906050715279	2.508780038050	-2.036341957713
H	-2.256834566801	3.369014814859	-1.866769590825
H	-2.350488199779	1.796288044408	-2.648683469607
H	-3.769483382412	2.847355632966	-2.621768080411
H	-4.238153506058	1.240928168279	-0.922834437026
H	-0.607911493377	-3.752060578292	-1.169825203358
C	1.349362084408	-3.212963794619	-1.849290311431
H	1.870716531737	-2.456107574361	-2.439797693507
H	1.752644666298	-3.182139288029	-0.837775921764
H	1.595216550520	-4.192394977252	-2.276817905686
C	-2.777072183700	-0.733310430937	-3.457727419940
H	-2.928191010269	-0.293184423716	-4.449891028208
H	-3.235613689143	-1.727135436580	-3.460145029456
H	-3.326509029324	-0.127508894446	-2.735362627961
H	-0.810440956573	0.166584491458	-3.329572420354
H	1.920680714453	1.795222828463	-2.615771285151
C	2.743404278812	-0.031858416936	-3.387025255750
H	3.480684634449	-0.804236171403	-3.149188479752
H	1.766274951388	-0.510132880364	-3.478286160004
H	3.000160772512	0.378600730961	-4.370530278528
C	3.180097906433	2.763748420681	1.388884368136
H	2.650493355408	3.675020528252	1.105469530147
H	2.559516602097	2.243858502051	2.120757660543
H	4.111660270263	3.056825625343	1.888592965875
H	4.347628490561	1.243023226234	0.420864180094
C	2.813225806326	-0.044774359381	3.511848951789
H	3.005286483016	0.589372582805	4.384723019546
H	3.197578807131	-1.045145887373	3.733502352871
H	3.398728358313	0.346552839647	2.678146969473
H	0.915914211601	0.944912385683	3.160696570601
H	0.518009388758	-3.363874840234	1.989705683288
C	-1.427517982608	-2.622415915238	2.484478654060
H	-1.928837597611	-1.725893784506	2.854823744375
H	-1.816640072708	-2.834529952771	1.489531655422
H	-1.713092236633	-3.455164093506	3.138019217861

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