

Trend-Analysis of Solid-State Structures: Low-Energy Conformational 'Reactions' Involving Directed and Coupled Movements in Half-Sandwich Compounds [CpFe(CO){C(=O)R}PPh₃]

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Dedicated to Professor Dr. M. P. Doyle on the occasion of his 75th birthday

Trends in solid-state structures were used to identify preferred intramolecular movements in half-sandwich compounds [CpFe(CO){C(=O)R}PPh₃]. Three weak interactions were analyzed: 1) the CH/π donor-acceptor interaction of phenyl rings in the PPh₃ ligand, 2) the Ph_{PPh₃} face-on Cp stabilization, and 3) the hydrogen bond between the oxygen atom of the acyl group and an *ortho*-C-H bond of one of the PPh₃ phenyl rings. Clockwise and counter-clockwise rotations established directed and coupled movements of the PPh₃ ligand, the acyl group, and the phenyl rings within the PPh₃ ligand.

Normally, the arrangement of sample points within an energy minimum is statistical (Figure 1, left side). A concentration, indicated by an inclined best-fit line, contains additional information (Figure 1, right side). For half-sandwich compounds [CpFe(CO){C(=O)R}PPh₃], we show that such trends in solid-state structures can be used to identify direction and coupling of movements inside the molecules. Such movements confirm and specify weak intramolecular interactions. This approach connects structure and movement by the relation: trends in solid-state structures—preferred movements.

Disregarding the conformational flexibility of the acyl substituent R at the outside of the molecules, there are five parameters in [CpFe(CO){C(=O)R}PPh₃] compounds that change the shape of the molecule: the three propeller angles τ of the phenyl rings of the PPh₃ ligand and the rotation angles ρ of

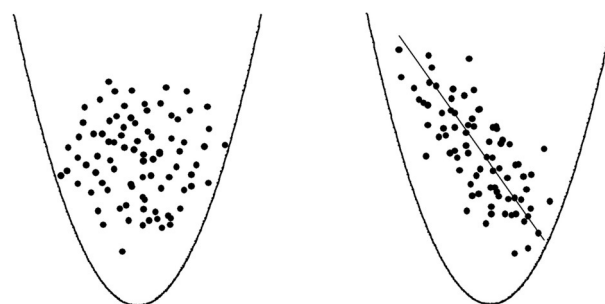


Figure 1. Statistical arrangement of sample points (left side) and concentration of sample points along an inclined best-fit line (right side).

the PPh₃ and acyl substituents. The propeller angles τ are defined as $C_o-C_i-P-Fe < 90^\circ$ (*i, o = ipso, ortho*), the rotation angle ρ_{PPh_3} as $C_i-P-Fe-Cp_{centr}$ and the rotation angle ρ_{acyl} as $O=C-Fe-Cp_{cent}$ (Figure 2). The rotation of the Cp ring around the axis $Cp_{cent}-Fe$ is not regarded to be a substantial change of the molecular shape.

The example CALWAN, [CpFe(CO){C(=O)sec-Bu}PPh₃], is shown in Figure 2, including the designations of the phenyl rings, as well as the propeller and rotation axes. In addition,

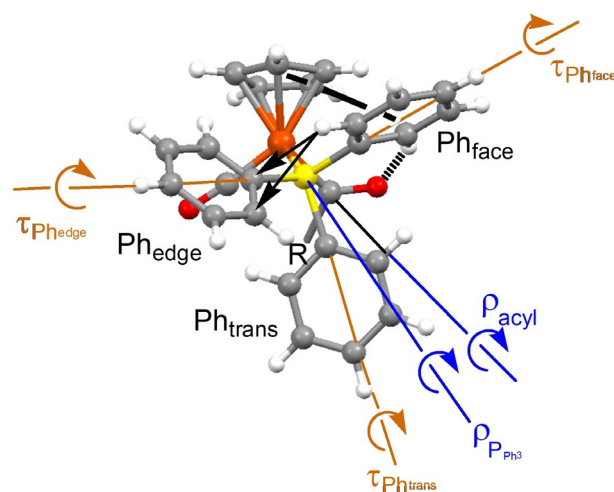


Figure 2. Labelling of phenyl rings, propeller angles τ , rotation angles ρ , and rotation axes in CALWAN [CpFe(CO){C(=O)sec-Bu}PPh₃]. The arrows indicate the CH/π interaction Ph_{face}→Ph_{edge} within the PPh₃ ligand. The bold line and the dashed line show the PPh₃ interaction with the fragment CpFe(CO)-{C(=O)R} by Ph_{PPh₃} face-on Cp interaction and CH...O hydrogen bond, respectively.

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Table 1. CSD symbols, rotation angles ρ , propeller angles τ , and torsion angle acyl and $(C_o)H-C_i-P-Fe$.

CSD symbol ^[a]	Ph _{edge} C _i -P-Fe-Cp _{cent} ρ [°]	C _o -C _i -P-Fe τ [°]	Ph _{trans} C _i -P-Fe-Cp _{cent} ρ [°]	C _o -C _i -P-Fe τ [°]	Ph _{face} C _i -P-Fe-Cp _{cent} ρ [°]	C _o -C _i -P-Fe τ [°]	Acyl O=C-Fe-Cp _{cent} ρ [°]	(C _o)H-C _i -P-Fe [°]
FIHTUL ^[b]	79.04	9.03	-165.76	-65.69	-40.67	-68.12	78.23	-70.03
LEZVAN	80.73	8.63	-160.05	-33.28	-37.40	-78.08	82.61	-81.74
DOKXIK	80.84	-1.38	-161.32	-57.71	-36.48	-70.33	91.28	-73.64
VOWTUW[1]	82.73	-3.05	-159.53	-49.34	-36.77	-65.70	83.61	-66.63
PIRDOJ	84.87	-3.48	-157.05	-56.56	-34.55	-63.23	61.39	-65.21
KEWSEK ^[b]	81.09	-3.58	-155.51	-26.69	-33.71	-75.84	84.61	-79.54
CUXBIG10	87.98	-3.79	-154.09	-57.89	-32.19	-60.24	68.97	_ ^[c]
LADFEB ^[b]	83.71	-5.32	-157.92	-59.19	-33.20	-66.97	75.22	-69.48
WAJYOV	79.90	-6.34	-163.87	-74.24	-39.26	-59.15	99.04	_ ^[c]
KEWSIO	79.40	-6.92	-161.40	-36.31	-41.99	-62.98	77.99	-68.11
JUDNEB	82.71	-8.91	-158.34	-50.62	-35.75	-67.62	70.74	-71.09
JUDNEB01	84.58	-9.76	-155.90	-50.64	-34.31	-68.43	75.80	-71.89
XIKFEC ^[b]	79.03	-9.86	-164.88	-71.46	-41.71	-56.33	99.61	-55.21
FAMNAI	80.50	-10.07	-162.25	-65.74	-39.69	-57.87	52.24	-67.29
NOCQEB	83.19	-10.22	-157.57	-46.40	-35.81	-65.18	66.63	-66.36
YOTBEO ^[b]	85.15	-12.11	-156.06	-52.35	-34.69	-54.24	50.66	-56.32
VOWTUW[2] ^[b]	81.07	-12.12	-160.50	-73.23	-38.80	-55.01	68.45	-56.33
YOTBIS	88.91	-13.65	-153.56	-53.45	-30.69	-57.43	61.20	-59.81
KITVAK	86.95	-13.96	-154.79	-48.33	-32.60	-60.97	80.54	-61.53
FIHTEV ^[b]	84.07	-14.00	-158.05	-63.76	-37.80	-54.57	51.05	-55.84
GOZYAX[1]	83.87	-14.00	-159.27	-73.97	-35.84	-57.89	69.54	-58.48
PIRDID ^[b]	85.91	-14.39	-157.08	-69.32	-34.47	-58.30	75.02	-58.37
FECPCB10 ^[b]	83.11	-15.17	-160.52	-60.74	-37.79	-51.15	66.12	-51.55
FIHTOF[1] ^[b]	82.64	-15.36	-159.82	-69.80	-37.20	-57.72	68.29	-57.82
GADWEN01 ^[b]	81.61	-15.48	-160.99	-76.90	-38.58	-57.92	75.60	_ ^[c]
VOWVAE	83.65	-16.78	-159.42	-74.77	-35.29	-58.73	78.35	-58.63
RARXAJ	84.10	-16.96	-159.45	-66.78	-38.52	-52.90	66.20	_ ^[c]
FEHTUH ^[b]	86.95	-17.26	-156.11	-65.67	-34.41	-54.11	72.82	-53.99
WAJYUB	83.83	-17.71	-157.91	-64.71	-35.84	-57.07	71.91	_ ^[c]
HAPSIA	75.30	-17.97	-167.06	-74.26	-45.37	-41.89	56.07	-42.97
ROXQEC	90.58	-18.15	-149.85	-41.19	-29.09	-62.14	75.61	-60.91
FIHTOF[2] ^[b]	83.45	-18.20	-159.93	-70.01	-37.13	-53.62	69.62	-55.12
FIHTIZ[1] ^[b]	84.55	-19.70	-157.11	-54.44	-35.32	-56.60	89.13	-58.59
CALWAN	86.80	-20.11	-156.13	-65.70	-34.67	-53.30	60.05	-52.86
GOZYAX[2] ^[b]	84.80	-20.40	-157.31	-70.70	-35.26	-55.45	80.73	-55.20
GOZXUQ ^[b]	88.66	-21.14	-153.25	-59.78	-32.22	-55.98	66.80	-57.68
FIHTIZ[2] ^[b]	88.01	-21.88	-154.55	-63.46	-32.70	-56.31	84.08	-58.19
DUHXOT	85.82	-22.10	-156.97	-65.58	-35.34	-52.67	65.57	-52.20
MCXCFE	89.53	-22.39	-150.81	-44.57	-28.87	-61.05	74.95	-63.77
RAZCEA	87.89	-23.44	-154.20	-57.69	-33.24	-53.26	77.40	-53.65
GIBTUG ^[b]	91.65	-23.56	-150.68	-64.58	-28.00	-56.04	67.41	_ ^[c]
ZIQGIP ^[b]	82.49	-24.04	-158.64	-65.88	-36.02	-58.25	83.15	-58.18
GADWEN02 ^[b]	81.41	-24.10	-160.15	-62.12	-39.98	-49.50	64.65	-46.94
FELFOR	87.60	-24.88	-155.07	-61.64	-33.20	-54.64	77.38	-54.37
SOGXOB	87.66	-25.34	-154.51	-59.99	-33.53	-53.11	73.84	-54.83
VIVTEZ	83.47	-28.54	-158.53	-72.92	-37.65	-47.14	59.90	-46.30
GAKJEH ^[b]	80.42	-29.01	-160.51	-57.99	-39.44	-52.64	57.58	-52.87
RARXEN	88.18	-29.06	-152.51	-51.88	-31.96	-54.11	80.17	_ ^[c]
JIDLUD ^[b]	80.19	-30.71	-159.51	-58.15	-38.60	-49.95	58.15	-51.79
DAWDUA	80.37	-31.39	-161.51	-72.20	-39.24	-55.36	51.92	-50.23
NOCQIF	86.50	-43.18	-153.19	-46.37	-31.60	-56.66	80.43	-57.20

[a] Brackets [] indicate independent molecules. [b] Inverted into the mirror image orientation. [c] No hydrogen atoms.

the arrows indicate the CH/ π interactions of the C-H bond of the donor Ph_{face} to the acceptor Ph_{edge} in the internal stabilization within the PPh₃ ligand. The interactions of the PPh₃ phenyl rings with the substituents of the fragment CpFe(CO)-{C(=O)R} are shown by a bold line for the Cp/Ph_{face} interaction and a dashed line for the hydrogen bond CH...O from Ph_{face} to the acyl oxygen atom.

A CSD search^[1] of the Cambridge Crystallographic Data Centre provided 47 [CpFe(CO){C(=O)R}PPh₃] compounds, the propeller and rotation angles of which are given in Table 1.^[2] Four compounds have two independent molecules in the unit cell. Thus, 51 different structures are available for analysis. In 23 cases, the CSD cif files were inverted to allow for a consistent stereochemistry in all the compounds.

The architecture of the PPh_3 propeller in half-sandwich compounds $[\text{CpFe}(\text{CO})\{\text{C}(=\text{O})\text{R}\}\text{PPh}_3]$ is determined by CH/π interactions.^[3,4] Contrary to the T-shaped benzene dimer, these CH/π interactions are intramolecular and entropically almost neutral.^[5] In the PPh_3 ligand, there are six $\text{C}_o\text{-H}$ bonds: three inside the propeller ($^{\text{in}}\text{C}_o\text{H}$) and three outside ($^{\text{out}}\text{C}_o\text{H}$). It is the interaction between the $^{\text{in}}\text{C}_o\text{-H}$ bonds and C_i , $^{\text{in}}\text{C}_o$, and $^{\text{out}}\text{C}_o$ atoms of neighboring phenyl rings that add up to an appreciable stabilization.^[3,4] Each of the three phenyl rings plays a specific role in the donor-acceptor interactions, as indicated by the arrows in Figure 2 for $\text{Ph}_{\text{face}} \rightarrow \text{Ph}_{\text{edge}}$.

In the histogram of Figure 3, a correlation of the propeller angles of the acceptor Ph_{edge} with the donor Ph_{face} is shown. The Ph_{edge} propeller angles span the range of $\tau = 9.0^\circ$ to -43.2° , and the Ph_{face} propeller angles from $\tau = -41.9^\circ$ to -78.1° . The best-fit line shows a good correlation with quality factors $R^2 = 0.5005$ and $p < 6.5 \times 10^{-9}$.

JIDLUD and FIHTUL are close to the best-fit line in Figure 3. The descent from JIDLUD to FIHTUL along the best-fit line implies not only a coupled movement of the propeller angles of Ph_{edge} and Ph_{face} but also preferred directions of this move-

ment. The change of the propeller angle of Ph_{edge} of JIDLUD from -30.7° to 9.0° of FIHTUL corresponds to a counter-clockwise (c-clw) rotation of Ph_{edge} by 39.7° around the $\text{C}_i\text{-P}$ bond, whereas the simultaneous change of the Ph_{face} angle from -50.0° to -68.1° is a clockwise (clw) rotation of 18.1° . A conformational change, such as the descent from JIDLUD to FIHTUL, will be called a 'reaction'. In such a 'reaction', a fragment changes, which two different molecules have in common. Here, the two molecules differ in the R substituents of their acyl ligands. In the 'reaction' JIDLUD \rightarrow FIHTUL, there is a concomitant change of the rotation angle of the PPh_3 ligand around the P-Fe axis from $\rho = -38.6^\circ$ to -40.7° . The other way round, the ascent from FIHTUL to JIDLUD is associated with a clockwise rotation of Ph_{edge} and a counter-clockwise rotation of Ph_{face} . Thus, in a conformational change of the type JIDLUD \rightarrow FIHTUL, Ph_{edge} and Ph_{face} do not move independently, but concertedly. The directions clockwise and counter-clockwise by no means are equal. There is a preferred direction for the synchronized movement of the two phenyl rings.

In the interaction $\text{Ph}_{\text{face}}/\text{Ph}_{\text{edge}}$ of JIDLUD, the $^{\text{in}}\text{C}_o\text{-H}$ bond of Ph_{face} is the donor to C_i and $^{\text{in}}\text{C}_o$ of Ph_{edge} (arrows in Figure 3).

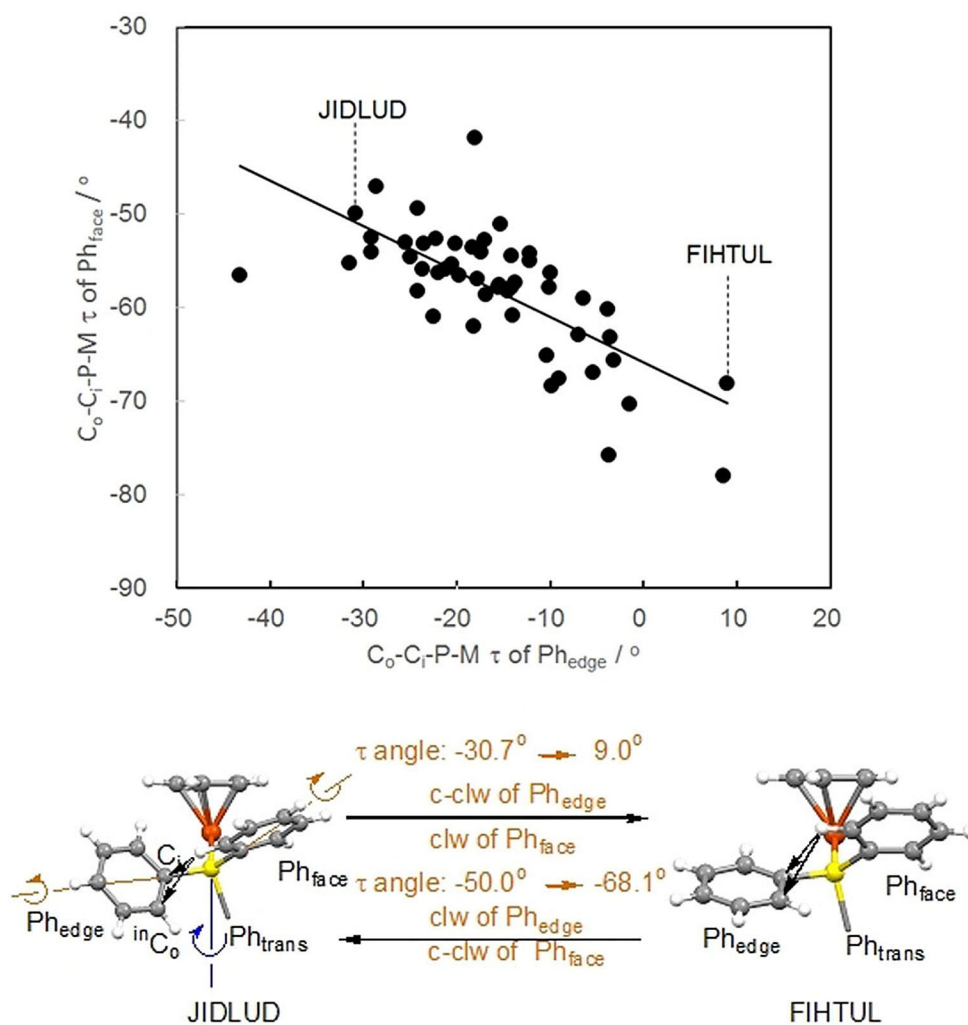


Figure 3. Correlation of the propeller angles of acceptor Ph_{edge} and donor Ph_{face} ($R^2 = 0.5005$, $p < 6.5 \times 10^{-9}$) (top). The 'reaction' JIDLUD \rightarrow FIHTUL (clw = clockwise, c-clw = counter-clockwise) (bottom).

For a CH/ π interaction, in JIDLUD the distance ${}^i\text{C}_o\text{H}-\text{C}_i$ (2.57 Å) is very short, whereas the distance ${}^i\text{C}_o\text{H}-{}^i\text{C}_o$ (2.85 Å) is relatively long. In the 'reaction' JIDLUD \rightarrow FIHTUL, Ph_{face} and Ph_{edge} of JIDLUD move to their positions in FIHTUL. In FIHTUL, the distances ${}^i\text{C}_o\text{H}-\text{C}_i$ (2.63 Å) and ${}^i\text{C}_o\text{H}-{}^i\text{C}_o$ (2.65 Å) are in the middle range. Given the counter-clockwise movement of Ph_{edge} in JIDLUD \rightarrow FIHTUL, a counter-clockwise instead of the observed clockwise movement of Ph_{face} would elongate both distances and weaken the CH/ π interaction. Had the CH/ π donor-acceptor interaction between Ph_{edge} and Ph_{face} not been established yet,^[3,4] the 'reaction' JIDLUD \rightarrow FIHTUL would indicate a weak bonding interaction between Ph_{edge} and Ph_{face} .

In (π -Ar)MPPH₃ complexes, a weak bonding stabilization is ascribed to the Ph_{PPh_3} face-on π -Ar interaction.^[6] For the complexes [CpFe(CO){C(=O)R}PPh₃], this means a weak attraction of Cp and Ph_{face} . In these molecules, a rotation around the P-Fe axis moves the PPh₃ ligand with respect to the fragment CpFe(CO){C(=O)R}. Figure 4 shows that the sample points of the three phenyl rings crowd within narrow ranges of their rotation angles, constraining the rotation around the P-Fe axis

to small degree intervals (Table 1). A change of the face/edge/*trans*-character of the phenyl rings would afford passage over higher transition states.

We had previously described the compression of the rotation angles of the face/edge/*trans*-phenyls of the PPh₃ ligand in half-sandwich complexes to narrow degree intervals, without recognizing the directionality, popping up in the best-fit lines of Figure 4.^[7] For Ph_{face} the 'reaction' VIVTEZ \rightarrow KEWSEK is shown at the bottom of Figure 4. Going down from VIVTEZ to KEWSEK, Ph_{face} performs a clockwise rotation of $\tau = 28.7^\circ$. Simultaneously, the PPh₃ ligand rotates in the counter-clockwise direction by $\rho = 4.0^\circ$. This is not much; however, it has to be kept in mind that PPh₃ rotation is strictly limited to narrow intervals and for the 'reaction' HAPSIA \rightarrow GIBTUG the PPh₃ rotation amounts to $\rho = 17.4^\circ$.

For the complexes [CpFe(CO){C(=O)R}PPh₃], the Ph_{PPh_3} face-on Cp stabilization requires that Ph_{face} is as close and as much face-on to the Cp ligand as possible. The decreasing rotation angle in the 'reaction' VIVTEZ \rightarrow KEWSEK brings Ph_{face} closer to Cp and the simultaneous clockwise rotation of Ph_{face} increases

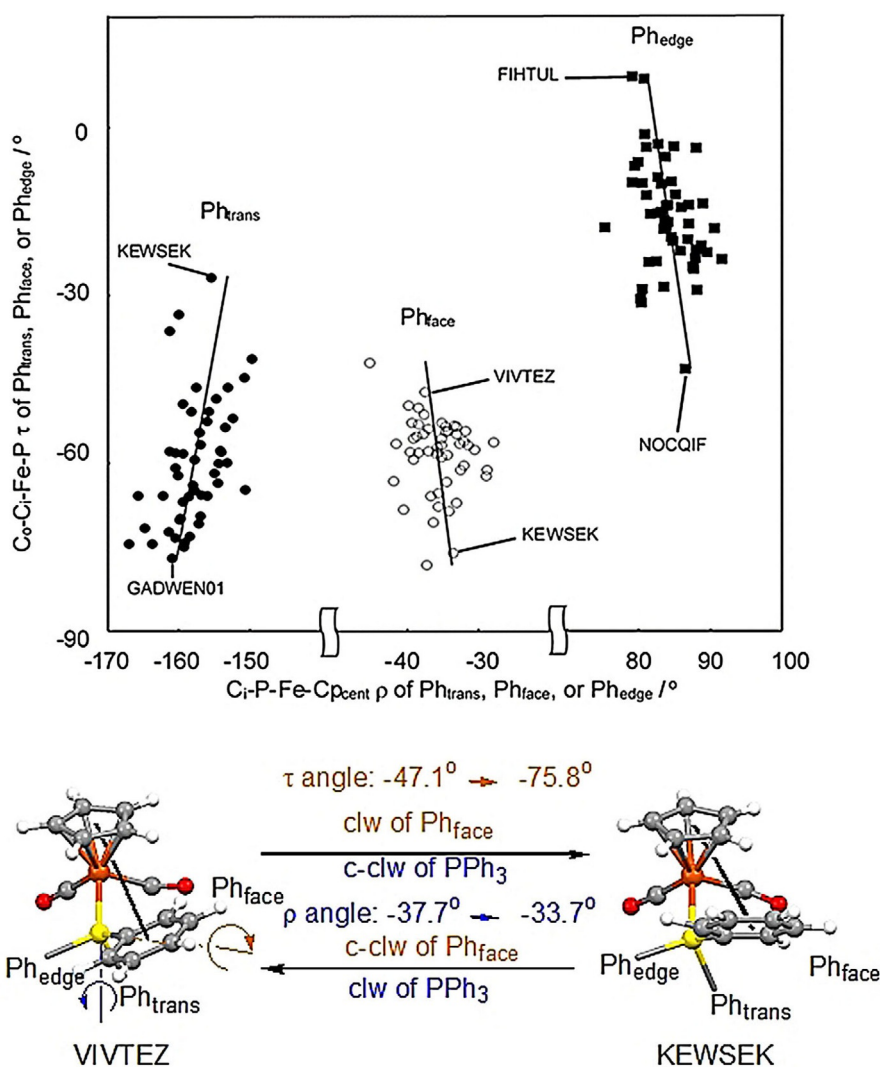


Figure 4. Correlation of the propeller angles τ of Ph_{trans} , Ph_{face} and Ph_{edge} and the rotation angle ρ of the PPh₃ ligand ($R^2 = 0.0399$, $p < 0.160$ for Ph_{face}) (top). The 'reaction' VIVTEZ \rightarrow KEWSEK (clw = clockwise, c-clw = counter-clockwise) (bottom).

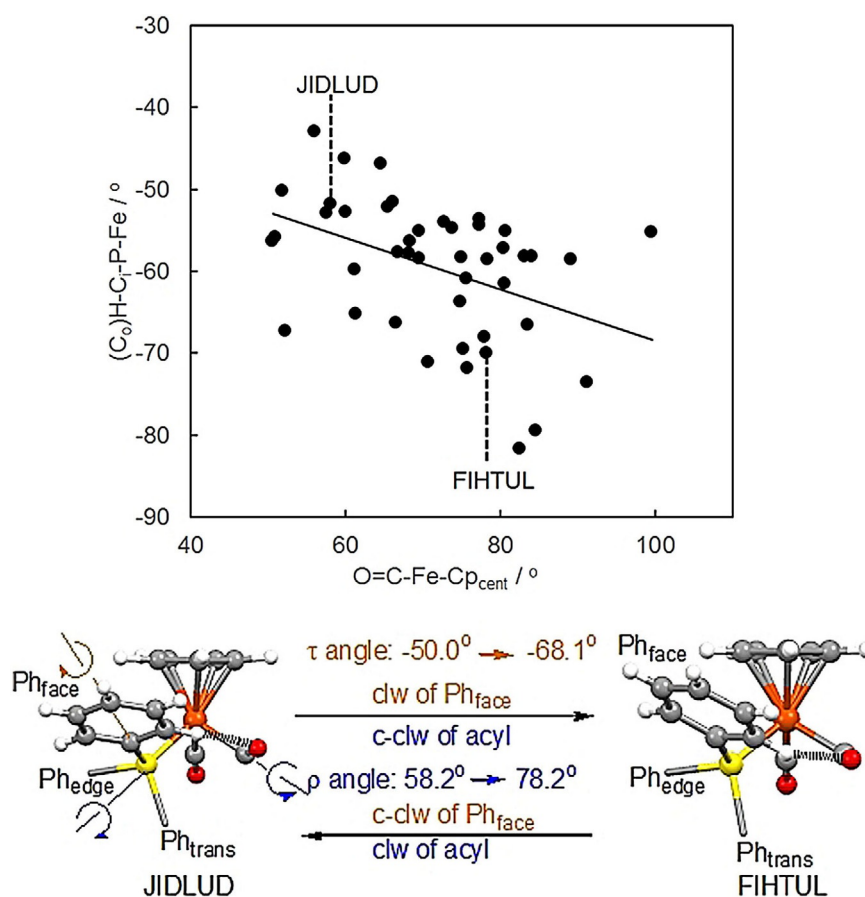


Figure 5. Correlation of the torsion angle $(C_o)H-C_i-P-Fe$ of Ph_{face} and the torsion angle $O=C-Fe-Cp_{cent}$ ($R^2=0.1807$, $p < 0.004026$) (top). The ‘reaction’ $JIDLUD \rightarrow FIHTUL$ (clw = clockwise, c-clw = counter-clockwise) (bottom).

its face-on character. The coupled movements work hand in hand to strengthen the Ph_{PPh_3} face-on Cp stabilization. Eclipsing of Ph_{edge} and Ph_{trans} with the carbonyl and acyl substituents prevents a further decrease of the rotation angle of Ph_{face} .^[6] In the back ‘reaction’ $KEWSEK \rightarrow VIVTEZ$, the increase of the rotation angle ρ weakens the Ph_{PPh_3} face-on Cp interaction. However, the counter-clockwise rotation of Ph_{face} increases its face-on character, making sure that as much stabilization as possible is maintained.

In the realm of Ph_{edger} the ‘reaction’ $FIHTUL \rightarrow NOCQIF$ results in a clockwise rotation of Ph_{edger} by $\tau=52.2^\circ$ and a counter-clockwise rotation of PPh_3 by $\rho=7.5^\circ$. For Ph_{trans} a ‘reaction’ with points close to the best-fit line is $KEWSEK \rightarrow GADWEN01$, involving a clockwise rotation of Ph_{edger} by $\tau=52.2^\circ$ and a counter-clockwise rotation of PPh_3 by $\rho=7.5^\circ$.

In the compounds $[CpFe(CO)\{C(=O)R\}PPh_3]$, the $^{out}C_o-H$ bond of Ph_{face} , abbreviated $(C_o)H$, forms a weak hydrogen bond to the oxygen atom of the acyl group (Figure 2).^[4] Figure 5 shows the correlation of the torsion angle $O=C-Fe-Cp_{cent}$ and the torsion angle $(C_o)H-C_i-P-Fe$ (Table 1). Although there is no bond between $(C_o)H$ and C_i in Ph_{face} , the torsion angle $(C_o)H-C_i-P-Fe$ perfectly positions $(C_o)H$, because it contains the propeller axis C_i-P of Ph_{face} and also the rotation axis $P-Fe$ of PPh_3 . Both axes contribute to the orientation of $(C_o)H$ within the molecule.

In Figure 5, $JIDLUD$ and $FIHTUL$ are close to the best-fit line. The descent from $JIDLUD$ to $FIHTUL$ changes the torsion angle $(C_o)H-C_i-P-Fe$ of Ph_{face} of $JIDLUD$ from 70.0° to 51.8° of $FIHTUL$, corresponding to a clockwise rotation of Ph_{face} of 18.2° , whereas the concomitant change of the acyl rotation angle from 58.2° to 78.2° is a counter-clockwise rotation of 20.0° . The change of the torsion angle $(C_o)H-C_i-P-Fe$ of Ph_{face} in the ‘reaction’ $JIDLUD \rightarrow FIHTUL$ implies two components: a clockwise rotation of Ph_{face} by 18.1° around the C_i-P axis and a clockwise rotation of the PPh_3 ligand around the $P-Fe$ axis by 2.1° . Vice versa, the ascent from $FIHTUL$ to $JIDLUD$ involves a counter-clockwise rotation of Ph_{face} , a counter-clockwise rotation of the PPh_3 ligand, and a clockwise rotation of the acyl group.

In all of the 51 structures of Table 1, a weak hydrogen bond from $^{out}C_oH$ of Ph_{face} to the oxygen atom of the acyl group is present. In the ‘reaction’ $JIDLUD \rightarrow FIHTUL$, there is a clockwise rotation of $(C_o)H$ of Ph_{face} and a counter-clockwise rotation of the acyl group (Figure 5). These concerted movements keep the hydrogen bond $^{out}C_oH \cdots O$ intact, as shown in the distances C_o-O of 3.22 Å in $JIDLUD$ and 3.15 Å in $FIHTUL$. A rotation of $(C_o)H$ and acyl in the same direction, both clockwise or counter-clockwise, would disrupt the hydrogen bond.

Using the correct absolute configuration, the trend analysis gives the correct chiral movements within the molecules—not

their mirror images. In molecules with a symmetry plane, the movements on the two sides are image and mirror image to each other.

The molecular movements described here are below full rotations around the C₁–P and P–Fe axes and even below the transition states, which interconvert the face/edge/trans-phenyl rings of the PPh₃ ligand.^[6] By trend analysis of solid-state structures, they are easily recognized. Directed and coupled movements may play a general role, for example, in biochemical processes such as protein folding.^[8,9]

Experimental Section

The Cambridge Structural Database^[11] was used for a search of the complexes discussed in this paper. The programs OLEX²,^[10] Mercury CSD ver. 3.9,^[11] and ConQuest ver. 1.19^[2] were used.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: donor–acceptor interactions · half-sandwich iron complexes · hydrogen bonding · propellers · triphenylphosphine

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