PPh₃ Propeller Diastereomers: Bonding Motif PhₚPPh₃ Face-On π-Ar in Half-Sandwich Compounds [(π-Ar)LL’MPPPh₃]

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Supporting Information

ABSTRACT: Chiral-at-metal compounds \((R_{Ru}(S))_{(S)}\)-[CyRu(1O-2N)PPh₃]PF₆ and \((R_{Ru}(S))_{(S)}\)-[CyRu(2O-1N)PPh₃]PF₆ were prepared using anions 1O-2N⁻ and 2O-1N⁻ of the Schiff bases, derived from the hydroxynaphthaldehydes and (S)-1-phenylethylamine. The pure \((R_{Ru}(S))\)-diastereomers were obtained by crystallization. In the unit cell of \((R_{Ru}(S))\)-[CyRu(1O-2N)PPh₃]PF₆ there are three independent molecules, which differ in the propeller sense of the PPh₃ ligand. Molecules [1] and [2] have \((M_{PPh3})\)-configuration and molecule [3] has \((P_{PPh3})\)-PPh₃ configuration. PPh₃ diastereoisomerism is discussed including other pairs of compounds, differing only in the PPh₃ configuration. A conformational analysis reveals an internal stabilization inside the PPh₃ ligand by a system of attractive CH/π interactions and a new bonding motif PhₚPPh₃ face-on π-Ar, both characteristic features of [(π-Ar)LL’MPPPh₃] compounds. The propeller diastereomers interconvert via a low-energy pathway and a high-energy pathway, corroborated by density functional theory calculations.

INTRODUCTION

In half-sandwich compounds of type [(π-Ar)LL’MPPPh₃], π-Ar = \(\eta^1\)-C₆H₆, \(\eta^3\)-C₆H₆, the triphenylphosphine ligand accounts for about half of the molecule. Figure 1 shows a hypothetical staggered conformation A in a Newman projection looking along P-M. Hypothetical staggered conformation (A). Propeller conformation (B), PhₚPPh₃, face-on π-Ar bonding conformation (C).

Figure 1. Newman projection of [(π-Ar)LL’MPPPh₃] looking along P-M. Hypothetical staggered conformation (A). Propeller conformation (B), PhₚPPh₃, face-on π-Ar bonding conformation (C).

staggered conformation A in a Newman projection looking along P-M, which differentiates the phenyl rings into gauche and trans with respect to π-Ar. In such a conformation, the inner ortho-hydrogen atoms of the phenyl rings would approximate each other to unacceptably short distances. The phenyl rings avoid this steric hindrance by rotation around their P-Cₖ₃ bonds, adopting a propeller structure B in Figure 1. When steric hindrance disappears, weak attractive forces such as CH/π interactions in the internal PPh₃ stabilization (see below) come into play.

In a 1983 paper, we showed that in half-sandwich compounds [(π-Ar)LL’MPPPh₃] there is an additional rotation about the P-M bond, differentiating the gauche phenyl rings into close and distant to π-Ar (C in Figure 1). The phenyls close to π-Ar have rotation angles \(0 < \rho < 60°\), and the phenyls distant to π-Ar have \(60° < \rho < 120°\). Subsequently, we will show that this rotation is part of bonding motif PhₚPPh₃ face-on π-Ar.

In the present paper, we describe the synthesis and characterization of compounds \((R_{Ru}(S))_{(S)}\)-[CyRu(1O-2N)PPh₃]PF₆ (Cy = cymene, 1-isopropyl-4-methylbenzene, 1O-2N⁻ = (S)-2-[(1-phenylethylimino)methyl]-1-naphthalenolate) and \((R_{Ru}(S))_{(S)}\)-[CyRu(2O-1N)PPh₃]PF₆ (2O-1N⁻ = (S)-1-[(1-phenylethylimino)methyl]-2-naphthalenolate). In the crystal, chiral-at-metal compound \((R_{Ru}(S))_{(S)}\)-[CyRu(1O-2N)PPh₃]PF₆ forms diastereomers, which differ only in the configuration of the triphenylphosphine propeller. In this context, we discuss eight pairs of such propeller diastereomers, develop the PhₚPPh₃ face-on π-Ar bonding concept, and reveal low- and high-energy pathways of the interconversion of the PPh₃ propeller.

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RESULTS AND DISCUSSION

Synthesis and X-ray Characterization. Diastereomerically pure compounds \((R_{Ru,S_C} )[\text{CyRu}(1O-2N)PPh_3]PF_6\) and \((R_{Ru,S_C} )[\text{CyRu}(2O-1N)PPh_3]PF_6\) were obtained in the following sequence of reactions. Deprotonated ligands \(\text{Ru, PPh}_3\) and \((\text{CyRu}(1O-2N)\text{PF}_6\) and then for the diastereomers of \((\text{CyRu}(2O-1N)\text{PF}_6\), \(2O-1N^-\) \((S)-1-[(1-\text{phenylethyl} \text{iminomethyl}] -1-\text{naphthalenolate, and (R}_{Ru,S_C} )[\text{CyRu}(2O-1N)PPh_3]PF_6 ((S)-2-[(1-\text{phenylethyl} \text{iminomethyl}] -1-\text{naphthalenolate}^d)

\[\text{Scheme 1.} \quad (R_{Ru,S_C} )[\text{CyRu}(1O-2N)PPh_3]PF_6, 1O-2N^- = (S)-2-[(1-\text{phenylethyl} \text{iminomethyl}] -1-\text{naphthalenolate}\]

in the following sequence of reactions. Deprotonated ligands \(10H-2N\) and \(2OH-1N^-\) were reacted with \([\text{CyRu}Cl]_2\) to give \((R_{Ru,S_C} )/[\text{CyRu}(10-2N)\text{Cl}]\) and \((R_{Ru,S_C} )/[\text{CyRu}(2O-1N)\text{Cl}]\), respectively. Treatment with PPh_3 and NH_4PF_6 afforded products \((R_{Ru,S_C} )/[\text{CyRu}(1O-2N)PF_6\] and \((R_{Ru,S_C} )/[\text{CyRu}(2O-1N)PF_6\] in both cases, the pure \((R_{Ru,S_C} )\) diastereomers were obtained by crystallization from CH_2Cl_2 as red crystals suitable for X-ray analysis (Table S1 in the Supporting Information). In the unit cell of \((R_{Ru,S_C} )[\text{CyRu}(10-2N)PF_6\] there are two different molecules \([1\) and \([2\) with the \((M,M,M)\)-configuration of the PPh_3 ligand and one molecule \([3\) with the \((P,P,P)\)-configuration of PPh_3.

The molecular structures will be discussed first for \((R_{Ru,S_C} )[\text{CyRu}(10-2N)PPh_3]PF_6\) and then for the diastereomers of \((R_{Ru,S_C} )[\text{CyRu}(2O-1N)PPh_3]PF_6\). The \(\pi\)-stack between the substituted phenyl ring of the naphthalene system and one of the phenyl rings of the PPh_3 ligand is a striking feature in the structure of \((R_{Ru,S_C} )[\text{CyRu}(2O-1N)PPh_3]PF_6\) (Figure 2, left side) and molecule \((R_{Ru,S_C} )[\text{CyRu}(10-2N)PPh_3]PF_6\) with \((P,P,P)\)-configuration of the PPh_3 propeller (right side). Hydrogen atoms omitted for clarity.

The internal CH/π interactions Ph3 \(\rightarrow\) Ph1, Ph2 \(\rightarrow\) Ph3, and Ph1 \(\rightarrow\) Ph2 looking along the P-M axis.

\[\text{Figure 3. CH/π interactions Ph3 \(\rightarrow\) Ph1, Ph2 \(\rightarrow\) Ph3, and Ph1 \(\rightarrow\) Ph2}\]
Propeller Chirality. Each of the three M-P-Ph systems in a PPh₃ ligand is an independent element of chirality.¹⁰,¹¹ The propeller angles Cᵢ-Cᵢ-Cᵢ-Pₚ-M < 90° are measures of the chirality of the M-P-Ph entities. They define (M)/M chirality of the M-P-Ph blades of the PPh₃ propeller according to the helicity rule of the CIP system.¹² Negative propeller angles correspond to (P) chirality, and positive propeller angles correspond to (M) chirality.

In (RₓRu₅CₛCₛ)⁻[CyRu(1O-2N)PPh₃]PF₆, the propeller angles Cᵢ-Cᵢ-Cᵢ-Pₚ-M < 90° in the PPh₃ ligand are +25.6°, +68.6°, and +44.3° (Table 1). As all torsion angles are positive, the (M,M,M)-configuration has to be assigned to the PPh₃ ligand. In (RₓRu₅CₛCₛ)⁻[CyRu(1O-2N)PPh₃]PF₆, the unit cell contains three independent molecules. Two of them, [1] and [2], have (M,M,M)-configuration due to positive torsion angles +14.2°, +82.6°, and +44.0° and +64°, +89.5° (−88.0°), and +44.7°. In the phenyl ring, with the highest torsion angle of the (M,M,M)-diastereomers of 2O-1N and 1O-2N, the two ortho positions are almost equivalent (large thermal ellipsoids). Use of one or the other will interchange the symbols (M) and (P). The torsion angles of [1] and [2] are very similar to those of (RₓRu₅CₛCₛ)⁻[CyRu(1O-2N)PPh₃]PF₆. However, the third molecule [3] in the unit cell of (RₓRu₅CₛCₛ)⁻[CyRu(1O-2N)PPh₃]PF₆ is very different. Its PPh₃ ligand has (P,P,P)-configuration due to its negative torsion angles −25.2°, −61.9°, and −69.5° (Table 1).

Our recent analysis of 119 compounds of type [(π-Ar)(LL)M(PPh₃)]⁺ showed that propeller configurations can be divided into two subgroups (P,P,P)/(M,M,M) (~90% abundance) and (M,P,P)/(P,M,M) (~10% abundance).¹⁰,¹¹ As all of the new cymene/naphthyl compounds and their parent benzene/phenyl compounds HEDYOE and HEDYIY belong to the (P,P,P) or (M,M,M) type, we will subsequently use symbols (P_PP₃) and (M_PP₃) for the propeller configuration of the PPh₃ ligand.

Rotation Angles. In ref 1, we demonstrated that 11 [(π-Ar)LL(MPPh₃)]⁺ compounds and 17 [(π-Ar)LL(MPPh₃)]⁻ compounds adopted structures of type C in Figure 1, with rotation angles far below 60°. This rotation brings the gauche phenyl 10° < ρ < 60° close and face-on toward π-Ar, whereas the gauche phenyl 10° < ρ < 120° becomes distant and edge-on toward π-Ar. It was argued that the steric hindrance of the π-Ar ligand with the ortho-CH bond of the edge-exposed phenyl is responsible for the rotation, which is wrong (see below).

Figure 4 shows Newman projections of the six salicylaldiminate compounds. They clearly subdivide into two types, which have surprisingly similar conformations, irrespective of their π-Ar and O-N substituents. In all of the compounds, Ph₃ is face-exposed to π-Ar with rotation angles ρ below 60°, whereas Ph1 is edge-exposed with rotation angles ρ above 60°. Taking into account the +/− signs of the rotation angles, the entire configurational symbols are (RₓRu₅CₛPₚ₃) for the compounds on the left and (RₓRu₅CₛPₚ₃) for those on the right of Figure 4. The rotation angles of Ph_face concentrate in the narrow range from 128.7° to 147.0°. With 89.2° to 176.7°, the rotation angles, ρ, of Ph_edge add up to 120° (Table S2 in the Supporting Information). The average of rotation angles ρ(Ph_face) is 140.0°.

In Table S2, we included another five pairs of diastereomers, which differ only in the propeller sense of the PPh₃ ligand: VOWTUV,¹⁵ GIRIYIP,¹⁶ ZINXOJ,¹⁷ FOMZEN,¹₈ and RCMXFE.¹⁹ These compounds are of types [CpFe(CO)(R)PPh₃]⁻ and [CpRe(NO)(R)PPh₃]⁻. In the unit cell of these compounds, there are two independent molecules with the same metal configuration and opposite PPh₃ configurations. This is similar to the four cymene/naphthyl compounds of the present paper, although they have an additional chiral center in the chelate ligand. For diastereomers HEDYIY and HEDYOE of (RₓRu₅CₛCₛ)⁻[CyRu(1O-2N)PPh₃]PF₆ however, the situation is different. We could isolate the diastereomers of this compound as separate single crystals.¹² Thus, HEDYOE and HEDYIY are two different modifications of (RₓRu₅CₛCₛ)⁻[CyRu(1O-2N)PPh₃]PF₆. We also included SEPZUI in Table S2. Its two diastereomers differ in the metal configuration, having the same PPh₃ propeller sense (P_PP₃).²₀

The rotation angles of Ph_face and Ph_edge of the CpFe(CO) and CpRe(NO) compounds hook up with the salicylaldiminato compounds, except for (M_PP₃), diastereomer GIRIYIP¹, which is not used for average calculations (Table S2). The overall average of rotation angles ρ(Ph_face) is −36.8° for the (P_PP₃) diastereomers and 40.0° for the (M_PP₃) diastereomers.

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| entry variant | CSD symbol or CCDC number | Table 1. Internal Stabilization in Compounds (RₓRu₅CₛCₛ⁻[CyRu(1O-2N)PPh₃]PF₆ (RₓRu₅CₛCₛ⁻[CyRu(2O-1N)PPh₃]PF₆ and (RₓRu₅CₛCₛ⁻[π-C₆H₆]Ru(O-N)PPh₃]PF₆)²² | 3 → 1 (Å) | M-P-Cₛ-Cₛ Cₛ-H-Cₛ Cₛ-Cₛ-Cₛ Pₛ₂ (deg) | M-P-Cₛ-Cₛ Cₛ-H-Cₛ Cₛ-Cₛ-Cₛ Pₛ₂ (deg) | 1 → 2 (Å) | M-P-Cₛ-Cₛ Cₛ-H-Cₛ Cₛ-Cₛ-Cₛ Pₛ₂ (deg) | M-P-Cₛ-Cₛ Cₛ-H-Cₛ Cₛ-Cₛ-Cₛ Pₛ₂ (deg) | 2 → 3 (Å) | M-P-Cₛ-Cₛ Cₛ-H-Cₛ Cₛ-Cₛ-Cₛ Pₛ₂ (deg) | M-P-Cₛ-Cₛ Cₛ-H-Cₛ Cₛ-Cₛ-Cₛ Pₛ₂ (deg) |
|-------------|-----------------------------|---------------------------------|-------------|-----------------------------|-----------------------------|-------------|-----------------------------|-----------------------------|-------------|-----------------------------|-----------------------------|
| 1 A/B        | 1519531 [1] (RₓRu₅CₛCₛ⁻[CyRu(1O-2N)PPh₃]PF₆ | 6.4 2.75 89.5 2.78 44.7 2.77 | 6.2⁷⁷⁺⁺⁺⁺ | 2.6⁷⁷⁺⁺⁺⁺ | 2.56⁺⁺⁺⁺ | | | | | | |
| 2 A/B        | 1519531 [2] (RₓRu₅CₛCₛ⁻[CyRu(1O-2N)PPh₃]PF₆ | 14.2 2.71 82.6 2.77 44.0 2.72 | 2.7⁷⁷⁺⁺⁺⁺ | 2.9⁷⁺⁺⁺⁺ | 2.58⁺⁺⁺⁺ | | | | | | |
| 3 A/B        | 1519532 (RₓRu₅CₛCₛ⁻[CyRu(2O-1N)PPh₃]PF₆ | −16.0 2.57 −67.6 2.80 −62.1 2.78 | 2.7⁷⁷⁺⁺⁺⁺ | 2.7⁷⁺⁺⁺⁺ | 2.64⁺⁺⁺⁺ | | | | | | |
| 4 A/B        | 1519531 [3] (RₓRu₅CₛCₛ⁻[CyRu(1O-2N)PPh₃]PF₆ | 25.6 2.62 86.2 2.74 44.3 2.77 | 2.7⁷⁷⁺⁺⁺⁺ | 2.7⁷⁺⁺⁺⁺ | 2.63⁺⁺⁺⁺ | | | | | | |
| 5 A/B        | 1519532 (RₓRu₅CₛCₛ⁻[CyRu(2O-1N)PPh₃]PF₆ | 23.9 2.58 77.9 2.63 53.7 2.76 | 2.8⁶⁺⁺⁺⁺ | 2.7⁷⁺⁺⁺⁺ | 2.54⁺⁺⁺⁺ | | | | | | |
| 6 A/B        | 1519531 [3] (RₓRu₅CₛCₛ⁻[CyRu(1O-2N)PPh₃]PF₆ | −25.2 2.59 −61.9 2.58 −69.5 2.73 | 2.8⁶⁺⁺⁺⁺ | 2.7⁷⁺⁺⁺⁺ | 2.54⁺⁺⁺⁺ | | | | | | |

Variants A and B, torsion angles M-P-Cₛ-Cₛ < 90°, and distances Cₛ-H-Cₛ, Cₛ-Cₛ-Cₛ, and Cₛ-Cₛ-Cₛ-Cₛ. Variant A refers to Cₛ-H-Cₛ distances and variant B refers to Cₛ-H-Cₛ-Cₛ distances for Ph₁ and Ph₂, respectively (see refs 10 and 11). Brackets [ ] indicate independent molecules. See ref 12.

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The face-on approximation of Ph$_{face}$ to $\pi$-Ar is an indication of a bonding attraction, considered next.

**Bonding Motif Ph$_{pph}$ Face-On $\pi$-Ar.** The bonding system Ph$_{pph}$ face-on $\pi$-Ar includes elements of the T-shape as well as of the $\pi$-stack benzene dimer, and it contains the Ru and the P atom. In addition to rotation angles $\rho$, angle $\phi$ between the planes of $\pi$-Ar and Ph$_{face}$ is a measure of the $\pi$-Ar/Ph$_{face}$ interaction. Figure 5 shows the arrangement of $\pi$-Ar and Ph$_{pph}$ in HEDYIY ($\phi = 27.6^\circ$, left side) and HEDYOE ($\phi = 28.6^\circ$, right side). In HEDYIY, distances C$_{Ar}$-C$_{i}$ 3.32 Å and C$_{Ar}$-C$_{o}$ 3.30 Å are below the graphite distance of 3.35 Å, indicating a $\pi$-stack interaction. T-shape benzene dimer interactions show up in distances such as...
(x-Ar)CH-C_6 = 2.76 Å and (x-Ar)CH-C_6 = 2.91 Å. The corresponding distances of propeller diastereomer HEDYOE are similar. In HEDYIY and HEDYOE, rotation angles \( \rho = 37.3 \) and \(-28.7^\circ\) of the face-on phenyls enforce rotation angles of \( \rho = -82.4 \) and \( 89.2^\circ\) for the corresponding edge-on phenyls.

In Figure 6, rotation angles \( \rho \) of the face-on and edge-on phenyls of the 18 diastereomers, differing only in the propeller configuration of the PPh_3 ligand, are shown as a function of \( \varphi \) for 140 cases of 119 compounds of type \([x-(C_6R_6)RuLL']PPh_3\]. The averages of \( \rho \) and \( \varphi \) for the face-on phenyls are \( \rho_{av} = -34.3^\circ \) and \( \varphi_{av} = 23.6^\circ \) for the \((P_{PPh})\) diastereomers and \( \rho_{av} = 40.0^\circ \) and \( \varphi_{av} = 24.2^\circ \) for the \((M_{PPh})\) diastereomers. The averages of \( \rho \) and \( \varphi \) for the edge-on phenyls are \( \rho_{av} = -81.0^\circ \) and \( \varphi_{av} = 55.3^\circ \) for the \((P_{PPh})\) diastereomers and \( \rho_{av} = 81.8^\circ \) and \( \varphi_{av} = 46.1^\circ \) for the \((M_{PPh})\) diastereomers.

The turning of PPh_3 face-on to x-Ar is a general phenomenon. In the histogram of Figure 7, this is shown for 140 cases of 119 compounds of type \([x-(C_6R_6)RuLL']PPh_3\], obtained in a CSD search for \([x-(C_6R_6)RuLL']PPh_3\). The sample points concentrate around averages \( \rho_{av} = -39.0^\circ \) and \( \varphi_{av} = 27.7^\circ \) for the \((P_{PPh})\) diastereomers and \( \rho_{av} = 39.3^\circ \) and \( \varphi_{av} = 25.7^\circ \) for the \((M_{PPh})\) diastereomers. This is surprising because L and L’ and the substituents in the x-Ar ligand of the (x-Ar)LL'Ru fragments vary considerably. In all of the 140 cases of Figure 7, there is no exception with \( \rho > 60^\circ \) such as GIRYIP[1] in Figure 6.

With a rotation angle of \( \rho = -51^\circ \), PIGJOG is almost in the middle between HEDYIY and HEDYOE (Figure 5). PIGJOG is even more perfectly stabilized than HEDYIY and HEDYOE, as apparent from distances C_{Ar}-C_i = 3.28 and 3.31 Å as well as \((x-Ar)CH-C_6 = 2.68\) and 2.75 Å and \((x-Ar)CH-C_6 = 2.84\) and 2.89 Å. When PIGJOG is very highly stabilized, the question arises, why do the rotation angles \( \rho \) of Ph_{face} concentrate around \( \pm 40^\circ \) and not around \( 0^\circ \)? The reason is the eclipsing interaction of the other two phenyls with substituents L and L’ in three-legged sandwich fragment \((x-Ar)LL'\). PIGJOG’s substituent L = H_2BHNMe_3 is in a plane with Arcent, Ru, and P perpendicular to the plane of the paper, and the two phenyls stagger L perfectly (Figure 5). Thus, \pm 40^\circ\) is a compromise of Ph_{face} to establish Ph_{face} face-x-Ar stabilization and to avoid eclipsing of the other two phenyls with L and L’.

Interconversion of Propeller Diastereomers. The interconversion of diastereomers HEDYIY and HEDYOE, differing only in the propeller configuration, can occur by two different pathways: (a) Ph_{face} of HEDYIY is converted to Ph_{face} of HEDYOE via a transition state about \( \rho = 0^\circ \) and vice versa and (b) Ph_{face} of HEDYIY is converted to Ph_{edge} of HEDYOE via a transition state about \( \rho = 60^\circ \) and vice versa (Figures 6 and 7). Both pathways require only small intramolecular rotations of \( \rho \) and \( \tau \), far below full phenyl rotations.

Pathway a inverts the chirality of Ru-Ph_{face} from \((M_{PPh})\) in HEDYIY to \((P_{PPh})\) in HEDYOE and exchanges \(^{13}C_{out/m}\) of Ph_{face} to \(^{13}C_{out/m}\). In addition, it brings Ph_{trans} of HEDYIY up into the position of Ph_{edge} of HEDYOE and it moves Ph_{edge} of HEDYOE down to the position of Ph_{trans} of HEDYOE. In pathway a, Ph_{face} passes through conformations with rotation angles \( \rho \) around \( 0^\circ \) similar to the conformation of PIGJOG in Figure 5. Because these conformations are highly stabilized, pathway a would be energetically favorable for Ph_{face}. However, as discussed above, rotation angles of Ph_{face} around \( 0^\circ \) imply the eclipsing of the other two phenyls with substituents L and L’, which makes the area of Ph_{face} around \( 0^\circ \) a transition state.

Pathway b, although interchanging diastereomers HEDYIY and HEDYOE, does not change the \((M_{PPh})\) chirality, and it does not exchange \(^{13}C_{out/m}\) of Ph_{face} to \(^{13}C_{out/m}\) of the phenyl in question. In addition, this rotation brings Ph_{edge} of HEDYIY into the position of Ph_{trans} of HEDYOE and it converts Ph_{trans} of HEDYOE to Ph_{trans} of HEDYOE. Thus, Ph_{trans} stays Ph_{trans}, but it inverts its chirality. Pathway b does not involve the eclipsing situation of pathway a.
It is well known that sample points of conformations, retrieved from the Cambridge Crystallographic Data file, concentrate in low-energy areas and thin out toward transition states.\(^{23}\) Therefore, the high population of the areas at about \(\rho = 140^\circ\) in Figures 6 and 7 by sample points means that these structures are favorable molecular conformations. On the other hand, the thinning out of sample points on the two sides of the energy minimum \(\rho = 140^\circ\) indicates the approximation to transition states. Furthermore, the distribution of sample points in the areas of the two transition states allows a differentiation between pathways a and b of the \((P_{\text{Ph}})/(M_{\text{Ph}})\) interconversion of Phface. At about \(\rho = 0^\circ\), sample points not only thin out but disappear completely (Figures 6 and 7). That means, rotation angles about \(\rho = 0^\circ\) correspond to a high-lying transition state. On the other hand, sample points of \((M_{\text{Ph}})\)-Phface and \((P_{\text{Ph}})\)-Phedge about \(\rho = 60^\circ\) overlap, indicating a low-lying transition state.

The process of diastereomer interconversion along pathways a and b is shown at the bottom of Figure 7 on the right side. In pathway b, starting with HEDYIY at \(\rho = 37.3^\circ\), the transition state is reached at about \(\rho = 60^\circ\) to finally arrive at HEDYOE with \(\rho = 80^\circ\). The process on the right side of Figure 6 would be similar. This low-energy pathway, far below full rotations around the C-P and P-Ru axes, is corroborated by the experimental sample points in Figure 7. The use of such experimental data to find reaction pathways has been pioneered by Dunitz et al.\(^{23}\)

Whereas in the crystal, the PPh\(_3\) ligand propeller configurations are fixed, in solution, they rapidly interconvert. For the 18 propeller diastereomers, pathway b seems to be the easiest mechanism of interconversion. This discussion concentrated on Phface and did not take into account a detailed consideration of Phedge and Phtrans. In addition, it must be kept in mind that each of the three phenyls has to carry out its duty in the internal stabilization of the PPh\(_3\) propeller.

**Density Functional Theory (DFT) Calculations.** We checked the results, obtained in the analysis of CSD sample points, by DFT calculations\(^{25}\) (RI\(^{25}\)-3LYP\(^{26}\)/def2-TZVP\(^{25b,27}\)). Using the cif files, we calculated the ground-state structures of HEDYIY and HEDYOE. HEDYOE turned out to be more stable than HEDYIY by 2.68 kJ/mol. The energy difference of 2.68 kJ/mol would account for a ratio HEDYIY/HEDYOE = 1:3 at 20 °C. Going from the conformation in the crystal to the conformation in the gas phase, the rotation angle changes for HEDYIY from \(\rho = 37.3\) to 47.4° and for HEDYOE from \(\rho = −28.7\) to −21.6°.

Our sample point analysis had predicted a low-lying transition state for the conversion of Phface of HEDYIY to Phedge of HEDYOE, resulting in the interconversion of the two diastereomers. This low transition state was reached after a counter-clockwise rotation of the PPh\(_3\) ligand in HEDYIY, which moved Phface from its position \(\rho = 37^\circ\) in the crystal to 60° (pathway b). We calculated the relative energies of HEDYIY with the PPh\(_3\) ligand rotated from its gas phase ground state \(\rho = 47.7\) to 50.3° and 59.4°. The relative energies rose from 0 via 0.75 to 4.66 kJ/mol (Figure 8), supporting a low-lying transition state at 60°.

In the sample point analysis, we had assigned a high-lying transition state to a clockwise rotation of Phface from \(\rho = 37.3\) to 0°, which converts Phface of HEDYIY to Phface of HEDYOE (pathway a). The calculation of the relative energies of HEDYIY with the PPh\(_3\) ligand rotated from \(\rho = 47.7\) to 21.9° and 11.1° gave relative energies from 0 via 13.50 to 24.31 kJ/mol (Figure 8). Thus, the transition state of pathway a is much higher than that of pathway b and the results of sample point analysis and DFT calculations are fully in accord. As expected, the relative energies of the transition states are much higher than the ground state energies of HEDYIY and HEDYOE.

**\(\alpha\)- and \(\beta\)-Effects.** In a recent paper, we reported CH/π interactions between cyclopentadienyl and phenyl rings in compounds of type CpM-L-E-Ph (Figure 9, left side), e.g.,

CpMo(CO)\(_2\)-amidinato and -thioamidato complexes.\(^{28}\) These compounds were among the earliest examples, for which CH/π interactions have been observed. The Cp/Ph attraction had been termed the \(\beta\)-phenyl effect because of the \(\beta\)-position of Ph in the ligands.\(^{29}\) In comparison, the Phpph, face-on π-Ar system of the present paper is an \(\alpha\)-phenyl effect.

In new compounds \(\langle R_{\text{Ru}}S_C\rangle: \text{CyRu(2O-1N)PPh}_3\text{PF}_6\) \(\langle R_{\text{Ru}}S_C\rangle: \text{CyRu(1O-2N)PPh}_3\text{PF}_6\) \(\langle 1\rangle, \langle 2\rangle, \text{and} \langle 3\rangle\) and in HEDYIY and HEDYOE, \(\pi\)-interactions are established between Ar and the phenyl ring of the CHMePh substituent, resulting in short (π-Ar)-CH-Ci and (π-Ar)-CH-Cc contacts far below the sum of the van der Waals radii. The dashed lines in Figure 9, right side, show the Cp\(_2\)H\(_2\)/Ph interactions in HEDYIY. An analysis according to ref 26 is given in Table S4 (Supporting Information).

The results in Table S4 reveal interesting differences between the compounds with and without π-stack stabilization. The two compounds \(\langle R_{\text{Ru}}S_C\rangle: \text{CyRu(1O-2N)PPh}_3\text{PF}_6\) \(\langle 3\rangle\) and HEDYOE, lacking π-stacks, have appreciably shorter (π-Ar)-CH-Ci, and (π-Ar)-CH-Cc distances than those in the four compounds containing π-stacks. Obviously, the π-stacks prevent a perfect build-up of the \(\beta\)-CH/π interactions and the better \(\beta\)-CH/π
stabilization seems to be a compensation for the absence of π-Stock formation.

**CONCLUSIONS**

Chiral-at-metal half-sandwich compounds [(π-Ar)LL’MPPPh3] form diastereomers, which differ in the propeller sense of the triphenylphosphine ligand. The inside of the PPh3 ligand is stabilized by a system of attractive CH/π interactions, in which each phenyl ring plays a specific role. One of the phenyl rings orients face-on toward the π-arene ligand, establishing a ubiquitous PPh3 face-π-Ar bonding motif. Interconversion of the propeller diastereomers occurs by a low-energy pathway, which exchanges Phface and Phedge of the diastereomers.

**EXPERIMENTAL SECTION**

**General Methods.** For IR, JASCO FT/IR4100ST was used. For 1H,31P{1H} NMR, Bruker Avance 400 (400/162 MHz, T = 293 K) or Bruker Avance III 500 (500/202 MHz, T = 293 K) were used. Tetramethylsilane was used as the internal standard, and H2PO4 was used as the external standard. For MS, Finnigan MAT 95 (EI, 70 eV) or ThermoQuest Finnigan TSP 7000 was used. All manipulations were carried out in purified nitrogen or argon. The Cambridge Structural Database ver. 5.38 (update May 31, 2017) for the 140 compounds of type [(π-Ar)RuLL’PPh3] was used. The OLEX2 program was used. All structures were solved using Eos and the Programs for Crystallographic Analyses, and ConQuest ver. 1.19 program was used for structural analyses.

**Preparation and Characterization.** (R,Ru)[(S,S)-Cloro[η⁴-1-methyl-4-(1-methylthelyl)benzene][1-[(1-phenylphosphino)iminomethyl]-2-naphthalenolato-κO]-ruthenium, (R,Ru)((S,S)-Cloro[CyRu(2O-1N)Cl]) to a solution of (S)-1-[(1-phenylphosphino)iminomethyl]-2-naphthalenol (300 mg, 0.73 mmol) in dichloromethane (20 mL) was added potassium t-butoxide (98 mg, 0.88 mmol). The solution was stirred for 1 h at room temperature and then cooled to −78 °C. [(η⁴-p-Cymene)RuCl3]Cl2 (250 mg, 0.36 mmol) was added to the cooled solution. The mixture was slowly warmed up to room temperature, stirred for 16 h, and then filtered on a short Celite column. After evaporation of the solvent, the residue was chromatographed on silica gel using EtOAc/hexane as an eluent. A reddish-brown band was collected and evaporated to give (R,Ru)((S,S)-Cloro[CyRu(2O-1N)Cl]). 88:12 as a red powder in 70% yield (280 mg). Mp 125 °C (color changed from red to brown) > 200 °C. IR (KBr): ν 1614 cm⁻¹ (N=C). 1H NMR (293 K, CDCl3, major (R,Ru)-diastereomer, minor (S,S)-diastereomer in brackets, if distinguishable): δ 8.75 (s, 1H, N=CH) [8.39 (s, 1H, N=CH)], 7.69 (d, 1H, JHH = 8.4 Hz, nap-H) [7.83 (d, 1H, JHH = 7.6 Hz, nap-H)], 7.62 (t, 2H, m-Ph-H), 7.56–7.07 (m, 8H, nap-H and Ph-H), 5.96 (q, 1H, JHH = 7.1 Hz, N-CH) [5.73 (q, 1H, JHH = 7.1 Hz, N-CH)], 5.25 (d, 1H, JHH = 6.0 Hz, Cy-H) [5.52 (d, 1H, JHH = 6.4 Hz, Cy-H)], 5.10 (d, 1H, JHH = 6.0 Hz, Cy-H) [5.44 (d, 1H, JHH = 6.4 Hz, Cy-H)], 5.02 (d, 1H, JHH = 5.7 Hz, Cy-H) [5.41 (d, 1H, JHH = 6.4 Hz, Cy-H)], 4.77 (d, 1H, JHH = 5.7 Hz, Cy-H) [5.20 (d, 1H, JHH = 6.4 Hz, Cy-H)], 2.63 (septet, 1H, JHH = 6.8 Hz, ipr-CH3) [2.83 (septet, 1H, JHH = 7.0 Hz, ipr-CH3)], 2.05 (s, 3H, Cy-CH3) [2.13 (s, 3H, Cy-CH3)], 1.81 (d, 3H, JHH = 7.1 Hz, CH3), 1.14 (d, 3H, JHH = 6.9 Hz, ipr-CH3) [1.14 (d, 3H, JHH = 7.0 Hz, ipr-CH3)], 0.98 (d, 3H, JHH = 6.9 Hz, ipr-CH3). MS (ESI, CH3Cl2/MeOH/MeOH/NaOAc): m/z 510 ([CyRu(20-1N)]; 100). Anal. Calcd for C29H38ClNORu: C, 63.90; H, 5.55; N, 2.57. Found: C, 63.90; H, 5.58; N, 2.45.

(R,Ru)((S,S)-Cloro[η⁴-1-methyl-4-(1-methylthelyl)benzene][1-[(1-phenylphosphino)iminomethyl]-2-naphthalenolato-κO]-ruthenium hexafluorophosphate, (R,Ru)((S,S)-Cloro[CyRu(2O-1N)PF6]). To a solution of (R,Ru)((S,S)-Cloro[CyRu(2O-1N)Cl]) (87 mg, 0.16 mmol) in chloroform (20 mL) was added PPh3 (42 mg, 0.16 mmol). The mixture was stirred for 3 h at room temperature. Then, [NH4]PF6 (26 mg, 0.16 mmol) was added while stirring for 12 h. The reaction mixture was filtered on a short Celite column. After evaporation of the solvent, the residue was washed with diethyl ether to give (R,Ru)((S,S)-Cloro[CyRu(20-1N)PF6]). 97:3 in 70% yield (102 mg). Crystalization from dichloromethane afforded orange crystals of pure diastereomer (R,Ru)((S,S)-Cloro[CyRu(2O-1N)PF6]) suitable for X-ray structure analysis. Mp 143 °C (color changed from orange to brown) > 200 °C. IR (KBr): ν 1616 (N=C), 1435 (P-F). 1H NMR (400 MHz, CDCl3, major (R,Ru)-diastereomer, minor (S,S)-diastereomer in brackets, if distinguishable): δ 8.68 (s, 1H, N=CH) [8.90 (s, 1H, N=CH)], 7.59–7.19 (m, 25H, nap-H and Ph-H), 6.93 (d, 1H, JHH = 9.1 Hz, nap-H), 5.56 (q, 1H, JHH = 7.0 Hz, N-CH), 5.49 (d, 1H, JHH = 6.5 Hz, JHH = 1.3 Hz, Cy-H) [6.30 (d, 1H, JHH = 6.0 Hz, Cy-H)], 5.29 (d, 1H, JHH = 6.5 Hz, 6.5 Hz, Cy-H) [6.11 (d, 1H, JHH = 6.0 Hz, Cy-H)], 5.26 (d, 1H, JHH = 6.0 Hz, Cy-H), 4.71 (brd, 1H, JHH = 6.0 Hz, Cy-H), 2.35 (septet, 1H, JHH = 7.0 Hz, ipr-CH) [2.70 (septet, 1H, JHH = 7.0 Hz, ipr-CH)], 1.58 (s, 3H, Cy-CH3) [1.76 (s, 3H, Cy-CH3)], 1.39 (d, 3H, JHH = 7.0 Hz, CH3) [2.09 (d, 3H, JHH = 6.7 Hz, CH3)], 1.07 (d, 3H, JHH = 7.0 Hz, ipr-CH3) [1.15 (d, 3H, JHH = 7.2 Hz, ipr-CH3)], 0.83 (d, 3H, JHH = 7.0 Hz, ipr-CH3) [1.14 (d, 3H, JHH = 7.2 Hz, ipr-CH3)]. 31P{1H} NMR...
(162 MHz, CDCl₃) major (Rₛₛ₋Sₛ) diastereomer, minor (Sₛₛ₋Sₛ) diastereomer in brackets): δ 32.80 (s, 1P, PPh₃), 29.60 (s, 1P, PPh₃) -142.81 (septet, 1P, 1J_F = 713.5 Hz, PF₃). MS (ESI, MeOH): m/z 772 ([CyRu(2O-1N)PPh₃]⁺), 100), 510 ([CyRu(2O-1N)PF₃]⁺), 10. Anal. Calc'd for C₅₇H₄₅F₆NOP₂Ru (916.87): C, 61.57; H, 4.75; N, 1.53. Found: C, 61.53; H, 4.88; N, 1.40.

Crystal structure and relative configuration of dimeric ruthenium complexes with phosphine and phosphite ligands. Angew. Chem. Int. Ed. 2013, 52, 1063-1068.

Crystallographic data of three complexes (Rₛₛ₋Sₛ-[CyRu(1O-2N)Cl], (Rₛₛ₋Sₛ-[CyRu(1O-2N)-PPh₃]PF₆, and (Rₛₛ₋Sₛ-[CyRu(2O-1N)PPh₃]PF₆) 1H NMR spectra and 31P{1H} NMR spectra of the complexes.

Table S1, crystallographic data of three complexes (Rₛₛ₋Sₛ-[CyRu(1O-2N)Cl], (Rₛₛ₋Sₛ-[CyRu(1O-2N)-PPh₃]PF₆, and (Rₛₛ₋Sₛ-[CyRu(2O-1N)PPh₃]PF₆) 1H NMR spectra and 31P{1H} NMR spectra of the complexes; Table S2, rotation angles ρ and angles γ plane Ph/plan π-Ar for the compounds in Table 1; Table S3, rotation angles ρ and angles γ plane Ph/plan π-Ar for the 119 compounds [(π-C₅H₅)Ru(OR)][PF₆], S4, CH/π interactions between π-Ar and Ph of the CHMePh substituent (β-phenyl effect) in compounds [(π-Ar)Ru(O-N)PPh₃]PF₆; Tables S5-S8, computational details (PDF)

Crystallographic data of three complexes (Rₛₛ₋Sₛ-[CyRu(1O-2N)Cl], (Rₛₛ₋Sₛ-[CyRu(1O-2N)-PPh₃]PF₆, and (Rₛₛ₋Sₛ-[CyRu(2O-1N)PPh₃]PF₆) (CIF)

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