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The synthesis and molecular structures of 2,5-diarylpyrroles, $[\mathrm{pyr}^{\mathrm{Ar}_2}]\mathrm{H}$ (Ar = Ph, 2,4-Xyl)

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2,5-Di(2,4-xylyl)pyrrole, $[\mathrm{pyr}^{2,5\text{-}\mathrm{Xyl}_2}]\mathrm{H}$, has been synthesized by reaction of the diketone $[\mathrm{XylC(O)CH}_2]_2$ with $\mathrm{NH}_4\mathrm{OAc}$ in AcOH; the diketone itself is obtained by condensation of XylC(O)Me with $\mathrm{XylC(O)CH}_2\mathrm{Br}$ in the presence of $\mathrm{Ti(OPr}^{\mathrm{i}})_4$. The molecular structures of both $[\mathrm{pyr}^{2,5\text{-}\mathrm{Ph}_2}]\mathrm{H}$ and $[\mathrm{pyr}^{2,5\text{-}\mathrm{Xyl}_2}]\mathrm{H}$ have been determined by single crystal X-ray diffraction, thereby demonstrating that an *ortho* methyl substituent increases the dihedral angle between the aryl and pyrrolyl groups from 14.5° in $[\mathrm{pyr}^{2,5\text{-}\mathrm{Ph}_2}]\mathrm{H}$ to 24.1° in $[\mathrm{pyr}^{2,5\text{-}\mathrm{Xyl}_2}]\mathrm{H}$.

KEY WORDS: pyrroles; interplanar angles; dihedral angles.

Introduction

Although much less ubiquitous than cyclopentadienyl, pyrrolyl ligands $[\mathrm{pyr}^{\mathrm{R}_n}]$(2) have applications in both main group and transition metal chemistry.[1] Pyrrolyl ligands may bind to a metal center by a variety of means, which include η^1-, η^5- and bridging coordination modes.[1,2] Substituents on the pyrrolyl ring play a key role in influencing the binding mode of the ligand, with bulky groups in the 2,5-positions increasing the relative stability of η^5-coordination. We are presently interested in the application of pyrrolyl ligands that feature aryl substituents, and in this paper we report on the synthesis and molecular structures of the pyrrole compounds, $[\mathrm{pyr}^{2,5\text{-}\mathrm{Ar}_2}]\mathrm{H}$ (Ar = Ph, 2,4-Xyl).

Results and Discussion

It has been proposed that bulky substituents in the 2- and 5-positions of the pyrrolyl ligand favor η^5-coordination over η^1-coordination, since the latter coordination mode would force the substituents directly toward the metal center.[1,3,4] For example, the 2,5-di-*t*-butylpyrrolyl ligand $[\mathrm{pyr}^{2,5\text{-}\mathrm{Bu}^t_2}]$ has been crystallographically identified to coordinate in an η^5-mode to elements as diverse as titanium[5] and the lanthanides.[6] In contrast, incorporation of substituents into the ortho positions of aryl groups of 2,5-diarylpyrrolyl ligands $[\mathrm{pyr}^{2,5\text{-}\mathrm{Ar}_2}]$ may, however, have the potential of promoting η^1-coordination as a result of destabilizing a conformation in which the pyrrolyl and aryl rings are coplanar (Fig. 1). For example, the phenyl-substituted complex $[\mathrm{pyr}^{2,5\text{-}\mathrm{Ph}_2}]\mathrm{Zr(NMe}_2)_3$ exhibits η^5-coordination, whereas the xylyl counterpart $[\mathrm{pyr}^{2,5\text{-}\mathrm{Xyl}_2}]\mathrm{Zr(NMe}_2)_3$ exhibits η^1-coordination.[7] To address further this issue, we sought to determine the influence of an ortho methyl substituent on the interplanar angle of the parent

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(2) Pyrrolyl ligands, $(\mathrm{C}_5\mathrm{R}_n\mathrm{H}_{4-n}\mathrm{N})$ are represented by the abbreviation $[\mathrm{pyr}^{\mathrm{R}_n}]$, where the superscript indicates the number and type of substituents.

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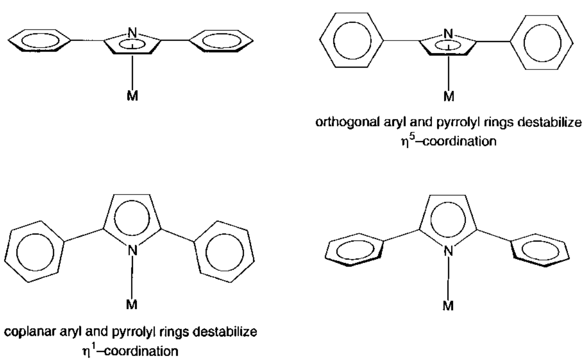
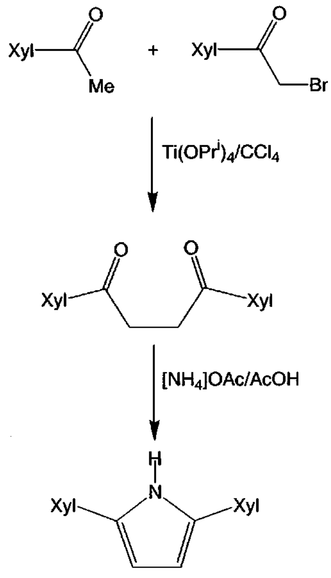


Fig. 1. Relative stability of η^1- and η^5-pyrrolyl coordination as a function of the aryl/pyrrolyl dihedral angle.

pyrrole derivatives, $[\mathrm{pyr}^{2,5\text{-}\mathrm{Ar}_2}]\mathrm{H}$ (Ar = Ph, 2,4-Xyl).

The compound 2,5-diphenylpyrrole $[\mathrm{pyr}^{2,5\text{-}\mathrm{Ph}_2}]\mathrm{H}$ is readily obtained by the reaction of the 1,4-diketone $[\mathrm{PhC(O)CH_2}]_2$ with $\mathrm{NH_4OAc}$ in AcOH.[8] Similarly, the corresponding reaction of $[\mathrm{XylC(O)CH_2}]_2$, obtained by the condensation of XylC(O)Me with $\mathrm{XylC(O)CH_2Br}$ promoted by $\mathrm{Ti(OPr^i)_4}$,[9] with $\mathrm{NH_4OAc}$ in AcOH yields $[\mathrm{pyr}^{2,5\text{-}\mathrm{Xyl}_2}]\mathrm{H}$ (Scheme 1).

The molecular structures of $[\mathrm{pyr}^{2,5\text{-}\mathrm{Ph}_2}]\mathrm{H}$ and $[\mathrm{pyr}^{2,5\text{-}\mathrm{Xyl}_2}]\mathrm{H}$ were determined by single crystal X-ray diffraction, as illustrated in Figs. 2 and 3. Selected bond lengths and angles are listed in Tables 1 and 2. The metrical parameters are unremarkable, with the dimensions of the pyrrole ring being very similar to those of 2,5-di-*tert*-butylpyrrole.[2] For example, the average N—C_α C_α—$\mathrm{C}_{\beta'}$ and C_β—$\mathrm{C}_{\beta'}$ bond lengths of 2,5-di-*tert*-butylpyrrole are 1.377(9) Å, 1.365(5) Å, and 1.420(3) Å, respectively; furthermore, these values are very similar to that of pyrrole itself [1.365(2) Å, 1.357(2) Å, and 1.423(3) Å, respectively].[10] The crystal structures of $[\mathrm{pyr}^{2,5\text{-}\mathrm{Ph}_2}]\mathrm{H}$ and $[\mathrm{pyr}^{2,5\text{-}\mathrm{Xyl}_2}]\mathrm{H}$ differ from pyrrole, however, in terms of their molecular packing. Specifically, pyrrole exhibits intermolecular N—H $\cdots$ π-system hydrogen bonding interactions involving the C_β—C_β bond. Examination of the molecular packing diagrams demonstrates that no such interactions are present in $[\mathrm{pyr}^{2,5\text{-}\mathrm{Ph}_2}]\mathrm{H}$ and $[\mathrm{pyr}^{2,5\text{-}\mathrm{Xyl}_2}]\mathrm{H}$ (Figs. 4 and 5).



Scheme 1.

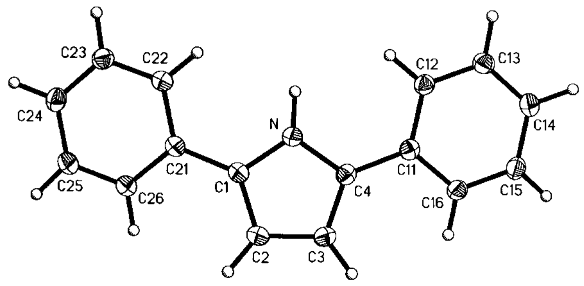


Fig. 2. Molecular structure of $[\mathrm{pyr}^{2,5\text{-}\mathrm{Ph}_2}]\mathrm{H}$.

The most noteworthy aspect of the structures of $[\mathrm{pyr}^{2,5\text{-}\mathrm{Ph}_2}]\mathrm{H}$ and $[\mathrm{pyr}^{2,5\text{-}\mathrm{Xyl}_2}]\mathrm{H}$ in the present study is concerned with the dihedral angle between the pyrrolyl and aryl groups. Specifically, the xylyl rings are twisted out of the pyrrolyl plane

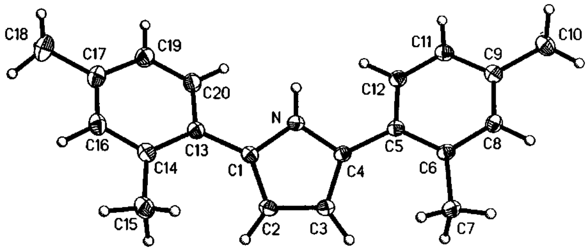


Fig. 3. Molecular structure of $[\mathrm{pyr}^{2,5\text{-}\mathrm{Xyl}_2}]\mathrm{H}$.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[\text{pyrr}^{2,5\text{-Ph}_2}]\text{H}$

Bond lengths			
N—C(1)	1.372(3)	N—C(4)	1.380(3)
C(1)—C(2)	1.384(4)	C(3)—C(4)	1.381(4)
C(2)—C(3)	1.408(4)	N—H(1)	0.99(4)
C(1)—C(21)	1.459(3)	C(4)—C(11)	1.455(4)
Bond angles			
N—C(1)—C(2)	106.5(2)	C(2)—C(3)—C(4)	108.3(3)
C(1)—C(2)—C(3)	108.0(2)	C(1)—N—C(4)	111.0(2)
C(3)—C(4)—N	106.2(2)	C(3)—C(4)—C(11)	130.4(3)
C(2)—C(1)—C(21)	130.0(2)	N—C(4)—C(11)	123.3(2)
N—C(1)—C(21)	123.5(2)	C(4)—C(11)—C(12)	122.7(2)
C(1)—C(21)—C(22)	122.5(2)	C(4)—C(11)—C(16)	120.1(3)
C(1)—C(21)—C(26)	119.9(3)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[\text{pyrr}^{2,5\text{-Xyl}_2}]\text{H}$

Bond lengths			
N—C(1)	1.379(2)	N—C(4)	1.380(2)
C(1)—C(2)	1.378(2)	C(3)—C(4)	1.379(2)
C(2)—C(3)	1.402(2)	N—H(1)	0.86(2)
C(1)—C(13)	1.465(2)	C(4)—C(5)	1.470(2)
Bond angles			
N(1)—C(1)—C(2)	105.6(1)	C(1)—C(2)—C(3)	108.7(1)
C(2)—C(3)—C(4)	108.4(1)	C(3)—C(4)—N	105.7(1)
C(1)—N—C(4)	111.5(1)	C(2)—C(1)—C(13)	133.8(1)
C(3)—C(4)—C(5)	133.9(1)	N—C(1)—C(13)	120.6(1)
N—C(4)—C(5)	120.3(1)	C(1)—C(13)—C(14)	123.4(1)
C(4)—C(5)—C(6)	123.2(1)	C(1)—C(13)—C(20)	119.0(1)
C(4)—C(5)—C(12)	119.3(1)		

of $[\text{pyr}^{2,5\text{-Xyl}_2}]\text{H}$ (24.1°)(3) to a greater degree than are the phenyl rings of $[\text{pyr}^{2,5\text{-Ph}_2}]\text{H}$ (14.5°)(4) as illustrated in Fig. 6; for comparison, the dihedral angle in simple polyphenyl complexes is ca. 13.3°.[11] Thus, steric interactions between the *ortho* methyl groups and the β-hydrogens of the pyrrolyl ring increase the orthogonality of the aryl and pyrrolyl groups, but the steric interaction is insufficient to overcome the completely planar structure that is favored by electronic delocalization across the three aromatic rings.

Experimental Section

General Considerations

NMR spectra were recorded on Bruker Avance 300wb DRX, Bruker Avance 400 DRX, and Bruker Avance 500 DMX spectrometers. ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) relative to SiMe_4 ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity or the ^{13}C resonances, respectively. All coupling constants are reported in hertz (Hz). Mass spectra were obtained using a JEOL LC Mate mass spectrometer in APCI+ ionization mode using a methanol/water solution (80/20). C, H, and N elemental analyses

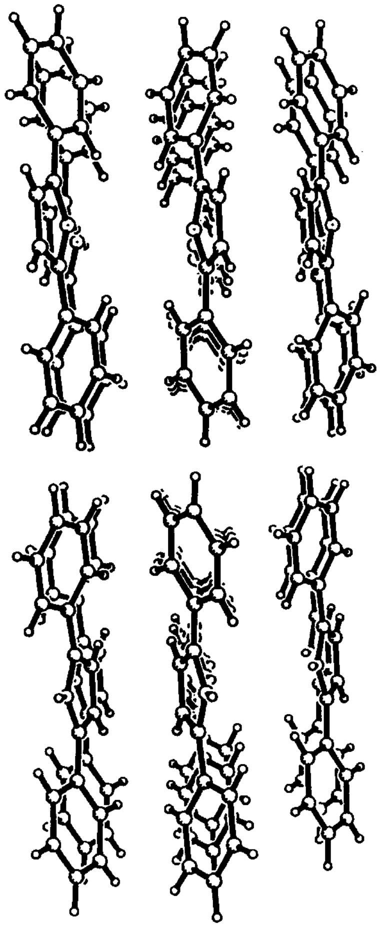


Fig. 4. Packing diagram of $[\text{pyr}^{2,5\text{-Ph}_2}]\text{H}$ (down *b* axis).

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(3) The individual dihedral values for $[\text{pyr}^{2,5\text{-Xyl}_2}]\text{H}$ are 21.5° and 26.7°.

(4) The individual dihedral values for $[\text{pyr}^{2,5\text{-Ph}_2}]\text{H}$ are 13.7° and 15.2°.

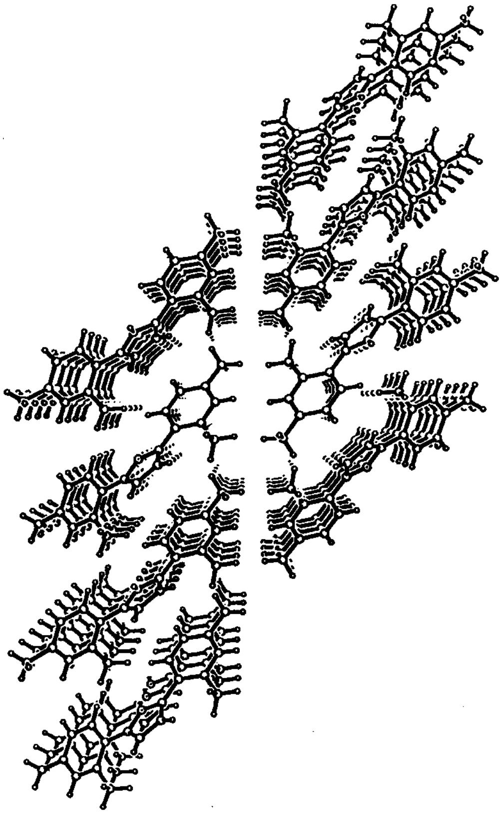

Fig. 5. Packing diagram of [pyr$^{2,5\text{-Xyl}_2}$]H (down *b* axis).

were measured using a Perkin-Elmer 2400 CHN Elemental Analyzer. 2,4-Dimethylacetophenone [(2,4-Xyl)C(O)Me] was obtained from Aldrich, 2-bromo-2′,4′-dimethylacetophenone [(2,4-Xyl) C(O)CH_2Br] was obtained from Maybridge Chemical Company, Cornwall, UK (*via* Ryan Scientific), and Ti(OPr^i)$_4$ was obtained from Aldrich. [pyr$^{2,5\text{-Ph}_2}$]H was prepared by the literature method.[8]

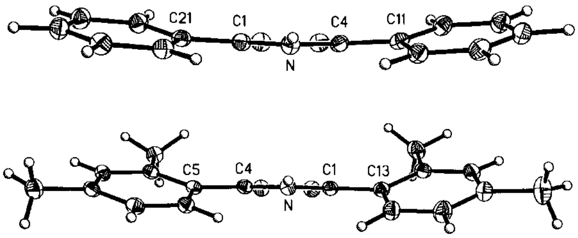

Fig. 6. Comparison of the aryl/pyrrolyl dihedral angles of [pyr$^{2,5\text{-Ph}_2}$]H (upper) and [pyr$^{2,5\text{-Xyl}_2}$]H (lower).

Synthesis of [XylC(O)CH_2]$_2$

A mixture of 2,4-XylC(O)Me (9.8 g, 66 mmol) and (2,4-Xyl)C(O)CH_2Br (10.0 g, 44 mmol) in dry CCl_4 (50 mL) was treated with freshly distilled Ti(OPr^i)$_4$ (20.8 mL, 20.0 g, 70 mmol) and stirred at room temperature under an inert atmosphere for 1 h. The mixture was allowed to stand for 1 week, over which period white crystals were deposited. The flask was cooled to 0°C, and the product was isolated by filtration, washed successively with cold (0°C) CCl_4, cold (0°C) HCl_{aq} (10%), and cold (0°C) methanol, and dried in vacuo, giving [XylC(O)CH_2]$_2$ (4.6 g, 35%—unoptimized). Analysis calcd. for $C_{20}H_{22}O_2$: C, 81.6%; H, 7.6%. Found: C, 79.8%; H, 7.6%. LC/MS(MeOH/H_2O): $m/z = 295.4$ (MH^+, 100%). ^{1}H NMR ($CDCl_3$): 2.34 [s, 2 C$\underline{H}_3$ of 2 Xyl], 2.46 [s, 2 C$\underline{H}_3$ of 2 Xyl], 3.30 [s, (C$\underline{H}_2$)$_2$], 7.01–7.08 [m, 4 *m*-$\underline{H}$ of 2 Xyl], 7.72 [d, $^3J_{\text{H-H}} = 7.8$, 2 *o*-$\underline{H}$ of 2 Xyl]. ^{13}C{^{1}H} NMR ($CDCl_3$): 21.4 [2 $\underline{C}H_3$ of 2 Xyl], 21.5 [2 $\underline{C}H_3$ of 2 Xyl], 35.4[($\underline{C}H_2$)$_2$], 126.3 [2 C of 2 Xyl (CH)], 129.1 [2 C of 2 Xyl (CH)], 132.8 [2 C of 2 Xyl (CH)], 134.8 [2 C of 2 Xyl (quarternary)], 138.6 [2 C of 2 Xyl (quarternary)], 141.8 [2 C of 2 Xyl(quarternary)], 202.0 [$\underline{C}$O].

Synthesis of [pyr$^{2,5\text{-Ph}_2}$]H

A mixture of [XylC](O)CH_2]$_2$ (4.5 g, 15 mmol) and NH_4OAc (15.9 g, 206 mmol) was refluxed in AcOH (50 mL) overnight under an inert atmosphere. The reaction mixture was allowed to cool to room temperature and poured into ice-cold water (1.5 L). The mixture was stirred for several hours, after which the white precipitate was isolated by filtration, washed with cold water, and dried in vacuo giving [pyr$^{2,5\text{-Xyl}_2}$]H (3.4 g, 81%). Analysis calcd. for $C_{20}H_{21}N$: C, 87.2%; H, 7.7%; N, 5.1%. Found: C, 87.4%; H, 7.8%; N, 4.6%. LC/MS(MeOH/H_2O): $m/z = 276.4$ (MH^+, 100%). ^{1}H NMR ($CDCl_3$): 2.33 [s, 2 *p*-C$\underline{H}_3$ of 2 Xyl], 2.47 [s, 2 *o*-C$\underline{H}_3$ of 2 Xyl], 6.36 [d, $^4J_{\text{H-H}} = 2.7$, 2 H of N ($C_4Xyl_2\underline{H}_2$), 7.04 [d, $^3J_{\text{H-H}} = 7.8$, 2 m-$\underline{\text{H}}$ of 2 Xyl], 7.08 [s, 2 m-$\underline{\text{H}}$ of Xyl], 7.28 [d, $^3J_{\text{H-H}} = 7.8$, 2 o-$\underline{\text{H}}$ of 2 Xyl], 8.21 [br s, N$\underline{\text{H}}$]. ^{13}C{^{1}H} NMR ($CDCl_3$): 21.0 [2 p-$\underline{\text{C}}H_3$ of 2 Xyl], 21.3 [2 o-$\underline{\text{C}}H_3$ of 2 Xyl], 109.4 [2 C of N($\underline{\text{C}}_4Xyl_2H_2$) (CH)], 126.8 [2 m-C of 2 Xyl (CH)], 127.7 [2 o-C of 2 Xyl (CH)], 129.9 [2 *ipso*-C of 2 Xyl (quarternary)], 131.4 [2 C of N($\underline{\text{C}}_4Xyl_2H_2$ (quarternary)], 131.9 [2 m-C of 2 Xyl (CH)], 134.7 [2 o-C of 2 Xyl (quarternary)], 136.4 [2 p-C of 2 Xyl (quarternary)].

X-ray Structure Determinations

Crystals of [pyr$^{2,5\text{-}Ph_2}$]H and [pyr$^{2,5\text{-}Xyl_2}$]H were obtained from benzene and $CDCl_3$, respectively. X-ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector, and crystal data, data collection, and refinement parameters are summarized in Table 3. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 5.03).[12] All hydrogen atoms were located and refined.

Table 3. Crystal, Intensity Collection, and Refinement Data

	[pyr$^{2,5\text{-}Ph_2}$]H	[pyr$^{2,5\text{-}Xyl_2}$]H
Lattice	Monoclinic	Monoclinic
Formula	$C_{16}H_{13}N$	$C_{20}H_{21}N$
CCDC deposit no.	CCDC-1003/6141	CCDC-1003/6142
Formula weight	219.17	275.38
Space group	$P2_1/n$	$C2/c$
a/Å	7.475(1)	47.431(3)
b/Å	5.967(1)	5.2104(4)
c/Å	26.301(5)	12.7162(10)
β/°	93.715(4)	97.817(1)
V/Å^3	1170.6(4)	3113.4(4)
Z	4	8
Temperature (K)	233	243
Radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.244	1.175
μ (Mo Kα), mm^{-1}	0.072	0.068
θ max, deg.	28.3	28.3
Total no. of data	7974	9807
No. of data	2726	3502
R_{merge}	0.0682	0.0276
No. of parameters	207	275
R_1	0.0774	0.0458
wR_2	0.2115	0.0993
GOF	1.070	1.085

Conclusions

2,5-Di(2,4-xylyl)pyrrole, [pyr$^{2,5\text{-}Xyl_2}$]H, has been synthesized by reaction of the diketone $[XylC(O)CH_2]_2$ with NH_4OAc in AcOH. The molecular structures of [pyr$^{2,5\text{-}Ph_2}$]H and [pyr$^{2,5\text{-}Xyl_2}$]H indicate that an *ortho* methyl substituent increases the dihedral angle between the aryl and pyrrolyl groups from 14.5° in [pyr$^{2,5\text{-}Ph_2}$]H to 24.1° in [pyr$^{2,5\text{-}Xyl_2}$]H.

Acknowledgment

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