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Zirconium Complexes Supported by an *N*-Perfluoro-Arylated Diamidopyridyl Ligand: Synthesis of Hydrazinediido Complexes

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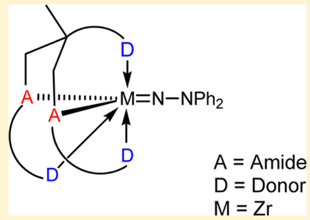
Supporting Information

ABSTRACT: The *N*-perfluoro-phenylated pyridyldiamine $H_2N_2^{PFP}N_{py}$ (**1**) has been prepared by a palladium-catalyzed coupling of hexafluorobenzene and the diamine $(H_2NCH_2)_2C(CH_3)(2\text{-}C_5H_4N)$ using the palladacycle *trans*-di(*μ*-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]palladium(II) as catalyst. Reactions of $H_2N_2^{PFP}N_{py}$ and $Zr(NMe_2)_4$ at room temperature or 90 °C led to the complexes $[(N^{PFP}N_2^{TFAP}N_{py})ZrF(NMe_2)]$ (**2**) and $[(N_2^{TFAP}N_{py})ZrF_2]$ (**3**) in which one or two dimethylamido groups replaced one or two ortho fluorine atoms of the pentafluorophenyl groups in the ligand. Reaction of Me_3SiX (X = Cl, I) with $[(N_2^{TFAP}N_{py})ZrF_2]$ (**3**) resulted in the formation of mixed halogenated complexes $[(N_2^{TFAP}N_{py})ZrFI]$ (**4**) and $[(N_2^{TFAP}N_{py})ZrFCl]$ (**5**) in which the axially bound fluorido ligand is substituted. Reaction of $[(N_2^{TFAP}N_{py})ZrF_2]$ (**3**) with $LiNHNPh_2$ afforded the monohydrazido(1−) complex $[(N_2^{TFAP}N_{py})ZrF(NHNPh_2)]$ (**6**) which was converted to the dimeric fluoro-potassium bridged hydrazinediido complex $[Zr(N_2^{TFAP}N_{py})FNNPh_2K]_2$ (**7**) using KHMDS. The corresponding reaction with LiHMDS yielded the monomeric, donor free complex $[Zr(N_2^{TFAP}N_{py})NNPh_2]$ (**8**).



■ INTRODUCTION

The choice of the appropriate ancillary ligand is crucial for controlling the reactivity of a metal complex, in particular for the stabilization of reactive molecular fragments in the coordination sphere of a metal. This applies both to the development of new molecular catalysts and to the stabilization of reactive molecular fragments at the metal with the aim of gaining an understanding of the key active species and intermediates involved in catalytic reactions. For complexes of high-valent Lewis acidic early transition metals polydentate amido ligands have found widespread application in this context.[1] These not only shield and thus protect a well-defined sector of the coordination sphere but also predefine the structures of the "reactive sector". For the group 4 metal, diamido-donor ligands,[2] in which the two negatively charged amido groups are combined with a neutral ligating unit, have proved to be particularly suited for the synthesis of complexes containing reactive M═N bonds.[3]

In particular, the tridentate diamidopyridyl ligand $[N_2^{PFP}N_{py}]^{2-4}$ has given rise to a rich organometallic chemistry of group 4 metal imido and hydrazido complexes and their derivatives.[3] Their characteristic M═N bond reactivity arises from the high polarity of this unit compared to the transition metals in middle of the d-block.[5] In order to raise the Lewis acidity of the metal center we became interested in the possibility of preparing a diamidopyridyl ligand of this type bearing pentafluorinated aryl groups. Given previous reports of the chemistry of *N*-fluoroarylated amido compounds,[6−8] we expected reactive behavior which differed from that of the silylated and arylated diamidopyridyl ligands studied to date.

In this work we report the synthesis of a pentafluorophenyl substituted $[N_2^{R}N_{py}]^{2-}$ ligand, its transformation upon reaction with $[Zr(NMe_2)_4]$, and the stepwise synthesis of hydrazinediido−zirconium complex. Interest in transition metal hydrazides has been due to the role they are thought to play in the stoichiometric and catalytic reduction of dinitrogen to ammonia.[9] In contrast to group 6 metals, the chemistry of group 4 metal hydrazinediido complexes has only been studied systematically during the past decade and has given rise to a variety of stoichiometric and catalytic reaction patterns.[10,11]

■ RESULTS AND DISCUSSION

Synthesis of the *N*-Pentafluorophenylated Protioligand $H_2N_2^{PFP}N_{py}$ (1). Reaction of the diamine $(H_2NCH_2)_2C(CH_3)(2\text{-}C_5H_4N)$[4b] ("$H_2N_2^{H}N_{py}$") and hexafluorobenzene in the presence of K_2CO_3, as had been described previously by Schrock and co-workers[6] for the synthesis of a tris(*N*-pentafluorophenylated) triaminoamine ligand, did not result in the formation of the target product. We therefore chose a Buchwald−Hartwig-type amination[12] to couple the aryl groups to the amine nitrogen atoms. Since the application of the most widely employed catalyst system, the combination of $Pd_2(dba)_3$ and *rac*BINAP, proved not to be successful for the coupling of bromopentafluorobenzene and $(H_2NCH_2)_2C(CH_3)(2\text{-}C_5H_4N)$,[13] we tested the palladacycle *trans*-di(*μ*-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]palladium(II) developed by Beller and Herrmann as precatalyst.[14] Unexpectedly, the reaction of the diamine with bromopentafluorobenzene resulted in a product mixture because both carbon−bromine and carbon−fluorine bond activation occurred. When hexafluorobenzene was used instead, the desired protioligand $H_2N_2^{PFP}N_{py}$ (**1**) was obtained in moderate yields (37%, Scheme 1), the major side

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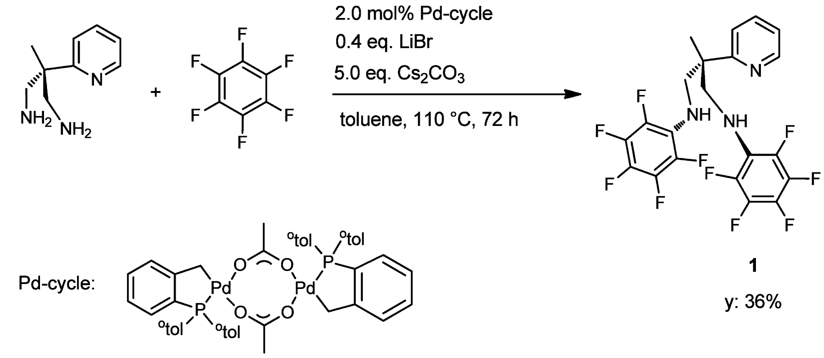
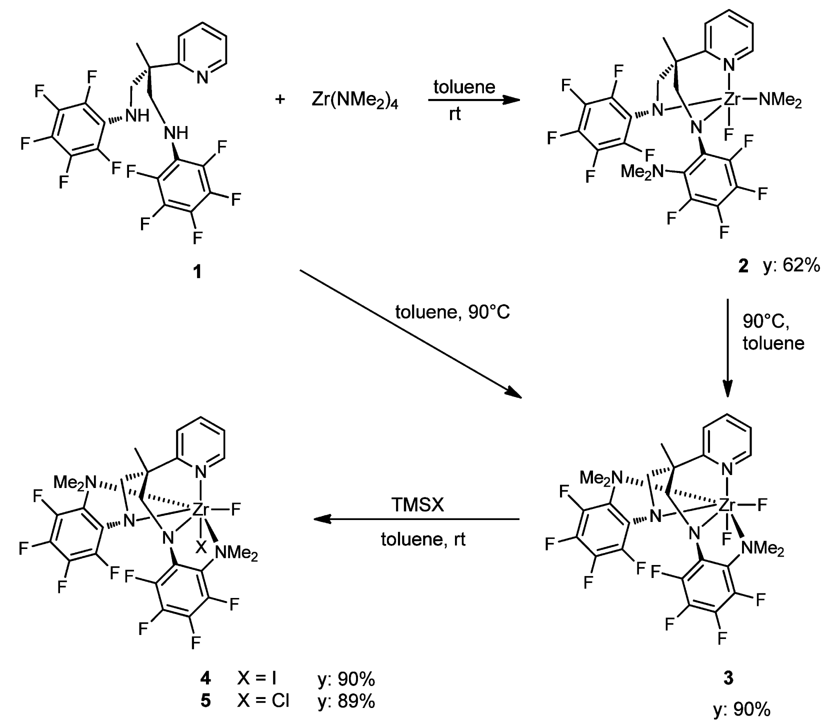
Scheme 1. Synthesis of the Pentafluorinated Ligand $H_2N_2^{PFP}N_{py}$ (1)



Scheme 2. Ortho Fluorido/Amido Exchange in the Ancillary Diamidopyridyl Ligand 1 upon Reaction with $[Zr(NMe_2)_4]$



product being the mono pentafluorophenylated compound which could be recycled. This is a relatively rare case in which palladium-catalyzed C−N coupling is carried out with the aryl fluoride.[15] The infrared spectra of the ligand $H_2N_2^{PFP}N_{py}$ (**1**) as well as of the complexes discussed below display strong bands at ν = 800 cm^{-1} to 1200 cm^{-1}, respectively, which are due to the C−F vibrations.[16]

Reaction of $H_2N_2^{PFP}N_{py}$ (1) with $[Zr(NMe_2)_4]$: Transfer of a Me_2N Group to the Ortho Position of the *N*-C_6F_5 Rings. The reaction of $H_2N_2^{PFP}N_{py}$ (**1**) and $[Zr(NMe_2)_4]$ at room temperature afforded $[(N_2^{PFP}N_2^{TFAP}N_{py})ZrF(NMe_2)]$ (**2**) as a yellow product in moderate yield. The ^{1}H and ^{19}F NMR spectra indicate a nonsymmetrical complex, which is reflected in the observation of eight signals in the ^{19}F NMR spectrum, seven in the aromatic region (−145 ppm to −180 ppm) and one at +72 ppm, indicating a Zr-bound fluorine. This can be explained by the exchange of one of the four ortho fluorine atoms in the *N*-C_6F_5 rings by a dimethylamido group originating from the tetraamido zirconium starting material. This assignment is also supported by the ^{1}H NMR spectrum showing two separate singlet resonances for both methyl groups of the coordinating dimethylamido unit and one singlet with an integral of six for the freely rotating dimethylamino group of the ligand. An exchange of this type was first reported by Schrock and co-workers for a related molybdenum complex[7a] and has been reported since for several other systems.[7,8] Upon heating compound **2** to 90 °C for six days the formation of the difluorido complex $[(N_2^{TFAP}N_{py})ZrF_2]$ **3** was observed (Scheme 2). Complex **3** could also be prepared directly by adding ligand $H_2N_2^{PFP}N_{py}$ (**1**) to $[Zr(NMe_2)_4]$ followed by application of the same reaction conditions.

The ^{19}F NMR spectrum of **3**, displaying four signals in the aromatic region (−150 ppm to −177 ppm) as well as two singlets at 72.5 ppm and 102.5 ppm, was consistent with a C_s-symmetric compound. An X-ray diffraction study revealed that two ortho fluorine atoms of the aryl rings had been replaced by dimethylamido groups. The molecular structure of 7-fold coordinated complex **3** is shown in Figure 1 along with selected bond lengths and angles.

The coordination geometry is best described as distorted pentagonal bipyramidal with the amido nitrogen atoms and the dimethylamino groups of the *N*-aryl rings of the ancillary ligand

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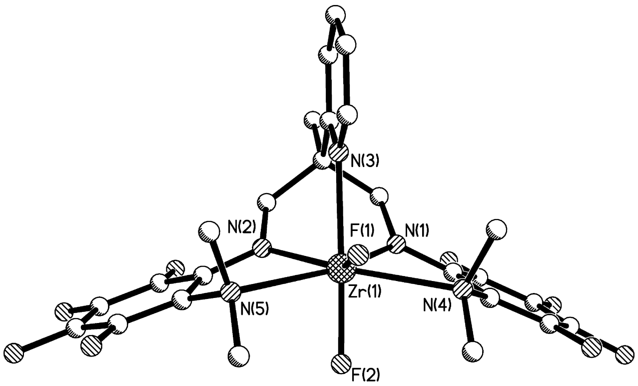


Figure 1. Molecular structure of complex **3**. Selected bond lengths (Å) and angles (deg): Zr(1)−N(1)/N(2) = 2.161(4)/2.152(4), Zr(1)−N(3) = 2.370(4), Zr(1)−N(4)/N(5) = 2.507(4)/2.529(4), Zr(1)−F(1)/F(2) = 1.978(2)/1.957(3); F(2)−Zr(1)−F(1) = 102.6(1), F(2)−Zr(1)−N(3) = 177.2(1); N(4)−Zr(1)−N(5) = 135.6(1). Hydrogen atoms are omitted for clarity.

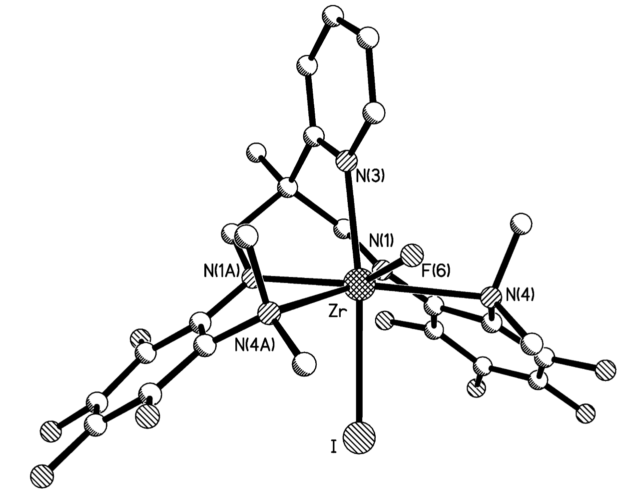


Figure 2. Molecular structure of complex **4**. Selected bond lengths (Å) and angles (deg): Zr−N(1) = 2.1320(13), Zr−N(3) = 2.3321(18), Zr−N(4) = 2.5262(13), Zr−F(6) = 1.974(1), Zr−I = 2.8951(2); F(6)−Zr−I = 110.75(4), N(3)−Zr−I = 167.96(4); N(4A)−Zr−N(4) = 132.05(6). Hydrogen atoms are omitted for clarity.

occupying four equatorial positions. The Zr(1)−N(1)/N(2) bonds are slightly longer (by 0.1−0.2 Å) than in related complexes with methyl-substituted aryl rings,[11g,13a] which can be explained by the electron withdrawing effect of the fluorine substituents. The pyridyl unit of the $N_2^{TFAP}N_{py}$ ligand and one fluorido ligand occupy the axial sites. The Zr−N(3) and the Zr−F bond lengths are in good agreement with those reported in literature.[7,8]

Halide exchange in **3** was attempted by reaction with a slight excess of trimethylsilyl chloride or trimethylsilyl iodide (Scheme 2).[17] In both cases only the mixed halogenated complexes were isolated in which the axially bonded fluorido ligand was replaced by the chloride or iodide. Even a large excess of the trimethylsilyl halide reagent did not result in the replacement of the equatorially bound fluorine atom as demonstrated by ^{19}F NMR spectroscopy (in both reactions only one signal between 90 ppm and 105 ppm corresponding to one zirconium bound fluorine atom was observed).

Single crystals suitable for X-ray diffraction were obtained from both complexes $[(N_2^{TFAP}N_{py})ZrFI]$ (**4**) and $[(N_2^{TFAP}N_{py})ZrFCl]$ (**5**) (see Supporting Information). The general structural features of both complexes are very similar, including C_s molecular symmetry. The molecular structure of $[(N_2^{TFAP}N_{py})ZrFI]$ (**4**) is shown in Figure 2. The zirconium is 7-fold coordinated by all nitrogen atoms of the facially coordinating diamidopyridyl ligand including the dimethylamino groups and both halogenides. The axial positions are occupied by the pyridine nitrogen of the ancillary ligand and the iodine atom (respectively the chlorine atom in **5**), the "trans" angle differing significantly from linearity (N(3)−Zr−I 167.96(4)° and N(3)−Zr−Cl 169.06(4)°, respectively).

Synthesis and Structural Characterization of Hydrazido−Zirconium Complexes. The synthesis of hydrazinediido zirconium complexes stabilized by the diamidopyridyl ligand with amido *N*-aryl substituents has been achieved by addition of the corresponding hydrazine to a solution of bisamido complex $[(N_2^{Xyl}N_{py})Zr(NMe_2)_2]$ along with an excess of 4-dimethylaminopyridine (DMAP).[11h,i] Herein we describe the synthesis of hydrazinediido complexes containing the *o*-NMe_2 substituted *N*-fluoroarylated ligand described in this work. Reaction of the difluorido complex $[(N_2^{TFAP}N_{py})ZrF_2]$ (**3**) with 1 molar equiv of $LiNHNPh_2$ selectively led to one of the possible isomers of the fluorohydrazido(1−) complex (**6**) (Scheme 3).

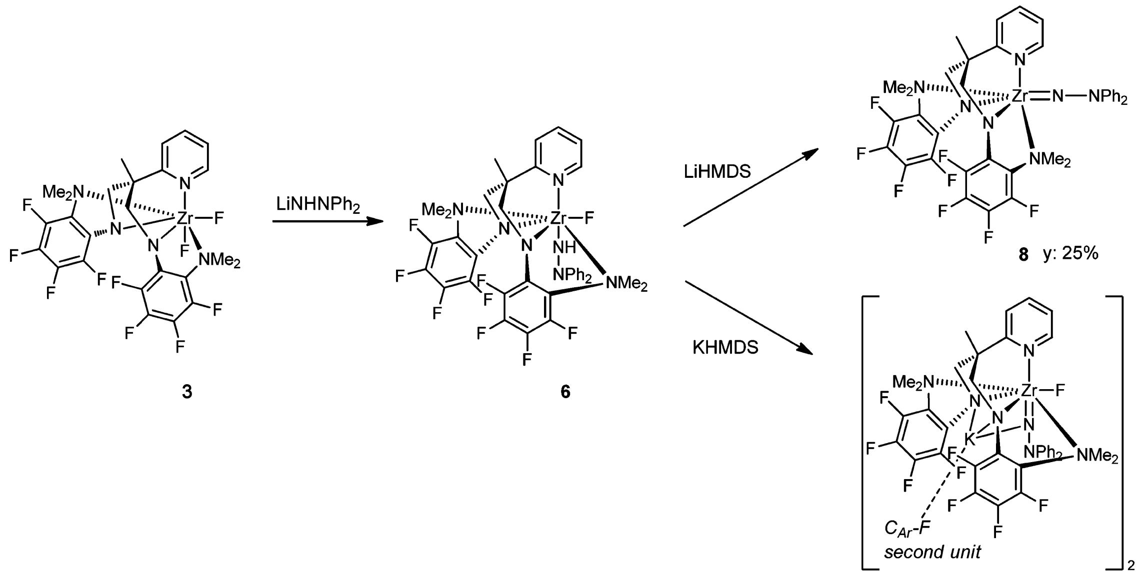
The ^1H NOESY NMR spectrum of **6** revealed cross relaxation between the N*H* proton and the dimethylamino groups at the aryl substituents of the ligand. Furthermore no cross relaxation was observed between the N*H* proton and the hydrogen atoms of the pyridyl fragment of the ligand. This pattern indicates an axial coordination of the hydrazido(1−) fragment as depicted in Scheme 3.

Conversion of the hydrazido(1−) zirconium complex **6** to a hydrazinediido complex was attempted by reaction with potassium hexamethyldisilazide in benzene. In view of the peripheral Me_2N-donor functions in the supporting ligand, no additional neutral donor was added. Although the ^1H NMR spectrum indicated abstraction of the N*H* proton by the base, the ^{19}F NMR spectrum of the isolated product **7** was consistent with the presence of a fluoride ligand bonded to Zr. An X-ray diffraction study revealed a dimeric structure in which the two zirconium complex units are formally KF adducts, in which the potassium cations associated with one of the hydrazido units are coordinated by the fluoraryl rings of the other complex fragment. The molecular structure of **7** is depicted in Figure 3, along with selected bond lengths and angles.

Coordination of each Zr atom is 7-fold by the diamidopyridyl ligand (including the dimethylamino groups), the hydrazinediido unit, and one fluorido atom. The molecular structure is therefore approximately pentagonal bipyramidal with the pyridyl fragment of the ligand and the near-linear hydrazinediido ligand occupying the axial positions. The Zr−N(6) and the N(6)−N(7) bond lengths are in good agreement with those found for other zirconium hydrazinediido complexes.[11] The two amido and the two dimethylamine nitrogen atoms as well as the remaining fluorido ligand are coordinated in the equatorial sites. The Zr−N(1)/N(2) bond lengths are longer [up to 0.2 Å] than in the halogenated complexes **3**−**5**, indicating a weaker coordination of the ligand to the zirconium atom.

It did not prove possible to induce KF elimination from compound **7**, in order to obtain the salt-free hydrazinediido complex, either by extended heating in toluene or K^+

Scheme 3. Synthesis of $\{N_2^{TFAP}N_{py}\}$ Zirconium Hydrazido Complexes



complexation with crown ethers or cryptants. However, reacting the hydrazido(1−) zirconium complex **6** with 1 equiv of lithium hexamethyldisilazide yielded the monomeric hydrazinediido complex **8** directly, the complete dehydrohalogenation being readily followed by ^{1}H and ^{19}F NMR spectroscopy. This may be due to the greater Lewis acidity of Li^+ compared to K^+ and the ability of the former to assist fluoride abstraction. Notably, an additional donor molecule like pyridine, hitherto employed in all isolated zirconium hydrazinediides, is not required.

The molecular structure of **8**, as determined by single crystal X-ray diffraction, is depicted in Figure 4. The zirconium atom is 6-fold coordinated, with five coordination sites being occupied by the diamidopyridyl ligand including the dimethylamino groups and the remaining position by the hydrazinediido fragment. In contrast to previously reported systems featuring an arylated diamidopyridyl ligand, the hydrazinediido ligand occupies an equatorial site which we attribute to the geometric constraints imposed by the pentadentate amido-donor ligand.[11j,k] The Zr−N(6) bond length and the Zr−N(6)−N(7) angle are in good agreement with those of other hydrazinediido zirconium complexes.[18] The binding of the dimethylamino groups to the zirconium is stronger compared to the complexes discussed so far, as reflected in the shorter Zr(1)−N(4)/N(5) bonds, and may result from the lower coordination number of six (Zr−N(4)/N(5) values: **3**, 2.507(4)/2.529(4); **4**, 2.526(1); **5**, 2.481(1); **7**, 2.522(1)/2.565(2); **8**, 2.436(1)/2.454(1)). Notably, one of the dimethylamino groups occupies an axial position, although the structural constraints of the ligand backbone lead to a considerable deviation of the "trans" angle N(4)−Zr−N(3).

■ CONCLUSION

In this work we have reported a new access to pentafluorophenyl substituted amine ligands using Pd coupling with hexafluorobenzene and *trans*-di(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]palladium(II) as catalyst. Moreover, the resulting protioligand $H_2N_2^{PFP}N_{py}$ (**1**) was subsequently transformed to a potentially pentacoordinate supporting ligand by reaction with $[Zr(NMe_2)_4]$. These additional donor functions proved to be important in the dehydrohalogenation of the monohydrazido(1−) complex **6** using LiHMDS giving the first donor free hydrazinediido zirconium complex. Further exploitation of this type of ancillary ligand is part of current and future work in our lab.

■ EXPERIMENTAL SECTION

General Experimental Procedures. All manipulations of air and moisture sensitive materials were carried out under an inert atmosphere of dry argon [argon 5.0] using standard Schlenk and glovebox techniques [glovebox: Unilab-2000, M. Braun]. Argon was dried over phosphorus pentoxide [Sicapent, Merck Chemicals] before use. Solvents were predried over molecular sieves and dried over Na/K alloy [pentane, diethyl ether] or K [toluene, THF, hexane, benzene] and distilled, or dried over activated alumina columns using a solvent purification system [M. Braun SPS 800] and stored over potassium or sodium mirrors [THF] in Teflon valve ampules. Deuterated solvents were purchased from Deutero GmbH, dried over K [benzene-d_6, THF-d_8], vacuum distilled, and stored in Teflon valve ampules under argon. Samples for NMR spectroscopy were prepared under argon in 5 mm Wilmad tubes equipped with J. Young Teflon valves. NMR spectra were recorded on Bruker DRX200, Bruker Avance II 400, or Bruker Avance III 600 (with QNP-CryoProbe) NMR spectrometers. NMR spectra are quoted in ppm and were referenced internally relative to the residual protio-solvent [^{1}H] or solvent [^{13}C] resonances or externally to $^{15}NH_3$ [^{15}N] and $C^{19}FCl_3$ [^{19}F]. Where necessary, NMR assignments were confirmed by the use of two-dimensional $^{1}H-^{1}H$, $^{1}H-^{19}F$, and $^{1}H-^{13}C$ correlation experiments. Infrared spectra of Nujol mulls were recorded on a Varian 3100 FT-IR. Elemental analyses were recorded by the analytical service of the Heidelberg Chemistry Department. The ligand precursor $(H_2NCH_2)_2C(CH_3)(2\text{-}C_5H_4N)$ ("$H_2N_2^{H}N_{py}$") was prepared according to a published procedure.[4b] Ph_2NNH_2 was prepared from the hydrochloride salt purchased from Acros, and purified by column chromatography (over silica, dichloromethane) prior to use. $LiNHNPh_2$ was synthesized according to the literature.[19] All other reagents were obtained from commercial sources [Acros/Thermo Fischer, ABCR/Strem and Sigma-Aldrich] and used as received unless explicitly stated. Trimethylsilyl reagents were degassed and stored in a glovebox.

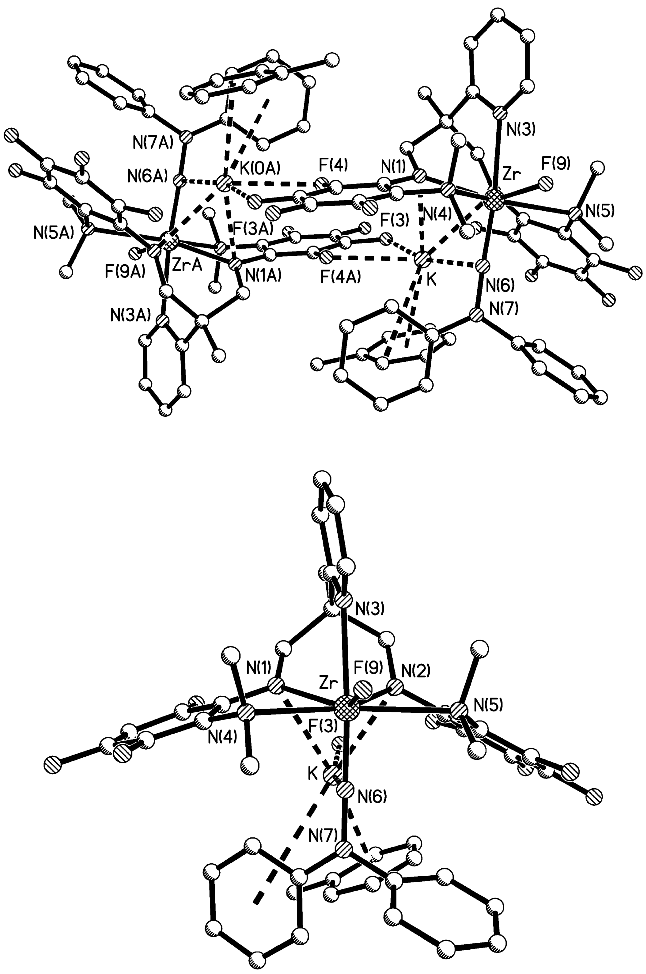


Figure 3. Molecular structure of complex **7**. Top: The dimer $[Zr(N_2^{TFAP}N_{py})FNNPh_2K]_2$. Bottom: A monomeric complex unit. Selected bond lengths (Å) and angles (deg): Zr–N(1)/N(2) = 2.722(1)/2.242(1), Zr–N(4)/N(5) = 2.522(1)/2.565(1), Zr–N(3) 2.492(1), Zr–N(6) = 1.896(1), N(6)–N(7) = 1.386(2), K–F(3) = 2.730(1); N(7)–N(6)–Zr = 175.0(1), N(6)–Zr–N(3) = 172.94(5), N(4)–Zr–N(5) = 143.44(4), F(4A)–K–N(1) = 93.80(3). Hydrogen atoms are omitted for clarity.

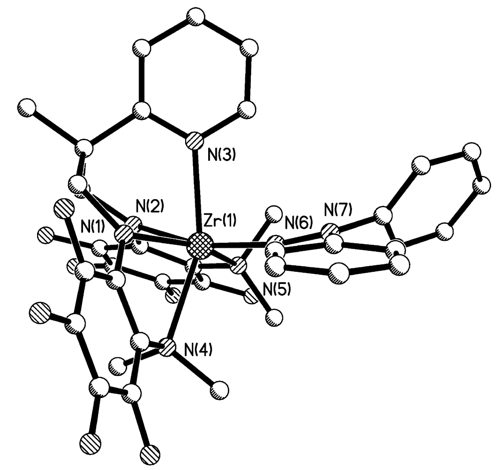


Figure 4. Molecular structure of complex **8**. Selected bond lengths (Å) and angles (deg): Zr(1)–N(1)/N(2) = 2.157(1)/2.251(1), Zr(1)–N(4)/N(5) = 2.436(1)/2.454(1), Zr(1)–N(6) = 1.895(1), N(6)–N(7) = 1.379(2); N(7)–N(6)–Zr(1) = 169.7(1), N(3)–Zr(1)–N(4) = 150.35(5), N(3)–Zr(1)–N(5) 104.65(5), N(6)–Zr(1)–N(3) = 90.47(6).

Preparation of Compounds. *$H_2N_2^{PFP}N_{py}$ (1).* Under an atmosphere of argon to a solution of *trans*-di(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]palladium(II) (92 mg, 0.10 mmol, 2.0 mol %), cesium carbonate (8.15 g, 25 mmol, 5.0 equiv), and lithium bromide (0.17 g, 2.0 mmol, 0.4 equiv) in toluene (50 mL) were added the diamine $MeC(2\text{-}C_5H_4N)(CH_2NH_2)_2$ (0.83 g, 5.0 mmol, 1.0 equiv) and hexafluorobenzene (1.86 g, 10.0 mmol, 2.0 equiv), and the reaction mixture was stirred for 72 h under reflux. Subsequently, the solvent was removed under reduced pressure. The brown residue was redissolved in diethyl ether (50 mL) the resulting solution was washed with water (2 × 30 mL) and then with a saturated aqueous solution of NaCl (2 × 30 mL). The combined organic phases were dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography on silica (pentane/diethyl ether 7:3, R_f = 0.23) to give the product as a light brown solid. Yield: 0.9 g (36%). The mono arylated ligand $H_2N_2^{mono\text{-}PFP}N_{py}$ could be retrieved in the chromatographic workup and appeared after the fractions of **1** together with the unreacted starting material (characterization data given below). The mixture of both could be reused as educt for synthesis of the diarylated compound.

$H_2N_2^{PFP}N_{py}$ (1). ^{1}H NMR (C_6D_6, 600.13 MHz, 296 K): δ = 1.02 (s, 3H, CH_3), 3.39 (dd, $^2J_{HH}$ = 12.6 Hz, $^3J_{CH2NH}$ = 6.0 Hz, 2H, CHH), 3.49 (dd, $^2J_{HH}$ = 12.9 Hz, $^3J_{CH2NH}$ = 7.9 Hz, 2H, CHH), 4.86 (s, 2H, NH), 6.50 (dd, $^3JH_{5pyH4py}$ = 7.8 Hz, $^3J_{H5pyH6py}$ = 4.9 Hz, 1H, $H5_{py}$), 6.79 (d, $^3J_{H3pyH4py}$ = 8.0 Hz, 1H, $H3_{py}$), 6.97 (td, $^3J_{H4pyH3py/H5py}$ = 7.8 Hz, $^4J_{H4pyH6py}$ = 1.9 Hz, 1H, $H4_{py}$), 8.31 (dt, $^3J_{H6pyH5py}$ = 4.9 Hz, $^4J_{H6pyH5py}$ = 0.8 Hz, 1H, $H6_{py}$). {^{1}H} ^{13}C NMR (C_6D_6, 150.92 MHz, 296 K): δ = 22.4 (CH$_3$), 45.7 (C-CH$_3$), 54.7 (CH$_2$), 121.3 ($C3_{py}$), 122.1 ($C5_{py}$), 124.6 ($C_{Ph\text{-}NH}$), 132.9, 135.0 ($C_{\text{-}mPh/pPh\text{-}F}$), 136.9 ($C4_{py}$), 138.0, 139.6 ($C_{\text{-}oPh/mPh\text{-}F}$), 148.8 ($C6_{py}$), 163.6 ($C2_{py}$).^{15}N NMR ($C_6D_6$, 60.84 MHz, 296 K): δ = 41.6 (NH), 307.3 (N_{py}).^{19}F NMR (C_6D_6, 376.27 MHz, 296 K): δ = −171.4 (tt, $^3J_{p\text{-}Fm\text{-}F}$ = 22.9, $^4J_{p\text{-}Fo\text{-}F}$ = 6.1, 2F, $F_{\text{-}pPh}$), −164.8 (t, $^3J_{m\text{-}Fo\text{-}F/p\text{-}F}$ = 20.7, 4F, $F_{\text{-}mPh}$), −158.7 (d, $^3J_{o\text{-}Fm\text{-}F}$ = 22.3, 4F, $F_{\text{-}oPh}$). IR (Nujol, NaCl, cm^{-1}): ν = 3440 w, 3307 w, 2963 vs, 2726 w, 2611 w, 1659 w, 1595 w, 1521 m, 1460 s, 1377 s, 1305 w, 1262 w, 1170 w, 1073 w, 1025 w, 970 w, 827 w, 721 m. HR-MS (FAB): [M]$^+$ = $C_{21}H_{21}F_{14}N_3$, calcd 498.1028, found 498.1030; diff, 0.2 mmu. Elemental analysis, $C_{21}H_{13}F_{10}N_3$: calcd C 50.72, H 2.63, N 8.45; found C 50.76, H 2.71, N 8.40.

$H_2N_2^{mono\text{-}PFP}N_{py}$. ^{1}H NMR ($C_6D_6$, 600.13 MHz, 296 K): δ = 1.03 (s, 3H, CH_3), 2.60 (d, $^2J_{HH}$ = 12.5 Hz, 1H, CHH), 3.20 (d, $^2J_{HH}$ = 12.5 Hz, 1H, CHH), 3.55 (dd, $^2J_{HH}$ = 12.5 Hz, $^3J_{CH2NH}$ = 4.8 Hz, 1H, CHH(PFP)), 3.66 (dd, $^2J_{HH}$ = 12.4 Hz, $^3J_{CH2NH}$ = 6.5 Hz, 1H, CHH(PFP)), 6.31 (s, 1H, NH(PFP)), 6.54–6.56 (m, 1H, $H5_{py}$), 6.96 (d, $^3J_{H3pyH4py}$ = 8.0 Hz, 1H, $H3_{py}$), 7.02–7.52 (m, 1H, $H4_{py}$), 8.34 (d, $^3J_{H6pyH5py}$ = 4.3 Hz, 1H, $H6_{py}$). {^{1}H} ^{13}C NMR (C_6D_6, 150.92 MHz, 296 K): δ = 23.5 (CH$_3$), 45.7 (C-CH$_3$), 51.0 (CH$_2$NH$_2$), 55.1 (CH$_2$(PFP)), 121.4 ($C3_{py}$), 121.4 ($C5_{py}$), 125.8 ($C_{PFP\text{-}NH}$), 136.3 ($C4_{py}$), 137.6, 139.3 ($C_{\text{-}oPh/mPh\text{-}F}$), 148.9 ($C6_{py}$), 164.9 ($C2_{py}$), $C_{\text{-}pPh\text{-}F}$ n. o. ^{15}N NMR (C_6D_6, 60.84 MHz, 296 K): δ = 46.7 (NH), 310.6 (N_{py}), NH_2 n. o. ^{19}F NMR (C_6D_6, 376.27 MHz, 296 K): δ = −174.4 (tt, $^3J_{p\text{-}Fm\text{-}F}$ = 22.5, $^4J_{p\text{-}Fo\text{-}F}$ = 7.4, 1F, $F_{\text{-}pPh}$), −164.8 to −165.6 (m, 2F, $F_{\text{-}mPh}$), −159.9 (m, 2F, $F_{\text{-}oPh}$).

$[Zr(N^{PFP}N^{TFAP}N_{py})(NMe_2)F]$ (2). Tetrakisdimethylamidozirconium(IV) (266 mg, 1.0 mmol, 1.0 equiv) and $H_2N_2^{PFP}N_{py}$ (500 mg, 1.0 mmol, 1.0 equiv) were dissolved in toluene and stirred overnight. Subsequently, the solvent was removed under reduced pressure and the crude product was washed with pentane to obtain $[Zr(N^{PFP}N^{TFAP}N_{py})(NMe_2)F]$ as a pale red solid. Yield: 0.43 g (62%). ^{1}H NMR (C_6D_6, 600.13 MHz, 296 K): δ = 1.05 (s, 3H, CH_3), 2.11 (s, 3H, C_{Ph}-N-CH_3), 2.65 (bs, 6H, Zr-N-(CH_3)$_2$), 2.87 (d, $^2J_{HH}$ = 11.8 Hz, 1H, CHH), 2.90–2.96 (m, 3H, C_{Ph}-N-CH_3), 3.04 (dd, $^2J_{HH}$ = 12.3 Hz, $^5J_{HF\text{-}Ar}$ = 5.4 Hz, 1H, CHH), 4.02 (d, $^2J_{HH}$ = 11.8 Hz, 1H, CHH), 4.44 (dd, $^2J_{HH}$ = 12.3 Hz, $^5J_{HF\text{-}Ar}$ = 6.6 Hz, 1H, CHH), 6.45–6.50 (m, 1H, $H5_{py}$), 6.79 (d, $^3J_{H3pyH4py}$ = 8.1 Hz, 1H, $H3_{py}$), 6.96 (td, $^3J_{H4pyH3/5py}$ = 7.8 Hz, $^4J_{H4pyH6py}$ = 1.7 Hz, 1H, $H4_{py}$), 8.98 (d, $^3J_{H6pyH5py}$ = 5.2 Hz, 1H, $H6_{py}$).^{13}C {^{1}H} NMR (C_6D_6, 150.92 MHz, 296 K): δ =

24.5 (s, CH_3), 41.7 (bs, Zr-N-$(CH_3)_2$), 46.6 (m, C_{Ph}-N-CH_3), 46.9 (s, C_{Ph}-N-CH_3), 47.3 (d, *C*-CH_3), 62.0 (d, CH_2), 63.0 (d, CH_2), 121.4 (s, $C3_{py}$), 122.0 (s, $C5_{py}$), 123.8 ($C_{F\text{-}Ar}$), 132.1 ($C_{F\text{-}Ar}$), 133.4($C_{F\text{-}Ar}$), 134.9 ($C_{F\text{-}Ar}$), 136.6 ($C_{F\text{-}ar}$), 137.4 ($C_{F\text{-}Ar}$), 138.2 ($C_{F\text{-}Ar}$), 139.0 ($C_{F\text{-}Ar}$), 139.3 ($C_{F\text{-}Ar}$), 139.6 (s, $C4_{py}$), 141.3 ($C_{F\text{-}Ar}$), 142.8 ($C_{F\text{-}Ar}$), 145.1 ($C_{F\text{-}Ar}$), 147.6 (d, $C6_{py}$), 163.3 (s, $C2_{py}$).^{15}N NMR (C_6D_6, 60.84 MHz, 296 K): δ = 135.9 (CH_2-*N*-Ar), 151.0 (CH_2-*N*-Ar), 183.5 (Ar-*N*-Me_2), 282.7 (N_{py}), n.b. (Zr-*N*Me_2). ^{19}F NMR (C_6D_6, 376.27 MHz, 296 K): δ = −176.7 (td, $^3J_{FF}$ = 22.8 Hz, $^4J_{FF}$ = 8.8, 1F, $F_{o/m}$), −171.5 (tt, $^3J_{FF}$ = 21.8 Hz, $^4J_{FF}$ = 5.9 Hz, 1 F, Cp_{Ph}-*F* (N-Pfb)), −167.0 (m, 2F, C_{oPh}-*F*, C_{mPh}-*F* (N-Pfb)), −159.4 (m, 1F, 1 F_m), −158.9 (m, 1F, *F*CCNMe_2), −153.3 (m, 2F, C_{oPh}-*F*, C_{mPh}-*F* (N-Pfb)), −149.7 (m, 1F, F_o), +71.2 (t, $^4J_{FH}$ = 27.4 Hz, 1F, Zr-*F*). IR (Nujol, NaCl, cm^{-1}): ν = 2924 vs, 2854 vs, 1462 s, 1377 m, 1260 m, 1101 m, 1059 m, 1015 m, 799 m. Elemental analysis, $C_{25}H_{23}F_{10}N_5Zr$: calcd C 44.50, H 3.44, N 10.38; found C 43.95, H 3.57, N 10.27.

[Zr($N_2^{TFAP}N_{py}$)F_2] (3). Tetrakisdimethylamidozirconium(IV) (399 mg, 1.5 mmol, 1.0 equiv) and $H_2N_2^{PFP}N_{py}$ (742 mg, 1.5 mmol, 1.0 equiv) were dissolved in toluene and heated for four days at 90 °C. Subsequently, the solvent was removed under vacuum and the crude product was washed with pentane. The complex was obtained as a yellow powder. Yield: 906 mg (90%). ^{1}H NMR (THF-d_8, 600.13 MHz, 296 K): δ = 1.64 (s, 3H, CH_3), 2.59 (s, 6H, N$(CH_3)_2$), 3.21–3.31 (m, 8H, 2 C*H*H + 6 N$(CH_3)_2$), 4.34–4.43 (m, 2H, CH*H*), 7.52 (t, $^3J_{H5pyH4py}$ = 6.5 Hz, 1H, $H5_{py}$), 7.81 (d, $^3J_{H3pyH4py}$ = 8.1 Hz, 1H, $H3_{py}$), 8.09 (t, $^3J_{H4pyH3/5py}$ = 7.7 Hz, 1H, $H4_{py}$), 9.25–9.31 (m, 1H, $H6_{py}$). ^{13}C {^{1}H} NMR (THF-d_8, 150.92 MHz, 296 K): δ = 25.1 (CH_3), 45.2 (N-$(CH_3)_2$), 46.6 (*C*-CH3), 46.8 (N-$(CH_3)_2$), 62.5 (CH_2), 62.6 (CH_2), 122.2, 122.5 (C_{Ar}-N), 123.3 ($C3_{py}$), 123.6 ($C5_{py}$), 125.9 (C_{ar}), 131.0 (C_{Ar}), 132.6 (C_{Ar}), 137.0 (C_{Ar}), 138.6 (C_{ar}), 140.0 (C_{Ar}), 140.9 (C_{Ar}), 141.6 ($C4_{py}$), 142.6 (C_{Ar}), 145.3 (C_{Ar}), 146.9 (C_{Ar}),148.2 ($C6_{py}$), 163.4 ($C2_{py}$). ^{15}N NMR (THF-d_8, 60.84 MHz, 296 K): δ = 151.7 (CH_2-*N*-Ar), 281.5 (N_{py}), n.b. (*N*Me_2). ^{19}F NMR (THF-d_8, 376.27 MHz, 296 K): δ = −178.8 (td, $^3J_{FF}$ = 22.3 Hz, $^4J_{FF}$ = 7.8, 2F, F_p or F_m), −162.6 (t, $^3J_{FF}$ = 20.8 Hz, $^4J_{FF}$ = 1.4 Hz, 2F, F_m or F_m), −158.6 to (−158.4) (m, 2F, F_m adjacent to C-NMe_2), −151.2 (d, $^3J_{FF}$ = 21.7 Hz, 2F, F_o), +70.5 (s, 1F, Zr-*F*), +102.5 (s, 1F, Zr-*F*). IR (Nujol, NaCl, cm^{-1}): ν = 3131 w, 2853 vs, 1607 s, 1498 s, 1376 m, 1295 w, 1259 m, 1164 m, 1104 m, 1064 w, 994 m, 844 m, 721 m, 673 m. Elemental analysis, $C_{25}H_{23}F_{10}N_5Zr$: calcd C 44.50, H 3.44, N 10.38; found C 44.02, H 3.74, N 9.92.

[Zr($N_2^{TFAP}N_{py}$)FI] (4). To a solution of [Zr($N_2^{TFAP}N_{py}$)F_2] (100 mg, 0.15 mmol, 1.0 equiv) in toluene (10 mL) was added TMSI (102 μL, 0.75 mmol, 5.0 equiv), and the reaction mixture was stirred for two days at room temperature. Subsequently, the solvent was removed under vacuum and the crude product was washed with pentane. The complex was obtained as a pale yellow powder. Yield: 104 mg (90%). ^{1}H NMR (THF-d_8, 600.13 MHz, 296 K): δ = 1.69 (s, 3H, CH_3), 2.52 (s, 6H, N$(CH_3)_2$), 3.29–3.25 (m, 2H, CH*H*), 3.42–3.50 (m, 6H, N$(CH_3)_2$), 4.46–4.54 (m, 2H, C*H*H), 7.58 (t, $^3J_{H5pyH4py}$ = 6.5 Hz, 1H, $H5_{py}$), 7.86 (d, $^3J_{H3pyH4py}$ = 8.2 Hz, 1H, $H3_{py}$), 8.15 (td, $^3J_{H4pyH3py/5py}$ = 7.8 Hz, $^4J_{H4pyH6py}$ = 1.6 Hz, 1H, $H4_{py}$), 9.14–9.19 (m, 1H, $H6_{py}$). ^{13}C {^{1}H} NMR (THF-d_8, 150.92 MHz, 296 K): δ = 24.9 (CH_3), 46.8 (*C*-CH3), 47.6, 48.3 (N-$(CH_3)_2$), 62.8 (CH_2), 62.9 (CH_2), 122.2, 122.4 (C_{Ar}-N), 123.8 ($C3_{py}$), 123.9 ($C5_{py}$), 127.4 (C_{Ar}-F), 132.0 (C_{Ar}-F), 133.6 (C_{Ar}-F), 136.0 (C_{Ar}-F), 137.4 (C-N-$(CH_3)_2$), 137.6 (C_{Ar}-F), 140.5 (C_{Ar}-F), 140.5 ($C4_{py}$), 144.2 (C_{Ar}-F), 145.9 (C_{Ar}-F), 147.9 ($C6_{py}$), 163.3 ($C2_{py}$). ^{15}N NMR (THF-d_8, 60.84 MHz, 296 K): δ = 277.9 (N_{py}), 173.2 (CH_2-*N*-Ar), n.b. (*N*$(CH_3)_2$)). ^{19}F NMR (THF-d_8, 376.27 MHz, 296 K): δ = −176.3 (td, $^3J_{FF}$ = 21.7 Hz, $^4J_{FF}$ = 7.0, 2F, C-*F*), −162.8 to (−162.7) (m, 2F, C-*F*), −156.7 to −156.6 (m, 2F, CH_2NCC*F*), −152.3 to −152.2 (m, 2F, *F* adjacent to C-NMe_2), +104.0 (s, 1F, Zr-*F*). IR (Nujol, NaCl, cm^{-1}): ν = 3120 w, 2899 vs, 2852 s, 1606 s, 1466 s, 1378 s, 1292 m, 1260 m, 1161 s, 1094 m, 1067 m, 1013 m, 992 m, 954 m, 837 s, 763 m, 675 m, 649 m. Elemental analysis, $C_{25}H_{23}F_9IN_5Zr$: calcd C 38.37, H 2.96, N 8.95; found C 38.08, H 3.26, N 8.78.

[Zr($N_2^{TFAP}N_{py}$)FCl] (5). To a solution of [Zr($N_2^{TFAP}N_{py}$)F_2] (50 mg, 0.07 mmol, 1.0 equiv) in toluene (3 mL) was added TMSCl (19 μL, 0.15 mmol, 2.0 equiv), and the reaction mixture was stirred for two days at room temperature. Subsequently, the solvent was removed under vacuum and the crude product was washed with pentane. The complex was obtained as a pale yellow powder. Yield: 45 mg (89%). ^{1}H NMR (C_6D_6, 399.89 MHz, 296 K): δ = 0.97 (s, 3 H, CH_3), 2.18 (s, 6 H, N$(CH_3)_2$), 2.83 (dd, $^2J_{HH}$ = 12.2 Hz, $^4J_{HH}$ = 2.5 Hz, 2 H, C*H*H), 3.29–3.40 (m, 6 H, N$(CH_3)_2$), 4.35–4.44 (m, 2 H, C*H*H), 6.47 (t, $^3J_{H5pyH6py/H4py}$ = 6.6 Hz 1 H, $H5_{py}$), 6.76 (d, $^3J_{H3pyH4py}$ = 8.3 Hz, 1 H, $H3_{py}$), 6.92–6.98 (m, 1 H, $H4_{py}$), 8.76–8.82 (m, 1 H, $H6_{py}$). ^{13}C {^{1}H} NMR (C_6D_6, 100.56 MHz, 296 K): δ = 24.6 (CH_3), 45.8 (*C*-CH_3), 46.6, 46.9 (N-$(CH_3)_2$), 62.0 (CH_2), 62.1 (CH_2), 122.2 ($C5_{py}$), 122.4 ($C3_{py}$), 140.1 ($C4_{py}$), 146.7 ($C6_{py}$), 162.4 (s, $C2_{py}$), C_q [*C*-F and *C*-N] could not be observed. ^{15}N NMR (C_6D_6, 60.84 MHz, 296 K): δ = 164.0 (CH_2-N_{ar}), 280.2 (N_{py}), *N*Me_2 n.o. ^{19}F NMR (C_6D_6, 376.27 MHz, 296 K): δ = −174.3 (td, $^3J_{FF}$ = 21.9 Hz, $^4J_{FF}$ = 7.2 Hz, 2 F, F_p or F_m), −160.3 (t, $^3J_{FF}$ = 21.0 Hz, 2 F, F_m or F_p) −155.6 to −155.4 (m, 2 F, F_m adjacent to C-NMe_2), −150.7 (dt, $^3J_{FoFm}$ = 21.9 Hz, $^4J_{FoFp}$ = 5.5 Hz, 2 F, F_o), 91.4 (s, 1 F, Zr-*F*). IR (Nujol, NaCl, cm^{-1}): ν = 2962 vs, 2857 vs, 2723 w, 1600 m, 1464 s, 1377 m, 1295 w, 1260 m, 1167 w, 1096 w, 1017 w, 991 m, 960 m, 802 m, 722 m. Elemental analysis, $C_{25}H_{23}ClF_9N_5Zr$: calcd C 43.44, H 3.35, N 10.13; found C 43.15, H 3.60, N 10.28.

[Zr($N_2^{TFAP}N_{py}$)FNHNPh$_2$] (6). To a solution of [Zr($N_2^{TFAP}N_{py}$)F_2] (1.6 g, 2.35 mmol, 1.0 equiv) in benzene (5 mL) was added lithium diphenylhydrazide (538 mg, 2.82 mmol, 1.2 equiv), and the reaction mixture was stirred for one day at 90 °C. The solvent was removed by filtration, the crude product was washed with pentane, and the complex was obtained as an orange powder. Yield: 1.2 g (61%). ^{1}H NMR (C_6D_6, 399.89 MHz, 296 K): δ = 1.07 (s, 3 H, CH_3), 2.21 (s, 6 H, N$(CH_3)_2$), 2.84 (d, $^2J_{HH}$ = 12.3 Hz, 2 H, C*H*H), 3.29–3.39 (m, 6 H, N$(CH_3)_2$), 4.16–4.29 (m, 2 H, CH*H*), 5.62 (s, 1 H, N*H*), 6.51 (t, $^3J_{H5pyH6py/H4py}$ = 6.4 Hz 1 H, $H5_{py}$), 6.78–6.88 (m, 3 H, $H3_{py}$ + $H_{p\text{-}Phenyl}$), 6.98 (t, $^3J_{H4pyH3py/5py}$ = 7.6 Hz, 1 H, $H4_{py}$), 7.04–7.22 (m, 8 H, $H_{m\text{-}Phenyl}$ + $H_{o\text{-}Phenyl}$ overlay with residual signal of C_6D_6), 8.89–8.94 (m, 1 H, $H6_{py}$). ^{13}C {^{1}H} NMR (C_6D_6, 100.56 MHz, 296 K): δ = 24.8 (CH_3), 45.8 (*C*-CH_3), 45.3 (N-$(CH_3)_2$), 47.9 (N-$(CH_3)_2$), 62.8 (CH_2), 62.9 (CH_2), 118.1 ($C3_{py}$), 119.6 (CH_{ar}, $C_{o/m\text{-}Phenyl}$), 121.7 (CH_{Ar}, $C_{p\text{-}Phenyl}$), 122.1 ($C5_{py}$), 125.6 (*C*-N$(CH_3)_2$), 129.5 (CH_{Ar}, $C_{o/m\text{-}Phenyl}$), 139.1 ($C4_{py}$), 146.9 ($C6_{py}$), 150.6 (NH-N-C_{Phipso}), 162.8 ($C2_{py}$), C_{Ar-F} n.o., C−N−$C_{Ph\text{-}Ligandipso}$ n.o. ^{15}N NMR (C_6D_6, 40.52 MHz, 296 K): δ = 117.0 (NH*N*Ph_2), 156.9 (CH_2N_{ar}), 197.8 (*N*H), 284.0 (N_{py}), *N*Me_2 n.o. ^{19}F NMR (C_6D_6, 376.27 MHz, 296 K): δ = −175.7 (td, $^3J_{FpFm}$ = 22.3 Hz, $^4J_{FpFo}$ = 7.5 Hz, 2 F, F_p), −160.7 (t, $^3J_{FmFp,\ FmFo}$ = 21.3 Hz, 2 F, F_m), −155.9 to −155.7 (m, 2 F, F_o), −151.1 to −150.9 (m, 2 F, F_m adjacent to C-NMe_2), 54.5 (s, 1 F, Zr-*F*). IR (Nujol, NaCl, cm^{-1}): ν = 2921 vs, 2853 s, 1780 w, 1601 m, 1461 s, 1377 m, 1293 w, 1259 m, 1168 m, 110 m, 1063 w, 993 m, 959 m, 845 m, 798 w, 721 w. Elemental analysis, $C_{37}H_{34}F_9N_7Zr$: calcd C 52.97, H 4.08, N 11.69; found C 52.83, H 4.14, N 11.40.

[Zr($N_2^{TFAP}N_{py}$)FNNPh$_2$K] (7). To a solution of [Zr($N_2^{TFAP}N_{py}$)-FNHNPh$_2$] (215 mg, 0.26 mmol, 1.0 equiv) in benzene (5 mL) was added potassium hexamethyldisilazide (52 mg, 0.26 mmol, 1.0 equiv), and the reaction mixture was stirred for one day at room temperature. Subsequently, the solvent was removed under vacuum and the crude product was washed with pentane. The complex was obtained as a light brown powder. Yield: 80 mg (36%). ^{1}H NMR (C_6D_6, 600.13 MHz, 296 K): δ = 1.18 (s, 6 H, 2*CH_3), 2.18 (s, 12 H, 2*N$(CH_3)_2$), 2.98 (d, $^2J_{HH}$ = 11.7 Hz, 4 H, 2*C*H*H), 3.08–3.17 (bs, 12 H, 2*N$(CH_3)_2$), 3.73–3.86 (m, 4 H, 2*CH*H*), 6.52 (d, $^3J_{Ho\text{-}Phenyl/Hm\text{-}Phenyl}$ = 7.7 Hz, 8H, 8*$H_{o\text{-}Phenyl}$), 6.58 (t, $^3J_{H5pyH6py/H4py}$ = 6.3 Hz 2 H, 2*$H5_{py}$), 6.71 (t, $^3J_{Hp\text{-}Phenyl/Hm\text{-}Phenyl}$ = 7.4 Hz, 4 H, 4*$H_{p\text{-}Phenyl}$), 6.89 (d, $^3J_{H3py/H4py}$ = 8.0 Hz, 2 H, 2*$H3_{py}$), 6.98–7.05 (m, 10 H, 8*$H_{m\text{-}Phenyl}$ + 2*$H3_{py}$), 9.37–9.40 (m, 2H, 2*$H6_{py}$). ^{13}C {^{1}H} NMR (C_6D_6, 150.91 MHz, 296 K): δ = 24.3 (CH_3), 44.9, 45.0, 45.1, 46.1, 46.1 (*C*-CH_3, N-$(CH_3)_2$), 63.7, 63.8 (CH_2), 118.1 ($C_{o\text{-}Phenyl}$), 119.8 ($C_{p\text{-}Phenyl}$), 120.1, 120.1 ($C5_{py}$, $C3_{py}$), 127.1 (*C*-N$(CH_3)_2$), 128.6 ($C_{m\text{-}Phenyl}$)136.9 ($C4_{py}$), 148.2, 148.4 (N-C_{Phipso}), 147.9 ($C6_{py}$), 163.0 ($C2_{py}$), $C_{ar\text{-}F}$ n.o., C−N−$C_{Ph\text{-}Ligandipso}$ n.o. ^{15}N NMR (C_6D_6, 40.52 MHz, 296 K): δ = 103.8 (CH_2-N_{ar}), 163.8 (N*N*Ph_2), 289.9 (N_{py}), *N*Me_2 n.o., *N*NPh_2 n.o. ^{19}F NMR (C_6D_6, 376.27 MHz, 296 K): δ =

Table 1. Details of the Crystal Structure Determinations of 3·0.5benzene, 4·2benzene, 5, 7, and 8·0.5toluene

	3·0.5benzene	4·2benzene	5	7	8·0.5toluene
formula	$C_{28}H_{26}F_{10}N_5Zr$	$C_{37}H_{23}D_{12}F_9IN_5Zr$	$C_{25}H_{23}ClF_9N_5Zr$	$C_{88}H_{82}F_{18}K_2N_{14}Zr_2$	$C_{40.50}H_{37}F_8N_7Zr$
M_r	713.76	950.89	691.15	1938.31	864.99
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/m$	$P2_1/m$	$P\bar{1}$	$P\bar{1}$
a/Å	8.973(2)	8.33711(8)	8.33527(4)	10.21010(10)	11.2275(2)
b/Å	14.563(3)	23.5742(2)	18.16024(9)	13.21438(13)	13.7650(3)
c/Å	22.387(5)	9.73416(10)	9.30851(5)	16.79443(15)	14.1485(3)
α/deg				93.1084(8)	112.625(2)
β/deg	97.987(4)	109.294(1)	110.9131(6)	95.7719(8)	105.1498(18)
γ/deg				111.0070(9)	101.2234(18)
V/Å^3	2898(1)	1805.68(3)	1316.21(1)	2094.62(4)	1838.17(8)
Z	4	2	2	1	2
F_{000}	1436	932	692	988	882
d_c/Mg·m^{-3}	1.636	1.749	1.744	1.537	1.563
X-radiation, λ/Å	Mo K_α, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Cu Kα, 1.5418
μ/mm^{-1}	0.472	1.242	0.610	0.444	3.173
max, min transm factors	0.9631, 0.8838	1.0000, 0.8027	0.947, 0.911	0.988, 0.952	0.965, 0.749
data collect. temp/K	100(2)	110(2)	115(2)	110(2)	110(2)
θ range/deg	2.3 to 25.1	3.3 to 29.0	3.2 to 27.9	3.2 to 32.4	3.6 to 71.8
index ranges (indep set) h, k, l	−10...10, 0...17, 0...26[a]	−11...11, −31...31, −13...13[b]	−10...11, −23...23, −12...12[b]	−15...15, −19...19, −25...24[b]	−13...13, −16...16, −17...17[b]
reflns measured	60392	141732	76245	73620	63489
unique [R_{int}]	5160 [0.1317]	4794 [0.0687]	3184 [0.0323]	14155 [0.0373]	7012 [0.0424]
obsd [$I \geq 2\sigma(I)$]	3529	4234	3028	13179	6619
params refined	375	258	205	574	534
GOF on F^2	1.047	1.054	1.067	1.174	1.047
R indices [$F > 4\sigma(F)$] $R(F)$, wR(F^2)	0.0543, 0.1070	0.0221, 0.0432	0.0189, 0.0507	0.0417, 0.0812	0.0245, 0.0588
R indices (all data) $R(F)$, wR(F^2)	0.0955, 0.1187	0.0306, 0.0458	0.0206, 0.0517	0.0470, 0.0831	0.0271, 0.0599
diff density: max, min/e·Å^{-3}	0.465, −0.677	0.503, −0.385	0.384, −0.341	0.686, −0.807	0.467, −0.429

[a]Independent set. [b]Complete set.

−177.4 (td, $^3J_{FpFm}$ = 21.4 Hz, $^4J_{FpFo}$ = 9.4 Hz, 4 F, 4*F_p), −164.0 (t, $^3J_{FmFp,Fo}$ = 21.4 Hz, 4 F, 4*F_m) −160.6 to −160.2 (m, 4 F, 4*F_o), −148.8 to −148.5 (m, 4 F, 4*F_m benachbart zu C-NMe$_2$), −17.3 to −17.1 (m, 2 F, 2*Zr-*F*). IR (Nujol, NaCl, cm^{-1}): ν = 2917 vs, 2853 s, 1886 w, 1605 m, 1465 s, 1377 m, 1294 w, 1259 m, 1164 m, 1099 m, 1068 w, 1017 m, 995 m, 955 w, 843 m, 722 w, 674 w. Elemental analysis, $C_{74}H_{66}F_{18}K_2N_{14}Zr_2$: calcd C 50.67, H 3.79, N 11.18; found C 50.44, H 4.45, N 10.60.

[Zr(N$_2^{TFAP}$N$_{py}$)NNPh$_2$] (**8**). To a solution of [Zr(N$_2^{TFAP}$N$_{py}$)-FNHNPh$_2$] (75 mg, 0.1 mmol, 1.0 equiv) in benzene (2 mL) was added lithium hexamethyldisilazide (19 mg, 0.1 mmol, 1.0 equiv), and the reaction mixture was stirred for one day at 60 °C. Subsequently, the solvent was removed under vacuum and the crude product was washed with pentane. The complex was obtained as a light brown powder. Yield: 20 mg (25%). ^{1}H NMR (C_6D_6, 600.13 MHz, 296 K): δ = 1.01 (s, 3H, C*H*$_3$), 2.58 (bs, 6H, N(C*H*$_3$)$_2$), 2.74 (bs, 6H, N(C*H*$_3$)$_2$), 3.38−3.65 (m, 4H, C*H*$_2$), 6.38 (t, $^3J_{H5pyH6py/H4py}$ = 6.5 Hz, 1H, *H*5$_{py}$), 6.73 (d, $^3J_{H3py/H4py}$ = 8.1 Hz, 1H, *H*3$_{py}$), 6.78 (t, $^3J_{Hp\text{-}Phenyl/Hm\text{-}Phenyl}$ = 6.8 Hz, 4 H, 2*$H_{p\text{-}Phenyl}$), 6.83−6.89 (m, 1H, *H*4$_{py}$), 7.13 (d, $^3J_{HArHAr}$ = 8.0 Hz, 4 H, 4*$H_{m\text{-}Phenyl}$), 7.31 (d, $^3J_{Ho\text{-}Phenyl/Hmeta\text{-}Phenyl}$ = 8.0 Hz, 4 H, 4*$H_{o\text{-}Phenyl}$), 9.31 (d, $^3J_{H6py/H5py}$ = 5.1 Hz, 1H, *H*6$_{py}$). ^{13}C {^{1}H} NMR (C_6D_6, 150.91 MHz, 296 K): δ = 22.5 (CCH$_3$), 41.8, 42.2, 44.3, 44.5 (N-(CH$_3$)$_2$), 45.3 (C-CH$_3$), 62.0, 63.5 (CH$_2$), 117.5 ($C_{o\text{-}Phenyl}$), 119.0 ($C_{p\text{-}Phenyl}$), 119.2, 119.3 (C5$_{py}$, C3$_{py}$), 126.8 ($C_{m\text{-}Phenyl}$), 137.3 (C4$_{py}$), 146.4 (C_{Phipso}), 149.4 (C6$_{py}$), 161.7 (C2$_{py}$), C_{Ar-F} n.o., C_{ipso}-N n.o. ^{19}F NMR (C_6D_6, 376.27 MHz, 296 K): δ = −160.6 to −159.8 (m, 2F), −150.2 to −149.2 (m, 2F). IR (Nujol, NaCl, cm^{-1}): ν = 3273 w, 2854 s, 2598 w, 1593 m, 1494 m, 1463 s, 1377 s, 1260 m, 1253 w, 1048 w, 976 m, 798 w, 722 m.

X-ray Crystal Structure Determinations. Crystal data and details of the structure determinations are listed in Table 1. Full shells of intensity data were collected at low temperature with a Bruker AXS Smart 1000 CCD diffractometer (Mo Kα radiation, sealed tube, graphite monochromator) (**3**·0.5benzene) or an Agilent Technologies Supernova-E CCD diffractometer (Mo or Cu Kα radiation, microfocus tube, multilayer mirror optics) (all others). Data were corrected for air and detector absorption and Lorentz and polarization effects;[20,21] absorption by the crystal was treated with a semiempirical multiscan method,[22−24] analytically,[21,25] or numerically (Gaussian grid).[21] The structures were solved by direct methods with dual-space recycling[26] (**3**·0.5benzene), by the heavy atom method combined with structure expansion by direct methods applied to difference structure factors[27] (**5**), or by the charge flip procedure[28] (all others) and refined by full-matrix least-squares methods based on F^2 against all unique reflections.[29] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and refined with a riding model. When found necessary, disordered groups and/or solvent molecules where subjected to suitable geometry and adp restraints. Crystals of **3**·0.5benzene were twinned; after detwinning (approximate twin fractions 0.76:0.24) refinement was carried out against all observations involving domain 1. In addition, due to severe disorder, electron density attributed to solvent of crystallization was removed from this structure with the BYPASS procedure,[30] as implemented in PLATON (SQUEEZE).[31] Partial structure factors from the solvent masks were included in the refinement as separate contributions to F_{obs}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figure of the molecular structure of complex **5** and selected bond parameters. CIF files giving crystallographic data for compounds **3**, **4**, **5**, **7**, **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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