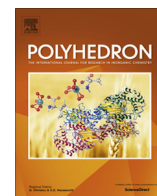




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Pyrrrolyl-based pincer complexes of iron – Synthesis and electronic structure

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ABSTRACT

Four- and five-coordinate high-spin ($S = 2$) Fe(II) complexes bearing the pyrrolyl-derived ^tBuPNP pincer ligand [^tBuPNP = 2,5-(*t*Bu₂PCH₂)₂(C₄H₂N)] have been prepared. All three complexes were characterized by X-ray diffraction, zero-field ⁵⁷Fe Mössbauer spectroscopy and solid-state magnetic susceptibility studies. Furthermore, the experimentally determined Mössbauer parameters of compounds **4–6** can be modeled satisfactorily by density functional theory (DFT) computations at the B97D level of theory. Introduction of the sterically demanding bis(trimethylsilyl)amido moiety induces significant distortions from ideal tetrahedral geometry in [(^tBuPNP)FeN(SiMe₃)₂] (**4**), featuring an Fe(II) high-spin state with large negative axial zero-field splitting and slow paramagnetic relaxation at low temperature, as evidenced by measurements of the solid-state magnetic susceptibility and zero-field ⁵⁷Fe Mössbauer spectroscopy. Replacing the chlorido ligand in [(^tBuPNP)FeCl] (**3**) by the bidentate acetylacetonato (acac) ligand enforces a trigonal-bipyramidal structure in [(^tBuPNP)Fe(acac)] (**5**), in which the Fe(II) atom also adopts a high-spin configuration. Reaction of **3** with adamantyl azide allowed us to confirm the inherent lability of the phosphine coordination, since the azide inserts into the Fe–P bond to form [(^tBuPNP^{N3}Adamantyl)FeCl] (**6**), in which the ^tBuPNP ligand is transformed to a phosphino-pyrrolyl-phosphazide ligand framework (^tBuPNP^{N3}Adamantyl). This motif can be considered as a trapped Staudinger intermediate along the reaction pathway of free phosphines with organic azides to form phosphinimines. Bidentate binding of the phosphazide sidearm in κN:κN-fashion to the Fe(II) atom enforces an *s-anti* coordination of the P1–N2–N3–N4 moiety, which raises the barrier for the thermodynamically favorable N₂ elimination and allows this intermediate to be trapped. Complex **6** contains a high-spin Fe(II) atom with a square-pyramidal structure.

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1. Introduction

Pincer compounds of 3d-transition metals have attracted significant interest in recent years because of their potential applications in small molecule activation and catalysis [1–9]. The flexible and readily adaptable architecture of pincer ligands, which may act as redox-active or non-innocent scaffolds participating in metal-ligand cooperativity [10–18], and the high thermal stability of the corresponding metal complexes have contributed to the rapid development of this field and several catalysts have emerged, e.g., for hydrofunctionalizations [19–25], cross-coupling reactions [26,27], activation and functionalization of C–H bonds [28], CO₂ [29,30] or N₂ [31–33], and dehydrogenation reactions [34,35]. Apart from the reaction chemistry of the pincer compounds, a detailed understanding of their structural and physical properties

is indispensable. Within the different and rapidly expanding classes of pincer ligands, pyrrolyl-based PNP systems (**I**, Chart 1) have only recently been introduced into the literature by the groups of Tonzetich [36], Gade [37] and Mani [38]. In contrast to the disilylamido- and diphenylamido-derived PNP-systems (**II** [39–43] and **III** [44–48] in Chart 1), which have long been known and are well-established, the coordination chemistry of the pyrrolyl-based ligand system **I** is still in its infancy [26,27,32,33,36–38,49–54].

We have recently prepared several iron compounds bearing the pyrrolyl-derived ^tBuPNP ligand scaffold, such as [(^tBuPNP)FeCl], [(^tBuPNP)FeN₂] and [(^tBuPNP)Fe(CO)₂] and studied their electronic ground-state properties by various physical techniques including solid-state magnetic susceptibility, zero-field ⁵⁷Fe Mössbauer and X-band EPR spectroscopy [54]. Furthermore, we found an exceptionally good correlation between the Mössbauer parameters determined by density functional theory (DFT) computations at the B97D level of theory and the experimentally determined data

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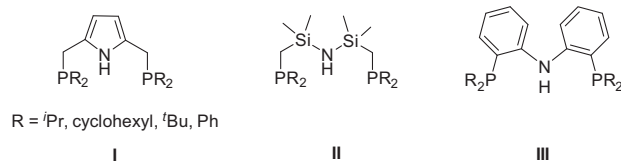


Chart 1.

[54]. This encouraged us to continue our investigations of iron(II) compounds adopting distorted square-planar, trigonal-bipyramidal and square-pyramidal structures and to investigate their electronic ground-state properties. These results are detailed in this manuscript.

2. Experimental

2.1. General considerations

All experiments were conducted under an atmosphere of purified dinitrogen, either in a Schlenk vessel or in a glovebox. The solvents tetrahydrofuran, toluene, diethyl ether, *n*-hexane, *n*-pentane or hexamethyldisiloxane (HMDSO) were dried and deoxygenated by distillation under a dinitrogen atmosphere over sodium. The following starting materials were prepared according to literature procedures: (^tBuPNP)H [50], [(^tBuPNP)Li] [50], [{Fe(N(SiMe₃)₂)₂] [55,56] and [Fe(acac)₂] [57]. Reaction of (Me₃Si)₂NH with *n*-BuLi in diethyl ether at 0 °C and crystallization of a concentrated solution at –30 °C yielded colorless, crystalline [Li(N(SiMe₃)₂(OEt₂))₂], which was isolated by filtration and shortly exposed to dynamic vacuum. All other chemicals were purchased from Acros Organics or Sigma Aldrich. C₆D₆ purchased from Eurisotope was refluxed for 3 days over sodium metal, vacuum transferred to a Teflon-sealable Schlenk flask containing 4 Å molecular sieves, and degassed via three freeze–pumpthaw cycles. Elemental analyses (C, H) by combustion and gas chromatography were carried out using an Elementar varioMICRO. NMR spectra were recorded on a Bruker 300 MHz AVANCE spectrometer. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents, which are internal standards for proton chemical shifts. UV–Vis spectra were recorded on a Varian Cary 50 Scan.

2.2. Synthesis of [(^tBuPNP)FeN(SiMe₃)₂] (4). Method 1

In a Schlenk flask a toluene solution (5 mL) of [Li(N(SiMe₃)₂(OEt₂))₂] (102 mg, 0.21 mmol) was added to a solution of [(^tBuPNP)FeCl] (3) (200 mg, 0.42 mmol) in toluene (5 mL) at ambient temperature. The reaction mixture immediately turned orange and after stirring for 12 h the solvent was removed under dynamic vacuum. The residue was extracted with *n*-hexane (2 × 5 mL) and filtered through Celite. The solvent was removed under dynamic vacuum leading to a brown viscous oil. Yellow crystals of [(^tBuPNP)FeN(SiMe₃)₂] (4) were obtained from a concentrated hexamethyldisiloxane solution at –24 °C. Yield: 186 mg (0.31 mmol, 74%). **Method 2.** In a Schlenk flask a toluene solution (5 mL) of KN(SiMe₃)₂ (84 mg, 0.42 mmol) was added to a solution of [(^tBuPNP)FeCl] (3) (200 mg, 0.42 mmol) in toluene (5 mL) at ambient temperature. The reaction mixture immediately turned orange and after stirring for 12 h the solvent was removed under dynamic vacuum. The residue was extracted with *n*-hexane (2 × 5 mL) and filtered through Celite. The solvent was removed under dynamic vacuum leading to a brown viscous oil. Crystals of (4) were obtained as above. Yield: 115 mg (0.19 mmol, 46%). **Method 3.** In a Schlenk flask a toluene solution (5 mL) of [{Fe(N(SiMe₃)₂)₂] (98 mg, 0.13 mmol) was added to a solution of [(^tBuPNP)H] (1)

(100 mg, 0.26 mmol) in toluene (5 mL) at ambient temperature. The reaction mixture immediately turned brown-orange and after stirring for 12 h the solvent was removed under dynamic vacuum. The residue was extracted with *n*-pentane (2 × 5 mL) and filtered through Celite. The solvent was removed under dynamic vacuum leading to brown viscous oil. Crystals of (4) were obtained as above. Yield: 119 mg (0.20 mmol, 76%). ¹H NMR (300 MHz, C₆D₆, 298 K): δ = 100.2 (br. s, $\nu_{1/2}$ = 500 Hz, 2H, Pyr-CH), 31.5 (br. s, $\nu_{1/2}$ = 930 Hz, 18H, N(SiMe₃)₂), –12.4 (br. s, $\nu_{1/2}$ = 520 Hz, 36H, *t*Bu-CH₃) ppm. UV–Vis (Et₂O, 298 K): λ_{\max} (ϵ , L mol^{–1} cm^{–1}) = 314 (5830). Elemental analysis calc. (%) for C₂₈H₆₀FeN₂P₂Si₂ (598.31): C 56.17, H 10.10, N 4.68; found: C 55.78, H 10.24, N 4.68.

2.3. Synthesis of [(^tBuPNP)Fe(acac)] (5)

In a Schlenk flask a THF solution (10 mL) of [(^tBuPNP)Li] (2) (307 mg, 0.79 mmol) was added to a suspension of [Fe(acac)₂] (200 mg, 0.79 mmol) in THF (10 mL) at ambient temperature. The reaction mixture immediately turned red and after stirring for 12 h the solvent was removed under dynamic vacuum. The residue was extracted with *n*-pentane (2 × 5 mL) and filtered through Celite. The *n*-pentane extract was concentrated to ca. 3 mL and cooled to –24 °C to yield orange crystals of [(^tBuPNP)Fe(acac)] (5). Yield: 380 mg (0.71 mmol, 87%). ¹H NMR (300 MHz, C₆D₆, 298 K): δ = 56.1 (br. s, $\nu_{1/2}$ = 300 Hz, 2H, CH), 31.2 (br. s, $\nu_{1/2}$ = 560 Hz, 4H, CH₂), 18.6 (br. s, $\nu_{1/2}$ = 510 Hz, 1H, CH), 5.8 (br. s, $\nu_{1/2}$ = 400, 36H, *t*Bu-CH₃), –63.1 (br. s, $\nu_{1/2}$ = 240, 6H, CH₃) ppm. UV–Vis (Et₂O, 298 K): λ_{\max} (ϵ , L mol^{–1} cm^{–1}) = 297 (13098), 348 (2431), 455 (1626). IR (ATR): 3084 (w), 3069 (w), 2951 (m), 2897 (m), 2864 (m), 1568 (s), 1514 (vs), 1470 (m), 1445 (m), 1358 (vs), 1313 (m), 1258 (m), 1180 (m), 1121 (m), 1049 (s), 1018 (m), 926 (m), 822 (s) cm^{–1}. Elemental analysis calc. (%) for C₂₇H₄₉FeNO₂P₂ (537.26): C 60.34, H 9.19, N 2.61; found: C 60.32, H 9.18, N 2.65. The E.I. mass spectrum showed a molecular ion at *m/e* = 537 amu. The parent ion isotopic cluster was simulated: (calcd%, observd%): 535(7, 7), 536 (3, 6), 537(100, 100), 538(33, 28), 539 (6, 7), 540 (1, 1).

2.4. Synthesis of [(^tBuPNP^{N3}Adamantyl)FeCl] (6)

Under an N₂ atmosphere a toluene solution (5 mL) of [(^tBuPNP)FeCl] (3) 100 mg, 0.21 mmol) in THF (15 mL) was added to a toluene solution (2 mL) of 1-azidoadamantane (37 mg, 0.21 mmol) at ambient temperature. The reaction mixture immediately turned yellow. After stirring for 12 h the suspension was filtered and the solvent was removed under dynamic vacuum. The yellow residue was washed with *n*-hexane and dried under dynamic vacuum. Yield: 88 mg (0.13 mmol, 64%). Single crystals were obtained by *n*-hexane diffusion into a concentrated dichloromethane solution of [(^tBuPNP^{N3}Adamantyl)FeCl] (6). ¹H NMR (300 MHz, CD₂Cl₂, 298 K): δ = 41.1 (br. s, $\nu_{1/2}$ ≈ 100 Hz, 1H), 38.0 (br. s, $\nu_{1/2}$ ≈ 120 Hz, 1H), 13.7, 12.6, 11.3 (br. s, overlapping resonances, ca. 27H), 6.8 (br. $\nu_{1/2}$ ≈ 20 Hz, 3H), 2.0 (br. s, $\nu_{1/2}$ ≈ 18 Hz, 3H), 1.2 (br. s, $\nu_{1/2}$ ≈ 6 Hz, 2H), 0.8 (br. s, $\nu_{1/2}$ ≈ 30 Hz, ca. 4H), –1.1 (sh.), –1.3 (br. s, $\nu_{1/2}$ ≈ 130 Hz) (overlapping resonances, ca. 13H), –2.7 (v. br. s, $\nu_{1/2}$ ≈ 180 Hz, 1H), –10.1 (br. s., $\nu_{1/2}$ ≈ 170 Hz, 1H), –36.0 (v. br. s., $\nu_{1/2}$ ≈ 620 Hz, 1H) ppm. UV–Vis (Et₂O, 298 K): λ_{\max} (ϵ , L mol^{–1} cm^{–1}) = 474 (770). IR (ATR): 3389 (w), 2941 (m), 2897 (m), 2868 (m), 26361 (w), 2341 (w), 2122 (w), 2064 (m), 1634 (w), 1543 (w), 1472 (s), 1367 (s), 1178 (m), 1113 (m), 1069 (s), 935 (w), 814 (vs), 731 (vs), 694 (m), 642 (m) cm^{–1}. Elemental analysis calc. (%) for C₃₂H₅₇ClFeN₄P₂ (650.31): C 59.03, H 8.82, N 8.61; found: C 58.56, H 9.03, N 7.65. The E.I. mass spectrum showed a molecular ion at *m/e* = 650 amu. The parent ion isotopic cluster was simulated: (calcd%, observd%): 648 (6, 7), 649(3, 4), 650(100, 100), 651(40, 36), 652(40, 39), 653(14, 13), 654(3, 3).

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