An iron(II) complex featuring κ^3 and labile κ^2-bound PNP pincer ligands – striking differences between CH_2 and NH spacers

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Electronic Supporting Information

General. All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques or in an MBraun inert-gas glovebox. The solvents were purified according to standard procedures.[1] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. The ligand N,N'-bis(diphenylphosphino)-2,6-diaminopyridine (PNP-Ph) (**1**) was prepared according to the literature.[2,3] ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on Bruker AVANCE-250, AVANCE-300 DPX, and AVANCE-400 spectrometers. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced internally to residual protio-solvent, and solvent resonances, respectively, and are reported relative to tetramethylsilane (δ = 0 ppm). ^{31}P{^{1}H} NMR spectra were referenced externally to H_3PO_4 (85%) (δ = 0 ppm).

[Fe(κ^3-*P,N,P*-PNP-Ph)(κ^2-*P,N*-PNP-Ph)Cl]BF_4 (2). To a suspension of anhydrous $FeCl_2$ (127 mg, 1 mmol) in THF (10 mL) PNP-Ph (**1**) (960 mg, 2.00 mmol) and $AgBF_4$ (195 mg, 1.0 mmol) was added and the mixture was stirred for 4h. The solvent was removed under reduced pressure and the remaining green solid was dissolved in CH_2Cl_2. The white precipitate (AgCl) was removed by filtration over Celite and the solution was evaporated under reduced pressure. The remaining green solid was washed twice with diethyl ether (10 mL) and dried under vacuum. The complex was further purified by growing crystals from a saturated CH_2Cl_2 solution at -20°C.Yield: 1.10 g (97%). Anal. Calcd. for $C_{58}H_{50}BClF_4FeN_6P_4 \cdot CH_2Cl_2$ (1218.01): C, 58.18; H, 4.30; N, 6.90. Found: C: 59.12; H, 4.51; N, 6.73. ^{1}H NMR (δ, CD_2Cl_2, 20°C): 6.2-8.7 (m, 50H, py, Ph, NH). ^{31}P{^{1}H} (δ, CD_2Cl_2, 20°C): A_2B spin system, δ_A = 108.7 (2P), δ_B = 100.9 (1P), J_{PP} = 50.0 Hz (shifts and J_{PP} determined from simulation), 47.0 (1P).
[Fe(κ^3-*P,N,P*-PNP-Ph)(κ^2-*P,N*-PNP-Ph)Cl]Cl (2Cl). This complex was prepared in similar fashion to **2** with anhydrous $FeCl_2$ (127 mg, 1 mmol) and PNP-Ph (**1**) (980 mg, 2.05 mmol). The reaction mixture was stirred in THF (10mL) for 4h and the solvent was then removed under reduced pressure. The green solid was washed with 10 mL of diethy ether (three times) and dried under vacuum. Yield: 1.06 g (98 %). All spectral data for **2Cl** were identical with those of **2**.

[Fe(κ^3-*P,N,P*-PNP-Ph)$_2$](Cl)$_2$ (3). A solution of complex **2Cl** (50mg) in 5 mL of CH_3CN was stirred for 15 min, whereupon the color changed from green to red. The solvent was evaporated and the remaining red solid was washed with diethyl ether and dried in vacuum. Yield: 45 mg (90 %yield). All spectral data for **2** were identical with those of the authentic sample reported previously.[4]

***trans*-[Fe(PNP-Ph)(CO)$_2$Cl]BF_4 (4).** A solution of **2** (50 mg, 0.044 mmol) in 10 mL of THF, was stirred for 1h under an atmosphere of CO, whereupon the color changed from green to red. The

solvent was then removed under reduced pressure. The remaining red solid was collected on a glass-frit, washed with diethyl ether and dried under vacuum. Yield: 26.0 mg (83.0 %). Anal. Calcd. for $C_{31}H_{25}BClF_4FeN_3O_2P_2$ (711.61): C, 52.32; H, 3.54; N, 5.90. Found: C: 52.22; H, 3.58; N, 5.79. ^{1}H NMR (δ, acetone-d_6, 20°C): 9.50 (s, 2H, NH), 8.10 (m, 5H, Ph, py), 7.71 (m, 18H, Ph, py). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2) 207.2 (t, *J* = 25.8 Hz, CO), 161.3 (py), 141.8 (py), 134.6 – 133.2 (Ph), 132.10 (Ph), 131.0 – 129.8 (Ph), 129.2 (t, *J* = 5.4 Hz, Ph), 102.2 (py). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20°C): 98.2. IR (ATR, 20°C, cm^{-1}): 2031 ($\nu_{C=O}$).

X-ray Structure Determination. X-ray diffraction data were collected at *T* = 100 K in a dry stream of nitrogen on Bruker Kappa APEX II diffractometer using graphite-monochromatized Mo-*K*α radiation (λ = 0.71073 Å) and fine sliced *φ*- and *ω*-scans. Data were reduced with the program SAINT-Plus[5] and corrections for absorption and detector effects were applied with the program SADABS.[14] The structure was solved with direct methods and refined with the SHELX program package.[6] All refinements were against F^2 data. Non-hydrogen atoms were refined anisotropically. The H atoms connected to C atoms were placed in calculated positions and thereafter refined as riding on the parent atoms. H atoms connected to N atoms were mostly located in difference Fourier maps and freely refined. Molecular graphics were generated with the program MERCURY.[7]

Computational Details. All calculations were performed using the GAUSSIAN 09 software package[8] on the Phoenix Linux Cluster of the Vienna University of Technology. The optimized geometries were obtained with the B3LYP functional,[9] without symmetry constraints. That functional includes a mixture of Hartree-Fock[10] exchange with DFT[11] exchange-correlation, given by Becke's three parameter functional with the Lee, Yang and Parr correlation functional, which includes both local and non-local terms. The basis set used for the geometry optimizations consisted of the Stuttgart/Dresden ECP (SDD) basis set[12] to describe the electrons of iron, and a standard 6-31g** basis set[13] for all other atoms. The inclusion of dispersion effects by means of Grimme DFT-D3 method[14] with Becke and Jonhson short distance damping[15] rises the stability difference between the two isomers of complex **2** from 6.9 to 9.0 kcal mol^{-1}.

Also, geometry optimizations of isomers **A** and **B** of complex **2** were performed with the M06 functional leading to same conclusions and a stability difference of 6.1 kcal mol^{-1}. The M06 functional is a hybrid meta-GGA functional developped by Truhlar and Zhao,[16] and it was shown to perform very well for the kinetics of transition metal molecules, providing a good description of weak and long range interactions.[17]

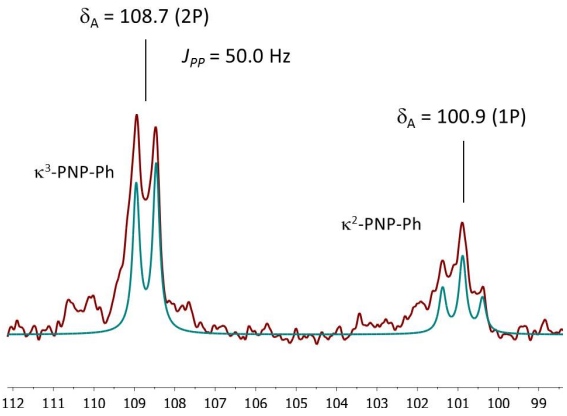

Figure S1 Part of the $^{31}P\{^{1}H\}$ NMR spectrum of **2** showing the resonances of the characteristic A_2B pattern the of the κ³-*P,N,P*- and κ²-*P,N*-bound PNP ligands (red). The simulated spectrum is shown in blue from which the chemical shifts δ_A and δ_B and the J_{PP} coupling constant were derived.

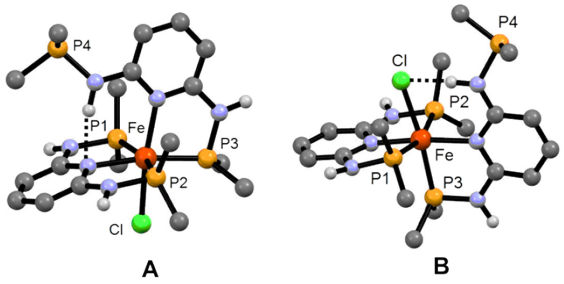

Fig. S2 Optimized B3LYP geometries of the two possible isomers **A** and **B** of [Fe(κ³-*P,N,P*-PNP-Ph)(κ²-*P,N*-PNP-Ph)Cl]⁺ (**2**). Most hydrogen atoms are omitted and only *ipso* carbon atoms of the Ph substituents are shown for clarity.

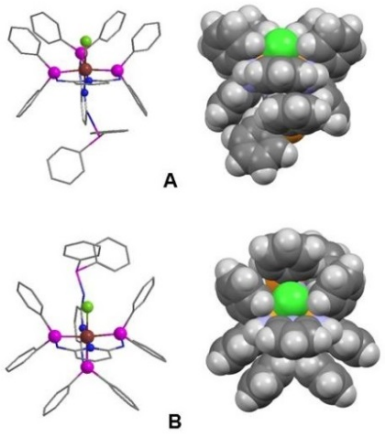

Fig. S3 Space filling representation of optimized B3LYP geometries of the two possible isomers **A** and **B** of [Fe(κ³-*P,N,P*-PNP-Ph)(κ²-*P,N*-PNP-Ph)Cl]⁺ (**2**) viewed along the Fe-N(py,κ³-PNP) bond to illustrate steric crowding around the Cl ligand (green).

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