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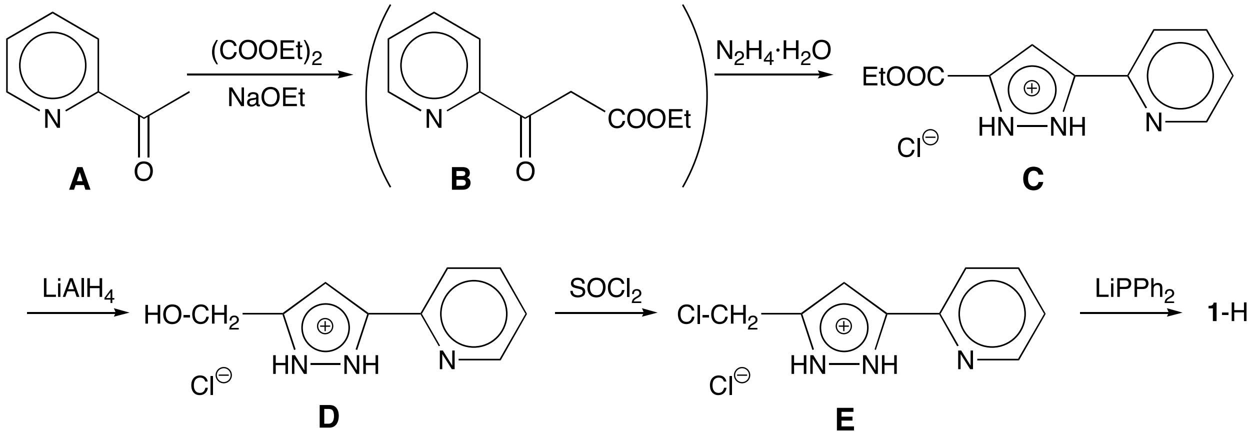
Supporting Information

Selective synthesis of isomeric heterodinuclear complexes with switched metal arrangements: Proton-induced reversible metal migration on an iridium complex with a novel dinucleating PNNN ligand (3-diphenylphosphinomethyl-5-pyridylpyrazolate)

Christian Dubs, Akiko Inagaki and Munetaka Akita*

Chemical Resources Laboratory, Tokyo Institute of Technology, R1-27, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Preparative procedures for PNNN-H (1-H).



Preparation of C: Sodium (2.5 g, 0.11 mol) was dissolved under argon in dehydrated ethanol (150 mL) at room temperature. To the resultant NaOEt solution was added diethyl oxalate (14.0 mL, 0.10 mol) followed by 2-acetylpyridine **A** (11.5 mL, 0.10 mol). After the solution was stirred for 18h, the volatiles were evaporated and the resultant dark-colored paste was dissolved in water (100 mL). The aqueous solution was neutralized with acetic acid and extracted with diethyl ether (100mL; 4 times). The combined organic phase was dried over $MgSO_4$ and filtered, and the solvent was evaporated to yield **B** (20.19g, 0.097 mol; crude yield: 97%) as a brownish- white solid. **B** was used as obtained without further purification.

The crude solid sample of **B** (20.19 g, 0.097 mol) was dissolved in dehydrated ethanol and then $NH_2NH_2 \cdot H_2O$ (4.26 mL, 1. eq) was added drop wise to the solution. After the mixture was refluxed for 3 hours, the volatiles were removed under educed pressure. The resultant brownish paste was dissolved in ether (100 mL) and the organic phase was washed with water (40 mL x 2). The combined aqueous solution was extracted again with ether (100 mL). The combined organic phase was dried over $MgSO_4$, filtered and evaporated to leave a sticky white solid. The solid was dissolved in ethanol (50 mL) and conc. HCl (4 mL) was added to form a HCl salt. Slow addition of ether gave the hydrochloride salt of 3-ethoxycarbonyl-5-(pyridin-2-yl)-pyrazole (**C**). A second crop was recovered from the filtrate by concentration and cooling of the filtrate. Combined yield of **C**: 71 % (22.0 g, 0.071 mol; with one mol of EtOH solvate)

B: ^{1}H-NMR (DMSO-d$_6$) δ_H 1.32 (t, 3H, J=6.8, CH$_3$), 4.34 (q, 4H, J=7.2 Hz, CH$_2$), 7.77- 7.86 (m, 2H, pz + py-H$_5$); 8.39 (m, 2H, py), 8.73 (d, 1H, J= 5.2 Hz, py-H$_6$); IR (KBr) 3106 (ν_{CH}; py), 2974, 2859 (ν_{CH}), 1725 cm^{-1} ($\nu_{C=O}$).

Preparation of D: 11.14 g (44 mmol) of **C** was dissolved in H_2O (30 mL). pH was adjusted to 8 by addition of sat. aq. Na_2HPO_4 solution. The aqueous phase was extracted with ether (3 times). The combined organic phase was dried over $MgSO_4$, filtered and evaporated to leave a slightly brown solid, which was dissolved in dry ether (300 mL). The ethereal solution was slowly added to $LiAlH_4$ (5 g) suspended in 50 ml dry ether and the mixture was refluxed for 10 h. The flask was immersed in an ice-water bath and the reaction mixture was hydrolyzed with water carefully. The volatiles were removed under reduced pressure and the obtained white cake was suspended in methanol (350 mL). CO_2 gas was bubbled through the solution for 10 minutes and the mixture was refluxed for 8 hours. Filtration and evaporation under reduced pressure gave a white solid. Water in this residue was removed by azeotropic distillation with ethanol. Dissolution of the resultant solid in ethanolic HCl solution followed by addition of ether gave the alcohol **D** (8.22g, 39 mmol, 89 % yield) as pale brown solid.

D: ^{1}H-NMR (DMSO-d$_6$) δ_H 4.57 (s, 2H, CH$_2$OH), 7.27 (s, 1H, pz), 7.82 (t, 1H, J= 5.9 Hz, py-H$_4$); 8.39 (d, 1H, J= 8.4 Hz, py-H$_3$), 8.48 (t, 1H, J= 7.6 Hz, py-H$_5$), 8.70 (d, 1H, J= 5.2 Hz, py-H$_6$); IR (KBr) 3292, 3129, 3003, 2768, 1608 cm^{-1}.

Preparation of E: **D** (6.02 g, 28.6 mmol) was dissolved in $SOCl_2$ (50 mL) and refluxed for 30 min. The excess $SOCl_2$ was removed under reduced pressure and the residue was dissolved in ethanol and filtered. The product **F** (5.95g, 26.0 mmol, 91 % yield) was obtained as a brownish solid by slow addition of ether.

E: ^{1}H-NMR (DMSO-d_6) δ_H 4.89 (s, 2H, CH_2Cl), 7.40 (s, 1H, pz), 7.79 (t, J= 6.6 Hz, py-H_4); 8.35 (d, J= 7.6 Hz, py-H_3) 8.43 (t, J= 7.6 Hz, py-H_5), 8.71 (d, 1H, J= 5.6 Hz, py-H_6); IR (KBr) 3122, 3067, 2953, 1631, 1616, 785 cm^{-1}.

Preparation of 1-H: To a dry THF solution of PPh_3 (2.82 g) was added lithium wire (186 mg) cut in small pieces. Stirring the mixture for 3 hours at ambient temperature gave $LiPPh_2$ as a dark red solution. The mixture was cooled with a dry ice-MeOH bath and **D** (1.31 g, 5.7 mmol) was added in one portion. After the mixture was stirred for 10 min at the same temperature, the mixture was further stirred for 2 hours at 0°C and then for 30 min at room temperature. Addition of deoxygenated water was followed by extraction with deoxygenated ether (3 times). The ether extract was dried over $MgSO_4$, filtered and concentrated to 10 ml. Products were separated by silica gel column chromatography under argon using dry and deoxygenated solvents. Elution with Et_2O-hexane (1:1) was followed by elution with ether. From the second ether eluent the PNNN-H ligand (**1**-H; 1.33 g, 3.9 mmol, 68 % yield) was isolated as a white solid after removal of the volatiles under reduced pressure.

Table S1. Spectroscopic data for PNNN-H and its metal complexes.

Complex	^{1}H-NMR (δ_H in CD_2Cl_2)	^{31}P-NMR (δ_P in CD_2Cl_2)	IR (KBr / cm^{-1})	ESI-MS (the largest peak)
1-H	3.52 (2H, s, CH$_2$P), 6.48 (1H, s, pz), 7.19- 7.22 (1H, m, py), 7.33-7.35 (6H, m, Ph), 7.46- 7.50 (4H, m, Ph), 7.61 (1H, d, J= 8.0 Hz, py-H$_3$), 7.71 (1H, dt, J= 8.0, 1.6 Hz, py-H$_4$), 8.56 (1H, d, J= 4.8 Hz, py-H$_6$)	-20.1	3259, 2962, 1428, 1467, 1431, 1096, 1024	343 [**1**-H] (FD-MS)
2$^{\mathbf{2}}$ $\cdot(BF_4)_2$	1.8-2.0 (4H, bm, cod), 2.4- 2.6 (2H, bm, cod), 2.6- 2.8 (2H, bm, cod), 3.2- 3.4 (m, 3H, CH$_2$P + cod), 3.7- 3.8 (1H, m, cod), 5.10 (1H, s, pz), 6.88 (2H, bs, cod), 7.29- 7.55 (8H, m, Ph + py), 7.7- 7.8 (4H, m, Ph), 7.88 (1H, t, J= 7.56, py-H$_4$), 7.98 (1H, d, J= 5.12, py-H$_6$)	-5.5 (0.6, solid)	2963, 1261, 1084,1028	642.6 [**2**], 942.5 [**2** + Ir(cod) –H] 1285.0 [**2** x 2 –H], 1373.0 [**2** x 2 + BF$_4$]
3a·BF$_4$	1.71 (2H, bs, cod), 1.92 (2H, bs, cod), 2.28 (4H, bs, cod), 2.68 (1H, bs, CH$_2$ in allyl), 3.70- 4.20 (8H, m, CH$_2$P + CH$_2$ in allyl + cod), 5.24 (1H, t, *J*=6.8, CH$_2$ in allyl), 5.69 (1H, m, CH in allyl), 6.76 (1H s, , pz), 7.37 (1H, td, J= 6.6,1.2 Hz, py-H$_5$), 7.40- 7.7 (10H, m, Ph), 7.76 (1H, d, *J*=7.6, py-H$_3$), 7.89 (1H, d, *J*=5.6, py-H$_6$), 8.00 (1H, td, J= 8, 1.2 Hz, py-H$_4$)	34.0	1608, 1464, 1084, 1053	790.3 [**3a**], 748.4 [**3a** – allyl]
3b·BF$_4$	1.5- 2.6 (16H, m, cod), 3.7-5.3 (8H, bm, cod), 4.03 (2H, d, J= 8.0, CH$_2$P), 6.71 (1H, s, pz), 7.3- 7.6 (11H, m, Ph + py), 7.74 (1H, d, J= 7.0 Hz, py-H$_3$), 7.87 (1H, d, J= 5.3 Hz, py-H$_6$), 8.01 (1H, t, J= 7.8 Hz, py-H$_4$)	38.79 (d, $J_{P\text{-}Rh}$=154.6 Hz)	2915, 2878, 2830, 1611, 1453, 1083	854.2 [**3b**], 744.4 [**3b** – cod]

Table S1. Spectroscopic data for PNNN-H and its metal complexes. (cont'd.)

Complex	^{1}H-NMR (δ_H in CD_2Cl_2)	^{31}P-NMR (δ_P in CD_2Cl_2)	IR (KBr / cm^{-1})	ESI-MS
4a·BF_4	1.73- 2.50 (8H, m, cod), 3.24 (2H, t, J= 10.7 Hz, CH_2 in allyl), 3.38 (1H, s, cod), 3.92- 4.01 (3H, m, cod + CH_2P), 4.11 (1H, d, J= 5.9 Hz, CH_2 in allyl), 4.58 (1H, d, J= 5.1 Hz, CH_2 in allyl), 5.22 (2H, s, cod), 5.81 (1H, m, CH in allyl), 6.83 (1H, s, pz), 7.38(1H, t, J= 6.1 Hz, py-H_5), 7.45- 7.70 (10H, m, Ph), 7.77 (1H, d, J= 8.0 Hz, py-H_3), 7.99 (1H, t, J= 7.8 Hz, py-H_4), 8.53 (1H, d, J= 4.9 Hz, py-H_6)	37.7	2915, 2880, 2834, 1606, 1449, 1054	790.3 [**4a**], 746.4 [**4a** – allyl]
4b·BF_4	1.35- 3.2 (16H, bm, cod), 3.30- 5.7 (10H, bm, cod + CH_2P), 6.80 (1H, s, pz), 7.33 (1H, t, J = 6.12 Hz, py-H_5), 7.40- 7.80 (12H, m, Ph + py), 7.96 (1H, t, J= 7.84 Hz, py-H_4)	38.1	2916, 2879, 2831, 1608, 1449, 1060	854.3 [**4b**]
5	2.10 (4H, bs, cod), 2.28 (4H, bs, cod), 3.33 (2H, s, cod), 3.59 (2H, d, J= 10.4 Hz, CH_2P), 5.79 (2H, s, cod), 6.73 (1H, s, pz), 7.07 (1H, dd, J= 7.42, 1.36 Hz, py-H_5), 7.42- 7.73 (11H, m, Ph + py), 8.00 (1H, d, J= 8.0 Hz, py-H_3), 8.50 (1H, d, J= 4.7 Hz, py-H_6)	31.2	2910, 2876, 2828, 1610, 1591, 1452, 1433, 1083	642.5 [**5** + H]

Details for X-ray crystallographic analysis

Singles crystals of **3a**·BF_4, **4a**·BF_4·$(CH_2Cl_2)_{0.5}$, **5**, and **8**·$(CH_2Cl_2)_2$ were obtained by recrystallization from CH_2Cl_2-ether. The crystallographic data are summarized in Table S2.

Diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with Mo Kα radiation (λ= 0.71069 Å). All the data collections were carried out at -60°C. Indexing was performed from 3 oscillation images, which were exposed for 5 min. The crystal-to-detector distance was 110 mm. Readout was performed with the pixel size of 100 μm x 100 μm. Neutral scattering factors were obtained from the standard source.[1] In the reduction of data, Lorentz, polarization, and empirical absorption corrections were made.[2]

The structures were solved by a combination of the direct methods (SHELXL 86)[3] and Fourier synthesis (DIRDIF).[4] Least-squares refinements were carried out using SHELXL97 [3] linked to teXsan.[5] Unless otherwise stated, non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at the calculated positions.

4a·BF_4·$(CH_2Cl_2)_{0.5}$: Because (i) the number of diffraction data with $I > 2\sigma(I)$ was insufficient owing to the small size of the crystal and (ii) attempted anisotropic refinements of the BF_4 anion and the CH_2Cl_2 solvate led to non-positive definition, the non-hydrogen atoms of the cationic parts were refined with anisotropic thermal parameters and the other atoms were refined isotropically.

8·BF_4·$(CH_2Cl_2)_2$: Because (i) the number of diffraction data with $I > 2\sigma(I)$ was insufficient owing to the small size of the crystal and (ii) attempted anisotropic refinements of the C2B and C6A atoms, the BF_4 anions and the CH_2Cl_2 solvates led to non-positive definition, the non-hydrogen atoms of the cationic parts except the two carbon atoms were refined with anisotropic thermal parameters and the other atoms were refined isotropically.

(1) *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1975, Vol. 4.

(2) T. Higashi *Shape - Program to obtain Crystal Shape using CCD camera*, Rigaku Corp.: Tokyo, Japan, 1999.

(3) (a) Sheldrick, G. M. *SHELXS-86: Program for crystal structure determination*, University of Göttingen, Göttingen, Germany, 1986. (b) Sheldrick, G. M. *SHELXL-97: Program for crystal structure refinement*, University of Göttingen: Göttingen, Germany, 1997.

(4) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program system, Technical Report of the Crystallography Laboratory*, University of Nijmegen, Nijmegen, The Netherland, 1992.

(5) *teXsan; Crystal Structure Analysis Package, ver. 1. 11*, Rigaku Corp., Tokyo, Japan, 2000.

Table S2. Crystallographic data.

complex	**3a**·BF_4	**4a**·BF_4·$(CH_2Cl_2)_{0.5}$	**5**	**8**·$(CH_2Cl_2)_2$
formula	$C_{32}H_{34}BN_3F_4$-$PPdIr$	$C_{32.50}H_{35}BN_3$-$F_4PClPdIr$	$C_{29}H_{29}N_3PIr$	$C_{60}H_{62}N_6$-$P_2Cl_4Ir_2$
formula weight	877.00	919.47	642.72	1455.3
crystal system	triclinic	triclinic	triclinic	triclinic
space group	P-1	P-1	P-1	P-1
a / Å	10.898(6)	13.877(9)	9.341(5)	11.130(18)
b / Å	11.791(8)	14.786(13)	9.958(5)	14.56(2)
c / Å	12.960(8)	16.189(14)	13.571(9)	18.75(2)
α / deg	96.74(2)	83.74(4)	92.45(5)	78.51(6)
β / deg	111.63(2)	79.66(3)	102.39(4)	85.37(6)
γ / deg	95.51(2)	88.57(3)	98.18(2)	71.38(6)
V/ Å^3	1519.8(16)	3248(5)	1216.9(13)	2823(7)
Z	2	2	4	2
d_{calcd} / g·cm^{-3}	1.916	1.880	1.754	1.712
μ / mm^{-1}	5.071	4.829	5.575	5.001
no of diffractions collected	11628	18654	4773	14895
no of variable	388	737	307	627
R1 for data with I > 2σ(I)	0.0732 (for 4764 data)	0.0633 (for 3480 data)	0.0584 (for 2686 data)	0.0727 (for 2858 data)
wR2	0.2569 (for all 6288 data)	0.2056 (for all 11925 data)	0.1468 (for all 3595 data)	0.2282 (for all 9937 data)

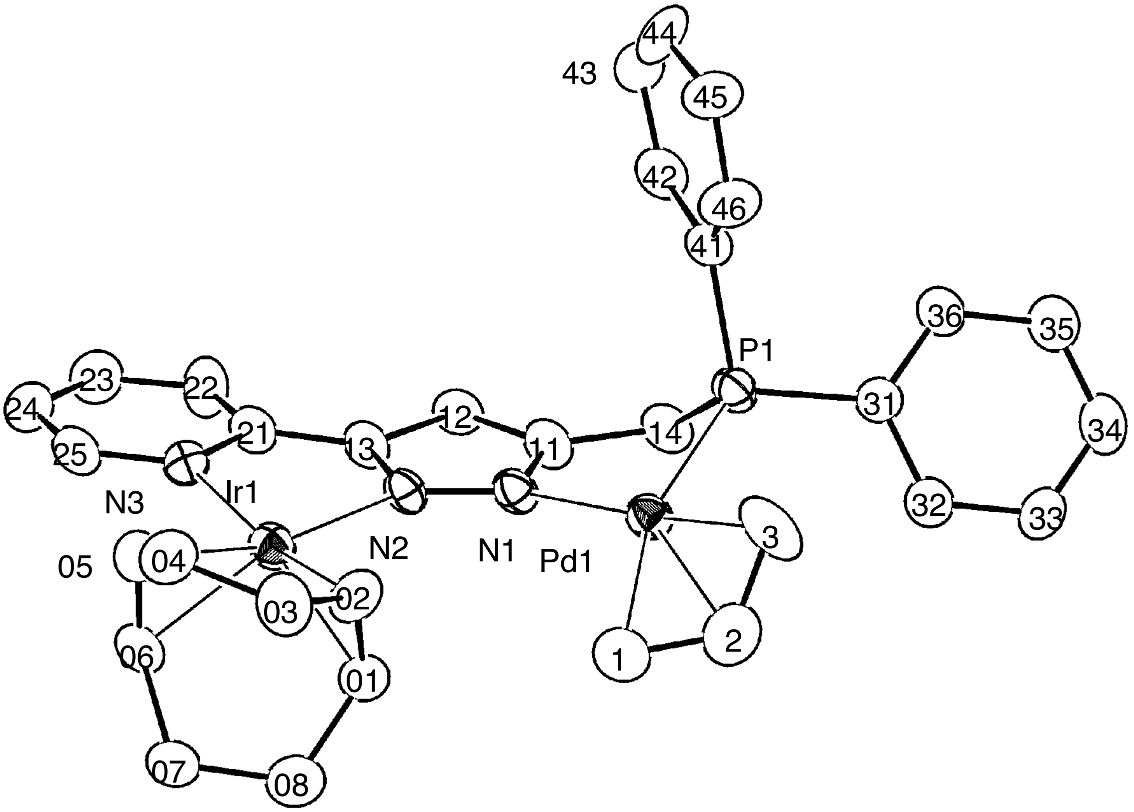


Figure S1. Atomic numbering scheme for the cationic part of **3a**·BF_4. Numbers without atom names are for carbon atoms.

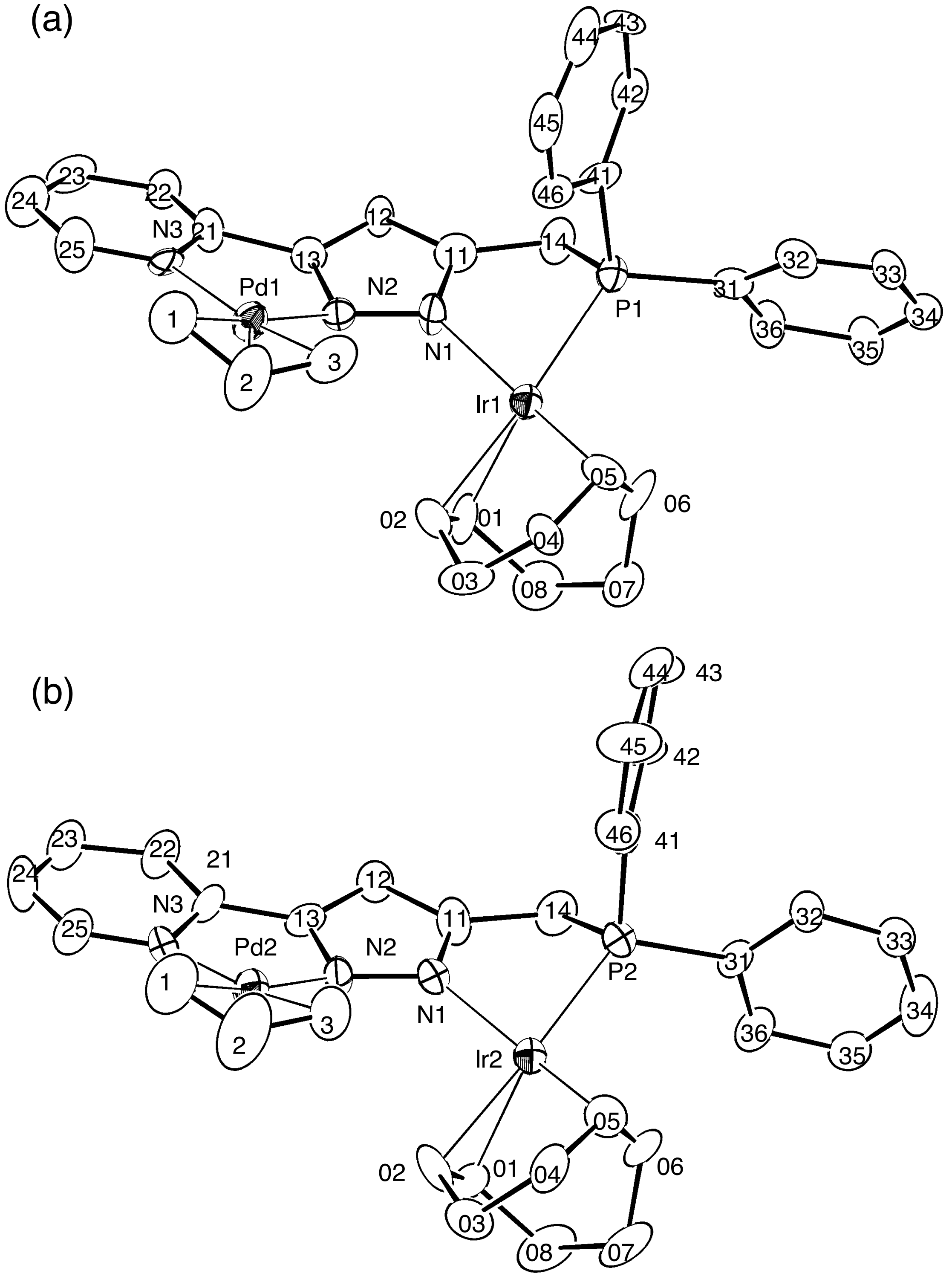


Figure S2. Atomic numbering scheme for the cationic part of **4a**·BF$_4$. Numbers without atom names are for carbon atoms. (a) molecule 1 (A-series). (b) molecule 2 (B-series).

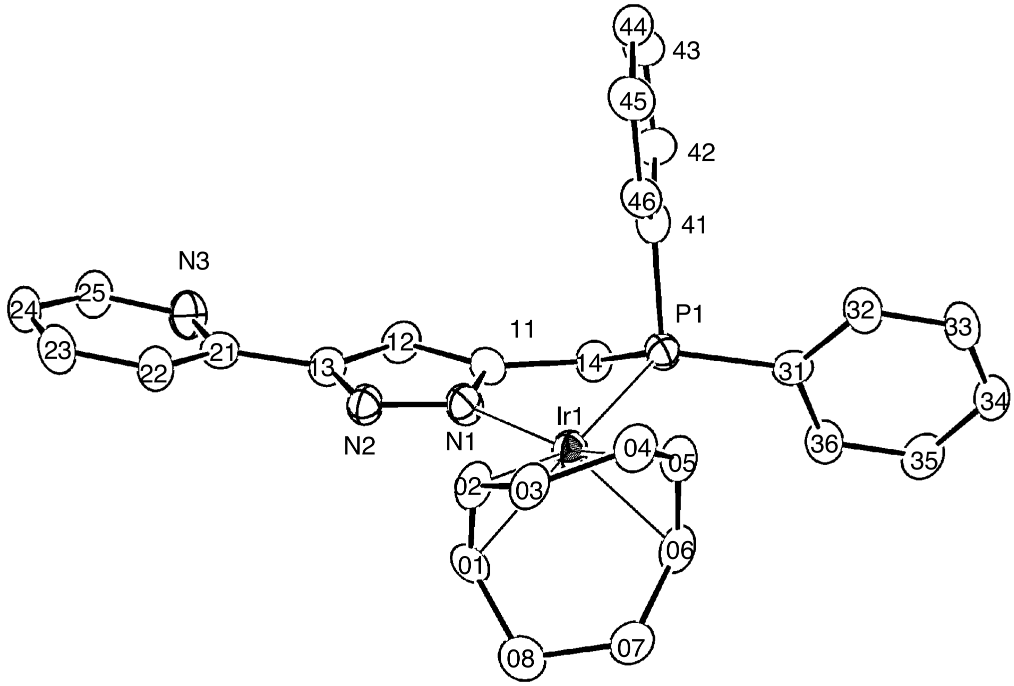


Figure S3. Atomic numbering scheme for the cationic part of **5**. Numbers without atom names are for carbon atoms.

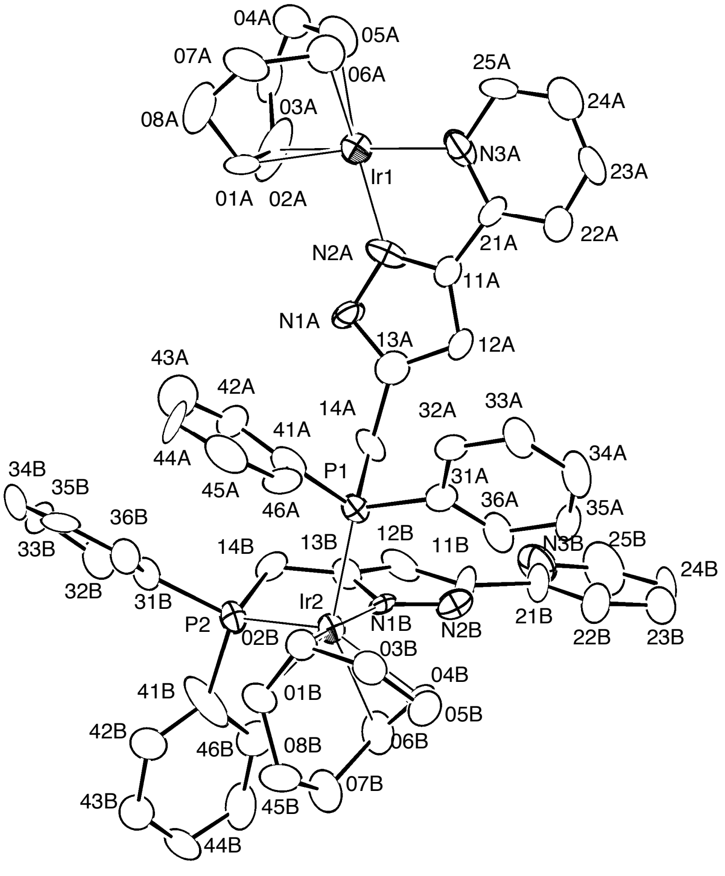


Figure S4. Atomic numbering scheme for the cationic part of **8**. Numbers without atom names are for carbon atoms.