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Electronic Supporting Information

For

Nickel(II) Complexes of the New Pincer-Type Unsymmetrical Ligands PIMCOP, PIMIOCOP, and NHCCOP: Versatile Bonding Motifs

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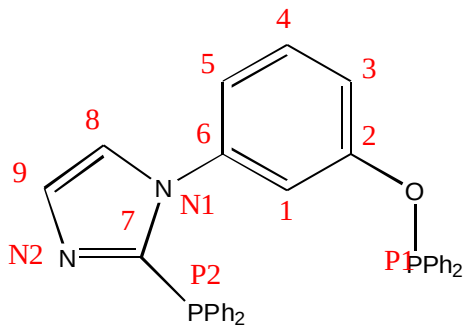
1. **General Comments.** Unless otherwise indicated, all manipulations were carried out using standard Schlenk and glove box techniques under nitrogen atmosphere. All solvents used for experiments were dried to water contents of less than 10 ppm (determined using a Mettler Toledo C20 coulometricKarl Fischer titrator) by passage through activated aluminum oxide columns (MBraun SPS) and freeze–thaw-degassed. All starting materials, including 3-bromoanisol, CuBr, imidazole, methyl trifluoromethanesulfonate, BuLi, Ph_2PCl, were purchased from Aldrich and used without further purification. Previous reports have described the syntheses of 3-methoxyphenyl-imidazole[1] and $NiBr_2(NC^iPr)$.[2] NMR chemical shift values are reported in ppm (δ) and referenced internally to the residual solvent signals (^1H and ^{13}C: 7.26 and 77.16 ppm for $CDCl_3$; 7.16 and 128.06 ppm for C_6D_6) or externally (^{31}P, H_3PO_4 in D_2O, δ = 0). Coupling constants are reported in Hz. High Resolution Mass Spectroscopy analyses were performed by the Centre Regional de Spectroscopie de Masse – Université de Montréal, and the Laboratoire de Chimie de Coordination du CNRS – Toulouse. The elemental analyses were performed by the Laboratoire de Chimie de Coordination du CNRS – Toulouse.

2. **Synthetic Procedures.** Details of the synthesis and characterization of the new compounds reported in the accompanying communication are provided below. All compounds are identified by their respective IUPAC names as well as the acronyms used to refer to them in the communication. In addition, we have provided a line-drawing for each compound to facilitate spectral assignments. It

should be noted that the numbering scheme used in these drawings are consistent with that used in the molecular views of the solid structures of complexes **3-5** (Figure 1 in the manuscript).

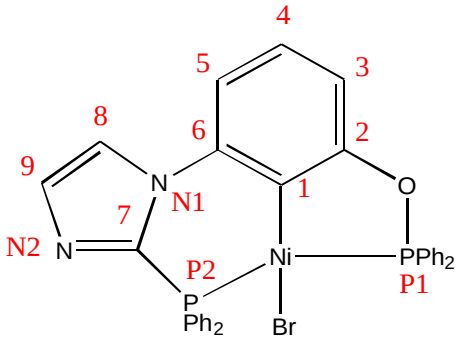
3-[2-(Diphenylphosphanyl)-1H-imidazol-1-yl]phenyl diphenylphosphinite, PIMC^{H}OP (2):



Drop-wise addition of BuLi (5.0 mL of a 2 M solution in cyclohexane, 10 mmol) to a solution of 3-hydroxyphenyl-imidazole **1** (800 mg, 5.0 mmol) in THF (75 mL) at –78 °C gave a pink suspension, which was allowed to warm to room temperature before adding $ClPPh_2$ (1.80 mL, 10.0 mmol). The resulting yellow solution was stirred for 10 min and then placed under vacuum to remove the volatiles. Extraction of the remaining solid residues with toluene (50 mL), followed by filtration and evaporation, gave the desired product as a beige solid (2.14 g, 81 %). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 7.64-7.71 (m, 4H, H_{Ar}), 7.49-7.57 (m, 10H, H_{Ar}), 7.26-7.42 (m, 10H, H_{Ar}), 7.03 (m, 2H, H8 & H9). ^{13}C NMR ($CDCl_3$, 25 °C): δ 157.7 (d, J_{CP}= 9.6, C2), 140.4 (d, J_{CP}= 17.0, *i*-C_{Ph}), 139.0 (d, J_{CP}= 4.5, C6), 135.6 (d, J_{CP}= 6.8, C7), 134.1 (d, J_{CP}= 20.0, *i*-C_{Ph}), 134.0 (d, J_{CP}= 20.7, CH_{ar}), 131.4 (d, J_{CP}= 7.5, CH_{ar}), 130.7 (d, J_{CP}= 22.7, CH_{ar}), 130.1 (s, CH_{ar}), 129.9 (s, CH_{ar}), 123.8 (s, CH_{ar}), 129.1 (s, CH_{ar}), 128.7 (d, J_{CP}= 7.5, CH_{ar}), 128.6 (d, J_{CP}=

8.4, CH_{ar}), 120.4 (d, J_{CP}= 6.5, CH_{ar}), 118.8 (d, J_{CP}= 13.0, CH_{ar}), 117.1 (dd, J_{CP}= 4.5 and 10.8, C1). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 25 °C): δ –29.2 (s, P2), +112.3 (s, P1). MS DCI-NH_3 *m/z* 529.1 $[MH]^+$. HRMS Calcd for $C_{33}H_{27}N_2OP_2^+$: 529.15917 found 529.15931.

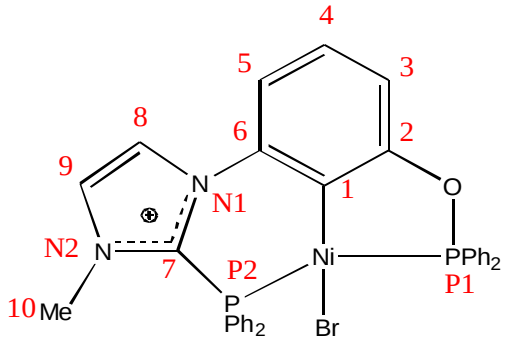
8-Bromo-7,7,9,9-tetraphenyl-10-oxa-2,5-diaza-7λ^5,9λ^5-diphospha-8-nickelatetracyclo[6.6.1.0^{2,6}.0^{11,15}]pentadeca-1(14),3,5,11(15),12-pentaene-7,9-bis(ylium), (PIMCOP)NiBr (3):



Stirring a mixture of **2** (1.72 g, 3.26 mmol), (*i*-PrCN)$NiBr_2$ (1.12 g, 3.91 mmol), and NEt_3 (4.86 mmol, 680 µL) in THF (50 mL) for 2 h at r.t. gave an orange suspension. Evaporation of the volatiles under vacuum, followed by extraction of the solid residues with toluene (75 mL), filtration, and evaporation of the filtrate, gave the crude product as a yellow solid. Slow evaporation of a saturated Et_2O solution of this solid gave analytically pure crystals of the desired product (1.70 g, 78 %). ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.93-7.98 (m, 4H, H_{Ar}), 7.60-7.65 (m, 5H, H_{Ar}), 7.52-7.56 (m, 2H, H_{Ar}), 7.42-7.50 (m, 7H, H_{Ar}), 7.35-7.39 (m, 4H, H_{Ar}), 7.10 (td, J_{HH}= 7.9, J_{HP} = 1.4, 1H, H_{Ar}), 6.89 (d, J_{HH}= 7.9, 1H, H_{Ar}), 6.86 (d, J_{HH}= 8.1,

1H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 25 °C): δ 167.8 (dd, J_{CP}= 5.0 and 17.5, C2), 143.7 (d, J_{CP}= 7.0, C6), 134.3 (d, J_{CP}= 11.2, CH_{Ar}), 133.3 (d, J_{CP}= 9.2, CH_{Ar}), 132.6 (d, J_{CP}= 11.9, CH_{Ar}), 132.3 (d, J_{CP}= 20.0, CH_{Ar}), 132.0 (d, $J_{CP=}$ 3.9, *i*-C_{Ph}), 131.8 (d, J_{CP}= 1.6, CH_{Ar}), 130.9 (d, J_{CP}= 1.8, CH_{Ar}), 128.6 (d, J_{CP}= 11.1, CH_{Ar}), 128.4 (d, J_{CP}= 11.8, CH_{Ar}), 128.1 (d, J_{CP} = 57.6, C7), 125.8 (dd, J_{CP}= 21.5 and 24.9, C1), 122.2 (s, CH_{Ar}), 114.6 (s, CH_{Ar}), 111.6 (d, J_{CP} = 14.1, CH_{Ar}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ +3.2 (d, J_{PP}= 358.0, P2), +145.7 (d, J_{PP}= 358.0, P1). HRMS Calcd for $C_{33}H_{26}N_2OP_2NiBr^+$: 665.0038 found 665.0057. Anal. Calcd. for $C_{33}H_{25}BrN_2NiOP_2$ (666,11): C, 59.60 ; H, 3.78 ; N, 4.21. Found: C, 59.62 ; H, 3.77 ; N, 4.21.

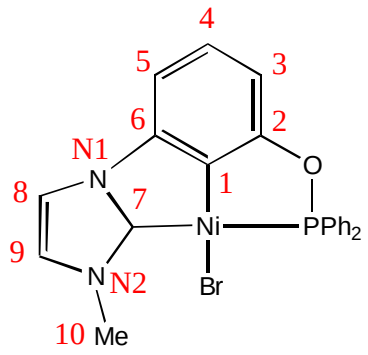
8-Bromo-5-methyl-7,7,9,9-tetraphenyl-10-oxa-2,5-diaza-7λ^5,9λ^5-diphospha-8-nickelatetracyclo[6.6.1.0^{2,6}.0^{11,15}]pentadeca-1(14),3,5,11(15),12-pentaen-5-ium-7,9-bis(ylium), (PIMIOCOP)NiBr (4):



Methyl trifluoromethanesulfonate (79.0 µL, 0.72 mmol) was added to a solution of **3** (0.48 g, 0.72 mmol) in CH_2Cl_2 (30 mL) cooled to –78 °C. The mixture was then allowed to warm to r. t. and stirred for 2 h. Evaporation of the volatiles under

vacuum, followed by washing of the solid residues with Et_2O (40 mL) afforded **4** as an orange solid (0.58 g, 97 %). Recrystallization at –20 °C from THF gave analytically pure **4** as orange crystals (m.p. 133-135 °C). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 8.12 (br s, 1H, H_{Ar}), 7.97-7.90 (m, 4H, H_{Ar}), 7.76-7.57 (m, 17H, H_{Ar}), 7.27 (t, J_{HH}= 7.5, 1H, H_{Ar}), 7.06 (d, J_{HH}= 7.8, 2H, H_{Ar}), 3.21 (s, 3H, CH_3). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 167.3 (dd, $J_{CP=}$ 5.4 and 17.6, C2), 141.5 (d, J_{CP}= 8.8, C6), 133.7 (d, J_{CP}= 11.3, CH_{Ar}), 133.0 (s, CH_{Ar}), 132.6 (d, J_{CP}= 11.3 Hz, CH_{Ar}), 132.5 (s, CH_{Ar}), 131.6 (d, J_{CP}= 26.4, *i*-C_{Ph}), 131.1 (d, J_{CP}= 49.1, *i*-C_{Ph}), 131.0 (s, CH_{Ar}), 130.1 (d, J_{CP}= 11.3, CH_{Ar}), 130.0 (s, CH_{Ar}), 128.8 (d, J_{CP}= 11.3, CH_{Ar}), 126.9 (pst, J_{CP}= 22.6 and 22.9, C1), 125.5 (s, CH_{Ar}), 122.9 (d, J_{CP} = 50.3 Hz, C7), 120.5 (q, J_{CF}= 320.0, $CF_3SO_3^-$), 116.8 (s, CH_{Ar}), 114.5 (d, J_{CP}= 15.1, CH_{ar}), 39.2 (s, CH_3). ^{31}P NMR (CD_2Cl_2, 25 °C): δ +147.0 (d, J_{PP}= 366.6, P1), +11.1 (d, J_{PP}= 366.6, P2). MS (ES): *m/z*: 679.0 $[M]^+$. HRMS (ES): calcd for $C_{34}H_{28}N_2OBrP_2Ni$ 679.0214; found, 679.0190.

1-Bromo-12-methyl-2,2-diphenyl-3-oxa-9,12-diaza-2λ^{5}phospha-1-nickelatetracyclo[6.5.1.0^{4,14}.0^{9,13}] tetradeca-1(13),4(14),5,7,10-pentaen-2-ylium, (NHCCOP)NiBr (5):



Tetra(ethyl)ammonium chloride (0.22 g, 1.33 mmol) and **4** (0.74 g, 0.89 mmol) were dissolved in CH_3CN (20 mL) and stirred at 60 °C for 24 h. Evaporation of the solution to dryness followed by purification of the remaining solid residues by flash chromatography on silica gel (CH_2Cl_2/hexane) gave a yellow solid that turned out to be a 1:2 mixture of the desired product and its Ni-Cl analogue, respectively. Treatment of this mixture with tetra(butyl)ammonium bromide (0.29 g, 0.89 mmol) in CH_3CN (10 ml), followed by filtration on silica gel (CH_2Cl_2), gave **5** as a yellow solid (0.17 g, 39 %). Recrystallization of the crude product at –20 °C from a THF/pentane mixture gave yellow crystals (m.p. 270-272 °C). ^{1}H NMR ($CDCl_3$, 25 °C): δ 8.06-8.02 (m, 4H, H_{Ar}), 7.52-7.46 (m, 6H, H_{Ar}), 7.23 (d, J = 1.9, 1H, H_{Ar}), 7.08 (t, J = 7.8, 1H, H_{Ar}), 6.80 (t, J = 1.9, 1H, H_{Ar}), 6.68 (dd, J = 3.5 and 7.8, 2H, H_{Ar}), 4.16 (s, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 173.8 (d, J_{CP} = 112.0, C7), 166.1 (d, J_{CP}= 16.3, C2), 148.2 (s, C6), 135.4 (d, J_{CP}= 31.4, C1), 132.6 (d, J_{CP}= 44.0, *i*-C_{Ph}), 132.4 (d, J_{CP} = 12.6, CH_{Ar}), 131.5 (s, CH_{Ar}), 128.5 (d, J_{CP} = 11.3, CH_{Ar}), 127.5 (s, CH_{Ar}), 122.8 (d, J_{CP} = 5.0 Hz, CH_{Ar}), 113.4 (s, CH_{Ar}),

109.2 (d, J_{CP} = 13.8, CH_{Ar}), 105.1 (s, CH_{Ar}), 38.2 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = +144.9 ppm. MS (ES): *m/z*: 415.1 $[M - Br]^+$. HRMS (ES): calcd for $C_{22}H_{18}N_2OPNi$ 415.0510; found, 415.0510.

3. **Procedure for electrochemical measurements.** Cyclic voltammetry measurements were carried out with a potentiostat Autolab PGSTAT100. Experiments were performed at room temperature in an homemade airtight three–electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of *ca* 1.0 cm^2 apparent surface. The working electrode was a glassy carbon microdisk (1.0 mm diameter). Voltammograms were recorded in dry CH_2Cl_2 solution (*ca* 3 x 10^{-3} M) in the presence of 0.1 M *n*-tetrabutylammonium hexafluorophosphate as the supporting electrolyte, under argon at 25°C. In these conditions, the redox couple $FeCp_2^+/FeCp_2$ was found at 0.44 V/SCE. All oxidation potentials reported are referenced to the $FeCp_2^+/FeCp_2$ redox couple.

4. **Procedure for crystal structure determinations.** Intensity data were collected at 180K on a Bruker Apex2 diffractometer. Structures were solved by direct methods using SIR92[3] or SHELXS,[4] and refined by full-matrix least-squares procedures using the program CRYSTALS.[5] Atomic scattering factors were taken from the International tables for X-ray Crystallography.[6] All non-hydrogen atoms

were refined anisotropically. Hydrogen atoms were refined using a riding model. Absorption corrections were introduced using the program MULTISCAN.[7]

Crystal data for **3**. $C_{37}H_{35}BrN_2NiO_2P_2$, M = 740.26 g.mol^{-1}, Triclinic, a = 10.8276(8), b = 12.6576(9), c = 14.1398(10) Å, α = 89.271(4), β = 69.270(4), γ = 67.245(4), V = 1653.9(2) Å^3, space group P -1, Z = 2, μ(Mo-Ka) = 1.928 mm^{-1}, 45525 reflections measured, 12897 unique (Rint = 0.023), 9265 reflections used in the calculations [I > 3σ(I)], 382 parameters, R1 = 0.0378, wR2 = 0.0475.

Crystal data for **4**. $C_{39}H_{36}BrF_3N_2NiO_5P_2S$, M = 902.35 g.mol^{-1}, Triclinic, a = 10.3522(6), b = 15.0431(9), c = 16.8048(9) Å, α = 91.599(3), β = 98.038(3), γ = 92.758(3), V = 2586.7(3) Å^3, space group P -1, Z = 2, μ(Mo-Ka) = 1.295 mm^{-1}, 53685 reflections measured, 10359 unique (Rint = 0.026), 7411 reflections used in the calculations [I > 3σ(I)], 523 parameters, R1 = 0.0312, wR2 = 0.0323.

Crystal data for **5**. $C_{26}H_{26}BrN_2NiO_2P$, M = 568.09 g.mol^{-1}, Triclinic, a = 9.8280(4), b = 11.2069(5), c = 13.2269(6) Å, α = 65.649(2), β = 69.724(2), γ = 68.158(2), V = 1199.39(9) Å^3, space group P -1, Z = 2, μ(Mo-Ka) = 2.568 mm^{-1}, 27313 reflections measured, 7770 unique (Rint = 0.027), 5414 reflections used in the calculations [I > 3σ(I)], 298 parameters, R1 = 0.0321, wR2 = 0.0326.

5. References

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