Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 302-304

Electrochemical and catalytic properties of nickel(II) complexes with bis(imino)acenaphthene and diazadiphosphacyclooctane ligands

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Diimines [S1-S5], $[Ni(MeCN)_6](BF_4)_2$ [S6], and $P^{Ph}{}_2N^{Ph}{}_2$ [S7] were prepared according to the literature procedures. The supporting electrolyte, Bu_4NBF_4, used for electrochemical studies was purchased from Sigma-Aldrich and dried overnight at 100 °C under vacuum prior to use. Anhydrous acetonitrile (> 99.8%) used for electrochemistry was purchased from Sigma-Aldrich.

Nickel(II) complexes with BIANs **1-7** were prepared according to the published procedures [S8-S11]. The Ni^{II} complexes with Ar-BIANs were obtained by treatment of 1 equivalent of nickel(II) salt $\{Ni(CH_3CN)_6(BF_4)_2$ (4 mM) with 1 equivalent of BIANs (4 mM) in acetonitrile until the components were completely dissolved at ambient temperature. The reaction mixture was filtered and solvent was removed under vacuum. The product was precipitated by diethyl ether and dried under vacuum. Yields of the nickel(II) complexes were up to 90 %.

The ^1H spectra were recorded using a Bruker Avance-400 NMR spectrometer. Elemental analysis was accomplished with the automated EuroVector EA3000 CHNS-O elemental analyzer (Euro-Vector, Milano, Italy). MALDI mass spectra were acquired using Ultra flex III TOF/TOF spectrometer (Bruker Daltonics, Germany). Infrared (IR) spectra were recorded on the Bruker Vector-22 FT-IR spectrometer.

1: brown-orange solid. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.88 (d, J = 8.2 Hz, 2H), 7.47 (t, J = 7.7 Hz, 4H), 7.37 (t, J = 7.8 Hz, 2H); 7.27 (t, J = 7.4 Hz, 2H), 7.14 (d, J = 7.8 Hz, 4H), 6.80 (d, J = 7.2 Hz, 2H). IR (cm^{-1}, KBr): 1647, 1612, 1597, 1578. MALDI TOF-TOF: 391.23. Anal. calcd for $C_{32}H_{28}B_2F_8N_6Ni$: C, 52.73; H, 3.87; N, 11.53; Found: C, 52.73; H, 3.87; N, 11.53.

2: orange solid. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03 (d, J = 8.2 Hz, 2H), 7.81 (m, 2H), 7.61 (m, 3H); 7.50 (t, J = 7.2 Hz, 2H); 7.25 (m; 1H), 7.18 (t, J = 6.6 Hz, 2H), 6.87 (d, J = 7.2 Hz, 2H). IR (cm^{-1}, KBr): 1645, 1601, 1580. MALDI TOF-TOF: 664.15. Anal. calcd for $C_{36}H_{24}B_2F_{20}N_6Ni$: C, 43.20; H, 2.42; N, 8.40; Found: C, 43.17; H, 2.45; N, 8.42.

3: red or orange crystals. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.88 (d, J = 8.2 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.10 (d, J = 9.0 Hz, 4H), 7.04 (t, J = 3.2 Hz, 4H), 6.70 (d, J = 7.2 Hz, 2H), 3.90 (s, 6H). IR (cm^{-1}, KBr): 1645, 1601, 1580. MALDI TOF-TOF: 452.24. Anal. calcd for $C_{34}H_{32}B_2F_8N_6NiO_2$: C, 51.76; H, 4.09; N, 10.65; Found: C, 51.73; H, 4.08; N, 10.66.

4: orange crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.98 (d, J = 8.4 Hz, 2H), 7.58 (m, 4H), 7.44 (t, J = 7.3 Hz, 2H), 7.00 (m, 4H); 6.70 (d, J = 7.2 Hz, 2H). IR (cm^{-1}, KBr): 1647, 1612, 1598, 1577. MALDI TOF-TOF: 442.23. Anal. calcd for $C_{34}H_{26}B_2F_8N_8Ni$: C, 52.43; H, 3.36; N, 14.39; Found: C, 52.43; H, 5.40; N, 14.40.

5: orange crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.98 (d, J = 8.4 Hz, 2H), 7.60 (m, 4H), 7.42 (t, J = 7.3 Hz, 2H), 7.10 (m, 4H); 6.70 (d, J = 7.2 Hz, 2H). IR (cm^{-1}, KBr): 1647, 1612, 1598, 1577. MALDI TOF-TOF: 427.18. Anal. calcd for $C_{32}H_{26}B_2F_{10}N_6Ni$: C, 50.25; H, 3.43; N, 10.99; Found: C, 50.23; H, 3.40; N, 11.00.

6: red crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.08 (d, J = 8.2 Hz, 2H), 7.95 (d, J = 7.8 Hz, 2H), 7.80 (d, J = 8.2 Hz, 4H), 7.56 (m, 3H), 7.45 (m, 2H), 7.26 (m, 3H), 7.22 (m, 2H), 6.64 (d, J = 7.2 Hz, 2H). IR (cm^{-1}, KBr): 1647, 1612, 1598, 1577. MALDI TOF-TOF: 492.11. Anal. calcd for $C_{40}H_{32}B_2F_8N_6Ni$: C, 57.95; H, 3.89; N, 10.14; Found: C, 57.94; H, 3.85; N, 10.10.

7: orange or red crystals. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, J = 8.8 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.34 (s, 4H), 6.73 (d, J = 7.6 Hz, 2H), 3.13 (m. 4H), 1.32 (d, J = 6.8 Hz, 12H), 1.06 (d, J = 6.8 Hz, 12H). IR (cm^{-1}, KBr): 1659, 1629, 1588. MALDI: *m/z* 558.44. Anal. calcd for $C_{44}H_{52}B_2F_8N_6Ni$: C, 58.90; H, 5.84; N, 9.37; Found: C, 58.93; H, 5.80; N, 9.30.

Electrochemical measurements. Cyclic voltammetry measurements were performed with an E2P potentiostat of BASi Epsilon (USA) composed of a measuring block, a Dell Optiplex 320 computer with installed an EpsilonES-USB-V200 program, and a C3 electrochemical cell. A stationary glassy-carbon electrode (with diameter of 3.0 mm) was used as a working electrode. Ferrocene was used as an internal standard. Ag/AgCl was used as a comparison electrode. Before and after each CV experiment, a 1.5 mM solution of ferrocene was recorded under similar conditions ($E_{1/2}$ = 0.45 V vs. Ag/AgCl). The potential was reproduced and remained constant in all the cases. A platinum wire of 0.5 mm diameter was used as an auxiliary electrode. Measurements were performed under an inert argon atmosphere.

X-ray diffraction data for the single crystals of **3** and **6** were collected in an ω/φ-scan mode on a Bruker Kappa Apex II CCD diffractometer using graphite monochromated Mo*K*α (0.71073 Å) radiation at 150(2) K (**3**) and 293(2) K (**6**). Diffractometer was equipped with an Oxford Cryostream LT device. Images were indexed and integrated using the *APEX*3 data reduction package (v2015.9-0, Bruker AXS). Data were corrected for absorption based on the Laue symmetry using equivalent reflections and for systematic errors. Structures were solved by the direct methods using SHELXT-2018/2 [S12] and refined by the full-matrix least-squares on F^2 using SHELXL-2018/3 [S13]. Non-hydrogen atoms were refined anisotropically. The positions of

hydrogen atoms of methyl groups were found using rotating group refinement with idealized tetrahedral angles. Other hydrogen atoms were inserted at the calculated positions and refined as riding atoms. The disorder of BF_4^- anions was resolved using free variables and reasonable restraints on geometry and anisotropic displacement parameters. All the compounds studied have no unusual bond lengths and angles.

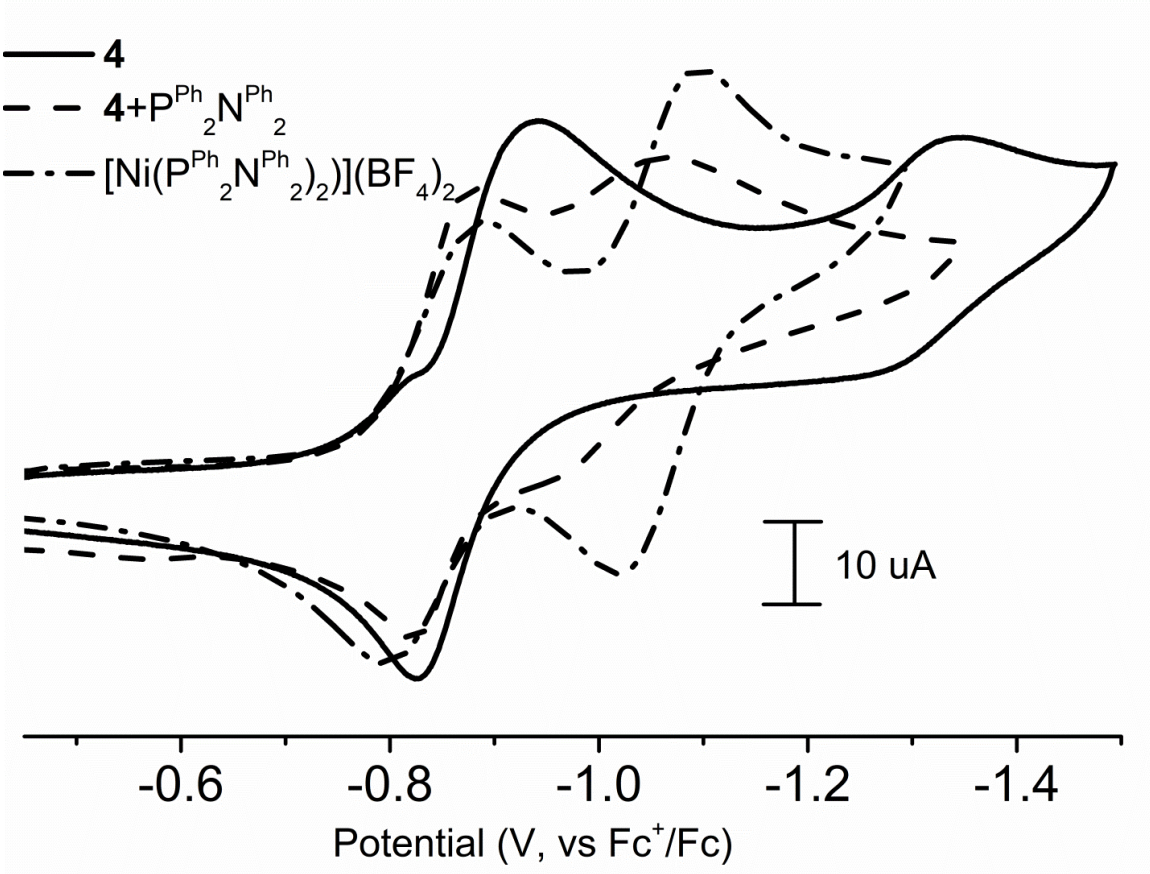

Figure S1 CVs for 1.5 mM solutions of **4**, mixed-ligand complex "**4** + $P^{Ph}_2N^{Ph}_2$", and $[Ni(P^{Ph}_2N^{Ph}_2)_2](BF_4)_2$ in acetonitrile.

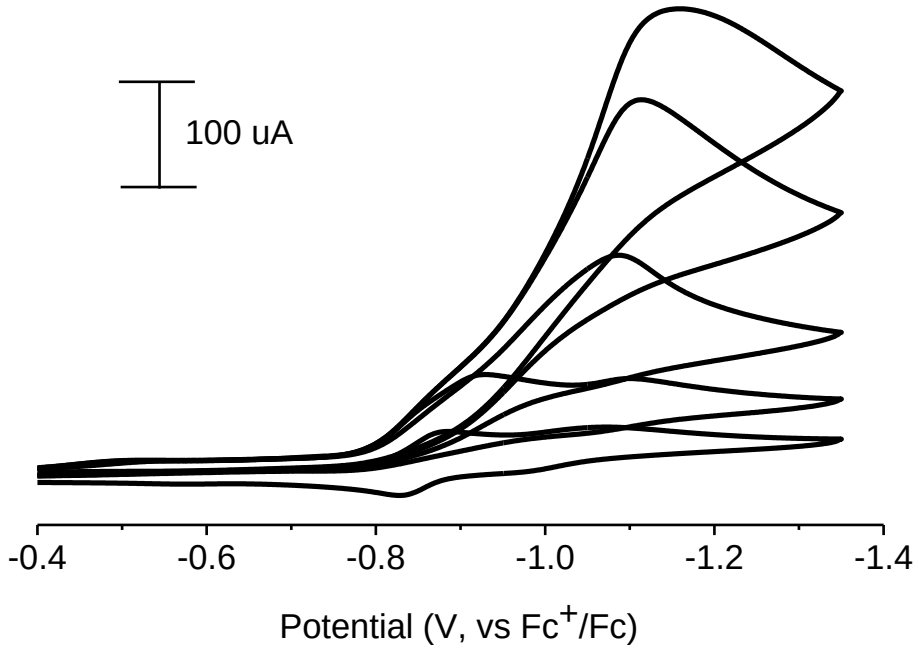

Figure S2 CVs for 1.5 mM solutions of mixed-ligand complex "**4** + $P^{Ph}{}_2N^{Ph}{}_2$" in acetonitrile in the presence of increasing amounts of [DMFH]OTf (0.01, 0.015, 0.020, 0.025 M).

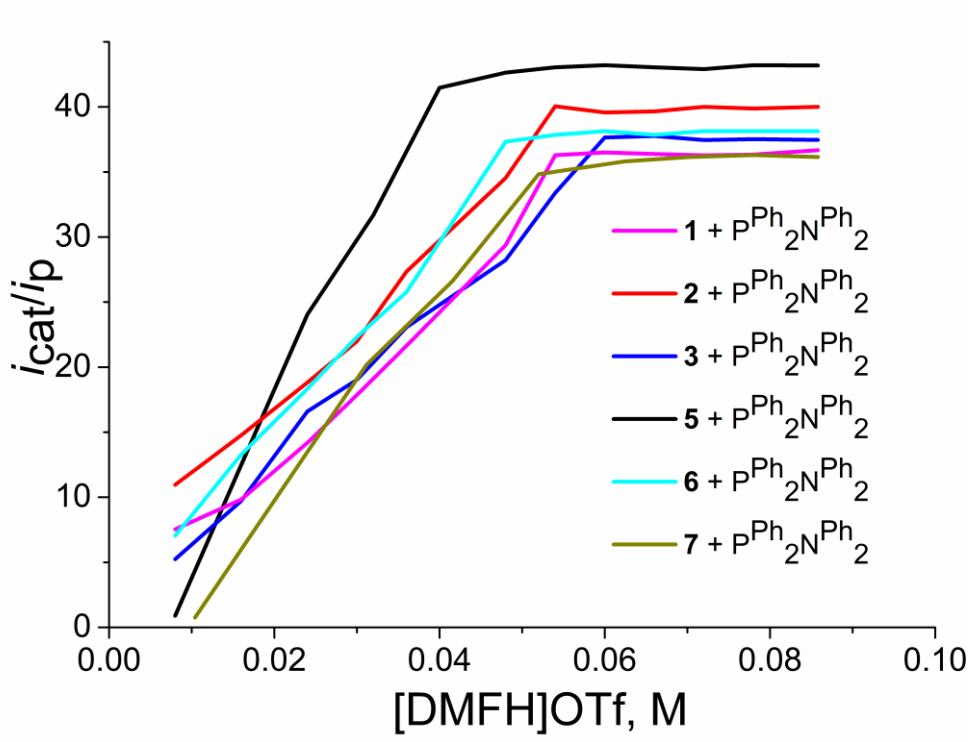

Figure S3 Plots of i_{cat}/i_p *vs*. acid concentration for 1.5 mM solution of **1**-**7** + $P^{Ph}{}_2N^{Ph}{}_2$ in acetonitrile.

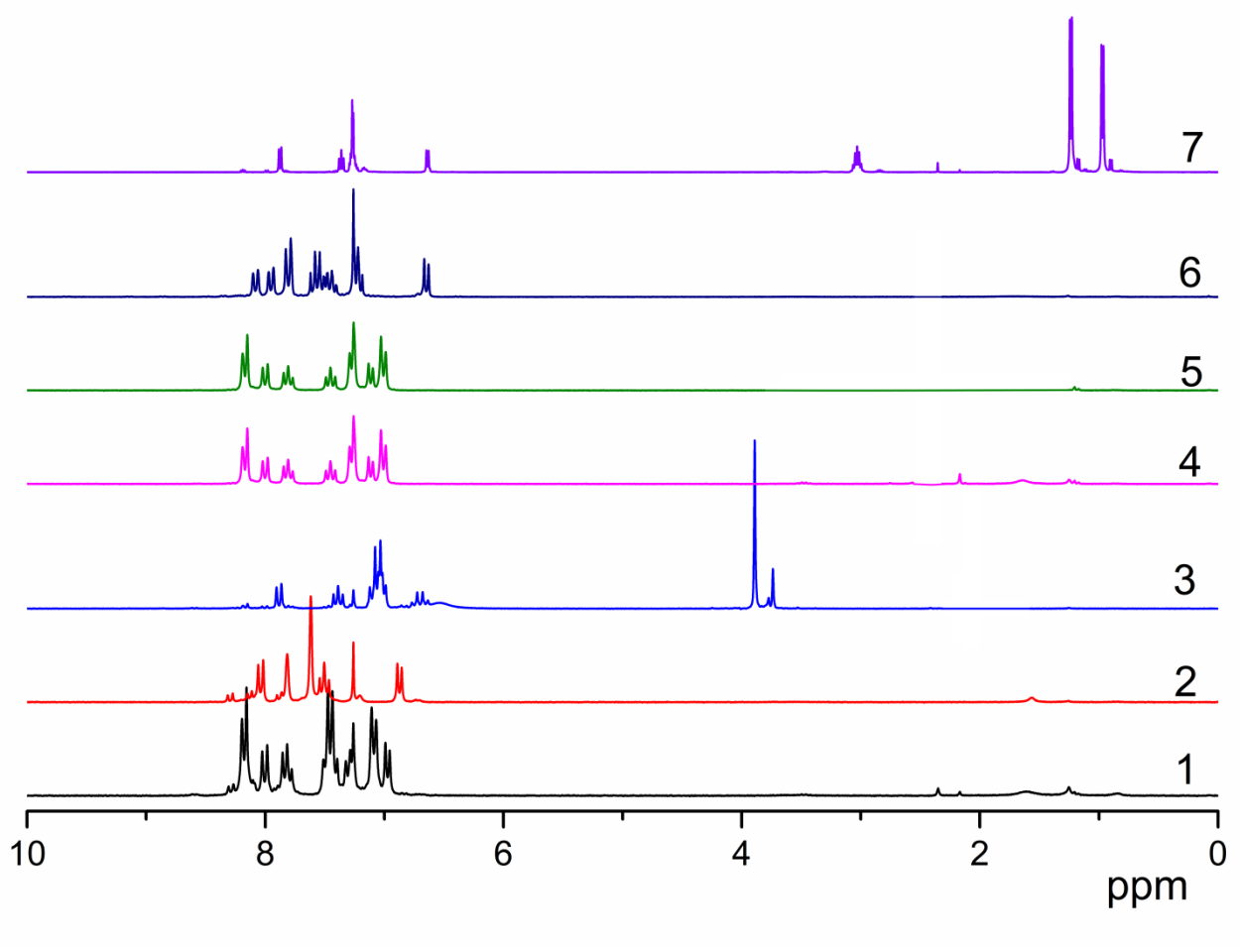

Figure S4 ^{1}H NMR spectra for **1-7** recorded in $CDCl_3$.

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