Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2020, **30**, 302–304

Mendeleev Communications

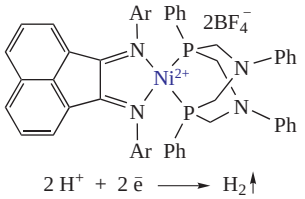
Electrochemical and catalytic properties of nickel(II) complexes with bis(imino)acenaphthene and diazadiphosphacyclooctane ligands

Vera V. Khrizanforova, Robert R. Fayzullin, Elvira I. Musina, Andrey A. Karasik and Yulia H. Budnikova*

A. E. Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of the Russian Academy of Sciences, 420088 Kazan, Russian Federation. E-mail: yulia@iopc.ru

DOI: 10.1016/j.mencom.2020.05.013

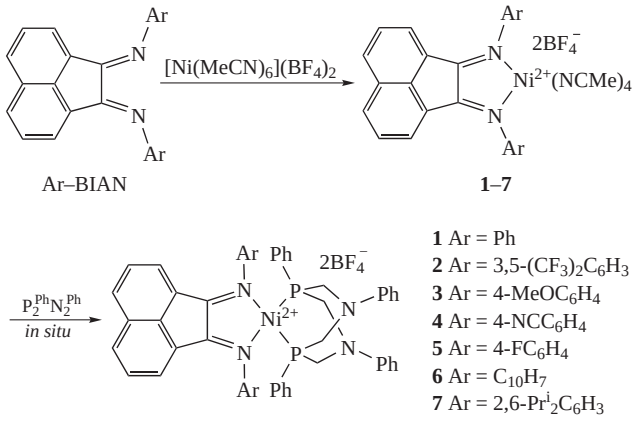
The title complexes were prepared, and their redox and catalytic properties in hydrogen evolution reaction were examined. The catalytic current increases in the presence of a proton source near the potential of the nickel(I/0) couple for a mixture of nickel(II) complexes with different ligands. Moreover, the catalytic activity of mixed-ligand complexes in the hydrogen evolution reaction was higher than that of a bis-chelated diphosphine nickel(II) complex.



Keywords: nickel complexes, α-diimines, phosphine, catalysis, hydrogen, electrochemistry.

Nickel(II) complexes with α-diimines exhibit good catalytic activity.[1–11] On the other hand, metal complexes with 1,2-bis(imino)-acenaphtenes (BIANs) can be used for creating new catalytic systems due to the non-innocent nature of ligand.[12–14] These ligands can accept to four electrons with the formation of stable anions and radical anions.[12] Nickel complexes with bis(imino)acenaphtenes exhibited high activity in the polymerization of ethylene,[15–21] and various nickel(II) complexes with substituted Ar–BIANs have been studied.[22–27] At the same time, the redox and electrocatalytic properties of nickel(II) complexes with BIANs are poorly understood.[28] Production of molecular H_2 through electrochemical hydrogen evolution reactions is crucial for the development of clean-energy technologies.

In this work, we synthesized nickel(II) complexes with Ar–BIANs (Scheme 1) as potential catalysts for hydrogen evolution reactions and studied their electrochemical properties by cyclic voltammetry in acetonitrile solution. A hydrogen evolution reaction with protonated dimethylformamide as a proton source was electrocatalyzed by the nickel(II) complexes in a mixed diimine and diphosphine medium.



Scheme 1

Nickel(II) complexes with Ar–BIANs were obtained from equimolar amounts of $[Ni(MeCN)_6](BF_4)_2$ and a ligand in acetonitrile at room temperature (Scheme 1). As a result, complexes **1**–**7** with equimolar metal-to-ligand ratios were formed, as confirmed by single-crystal X-ray diffraction analysis (for complexes **3** and **6**), MALDI mass spectrometry, and elemental analysis. The nickel center in an octahedral configuration in complexes **3** and **4**, was additionally coordinated with four acetonitrile molecules (Figure 1).†

† *Crystal data for* **3**. The crystals were grown by slow liquid diffusion of diethyl ether into an acetonitrile solution at room temperature. $C_{36}H_{35}B_2F_8N_7NiO_2$, M_r = 830.04, triclinic, $P\bar{1}$ (No. 2), a = 10.4619(6), b = 11.9692(7) and c = 17.1624(10) Å, α = 72.632(3)°, β = 78.308(2)°, γ = 74.102(2)°, V = 1955.5(2) Å^3, Z = 2, Z' = 1, d_{calc} = 1.410 g cm^{-3}, μ = 0.576 mm^{-1}, $F(000)$ = 852, $T_{max/min}$ = 0.6848/0.6035; 53862 reflections were collected (2.698° ⩽ θ ⩽ 27.098°; index ranges: –13 ⩽ h ⩽ 11, –15 ⩽ k ⩽ 15, –21 ⩽ l ⩽ 21), 8499 of which were unique, R_{int} = 0.0363, R_y = 0.0312; completeness to 25.242° of 98.9%. The refinement of 558 parameters with 256 restraints converged to R_1 = 0.0356, wR_2 = 0.0814 for 6959 reflections with $I > 2\sigma(I)$ and R_1 = 0.0488, wR_2 = 0.0879 for all data with S = 1.037 and residual electron density, $c_{max/min}$ = 0.431/–0.381 e Å^{-3}.

Crystal data for **6**. The crystals were grown as described above. The unit cell contains highly disordered solvent molecules of acetonitrile and/or diethyl ether, which were treated as a diffuse contribution to the overall scattering without specific atom positions by PLATON/SQUEEZE.[14] Squeezed solvent info is not included in the formulae and related items such as molecular weights and calculated densities. $C_{40}H_{32}B_2F_8N_6Ni$, M_r = 829.04, monoclinic, $P2_1/n$ (No. 14), a = 11.7829(14), b = 20.642(2) and c = 17.823(2) Å, β = 92.610(2)°, V = 4330.6(9) Å^3, Z = 4, Z' = 1, d_{calc} = 1.272 g cm^{-3}, μ = 0.517 mm^{-1}, $F(000)$ = 1696, $T_{max/min}$ = = 0.7239/0.6044; 29047 reflections were collected (1.973° ⩽ θ ⩽ 25.249°; index ranges: –14 ⩽ h ⩽ 14, –20 ⩽ k ⩽ 24, –21 ⩽ l ⩽ 21), 7846 of which were unique, R_{int} = 0.0860, R_y = 0.0888; completeness to 25.242° of 100%. The refinement of 610 parameters with 577 restraints converged to R_1 = = 0.0687, wR_2 = 0.1685 for 4501 reflections with $I > 2\sigma(I)$ and R_1 = 0.1280, wR_2 = 0.1965 for all data with S = 1.027 and residual electron density, $c_{max/min}$ = 0.940 and –0.455 e Å^{-3}.

CCDC 1970432 and 1970433 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

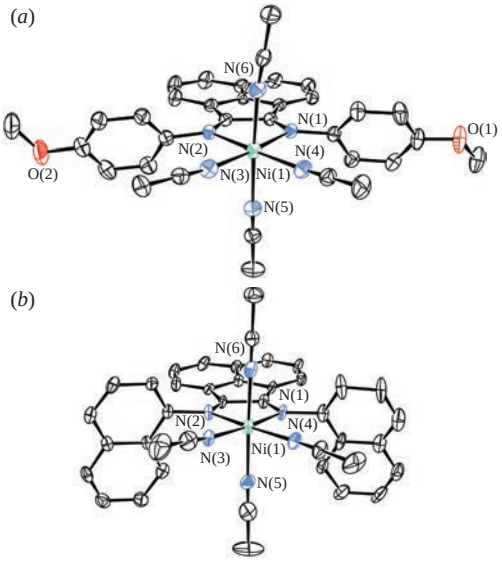


Figure 1 ORTEP of cationic parts of nickel(II) complexes (*a*) **3** and (*b*) **6** at 50 and 30% probability levels, respectively. Hydrogen atoms, solvent molecules, and tetrafluoroborate anions are omitted for clarity.

The complexes demonstrated similar electrochemical properties. Four reversible reduction peaks corresponding to the $Ni^{2+/1+/0}$ and Ar–BIAN$^{0/1-/2-}$ redox couples were observed for **1**–**7** in MeCN on CVs. The formation of stable Ni^{+} complexes at the first reduction peak potential during potential-controlled electrolysis was previously approved by UV-VIS and EPR spectroscopy.[28] The reduction potentials of **1**–**7** (Table 1) demonstrate that substituents in the *para* position of the aromatic ring of a diimine fragment affect significantly the first reduction potential of the complexes. In particular, acceptor substituents cause a negative shift of first reduction peak potentials in complexes **3**–**5**, as compared to unsubstituted complex **1**. In complexes **2** and **7** bearing isopropyl and trifluoromethyl moieties, the substituents have almost no effect on the reduction potentials.

Previously, the electrocatalytic properties of iron complexes with Ar–BIANs were studied in the hydrogen evolution from protonated DMF in acetonitrile solution.[29] Complexes **1**–**7**, which are stable in strongly acidic solutions, did not exhibit electrocatalytic activity in an analogous reaction. On the other hand, it is well known that bis-chelated nickel(II) complexes with 1,5-diaza-3,7-diphosphacyclooctanes are effective electrocatalysts for hydrogen evolution from different acids in organic media.[30–34] The catalytic current for these electrocatalysts was observed near the reduction potential of $Ni^{II/I}$ couple. The high catalytic activity of such complexes is mainly caused by a pendant amine group near the metal center, which provides effective proton binding and the subsequent hydrogen formation.[30–34]

Here, we proposed to combine the advantages of both aminomethylphosphine and diimine ligands in one structure and analyze the catalytic efficiency of the resulting mixed-ligand nickel complexes in the hydrogen evolution reaction. The addition of the diphosphine ligand $P_2^{Ph}N_2^{Ph}$ to nickel(II) complexes **1**–**7** in acetonitrile led to mixed-ligand complexes (see Scheme 1) and caused a small (~80 mV) anodic potential shift of the $Ni^{II/I}$ couple and a significant anodic potential shift of the $Ni^{I/0}$ couple on CVs in acetonitrile (Figure S1, see Online Supplementary Materials). The nickel(II) complex $[Ni(P_2^{Ph}N_2^{Ph})_2](BF_4)_2$[30] demonstrated two reversible reduction peaks at –0.89 and –1.09 V (*vs.* Fc^+/Fc) corresponding to $Ni^{II/I/0}$ redox couples.

The addition of $DMFH^+$ (pK_a^{MeCN} = 6.1)[35] to the complex $[Ni(P_2^{Ph}N_2^{Ph})_2](BF_4)_2$ in acetonitrile solution provides catalytic current enhancement at the $Ni^{II/I}$ couple potential. The maximum ratio of the catalytic current (i_{cat}) to the current of catalyst without acid (i_p), i_{cat}/i_p, was 30 at a scan rate of 0.1 V s^{-1},[36] which corresponded to the TOF value of 170 s^{-1}. Similarly, in the mixed-ligand nickel(II) complexes, significant current enhancement was observed on CVs in the presence of an acid in acetonitrile solution (Figure 2). A small increase in the first peak current (*i.e.*, near the $Ni^{II/I}$ couple potential) was observed only at low acid concentrations, a maximum i_{cat}/i_p ratio at the first reduction peak was 1.1–2.0, which is significantly lower than the catalytic increase in current for the nickel complex $[Ni(P_2^{Ph}N_2^{Ph})_2](BF_4)_2$ under similar conditions (Figure S2). Most likely, this is due to the fact that a certain amount of the monoligand complex $[Ni(P_2^{Ph}N_2^{Ph})_2](BF_4)_2$ is present in the mixture solution, which is just characterized by catalysis at the potential of the first peak. With increasing acid concentration, this peak disappears, merges with the main one, and one catalytic peak is observed at the $Ni^{I/0}$ potentials. However, when the acid is present in a huge excess, the reaction is of pseudo-first order, the current reaches a plateau, and k_{eff} and TOF under such conditions can be calculated and compared with each other and with published data. It can be assumed that, when the $P_2^{Ph}N_2^{Ph}$ ligand is added to the Ni–BIAN complex, a mixture of Ni–BIAN, $Ni(P_2^{Ph}N_2^{Ph})_2$ and $Ni(BIAN)(P_2^{Ph}N_2^{Ph})$ complexes is obtained. However, in the voltammograms of the Ni–BIAN complexes in the presence of a proton donor ([DMF]HOTf, AcOH, *etc.*), there is no catalytic increase in current. The catalytic activity of $Ni(P_2^{Ph}N_2^{Ph})_2$ is noticeably lower than that of a system with two different ligands (according to TOF calculations). Thus, for the complex $[Ni(P_2^{Ph}N_2^{Ph})_2](BF_4)_2$ in acetonitrile, the TOF of the catalytic cycle is 170 s^{-1}, and the current of the first peak increased by a factor of 30 with the use of [DMF]HOTf as a proton donor. A system with two ligands gave a TOF of 740 s^{-1},[37] and the second peak increased by a factor of 46. That is, if we assume that we have a mixture of nickel complexes in a solution

Table 1 Reduction potentials of complexes **1**–**7** in acetonitrile *vs.* Fc^+/Fc couple.

Complex	$E_p(Ni^{II/I})$ / V	$E_p(Ni^{I/0})$ / V
1	–0.74	–1.23
2	–0.76	–1.13
3	–0.97	–1.38
4	–0.86	–1.12
5	–0.88	–1.27
6	–0.90	–1.33
7	–0.77	–1.45

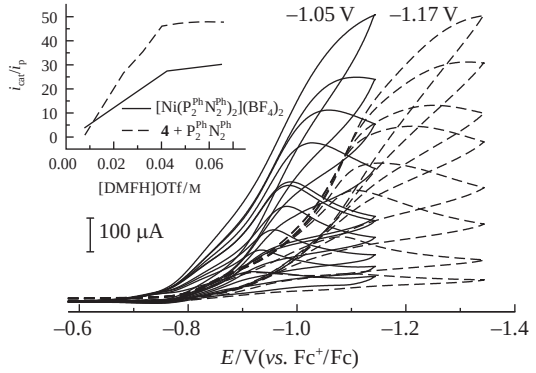


Figure 2 CVs for a 1.5 mM solution of $[Ni(P_2^{Ph}N_2^{Ph})_2](BF_4)_2$ (solid lines) and mixed-ligand complex **4** + $P_2^{Ph}N_2^{Ph}$ (dash lines) in acetonitrile in the presence of protonated DMF and corresponding plots of i_{cat}/i_p *vs.* acid concentration (0.008, 0.016, 0.024, 0.032, 0.040, 0.048, 0.056, 0.064, 0.072 M). Conditions: working electrode, glassy carbon; auxiliary electrode, Pt; and supporting electrolyte, Bu_4NBF_4. Potentials are referenced *vs.* Fc^+/Fc [$E_{1/2}$ (MeCN) = 0.45 V *vs.* Ag/AgCl].

of Ni–BIAN, Ni($P_2^{Ph}N_2^{Ph}$)$_2$, and mixed-ligand Ni(BIAN)($P_2^{Ph}N_2^{Ph}$), then the observed catalytic activity should be the sum of the activities of each, where Ni–BIAN is not active at all, and Ni($P_2^{Ph}N_2^{Ph}$)$_2$ is less active than nickel with a mixture of ligands. Nevertheless, it is reasonable to assume the predominance of a mixed-ligand complex with activity (TOF) exceeding the activity of mono-ligand complexes in the solution. The maximum i_{cat}/i_p ratio was ~46 at a scan rate of 0.1 V s^{-1}, which corresponded to the TOF value of 740 s^{-1}.[37] The potential of catalysis was –1.15 V (*vs.* Fc^+/Fc), which corresponded to an overpotential of 660 mV. The maximum i_{cat}/i_p ratio for complexes **1**–**7** + $P_2^{Ph}N_2^{Ph}$ is 35–46, which corresponds to TOFs of ~230–740 s^{-1} with an overvoltage of 0.660–0.820 V (Figure S3).

Thus, the replacement of one of two diphosphine ligands by an α-diimine ligand changes the mechanism of hydrogen evolution reaction and supports the catalytic activity. However, such modifications lead to an increase in the overpotential by ~100 mV. Thus, in the case of bis-chelated [Ni($P_2^{Ph}N_2^{Ph}$)$_2$](BF_4)$_2$, catalysis occurs at the $Ni^{II/I}$ couple potential, while for mixed-ligand nickel(II) complexes catalysis is observed at the potential of $Ni^{I/0}$ couple. The adjustment of the nickel ligand environment stabilizing the Ni^{I} active catalyst form allows one to increase the catalytic characteristics of the complex in the hydrogen evolution reaction. The combination of ligands of different nature, individually determining the low activity of the catalyst (diazadiphosphacyclooctane with a pendant amine base) and completely inactive complexes (BIAN), gives gross high catalytic TOFs due to the synergistic effect.

This work was supported by the Russian Foundation for Basic Research (grant no. 19-03-00084). The spectroscopic and diffraction data were obtained using the equipment of the Assigned Spectral-Analytical Center of the FRC Kazan Scientific Center of the Russian Academy of Sciences.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.013.

References

1 M. W. van Laren and C. J. Elsevier, *Angew. Chem., Int. Ed.*, 1999, **38**, 3715.
2 G. A. Grasa, R. Singh, E. D. Stevens and S. P. Nolan, *J. Organomet. Chem.*, 2003, **687**, 269.
3 A. Heumann, L. Giordano and A. Tenaglia, *Tetrahedron Lett.*, 2003, **44**, 1515.
4 A. E. Cherian, E. B. Lobkovsky and G. W. Coates, *Chem. Commun.*, 2003, **20**, 2566.
5 F. Al-Abaidi, Z. Ye and S. Zhu, *Macromol. Chem. Phys.*, 2003, **204**, 1653.
6 V. Fassina, C. Ramminger, M. Seferin, R. S. Mauler, R. F. de Souza and A. L. Monteiro, *Macromol. Rapid Commun.*, 2003, **24**, 667.
7 M. D. Leatherman, S. A. Svejda, L. K. Johnson and M. Brookhart, *J. Am. Chem. Soc.*, 2003, **125**, 3068.
8 C. M. Killian, D. J. Tempel, L. K. Johnson and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 11664.
9 C. Pellecchia, A. Zambelli, M. Mazzeo and D. Pappalardo, *J. Mol. Catal. A: Chem.*, 1998, **128**, 229.
10 A. E. Cherian, J. M. Rose, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2005, **127**, 13770.
11 J. M. Rose, A. E. Cherian and G. W. Coates, *J. Am. Chem. Soc.*, 2006, **128**, 4186.
12 M. M. Khusniyarov, K. Harms, O. Burghaus and J. Sundermeyer, *Eur. J. Inorg. Chem.*, 2006, 2985.
13 V. G. Sokolov, T. S. Koptseva, V. A. Dodonov, R. V. Rumyantsev and I. L. Fedushkin, *Russ. Chem. Bull., Int. Ed.*, 2018, **67**, 2164 (*Izv. Akad. Nauk, Ser. Khim.*, 2018, 2164).
14 A. L. Gushchin, N. F. Romashev, A. A. Shmakova, P. A. Abramov, M. R. Ryzhikov, I. S. Fomenko and M. N. Sokolov, *Mendeleev Commun.*, 2020, **30**, 81.
15 L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414.
16 W. C. Anderson, J. L. Rhinehart, A. G. Tennyson and B. K. Long, *J. Am. Chem. Soc.*, 2016, **138**, 774.
17 C. M. Killian, L. K. Johnson and M. Brookhart, *Organometallics*, 1997, **16**, 2005.
18 S. A. Svejda and M. Brookhart, *Organometallics*, 1999, **18**, 65.
19 C. S. B. Gomes, P. T. Gomes and M. T. Duarte, *J. Organomet. Chem.*, 2014, **760**, 101.
20 M. D. Leatherman and M. Brookhart, *Macromolecules*, 2001, **34**, 2748.
21 R. J. Maldanis, J. S. Wood, A. Chandrasekaran, M. D. Rausch and J. C. W. Chien, *J. Organomet. Chem.*, 2002, **645**, 158.
22 I. E. Soshnikov, K. P. Bryliakov, A. A. Antonov, W.-H. Sun and E. P. Talsi, *Dalton Trans.*, 2019, **48**, 7974.
23 L. Guo, W. Kong, Y. Xu, Y. Yang, R. Ma, L. Cong, S. Dai and Z. Liu, *J. Organomet. Chem.*, 2018, **859**, 58.
24 C. S. B. Gomes, P. T. Gomes and M. T. Duarte, *J. Organomet. Chem.*, 2014, **760**, 101.
25 Q. Zhang, R. Zhang, Y. Ma, G. Solan, T. Liang and W.-H. Sun, *Appl. Catal., A*, 2019, **573**, 73.
26 Z. Wang, Q. Liu, G. A. Solan and W.-H. Sun, *Coord. Chem. Rev.*, 2017, **350**, 68.
27 W. Shaoli, W. Sun and C. Redshaw, *J. Organomet. Chem.*, 2014, **751**, 717.
28 V. V. Khrizanforova, R. R. Fayzullin, V. I. Morozov, I. F. Gilmutdinov, A. N. Lukoyanov, O. N. Kataeva, T. P. Gerasimova, S. A. Katsyuba, I. L. Fedushkin, K. A. Lyssenko and Yu. H. Budnikova, *Chem. – Asian J.*, 2019, **14**, 2979.
29 V. V. Khrizanforova, V. I. Morozov, M. N. Khrizanforov, A. N. Lukoyanov, O. N. Kataeva, I. L. Fedushkin and Yu. H. Budnikova, *Polyhedron*, 2018, **154**, 77.
30 A. D. Wilson, R. H. Newell, M. J. McNevin, J. T. Muckerman, M. R. DuBois and D. L. DuBois, *J. Am. Chem. Soc.*, 2006, **128**, 358.
31 E. I. Musina, V. V. Khrizanforova, I. D. Strelnik, M. I. Valitov, Yu. S. Spiridonova, D. B. Krivolapov, I. A. Litvinov, M. K. Kadirov, P. Lönnecke, E. Hey-Hawkins, Yu. H. Budnikova, A. A. Karasik and O. G. Sinyashin, *Chem. – Eur. J.*, 2014, **20**, 3169.
32 V. V. Khrizanforova, E. I. Musina, M. N. Khrizanforov, T. P. Gerasimova, S. A. Katsyuba, Yu. S. Spiridonova, D. R. Islamov, O. N. Kataeva, A. A. Karasik, O. G. Sinyashin and Yu. H. Budnikova, *J. Organomet. Chem.*, 2015, **789**, 14.
33 V. V. Khrizanforova, Yu. G. Budnikova, I. D. Strelnik, E. I. Musina, M. I. Valitov, M. K. Kadirov, A. A. Karasik and O. G. Sinyashin, *Russ. Chem. Bull., Int. Ed.*, 2013, **62**, 1003 (*Izv. Akad. Nauk, Ser. Khim.*, 2013, 1003).
34 V. V. Khrizanforova, V. I. Morozov, A. G. Strelnik, Yu. S. Spiridonova, M. N. Khrizanforov, T. I. Burganov, S. A. Katsyuba, Sh. K. Latypov, M. K. Kadirov, A. A. Karasik, O. G. Sinyashin and Yu. H. Budnikova, *Electrochim. Acta*, 2017, **225**, 467.
35 A. M. Appel and M. L. Helm, *ACS Catal.*, 2013, **4**, 630.
36 R. T. Jane, P. D. Tran, E. S. Andreiadis, J. Pécaut and V. Artero, *C. R. Chim.*, 2015, **18**, 752.
37 M. L. Helm, M. P. Stewart, R. M. Bullock, M. R. DuBois and D. L. DuBois, *Science*, 2011, **333**, 863.

Received: 21st January 2020; Com. 20/6112