Electronic supplementary materials *Mendeleev Commun*., 2016, **26**, 131−133

First example of organonickel complex bearing three cyclic substituents in the σ-bonded aromatic ring: bromo[(2,2'-bipyridine)-2,4,6-tricyclohexylphenylnickel]

Il'yas F. Sakhapov, Zufar N. Gafurov, Vasily M. Babaev, Ildar Kh. Rizvanov, Alexey B. Dobrynin, Dmitry B. Krivolapov, Khasan R. Khayarov, Oleg G. Sinyashin and Dmitry G. Yakhvarov

All manipulations and reactions were carried out under an atmosphere of dry nitrogen. All solvents were purified and dried prior to use. DMF was dried with calcium hydride and purified by distillation. [$NiBr_2$(bpy)] was synthesized according to modified literature procedure;[S1] 2,2'-bipyridine (Alfa Aesar), 1-bromo-2,4,6-tricyclohexylbenzene (TchpBr, Sigma-Aldrich) and (NBu_4)BF_4 (Acros Organics) were commercial products. The supporting electrolyte (NBu_4)BF_4 was dried by melting in vacuum and stored under nitrogen.

Elemental analysis was performed on a EuroVector CHNS-O Elemental Analyser EA3000. ESI-MS measurements were performed using an AmazonX (Bruker Daltonics, Germany) ion trap mass spectrometer in positive mode in the mass range of 250–2000 Da. The optimized ESI-MS conditions were as follows: capillary voltage, – 4.5 kV; nitrogen drying gas, 10 L/min, 300 C. The NMR spectra were recorded on Bruker Avance III 400 spectrometer. Melting points were measured with an Electrothermal IA9000 SERIES Digital Melting Point Apparatus in capillary tubes. The macroscale electrolysis was performed using direct current power supply B5-49 (USSR).

X-ray diffraction analysis was performed on automatic diffractometer "Bruker Smart APEX II CCD (λMoKα). The structure was solved by direct method using SIR program[S2] and refined by the full matrix least-squares using SHELXL-97 program.[S3] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed into the geometrically calculated positions and refined as riding atoms. All calculations were performed using WinGX program.[S4] Analysis of intermolecular interactions were performed using PLATON program.[S5] All the figures were produced by MERCURY program.[S6] However, it was not

possible to obtain acceptably low values of the R-factor due to the low reflecting ability of the crystal.

The electrochemical synthesis of [NiBr(Tchp)(bpy)] (**1**) was carried out at room temperature in galvanostatic conditions [the potential of the working electrode was in the region –1.48 to -1.55 V *vs.* $Ag/AgNO_3$ (0.01 $mol \cdot L^{-1}$ solution in CH_3CN)]. The electrolysis was performed in a single electrochemical cell (three-electrode cell, 50 mL) without separation of anodic and cathodic compartments supplied with a nickel anode.[S7] A nickel porous muss electrode with a surface area of 60 cm^2 was used as cathode. Nitrogen was continuously bubbled through the stirred electrolyte during the electrolysis.

*Preparation of bromo[(2,2'-bipyridine)-2,4,6-tricyclohexylphenylnickel] (**1**).* A solution for electrolysis was prepared by mixing [$NiBr_2$(bpy)] (0.187 g, 0.5 mmol), TchpBr (0.2 g, 0.5 mmol) in DMF (50 mL). A constant current of 13.4 mA was passed through the solution for 1 hour (the potential of the working electrode was in the region –1.48 to -1.55 V *vs*. $Ag/AgNO_3$, 0.01 $mol \cdot L^{-1}$ solution in CH_3CN). After the electrolysis was completed, the solution was transferred to a flask, the solvent (DMF) was evaporated in vacuum and the residue was extracted with acetone (three times). The product was recrystallized from hot acetone cooling to +4°C, gave 0.18 g (58 %) of dark-red crystals of **1** suitable for X-ray analysis. Compound **1** was dried in vacuum at room temperature prior to NMR studies (for numbering of the atoms in **1** and ^1H-^{13}C heteronuclear single quantum coherence (HSQC) spectrum, see Figures S1 and S2).

^1H-NMR (400.1 MHz, [D_6]-acetone, 25 ºC): δ = 9.52 (d $^3J_{H2H3}$ = 5 Hz, 1H, H_{bpy}-2), 8.37 (d, $^3J_{H5H4}$ = 8.0 Hz, 1H, H_{bpy}-5), 8.32 (d, $^3J_{H6H7}$ = 8.0 Hz, 1H, H_{bpy}-6), 8.22 (t, 1H, H_{bpy}-4), 8.13 (t, 1H, H_{bpy}-7), 7.72 (t, 1H, H_{bpy}-3), 7.29 (t, 1H, H_{bpy}-8), 7.17 (d $^3J_{H9H8}$ = 6 Hz, 1H, H_{bpy}-9), 6.59 (s, 2H, m-H_{aryl}), 5.39 (m, 2H, $H_{c\text{-}hex}$-1, $H_{c\text{-}hex}$-23), 2.39 (m, 1H, $H_{c\text{-}hex}$-16), 1,83 (m, 12H $H_{c\text{-}hex}$-2, $H_{c\text{-}hex}$-3, $H_{c\text{-}hex}$-10, $H_{c\text{-}hex}$-11, $H_{c\text{-}hex}$-13, $H_{c\text{-}hex}$-14, $H_{c\text{-}hex}$-21, $H_{c\text{-}hex}$-22, $H_{c\text{-}hex}$-24, $H_{c\text{-}hex}$-25, $H_{c\text{-}hex}$-32, $H_{c\text{-}hex}$-33), 1.65 (m, 6H $H_{c\text{-}hex}$-4, $H_{c\text{-}hex}$-6, $H_{c\text{-}hex}$-8, $H_{c\text{-}hex}$-26, $H_{c\text{-}hex}$-28, $H_{c\text{-}hex}$-30), 1,52 (m, 3H $H_{c\text{-}hex}$-16, $H_{c\text{-}hex}$-18, $H_{c\text{-}hex}$-20), 1.29-1.26 (m, 9H $H_{c\text{-}hex}$-15, $H_{c\text{-}hex}$-17, $H_{c\text{-}hex}$-19, $H_{c\text{-}hex}$-5, $H_{c\text{-}hex}$-7, $H_{c\text{-}hex}$-9, $H_{c\text{-}hex}$-27, $H_{c\text{-}hex}$-29, $H_{c\text{-}hex}$-31).

$^{13}C\{^1H\}$-NMR (100.6 MHz, [D_6]-acetone, 25 ºC): δ = 156.6 (C_{aryl}-2), 153.7 (C_{aryl}-6), 151.9 (C_{bpy}-6), 151.7 (C_{bpy}-1, C_{bpy}-7), 151.5 (C_{bpy}-8), 143.8 (C_{aryl}-4), 142.1 (C_{aryl}-1), 140 (C_{bpy}-4), 139.3 (C_{bpy}-10), 127.3 (C_{bpy}-5), 126.9 (C_{bpy}-8), 122.5 (C_{bpy}-3), 121.9 (C_{bpy}-11), 121.3 (C_{aryl}-3, C_{aryl}-5), 48.5 ($C_{c\text{-}hex}$-1, $C_{c\text{-}hex}$-13), 45 ($C_{c\text{-}hex}$-7), 36 ($C_{c\text{-}hex}$-8, $C_{c\text{-}hex}$-12), 35.1 and 35 ($C_{c\text{-}hex}$-9, $C_{c\text{-}hex}$-10, $C_{c\text{-}hex}$-11), 28.3 ($C_{c\text{-}hex}$-2, $C_{c\text{-}hex}$-6), 28.1 ($C_{c\text{-}hex}$-13, $C_{c\text{-}hex}$-18), 27.9 ($C_{c\text{-}hex}$-3, $C_{c\text{-}hex}$-5, $C_{c\text{-}hex}$-15, $C_{c\text{-}hex}$-17), 27.3 ($C_{c\text{-}hex}$-4), 27.1 ($C_{c\text{-}hex}$-16).

Anal. Calcd (%) for $C_{34}H_{43}BrN_2Ni$ (618.32 g mol^{-1}): C 66.04; H 7.01; N 4.53, Ni 9.49. Found (%): C 65.50; H 7.63; N 4.31; Ni 9.66.

IR: ν(Ni-Br) 216, 191 cm^{-1}.

Mp > 320 °C (decomp.).

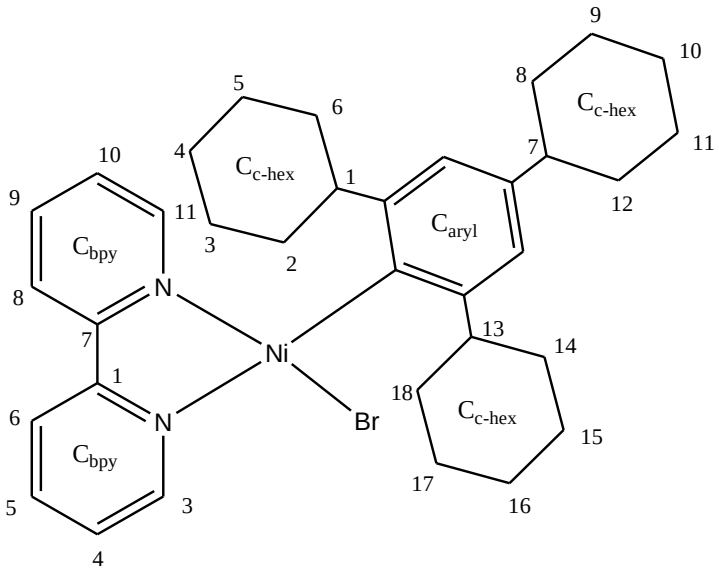

Figure S1 The numbering of H and C atoms in **1** for NMR study.

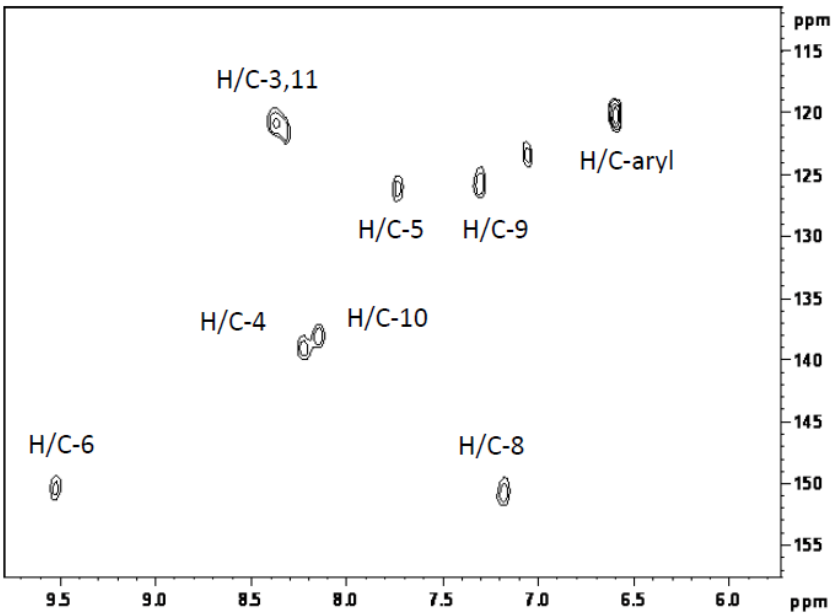

Figure S2 Signal assignments for the ^{1}H-^{13}C HSQC NMR spectrum (400/100.6 MHz, acetone-d6).

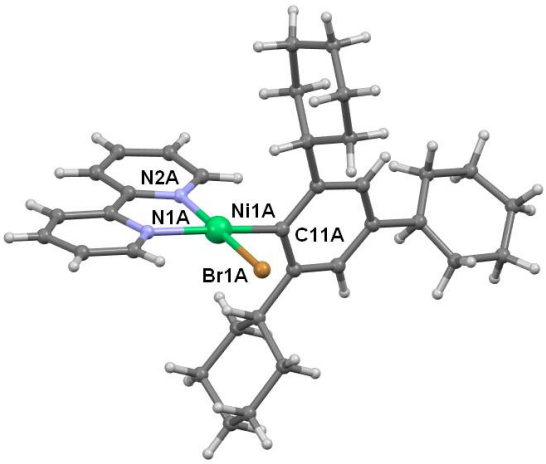

Figure S3 Molecular structure of **1** with 50 % thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) for **1** Ni(1a)-C(11a) 1.896(10), Ni(1A)-N(1A) 1.982(8), Ni(1A)-N(2A) 1.937(7), Br1(A)-Ni(1A) 2.3012(17), Ni(1B)-C(11B) 1.911(8), Ni(1B)-N(1B) 1.976(7), Ni(1B)-N(2B) 1.925(8), Br(1B)-Ni(1B) 2.3007(17); Br(1A)-Ni(1A)-N(1A) 96.7(2), Br(1A)-Ni(1A)-N(2A) 179.27(19), Br(1A)-Ni(1A)-C(11A) 88.4(3), N(1A)-Ni(1A)-N(2A) 82.6(3), N(1A)-Ni(1A)-C(11A) 173.5(3), N(2A)-Ni(1A)-C(11A) 92.3(3), Br(1B)-Ni(1B)-N(1B) 96.5(2), Br(1B)-Ni(1B)-N(2B) 174.2(2), Br(1B)-Ni(1B)-C(11B) 88.7(3), N(1B)-(Ni1B)-N(2B) 81.8(3), N(1B)-Ni(1B)-C(11B) 171.6(3), N(2B)-Ni(1B)-C(11B) 93.6(3).

Table S1 Crystal data and structure refinement for **1**.

	1
Formula	C34 H43 Br N2 Ni
FW	618.29
Crystal system	triclinic
Space group	P-1
a/A	10.825(4)
b/A	14.705(6)
c/A	20.915(8)
α/°	80.608(8)
β/°	86.773(11)
γ/°	89.694(8)
V/A^3	3279(2)
Z	4
Crystal size/mm^3	0.4 × 0.2 × 0.19
θ range/°	3.2, 27.0
Completeness to θmax	0.991
Reflections collected, R(int)	14209, 0.0000
Independent reflections	14209
GooF	0.93
Final R indices [I>2σ(I)]	R1 = 0.1020
	wR2 = 0.2539
R indices (all data)	R1 = 0.2073
	wR2 = 0.2901

References

S1 M. Uchino, K. Asagi, A. Yamamoto and S. Ikeda, *J. Organomet. Chem.*, 1975, **84**, 93.

S2 A. Altomare, G. Cascarano, C. Giacovazzo and D. Viterbo, *Acta Crystallogr., Sect. A*, 1991, **47,** 744.

S3 G. M. Sheldrick, *SHELX-97. Programs for Crystal Structure Analysis (Release 97-2).* University of Göttingen, 1997, vols. 1, 2.

S4 L. J. Farrugia, *J. Appl. Crystallogr.,* 1999, **32,** 837.

S5 A. L. Spek, *Acta Crystallogr., Sect. D.,* 2009, **65,** 148

S6 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466.

S7 D. G. Yakhvarov, E. A. Trofimova, I. Kh. Rizvanov, O. S. Fomina and O. G. Sinyashin, *Russ. J. Electrochem.,* 2011, **47**, 1100 (*Elektrokhimiya*, 2011, **47**, 1180).