Supplementary Information

Nickel(II)-2-amino-4-alkoxy-1,3,5-triazapentadienate complexes as catalysts for Heck and Henry reactions

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Experimental

Material and Instrumentations

Solvents and starting materials were obtained from commercial sources (Aldrich) and used as received. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ^{1}H and ^{13}C NMR spectra (in D_2O/[D_6]DMSO) were measured on a Bruker Avance II 300 MHz (UltraShield Magnet) spectrometer at ambient temperature. Infrared spectra (4000– 400 cm^{-1}) were recorded on a Brucker VERTEX 70 instrument as KBr pellets. ESI$^+$ mass spectra were obtained in methanol on a VARIAN 500-MS LC ion-trap mass spectrometer equipped with an electrospray ion source. A microwave reactor Anton Paar, Monowave 300, was used for the catalytic studies of the Heck reaction. 1-Butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6], and 1-butyl-3-methylimidazolium bis(trifluoromethane-sulfonyl)imide, [bmim][NTf_2], were prepared, by anion exchange of 1-butyl-3-methylimidazolium bromide upon reaction with $NaPF_6$ and $LiNTf_2$, respectively, using standard literature methods[1] and used after drying for 24 h at 60°C under a high vacuum whilst stirring.

Synthesis of Cu(II)-tap complexes were performed according the procedure described by us earlier.[2] Thus, $Cu(AcO)_2\cdot H_2O$ (200 mg, 1.0 mmol) or $Cu(NO_3)_2\cdot 2.5H_2O$ (233 mg, 1.0 mmol) and cyanoguanidine (168 mg, 2 mmol) were added to a flask with ROH (15 mL of methanol or ethanol, respectively), equipped with a magnetic stirrer, and the resulting mixture was heated at reflux for 24 h. Then the reaction mixture was filtered off, the eluate was evaporated under vacuum and the pink residue was washed with acetone and then recrystallized from methanol. The identity of the complex $[Cu(NH{=}C(OCH_3)NHC(NH_2){=}NH)_2](CH_3COO)_2$ (**1**) (yield 82%) was confirmed by IR, ESI$^+$-MS and elemental analysis.[2]

$[Cu(NH{=}C(OCH_2CH_3)NHC(NH_2){=}NH)_2](NO_3)_2$ (**2**): Yield 96%. IR (KBr, selected bands): 3340(s), 3245(s) ν(N-H); 2915(m) ν(C-H); 1625(s) ν(C=N); 1561(s) δ(N-H); 1130(s), 1090(s) ν(C-O); 1219 ν(C-N). ESI$^+$-MS (Calcd. for $[M-H^+-2NO_3]^+$), m/z: 322.09 (100%), 324.09 (44.9%), 323.1 (8.9%); (found), m/z: 321.9 (100%), 323.9 (45%). Elemental Analysis (Calcd.): C 21.45% N 31.28% H 4.50%; (found): C 21.40% N 31.33% H 4.40%.

The liberation of the tap salts was performed according the procedure described by us ealier,[2] namely by the reaction of corresponding copper(II)-tap complexes with acetylacetonate (Hacac) in aqueous medium at 25°C. The identity of the salt

$(NH{=}C(OCH_3)NHC(NH_3){=}NH)(CH_3COO)$ (**3**) (yield 92%) was confirmed by ^1H and ^{13}C NMR.[2]

$(NH{=}C(OCH_2CH_3)NHC(NH_3){=}NH)(NO_3)$ (**4**) Yield 91%. IR (KBr, selected bands): 3360(s) ν(N-H); 2983(m) ν(C-H); 1642(s) ν(C=N); 1590(s) δ(N-H); 1093(s) ν(C-O); 1540(s), 1385(s). ESI$^+$-MS (Calcd. for $[M-NO_3]^+$), m/z: 131.09 (100%); (found), m/z: 131.1 (100%). Elemental Analysis (Calcd.): C 24.87% N 36.26% H 5.74%; (found): C 24.81% N 36.21% H 5.63%. ^1H NMR (D_2O): δ = 1.29 (t, 3H; CH_3CH_2O), 4.21 ppm (q, 2H; CH_3CH_2O); $^{13}C\{^1H\}$ NMR (D_2O): δ = 13.31 (CH_3CH_2O), 65.31 (CH_3CH_2O), 160.29 ($C_2H_5OC{=}NH$), 162.25 ppm ($NHC{=}NH$).

Synthesis of Ni(II)-tap complexes

Route A (standard method): Nickel(II) nitrate hexahydrate $Ni(NO_3)_2•6H_2O$ (0.145 g, 0.5 mmol) was dissolved in distilled water (25 mL) and was treated with NaOH (1M) (2.5 mL). The solution is allowed to stand for 30 minutes to produce nickel(II) hydroxide as a green amorphous precipitate, which was then filtered off, washed with water and dried. Nickel(II) hydroxide (0.5 mmol), the corresponding triazapentadiene salt (1 mmol, obtained by liberation from the corresponding Cu^{II} complex **1** or **2** upon reaction with Hacac)[2] and distilled water (10 mL) were placed in round bottom flask equipped with a magnetic stirrer. The reaction mixture was stirred for 6 h at 25°C to produce an orange precipitate, which was filtered off, washed with NaOH (1M) and further with distilled water. Recrystallization from acetone yielded suitable crystals for single crystal X-ray diffraction.

Route B (template method): Nickel(II) nitrate hexahydrate $Ni(NO_3)_2•6H_2O$ (0.145 g, 0.5 mmol) was dissolved in the corresponding alcohol (25 mL), and cyanoguanidine (0.098 g, 1 mmol) was added afterwards. The reaction mixture was refluxed for 72 h to produce an orange precipitate that was filtered off, washed with NaOH (1M) and further with distilled water (yields of 11% for $[Ni\{N{=}C(OCH_3)NHC(NH_2){=}NH\}_2]$ (**5**) and 9% for $[Ni\{N{=}C(OCH_2CH_3)NHC(NH_2){=}NH\}_2]$ (**6**)). The identity of the thus formed Ni(II)-tap complexes was confirmed via comparison of their IR and elemental analysis data with those obtained via the route A (standard method).

$[Ni\{N{=}C(OCH_3)NHC(NH_2){=}NH\}_2]$, (**5**): Yield 87%. IR (KBr, selected bands): 3467(s), 3358(s), 3213(s) ν(N-H); 2946(m) ν(C-H); 1618(s) ν(C=N); 1570(s) δ(N-H); 1298(s), 1090(s) ν(C-O); 1224 ν(C-N). ESI$^+$-MS (Calcd. for $[M+H]^+$), m/z: 288.1 (100%), 290.1 (39.4%), 289.1 (9.9%); (found), m/z: 289.0 (100%), 290.9 (40%), 289.9 (10%). Elemental Analysis (Calcd.): C 24.94% N 38.78% H 4.88%; (found): C 25.01% N 38.86% H 4.84%.

$[Ni\{N{=}C(OCH_2CH_3)NHC(NH_2){=}NH\}_2]$ (**6**): Yield: 81%. IR (KBr, selected bands): 3466(s), 3364(s), 3336(m) ν(N-H); 2980(m) ν(C-H); 1626(s) ν(C=N); 1589(s) δ(N-H); 1292(s), 1096(s) ν(C-O); 1241(m) ν(C-N); ESI^+-MS (Calcd. for $[M+H]^+$): 317.1(100%), 319.09(38.6%), 318.1(11.9%); (found), m/z: 316.9(100%), 318.9(40%), 317.9(11%); Elemental Analysis (Calcd.): C 30.31, N 35.35 H 5.72; (found): C 30.39, N 35.21 H 5.76.

General procedure for the catalytic Heck reaction studies

[bmim]$[PF_6]$ (0.50 g, 1.75 mmol), catalyst (0.02 mmol) and triphenylphosphine (24 mg, 0.08 mmol) were mixed in a vial (10 mL) equipped with a magnetic stirrer and heated to 80 °C for 5 min in a heating block to form the ionic liquid solution of the catalyst. Butyl acrylate (0.256 g, 2.0 mmol), triethylamine (0.152 g, 1.5 mmol), and the corresponding aryl halide (1.0 mmol) were added, and the reaction mixture was heated to the predefined temperature for the established time in a microwave synthesizer (using 100 W of power). The products were analyzed by NMR, using literature reports and an internal standard.[3]

General procedure for the catalytic Henry reaction studies

The catalyst **5** or **6** (5.0 μmol) was placed, under air, in a 5 mL vial. Methanol (2 mL), nitroethane (286 μL, 4 mmol) and the selected aldehyde (1 mmol) were added to the vial in that order. The reaction mixture was stirred during 12 – 24 h (see Table S3 for the details) at 25°C temperature and air atmospheric pressure. The reaction mixture was evaporated to dryness under a stream of dinitrogen, and the residue was dissolved in deuterated DMSO and analysed by ^1H NMR spectroscopy. The yield of β-nitroalkanol (relatively to the aldehyde) was established using 1,2-dimethoxyethane as internal standard, taking into consideration the relative amounts of these compounds, as given by ^1H NMR spectra and previously reported.[4] The ratio between the *anti* and *syn* isomers was also determined by ^1H NMR spectroscopy.[5] Blank experiments were performed under the same reaction conditions in the presence of $Ni(NO_3)$ •$2.6H_2O$ instead of **5** or **6**.

Crystal Structure Determination

X-ray quality single crystals of the compounds were immersed in cryo-oil, mounted in a nylon loop and measured at room temperature. Intensity data were collected using a Bruker APEX-Kappa CCD diffractometer with graphite monochromated Mo-Kα (λ 0.71069) radiation. Data were collected using phi and omega scans of 0.5° per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT[6] on all the observed reflections. Absorption corrections were applied using SADABS.[6] Structures were solved by direct methods by using the SHELXS-97 package[7] and refined with SHELXL2014.[7] Calculations were performed using the WinGX System v2014.1.[8] All non-hydrogen atoms were refined anisotropically. Those H-atoms bonded to carbon were included in the model at geometrically calculated positions and refined using a riding model. $U_{iso}(H)$ were defined as $1.2U_{eq}$ of the parent carbon atoms for phenyl and methylene residues and $1.5U_{eq}$ of the parent carbon atoms for the methyl groups. The other hydrogen atoms (N–H) were located in the difference Fourier synthesis and refined, in some cases with the help of distance restraints, their isotropic thermal parameter set at 1.5 times the average thermal parameter of the parent nitrogen atom. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic ones for the remaining atoms were employed.

1. V. Cimpeanu, V. Parvulescu, V. I. Parvulescu, J. M. Thompson, C. Hardacre, *Cat. Today*, 2006, **117**, 126–132.
2. M. N. Kopylovich, Y. Y. Karabach, M. F. C. Guedes da Silva, P. J. Figiel, J. Lasri and A. J. L. Pombeiro, *Chemistry – A European Journal*, 2012, **18**, 899-914.
3. L. Xu, W. Chen, J. Xiao, *Organometallics*, 2000, **19**, 1123-1127.
4. a) A. Cwik, A. Fuchs, Z. Hell and J. M. Clacens, *Tetrahedron*, 2005, **61**, 4015-4021; b) M. Sutradhar, M. da Silva and A. J. L. Pombeiro, *Catalysis Communications*, 2014, **57**, 103-106; c) A. Paul, A. Karmakar, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *RSC Advances*, 2015, **5**, 87400-87410; d) A. Karmakar, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Dalton Transactions*, 2014, **43**, 7795-7810; e) A. Karmakar, S. Hazra, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *New Journal of Chemistry*, 2014, **38**, 4837-4846.
5. S. E. Denmark, B. S. Kesler and Y. C. Moon, *The Journal of Organic Chemistry*, 1992, **57**, 4912-4924.
6. Bruker, *APEX2 & SAINT*; AXS Inc.: Madison, WI, 2004.
7. G. M. Sheldrick, *Acta Crystallogr.Sect. A,* 2008, 64, 112–122.
8. L. J. Farrugia, *J. Appl. Cryst.* 2012, **45**, 849-854.

(a) (b)

Scheme S1. Schematic representation of (a) 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6], and (b) 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [bmim][NTf_2].

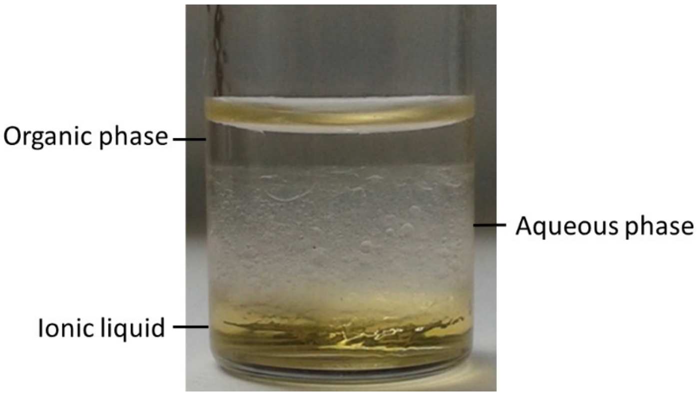


Fig. S1. A triphasic mixture of bromoanisole, butyl acrylate, [Ni{N=C(OCH_3)NHC(NH_2)=NH}$_2$] (**5**), Et_3N and products of the Heck reaction in [bmim][PF_6] (lower layer), water (mid layer), and diethyl ether (top layer).

Table S1. Heck reaction catalyzed by nickel(II)-tap complexes **5** and **6.**[a]

Run	Cat.	Aryl halide	n(IL) mmol	n(PPh_3) mmol	Base	T, °C	Time, min	Yield, %	TON[b]
1	-	bromoanisole	1.75	0.08	Et_3N	180	180	0	0
2	-	iodoanisole	1.75	0.08	Et_3N	180	180	0	0
3[c]	-	bromoanisole	1.75	0.08	Et_3N	180	180	0	0
4[c]	-	iodoanisole	1.75	0.08	Et_3N	180	180	0	0
5	$Ni(acac)_2$	iodoanisole	1.75	0.08	Et_3N	180	180	0	0
6[c]	$Ni(acac)_2$	iodoanisole	1.75	0.08	Et_3N	180	180	0	0
7	**5**	bromoanisole	1.75	-	Et_3N	180	90	0.5	0.3
8	**6**	bromoanisole	1.75	-	Et_3N	180	90	0.3	0.2
9	**5**	bromoanisole	1.75	0.02	Et_3N	180	90	1.3	0.7
10	**5**	bromoanisole	1.75	0.04	Et_3N	180	90	2.9	1.5
11	**5**	bromoanisole	1.75	0.08	Et_3N	180	90	10.0	5.0
12	**5**	bromoanisole	1.75	0.08	Et_3N	180	30	3.6	1.8
13	**5**	bromoanisole	1.75	0.08	Et_3N	180	180	19.0	9.5
14	**5**	bromoanisole	1.75	0.08	Et_3N	180	420	12.0	6.0
15	**5**	bromoanisole	1.75	0.08	Et_3N	130	90	7.3	3.9
16	**5**	bromoanisole	1.75	0.08	Et_3N	230	90	6.0	3.0
17	**5**	bromoanisole	0.875	0.08	Et_3N	180	90	2.1	1.1
18	**5**	bromoanisole	1.75	0.08	$NaHCO_3$	180	90	2.3	1.2
19	**5**	bromoanisole	1.75	0.08	$CsCO_3$	180	90	3.6	1.8
20	**5**	iodoanisole	1.75	0.08	Et_3N	180	90	3.4	1.7
21	**5**	iodoanisole	1.75	0.08	Et_3N	180	180	20.4	10.2
22	**6**	bromoanisole	1.75	0.08	Et_3N	180	180	1.0	0.5
23	**6**	iodoanisole	1.75	0.08	$CsCO_3$	180	90	0	0
24[c]	**5**	bromoanisole	1.75	0.08	Et_3N	180	180	2.5	1.3
25[c]	**5**	iodoanisole	1.75	0.08	Et_3N	180	180	1.9	1.0
26[c]	**6**	bromoanisole	1.75	0.08	Et_3N	180	180	1.3	0.7
27[c]	**6**	iodoanisole	1.75	0.08	Et_3N	180	180	1.0	0.5
28[c]	**5**	bromoanisole	1.75	0.08	Et_3N	130	90	3.4	1.7

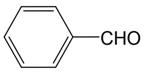
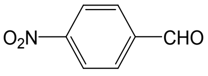
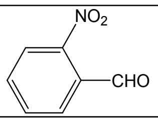
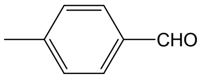
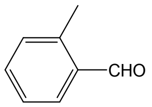
[a]Reaction conditions: [bmim][PF_6] (1.75 mmol), catalyst (0.02 mmol), and triphenylphosphine (24 mg, 0.08 mmol) were mixed in a vial (10 mL) and heated to 80 °C for 5 min in a heating block. Butyl acrylate (0.256 g, 2.0 mmol), triethylamine (0.152 g, 1.5 mmol), and the corresponding aryl halide (1.0 mmol) were then added and the vial was then placed in a MW reactor, heated to the desired temperature, using up to 100 W of power; [b] TON (Total turnover number) = moles of product per mol of catalyst; [c][bmim][NTf_2] (1.75 mmol) was used instead of [bmim][PF_6].

Table S2. Recycling studies for the Heck reaction catalyzed by nickel(II)-tap complexes.[a]

Run	Cat.	Aryl halide	Alkene	Base	T, °C	Time, min	Yield, %	TON[b]
1	**5**	iodoanisole	butyl acrylate	Et_3N	180	180	20.4	10.2
2	**5**	iodoanisole	butyl acrylate	Et_3N	180	180	13.3	6.7
3	**5**	iodoanisole	butyl acrylate	Et_3N	180	180	4.0	2.0
4	**5**	bromoanisole	butyl acrylate	Et_3N	180	180	19.0	9.5
5	**5**	bromoanisole	butyl acrylate	Et_3N	180	180	5.4	2.7
6	**5**	bromoanisole	butyl acrylate	Et_3N	180	180	1.0	0.5

[a] Reaction conditions: [bmim][PF_6] (0.50 g, 1.75 mmol), catalyst (0.02 mmol), and triphenylphosphine (24 mg, 0.08 mmol) were mixed in a process vial (10 mL) and heated to 80 °C for 5 min in a heating block. Butyl acrylate (0.256 g, 2.0 mmol), triethylamine (0.152 g, 1.5 mmol), and the corresponding aryl halide (1.0 mmol) were then added and the vial was then placed in a MW reactor, heated to the desired temperature, using up to 100 W of power; [b] TON (Total turnover number) = moles of product per mol of catalyst.

Table S3. Catalytic activity of **5** and **6** in the Henry reaction.[a]

Run	Catalyst	Substrate	Yield (%)[b]	Selectivity *anti:syn* [b]	TON[c]
1	**5**		92.6	67:33	185
2	**6**		100.0	71:29	200
3[d]	**6**		84.8	79:21	170
4	-		0	-	-
5	$Ni(NO_3)_2.6H_2O$		3.1	52:48	6
6	**5**		85.9	58:42	172
7	**6**		92.8	61:39	186
8[d]	**6**		79.4	74:26	159
9	$Ni(NO_3)_2.6H_2O$		2.0	49:51	4
10	**5**		82.7	61:39	165
11	**6**		89.1	63:37	178
12	$Ni(NO_3)_2.6H_2O$		1.2	52:48	2
13	**5**		15.3	60:40	31
14	**6**		41.7	69:31	83
15	$Ni(NO_3)_2.6H_2O$		0	-	-
16	**5**		11.5	68:32	23
17	**6**		36.4	66:34	73
18	$Ni(NO_3)_2.6H_2O$		0	-	-

[a] Reaction conditions: 5 µmol of catalyst, methanol (2 mL), nitroethane (4 mmol) and aldehyde (1 mmol), under air, at room temperature, 24 h; [b] Determined by ^1H NMR analysis (see Experimental part); [c] TON (Turnover number) = moles of product per mol of catalyst; [d] 12 h reaction time.

Table S4. Selected Bond Lengths (Å) and Angles (deg) for **5** and **6**.[a]

Compound **5**			
Ni1–N1	1.847	N4–C2	1.311(2)
Ni1–N4	1.857	O1–C1	1.352(2)
Ni1–N1^{i}	1.847	O1–C3	1.442(2)
Ni1–N4^{i}	1.857	N1–Ni1–N1^{i}	180.0
N1–C1	1.304(2)	N4–Ni1–N4^{i}	180.0
N2–C1	1.328(3)	N1–Ni1–N4	89.34
N2–C2	1.355(2)	N1–Ni1–N4^{i}	90.66
N3–C2	1.353(3)		
Compound **6**			
Ni1–N1	1.850	N4–C2	1.361(4)
Ni1–N2	1.860	O1–C1	1.357(3)
Ni1–N1^{i}	1.850	O1–C3	1.442(4)
Ni1–N2^{i}	1.860	N1–Ni1–N1^{i}	180.0
N1–C1	1.307(4)	N2–Ni1–N2^{i}	180.0
N3–C1	1.337(4)	N1–Ni1–N2	89.28
N3–C2	1.358(4)	N1–Ni1–N2^{i}	90.72
N2–C2	1.311(5)		

[a] Symmetry transformations used to generate equivalent atoms: **5**: (i) 1−x, 2–y, 2−z; **6**: (i) 1/2–x,1/2–y, 1–z.