Oxo-functionalised mesoionic NHC nickel complexes for selective electrocatalytic reduction of CO2 to formate†

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Strategies for the conversion of CO2 to valuable products are paramount for reducing the environmental risks associated with high levels of this greenhouse gas and offer unique opportunities for transforming waste into useful products. While catalysts based on nickel as an Earth-abundant metal for the sustainable reduction of CO2 are known, the vast majority produce predominantly CO as a product. Here, efficient and selective CO2 reduction to formate as a synthetically valuable product has been accomplished with novel nickel complexes containing a tailored C2O-bidentate chelating mesoionic carbene ligand. These nickel(II) complexes are easily accessible and show excellent catalytic activity for electrochemical H+ reduction to H2 (from HOAc in MeCN), and CO2 reduction (from CO2-saturated MeOH/MeCN solution) with high faradaic efficiency to yield formate exclusively as an industrially and synthetically valuable product from CO2. The most active catalyst precursor features the 4,6-di-tert-butyl substituted phenolate triazolylidene ligand, tolerates different proton donors including water, and reaches an unprecedented faradaic efficiency of 83% for formate production, constituting the most active and selective Ni-based system known to date for converting CO2 into formate as an important commodity chemical.

Introduction

The conversion of environmentally harmful CO2 into synthetically and industrially valuable products has become a pressing challenge for mitigating the threats associated with increased CO2 levels in the atmosphere.1–3 Among the various technologies developed for CO2 fixation,4–6 electrochemical reduction is particularly attractive7,8 since it allows for direct transformation of CO2 into synthetically or industrially valuable platform chemicals such as formate,9,10 alcohols,11–14 and unsaturated hydrocarbons (e.g., ethylene).15–17 In addition, electrochemical processes have the benefit to be fully sustainable, especially if they are powered by renewable energy sources (e.g., solar, wind, or hydro). The key critical parameter is then the nature of the catalyst, which is preferably derived from Earth-abundant metals in order to provide a truly sustainable process.18,19

While several complexes based on Earth-abundant Mn, Fe, and Ni metals have been known to catalyze the reduction of CO2,20–25 the vast majority of these catalysts produce CO as a predominant product.26,27 Only two Ni systems have been reported to yield formate,28 namely Sauvage’s Ni(cyclam) system from over 30 years ago,29–32 and Fontecave’s Ni(ni) catalyst,33 though selectivity is a major issue in both systems due to significant formation of CO. Formate formation is highly desirable as it constitutes a pathway to convert waste to a valuable product for synthesis, hydrogen storage, formic acid fuel cells, and for other industrial uses.

Inspired by the work of Kirchner and others on manganese pincer complexes,34–36 which demonstrated a key relevance of the metal-hydride intermediate to promote CO2 insertion rather than direct CO2 bonding, we became interested in exploiting the potential of triazolylidenes37,38 as a specific subclass of N-heterocyclic carbene (NHC) ligands39–41 for imparting such reactivity. In order to increase the robustness of the
M–C\textsubscript{NHC} bond and hence the reliability of the carbene as a spectator ligand to the nickel active site,\textsuperscript{42} oxygen chelating groups were introduced.\textsuperscript{43} Here we show that this approach provides a set of new, tunable, and highly active catalysts for the electrochemical reduction of CO\textsubscript{2} to formate. Catalyst screening in half-cell measurements revealed that the most active system accomplishes unrivalled faradaic efficiency and outstanding selectivity towards formate, largely outperforming currently known catalyst systems based on nickel.

Results and discussion

The new phenolate-substituted triazolium salts 2a–c were synthesized from 2-azidophenol 1 by [3 + 2] cycloaddition reaction through variation of the alkyne precursor (R = Ph, Bu, Mes; Scheme 1), followed by selective alkylation (>60% overall yield). Metalation was accomplished with NiCl\textsubscript{2} as a simple and cheap nickel precursor in the presence of K\textsubscript{2}CO\textsubscript{3}. The new bis-carbene nickel(II) complexes 3a–c and 4 were obtained as yellow solids that are stable towards air and moisture for >2 months.

The \textsuperscript{1}H NMR spectra of the complexes reveal the presence of only one isomer. While complexes 3a,\textsubscript{b} and 4 feature the phenolate proton resonances in the expected aromatic region (Fig. S20\textsuperscript{†}), the spectrum of complex 3c is distinct with a markedly upfield shifted phenolate ortho proton (\(\delta_{\text{trans}} = 4.8 \text{ ppm}\); Fig. S20\textsuperscript{†}). This shift of more than 2 ppm suggests a trans arrangement of the two \textsubscript{C,O}-bidentate ligands, with the phenolate H\textsubscript{ortho} influenced by ring current anisotropy of the mesityl group of the other ligand. No such effect has been observed in the NMR spectrum of complex 3b featuring a phenyl-substituted triazolylidene, which suggests a cis configuration. These ligand arrangements were unambiguously confirmed by single crystal X-ray diffraction (Fig. 1). In the trans configuration of 3c, the mesityl ring is essentially orthogonal to the carbene–Ni plane and close to H\textsubscript{ortho} (H\textsubscript{ortho}–arene = 2.75 Å), which accounts for the ring anisotropy observed by NMR spectroscopy. The cis configuration of the other complexes places the carbene wingtip groups R in close proximity, which results in a substantial distortion from square-planar to tetrahedral (\(\tau_{4} \geq 0.15\)).\textsuperscript{44} The distortion is larger for bulky wingtip groups (Bu, Ph, in 3a,\textsubscript{b}, respectively) than with methyl substituents (4), and negligible in the trans complex 3c (\(\tau_{4} < 0.01\); Table S7\textsuperscript{†}).

All four nickel complexes 3a–c, 4 display (quasi)reversible redox processes around +0.7 V and –2.0 V, tentatively attributed to Ni\textsuperscript{II}/Ni\textsuperscript{III} and Ni\textsuperscript{II}/Ni\textsuperscript{I} transitions, respectively (Fig. 2, S21 and 22;\textsuperscript{†} potentials vs. Ag/AgCl).\textsuperscript{33} Comparison of the redox potentials consistently indicates that triazolylidenes are stronger donor ligands than imidazolylidene,\textsuperscript{45} and that the wingtip group R directly affects the electron density on the nickel center with oxidation potentials increasing along the series R = Bu (\(E_{1/2} = 0.59\)) \(< R = \text{Mes} (E_{1/2} = 0.64) < R = \text{Ph} (E_{1/2} = 0.69\); Table 1).

The electrocatalytic performance of complexes 3a–c, 4 was first investigated in H\textsuperscript{+} reduction. A significant cathodic current was observed when acetic acid (AcOH) was present as proton donor in a MeCN solution of the Ni complex. Increasing the AcOH concentration from 5 to 400 eq. with respect to the Ni complex led to an enhanced current density,
Evident upon complex reduction, indicative of CO$_2$ transformation, reveals a significant enhancement of the cathodic currents in the MeCN solution of the nickel complex (Bu$_4$N)PF$_6$ as supporting electrolyte, 250 mV s$^{-1}$ scan rate, Fe$^3$/Fe as internal standard with $E_{1/2} = 0.36$ V vs. Ag/AgCl. Cathodic peak potential $E_{pc}$ for Ni$^{II}$/Ni$^{I}$ reduction and half-wave potential $E_{1/2}$ (in parentheses) $\Delta E_{pa} = E_{pa} - E_{pc}$ in mV for Ni$^{II}$/Ni$^{I}$ redox process$^b$ Catalytic conditions; 1 mM complex in MeCN, AcOH (0.8 M), (Bu$_4$N)PF$_6$ as supporting electrolyte, $k_{obs}$ determined by foot of the wave analysis (see ESI for details$^b$).

| Entry | Complex | $E_{pc}$ | $E_{1/2}(\text{Ni}^{III}/\text{II})$ | $k_{obs}$ [s$^{-1}$] |
|-------|---------|----------|-----------------------------------|---------------------|
| 1     | 3a      | -2.16    | 0.59 (130)                        | 440                 |
| 2     | 3b      | -2.09    | 0.69 (110)                        | 300                 |
| 3     | 3c      | -2.12    | 0.64 (120)                        | 10                  |
| 4     | 4       | -1.92 (110) | 0.75 (120)                     | 200                 |

$^a$ All values in V vs. Ag/AgCl; 1 mM MeCN solution of Ni complex with (Bu$_4$N)PF$_6$ as supporting electrolyte, 250 mV s$^{-1}$ scan rate, Fe$^3$/Fe as internal standard with $E_{1/2} = 0.36$ V vs. Ag/AgCl. $^b$ Cathodic peak potential $E_{pc}$ for Ni$^{II}$/Ni$^{I}$ reduction and half-wave potential $E_{1/2}$ (in parentheses) $\Delta E_{pa} = E_{pa} - E_{pc}$ in mV for Ni$^{II}$/Ni$^{I}$ redox process$^c$ Catalytic conditions; 1 mM complex in MeCN, AcOH (0.8 M), (Bu$_4$N)PF$_6$ as supporting electrolyte, $k_{obs}$ determined by foot of the wave analysis (see ESI for details$^c$).

indicative of catalytic H$^+$ reduction (Fig. 3). Extraction of $k_{obs}$ by foot-of-the-wave analysis (FOWA)$^{46,47}$ reveals a direct influence of the steric and electronic properties of the ligand in promoting catalytic reduction (Table S8$^b$). Specifically, the trans arrangement imposed by the very bulky mesityl wingtip groups is strongly deactivating, while all the cis-complexes are active. Moreover, the activity of the cis-complexes directly correlates with the ligand donor properties deduced from CV data: the alkyl-substituted triazolyldiene induces more than a twice higher active than the analogous imidazolyldiene ($k_{obs}$ = 440 s$^{-1}$ for 3a vs. 200 s$^{-1}$ for 4$^d$).

Prompted by the promising catalytic activities, complexes 3a–c, 4 were evaluated as catalyst precursors for electrochemical reduction of CO$_2$. Initial experiments with a 1 mM MeCN solution of the nickel complex 3a under a CO$_2$ atmosphere reveal a significant enhancement of the cathodic current upon complex reduction, indicative of CO$_2$ transformation (Fig. 4). For complex 4 the reversibility of the Ni$^{II}$/Ni$^{I}$ reduction was lost upon saturation with CO$_2$ gas. All the complexes were active in the process, with only the trans isomer 3c induces low catalytic current, suggesting lower activity. The catalytic current enhances further when the reaction was performed in the presence of MeOH (40 eq. with respect to the Ni complex), suggesting a beneficial role of proton sources.$^{49}$ Trifluoroethanol and phenol show similar effects, though the current increase is largest when using MeOH (Fig. 4). Blank measurements indicate no catalytic current with CO$_2$-saturated solutions in the absence of the Ni complex, or when the complex is reduced in the presence of methanol yet without CO$_2$ (Fig. S34†).

The robustness of the catalytically active species over time was investigated by chronoamperometry at −1.9 V vs. Ag/AgCl in MeOH/MeCN 1 : 50 v:v (Fig. S26–S29f). The observed catalytic current is constant over 2 h, suggesting no significant degradation during that time. More extended reaction reveals a gradual decrease of activity. Comparison of the different complexes reveals catalytic activity for CO$_2$ reduction follows the same trends observed for H$^+$ reduction, with highest rates for the nickel complex with the strongest donating triazolyldiene ligand (3a, $k_{obs}$ = 280 s$^{-1}$), which is essentially twice as fast as the corresponding imidazolyldiene analogue 4 ($k_{obs}$ = 150 s$^{-1}$; Table 2). Again, the cis ligand arrangement is essential for ensuing catalytic activity as the nickel complex 3c with the ligands in trans configuration is almost inactive ($k_{obs}$ = 10 s$^{-1}$), and enhanced electron density at the nickel center increases catalytic activity (3a > 3b > 4$).

Product identification focused first on gas-phase analysis of volatiles products as most hitherto known Ni catalysts for CO$_2$ reduction produce CO.$^{10,11}$ Remarkably, only traces of H$_2$ were detected in the gas phase, and CO quantities were below the detection limit (less than 2% faradaic efficiency after 4 h, Table 2). Analysis of the solution phase by ion-exchange...
chromatography (IC), HPLC and NMR measurements identified formate as the principal product of CO2 reduction with complexes 3a–c, 4. Complex 3a does not display only the highest activity but also imparts the highest selectivity. Optimization of reaction times afforded faradaic efficiencies up to 70% for formate formation, one of the highest known so far for homogeneous Ni-based electrocatalysts. 10,11 Ligand tailoring has been used to further improve the catalytic activity of these nickel complexes, in particular through introduction of electron-donating substituents on the phenolate. Substitution of the 4,6-positions moreover avoids undesired radical reactions of the phenolate, which may infer from one-electron-reduction upon catalyst activation. To this end the 4,6-Me2-phenol-triazolium salt 5a was nickelated via the procedure established for the synthesis of 3a, while the tBu analogue 5b required nBuLi as a stronger base to accomplish nickel complexation (Fig. 5a). The new O,C-bidentate chelated trz Ni(II) complexes 6a and 6b showed NMR characteristic reminiscent of those of 3a,b, indicating the formation of the cis-isomers exclusively. This structural assignment was further confirmed by single crystal X-ray diffraction studies of complexes 6a,b (Fig. 5b). The distortion from square planar geometry in these complexes is slightly less than in the parent complex 3a with τ values of 0.15 and 0.18 for 6a and 6b, respectively (cf. 0.21 for 3a, Table S7†).

The electrochemical properties of complexes 6a,b are comparable to those of complexes 3a–c, featuring a quasi-reversible oxidation at 0.49 and 0.45 V vs. Ag/AgCl, respectively, and an irreversible reduction below ~2.0 V (Fig. S21 and 22†). The incorporation of donating groups on the phenolate lowers the redox potentials by about 90 (R = Me, 6a) and 150 mV (R = tBu, 6b) relative to the parent phenolate complex 3a (Table 3). These potential shifts indicate enhanced electron density at the metal center and efficient electronic tailoring of the nickel center by ligand modifications.

In these cis triazolylidene Ni complexes, lower reduction potentials are correlated with higher electrocatalytic CO2 reduction activity (cf. Table 2). Indeed, the stronger donor ligands in complexes 6a,b and the associated low reduction potential improved the catalytic performance. Foot of the wave data analysis revealed a higher kobs for CO2 reduction for 6a than for the parent complex 3a (300 vs. 280 s−1; Table 3), and more significantly for 6b with the lowest reduction potential (kobs = 370 s−1). Moreover, the robustness of the catalytically active species is demonstrated by a constant catalytic current over the first 2 h (Fig. 6 and S31†). Formate was identified as exclusive product of CO2 reduction also with complexes 6a,b with only traces of H2 and CO as side products. Complex 6b revealed the highest FE of 83% for formate formation and represents a new benchmark for Ni in this transformation. Moreover, these results demonstrate that ligand tailoring on a molecular level through incorporation of electron-donating substituents provides an efficient strategy for catalyst optimization for this CO2 reduction and leads in this case to a marked increase of the FE to unprecedented 83%.

While this work is focused on catalyst optimization for the CO2 reduction half-reaction, obviously also the availability of protons is elementary as the efficiency of the CO2 to formate transformation is associated with a coupled electron/proton transfer. Variation of the proton source has been accomplished confirmed by single crystal X-ray diffraction studies of complexes 6a,b (Fig. 5b). The distortion from square planar geometry in these complexes is slightly less than in the parent complex 3a with τ values of 0.15 and 0.18 for 6a and 6b, respectively (cf. 0.21 for 3a, Table S7†).

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**Table 2** Faradaic efficiencies (FE) and catalytic rates for CO2 conversion with complexes 3a–c and 4†

| Entry | Complex | FEHCO2 (4 h) [%] | FEHCOO− (8 h) [%] | FEH2+CO (4 h) [%] | kobs (s−1) |
|-------|---------|-----------------|-----------------|-----------------|------------|
| 1     | 3a      | 54              | 68              | 3               | 280        |
| 2     | 3b      | 43              | 47              | 4               | 220        |
| 3     | 3c      | 10              | 10              | 2               | 10         |
| 4     | 4       | 25              | 25              | 3               | 150        |

† General conditions: 1 mM complex, at −1.9 V vs. Ag/AgCl, glassy carbon working electrode and Pt foil as counter electrode (see ESI for details†) in MeOH/McCN 1:50 v:v with 0.1 M (Bu4N)PF6 as supporting electrolyte. 1 Determined from foot of the wave data treatment (see ESI for details†).

![Fig. 5](image-url) (a) Synthesis of complexes 6a,b. (b) ORTEP diagrams of Ni complexes 6a,b (50% probability thermal ellipsoids, hydrogen atoms omitted for clarity, a denotes symmetry-related atoms). One tBu group in 6b is disordered about 2 conformations. Selected bond lengths (Å) for 6a: Ni–C1 = 1.862(2), Ni–O1 = 1.887(1). Selected bond lengths (Å) for 6b: Ni–C1 = 1.835(1), Ni–O1 = 1.889(1).

**Table 3** Faradaic efficiencies (FE) and catalytic rates for CO2 conversion with complexes 6a,b†

| Entry | Complex | Ecroc [V] | FEHCO2 (8 h) [%] | FEHCOO− (8 h) [%] | FEH2+CO (4 h) [%] | kobs (s−1) |
|-------|---------|----------|-----------------|-----------------|-----------------|------------|
| 1     | 6a      | −2.23    | 74              | 4               | 300            |
| 2     | 6b      | −2.31    | 83              | 3               | 370            |

† General conditions: 1 mM complex, at −1.9 V vs. Ag/AgCl, glassy carbon working electrode and Pt foil as counter electrode (see ESI for details†) in MeOH/McCN 1:50 v:v with 0.1 M (Bu4N)PF6 as supporting electrolyte. Cathodic peak potential Ecroc for NiII/NiI reduction in V vs. Ag/AgCl; 1 mM MeCN solution of Ni complex with (Bu4N)PF6 as supporting electrolyte, 250 mV s−1 scan rate, Fe3+/Fe2 as internal standard with E1/2 = 0.36 V vs. Ag/AgCl. ² Determined from foot of the wave data treatment (see ESI for details†).
by varying the additive to the aprotic solvent (MeCN) from MeOH to different proton donors including PhOH, iPrOH, CF₃CH₂OH (TFE), and H₂O (Fig. 7 and S32†). All these proton sources are mediating CO₂ reduction, yet with variable efficiency. Notably, water as the cleanest proton source is tolerated and affords considerable yields of formic acid. Best performance was achieved with TFE, reaching FEs up to 82% within 2 h. These data indicate that formate is exclusively formed at the cathode and not anodically, e.g. by partial MeOH oxidation, and that MeOH is not required to achieve high formate yields. Moreover, the broad tolerance of a variety of proton sources provides ample opportunities for optimizing also the oxidation half-reaction for designing an efficient full cell electrolyzer.

Total FE values below 100% suggest parasitic side reactions and catalyst deactivation, which might be triggered by several factors, including acidification of the reaction medium due to the generated formate, (cf. H⁺ reduction with high HOAc concentrations above). This limitation should be easily mitigated, for example, by using a flow reactor. Catalyst deactivation during CO₂ electroreduction was evidenced by a combination of high-resolution scanning electron microscopy (HR-SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) analyses with an electrode containing complex 6b after 2 h of operation at −1.9 V vs. Ag/AgCl. Post-electrolytic HR-SEM and XRD analyses identified Ni oxide nanoparticles on the working electrode surface, while EDX suggests formation of films that are too thin for detection (Fig. S37†).

Specifically, XRD revealed trace 20 intensities that are characteristic of NiO and Ni₂O₃ on the electrode surface (Fig. S38†). Nickel oxide formation may be rationalized by partial reduction of the complexed nickel to Ni⁰ under the cathodic potential applied during electrolysis, which induces complex decomposition and formation of Ni nanoparticles. These electrochemically generated Ni nanoparticles were probably transformed to Ni oxides (NiO/Ni₂O₃) only when the electrode was exposed to air after the experiment. Such partial complex degradation thus provides a plausible rationale for the gradual loss of activity during extended reaction times and may account for the uncompensated charge from chronoamperometric experiments as some cathodic charge is involved in the in situ reduction of Ni⁰ to Ni⁰ during the CO₂ reduction process. It must be noted, however, that Ni nanoparticles are unable to catalyze CO₂ reduction and only induce H₂ formation (HER), independent of size and shape of these nanoparticles. Therefore the highly selective reduction of CO₂ to formate as observed here is confidently attributed to the distinct catalytic activity of the molecularly defined NHC Ni complexes.

The production of formate as valuable product from CO₂ reduction is very rare for nickel-based catalysts, as most Ni systems produce CO.⁹ The best complex of the series, complex 6b shows high faradaic efficiency and exquisite formate vs. CO selectivity. The two other known Ni systems generating formate are less efficient in comparison and produce considerable amounts of CO as by-product (Table S11†).¹⁰,¹¹ The triazolylidene system presented here offers unique potential, due to the intrinsically high selectivity towards formate production, and because the catalytic rate can be further optimized due to the correlation of rational ligand design and reduction potentials with catalytic activity. Moreover, a variety of proton sources are tolerated, including water. The largest drawback is probably the high overpotential required in comparison to the Kubiak-Sauvage electrocatalyst (ΔE = 0.5 V).¹¹

The poor catalytic activity of the trans isomer points to a key role of the complex geometry. Either, the distortion from square-planar in the cis complexes may facilitate the formation of a penta-coordinate nickel(i) intermediate, or more likely, the cis-arrangement of the two oxygen donors produces a proton acceptor pocket, especially after one-electron reduction to either a formal nickel(i) complex or a phenoxide radical anion.¹¹,¹² Proton chelation by the two oxygen units is therefore suggested to form the reduced complex A (Scheme 2), presumably through a proton-coupled electron transfer (PCET). This intermediate facilitates the formation of a nickel(II)
hydride intermediate B for CO₂ insertion and generation of the formate complex C, which is then readily reduced to release the formate product. Formation of the nickel hydride intermediate is presumed to be key for the product selectivity, as most known nickel catalysts for CO₂ reduction bind CO₂ directly and therefore produce CO rather than formate. Alternatively, the proton scavenging may localize the negative charge on the oxygen, which facilitates the formation of the n1-OCO Ni adduct B’ as another potentially critical intermediate for formate formation. Attempts to characterize the putative nickel(i) intermediate by spectroelectrochemistry were not successful, as a solution of complex 3a or 4 did not produce any EPR signal after electrolysis at −2.0 V vs. Ag/AgCl, presumably because the nickel(i) species is not sufficiently stable in the absence of substrates. Nonetheless, this mechanistic proposal provides a rationale for the strong divergence of catalytic activity of the cis vs. trans complexes.

Conclusions

In summary, we have synthesized and characterized a new class of bis-carbene nickel(i) complexes containing C₂O-bidentate chelating phenolate-NHC ligands. These complexes are active in the selective electroreduction of CO₂ to formate, reaching up to 83% faradaic efficiency, which is the highest value reported for a Ni-based electrocatalyst to date. Tailoring of the complexes substantially affects activity, with the cis isomers outperforming the trans analogue and a more nucleophilic nickel center achieving higher activities. The requisite selectivity towards formate combined with the tolerance of a variety of proton sources hold great promises for optimizing also the anodic half-reaction and to develop a whole cell system for process operation. The unique aspects of this new class of complexes together with the viability of ligand modification, will provide new perspectives towards the design of novel electrocatalytic systems suitable for small molecules activation.

Experimental section

General

2-Azidophenol 1, 1-(2-phenol)-imidazole 7 and 2-amino-4,6-diterbutylyphenol were synthesized following procedures reported in literature. The synthesis of all triazolium salt ligand precursors (2a-c, 5a–b) is detailed in the ESL. All other reagents were commercially available and used as received. Unless specified otherwise, NMR spectra were recorded at 25 °C with Bruker spectrometers operating at 300 or 400 MHz (1H NMR), and 100 MHz (13C NMR), respectively. Chemical shifts (δ in ppm, coupling constants J in Hz) were referenced to residual solvent signals (1H, 13C). Assignments are based on homo- and heteronuclear shift correlation spectroscopy. The purity of bulk samples of the complexes has been established by NMR spectroscopy, and by elemental analysis, which were performed at the University of Bern Microanalytic Laboratory by using a Thermo Scientific Flash 2000 CHNS-O elemental analyzer. Residual solvent was confirmed by NMR spectroscopy and also by X-ray structure determinations. High-resolution mass spectrometry was carried out with a Thermo Scientific LTQ Orbitrap XL (ESI–TOF).

Synthesis of cis-[Ni(trzBuOPh)₂] (3a)

According to the general procedure, reaction of 2a (200 mg, 0.22 mmol), K₂CO₃ (1 mmol) and NiCl₂ (0.3 mmol) were suspended in dry MeCN under N₂ atmosphere. The mixture was stirred at reflux temperature for 16 h and filtered through Celite (5 g). The filtrate was evaporated to dryness and the residue was extracted with CH₂Cl₂ and dried in vacuo. The residual powder was purified by column chromatography (Al₂O₃ basic; CH₃CN/CH₂Cl₂ 1 : 1). Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a CH₂Cl₂ solution of the complex.
The reaction of triazolium salt 2c (200 mg, 0.45 mmol), NiCl₂ (44 mg, 0.34 mmol) and K₂CO₃ (124 mg, 0.9 mmol) in MeCN (10 mL) according to the general procedure yielded complex 3c as a yellow crystalline powder (51 mg, 35%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.80 (d, J = 8.5 Hz, 1H, H₃Ph), 7.02 (s, 2H, H₃Mes), 6.64 (t, J = 8.5 Hz, 1H, H₃PhO), 6.35 (t, J = 8.5 Hz, 1H, H₃PhO), 4.97 (d, J = 8.5 Hz 1H, H₃PhO), 3.67 (s, 3H, CH₃-N), 2.39 (s, 3H, CH₂-Mes), 2.25 (s, 6H, CH₃-Mes). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂): δ 157.79 (C-O), 148.98 (C₃Ph-N), 144.33 (C₃Ph=N), 138.72 (C₃Ph-N), 137.93 (C₃Ph=N), 128.40 (C₃Mes-H), 127.59 (C₃Ph-O), 127.34 (C₃Mes-C₃H), 127.59 (C₃Ph-O), 122.91 (C₃Mes-H), 112.23 (C₃Ph-N), 112.71 (C₃Mes-C₃H), 35.32 (CH₃-N), 21.02 (CH₃-C₃H), 20.32 (CH₃-C₃H). HR-MS (ESI): calcd for C₃₀H₂₄N₆NiO₂ [M + Na]^⁺ m/z = 665.2130 (found 665.2145). Anal. calcd for C₃₀H₂₄N₆NiO₂ (643.42): C, 67.20; H, 5.64; N, 13.06. Found: C, 67.00; H, 5.98; N, 12.95.

Synthesis of cis-[Ni(imiMe₂-O)Ph₂] (4)

According to the general procedure, reaction of 1-(2-phenyl)-3-methylimidazolium iodide 9 (200 mg, 0.61 mmol), NiCl₂ (42 mg, 0.33 mmol), and K₂CO₃ (200 mg, 1.4 mmol) in MeCN (10 mL) and purification by column chromatography (Al₂O₃; CH₃CN/CH₂Cl₂ 1:2) gave complex 4 as a yellow crystalline powder (90 mg, 70%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.33–7.12 (m, 3H, 2HPh + 1HPhO), 7.03 (t, J = 8.5 Hz, 1H, H₃PhO), 6.92 (s, 1H, H₃Mes), 6.61 (t, J = 8.5 Hz, 1H, H₃PhO), 3.19 (s, 3H, CH₃-N). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂): δ 159.22 (C-O), 157.62 (C₃im-N), 127.77 (C₃Ph-N), 127.62 (C₃Ph-H), 124.06 (C₃im-H), 122.42 (C₃Ph-H), 118.23 (C₃im-H), 117.57 (C₃Ph-N), 113.64 (C₃Mes-H), 37.01 (CH₃-N). HR-MS (ESI): calcd for C₂₃H₂₃NiNO₂ [M + Na]^⁺ m/z = 426.0597 (found 426.0603). Anal. calcd for C₂₃H₂₃NiNO₂ (404.08): C, 59.45; H, 4.24; N, 13.87. Found: C, 59.81; H, 3.95; N, 14.01.

Synthesis of cis-[Ni(trz²⁺-O)Ph₂]₃ (6a)

According to the general procedure, triazolium salt 5a (200 mg, 0.5 mmol), K₂CO₃ (140 mg, 1.0 mmol) and NiCl₂ (42 mg, 0.3 mmol) were suspended in dry MeCN (10 mL). The residual powder was purified by column chromatography (Al₂O₃ basic; CH₃CN/CH₂Cl₂ 1:1) to afford complex 6a as a bright yellow crystalline solid (100 mg, 71%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.27 (s, 1H, H₃Ph), 6.82 (s, 1H, H₃Ph), 3.88 (s, 3H, N-CH₃), 2.18 (s, 3H, CH₃), 2.16 (s, 3H, CH₃), 1.91 (s, 1H, CH-Pr), 1.81 (s, 1H, CH-Pr), 1.56 (s, 1H, CH-Et), 1.43 (s, 1H, CH-Et), 1.23–1.14 (m, 2H, CH₂-CH₃), 0.66 (t, J = 4 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂): δ 156.33 (C-O), 146.28 (C₃trz-N), 131.26 (C₃ph-N), 130.67 (C₃ph-N), 126.21 (C₃ph-N), 121.10 (C₃ph-N), 117.13 (C₃ph-N), 36.47 (CH₃-N), 32.25 (CH₂-Pr), 24.99 (CH₃), 22.98 (CH₂-Et), 20.74 (CH₃), 17.15 (CH₂-CH₃), 13.72 (CH₃). HR-MS (ESI): calcd for C₃₀H₃₈N₆NiO₂ [M + H]^⁺ m/z = 755.2639 (found 757.2638). Anal. calcd for C₃₀H₃₈N₆NiO₂ (755.38): C, 62.62; H, 7.01; N, 14.61. Found: C, 62.33; H, 7.12; N, 14.54.

Synthesis of cis-[Ni(trz²⁺-O)Ph(bu)₂] (6b)

Triazolium salt 5b (300 mg, 0.61 mmol) was dissolved in 10 mL of THF in a Schlenk tube under inert atmosphere and the solution stirred at –78 °C for 5 min. After that time a 2.5 M solution of BuLi in hexane (0.56 mL, 1.40 mmol) was added, and the reaction mixture stirred for 30 min and then cannulated to another Schlenk tube containing NiCl₂ (44 mg, 0.34 mmol) suspended in 5 mL of THF. The reaction mixture was stirred for 16 h at room temperature. After that time, the reaction was quenched, and the solvent removed under vacuum. DCM (30 mL) was added to the solid and the suspension was filtrated through a short Celite pad. The solvent was removed to leave a bright orange solid, which was then purified by column chromatography (basic Alox CH₃CN/DCM 1:5) to obtain complex 6b as a dark yellow powder (280 mg, 62%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.44 (d, J = 2.1 Hz, 1H, H₃PhO), 7.30 (d, J = 2.1 Hz, 1H, H₃PhO), 4.23 (s, 3H, CH₃), 2.34 (t, J = 6.0 Hz, 2H, CH₂-C₃H), 1.67 (s, b, 1H, CH₂-C₃H), 1.47 (s, b, 1H, CH₂-C₃H), 1.37–1.29 (m, 10H, (CH₃)₃-C + CH₂-C₃H), 1.28–1.24 (m, 10H, (CH₃)₃-C + CH₂-C₃H), 0.76 (t, 3H, J = 6.0 Hz, CH₃). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ 154.24 (C-O), 145.50 (C₃Ph), 141.85 (C₃ph-N), 138.89 (C₃trz-N), 125.33 (C₃ph-N), 126.22 (C₃ph-N), 122.42 (C₃trz-Bu), 121.58 (C₃ph-N), 38.89 (C(CH₃)), 36.19 (C(CH₃)), 34.73 (CH₃-N), 31.70 (CH₃), 29.23 (CH₃), 28.52 (CH₂-C₃H), 23.49 (CH₂-C₃H), 23.25 (CH₂-C₃H), 13.77 (CH₃). HR-MS (ESI): calcd for C₃₂H₃₈N₆NiO₂ [M + H]^⁺ m/z = 743.4517 (found 743.4495). Anal. calcd for C₃₂H₃₈N₆NiO₂ (743.70): C, 67.83; H, 8.67; N, 11.30. Found: C, 67.76; H, 8.88; N, 11.35.

Crystal structure determinations. Suitable crystals of 3a–c, 4 and 6a-b were grown in air at ambient conditions and measured on an Oxford Diffraction SuperNova area-detector diffractometer at T = 173(2) K by using mirror optics monochromated MoKα radiation (λ = 0.71073 Å) and Al filtered. Data reduction was performed by using the CryAlisPro
program.\textsuperscript{65} The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method by using SCALE3 ABSPACK in CrysAlisPro was applied. The structures were solved by direct methods by using SHELXT, and all non-hydrogen atoms were refined anisotropically.\textsuperscript{66} All hydrogen atoms were placed in geometrically calculated positions and refined by using a riding model with each hydrogen atom assigned a fixed isotropic displacement parameter (1.2\textit{Ueq} of its parent atom, 1.5\textit{Ueq} for the methyl groups). Structures were refined on \textit{F}\textsuperscript{2} by using full-matrix least-squares procedures. The weighting schemes were based on counting statistics and included a factor to downweight the intense reflections. All calculations were performed by using the SHELXL-2014 program.\textsuperscript{67} Further crystallographic details are compiled in Tables S1–6 in the ESI.\textsuperscript{†} Crystallographic data for all structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers 2004183 (20050372), 2004184 (2050371 (6a)), 2004185 (3b), 2004184 (3c), and 2004181 (4).

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

We thank the Swiss National Science Foundation (200020_182663 and 200020_172507), the Marie Skłodowska Curie ITN NoNoMeCat (grant 675020-MSCA-ITN-2015-ETN), and the European Research Council (CoG 615653) for generous financial support of this work. We also thank the crystallography service unit of the University of Bern for analytical work (funded through SNSF R’equip 206021_128724). A.R. acknowledges support from the Ministry of Science and Higher Education of the Russian Federation.

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Chronoamperometric measurements indicate a gradual decrease of the catalytic current when performing measurements over time periods larger than 10 min, which complicated the determination of catalytic efficiency, see ESI for details.†