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Preliminary communication

A new tetradentate nitrogen ligand for organometallic catalysis: electrochemical nickel-catalyzed intramolecular cyclization

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Abstract

The new tetraaza-molecule, **1** has been synthesized and used as a ligand for a cationic mononuclear nickel(II) complex. This complex is an efficient catalysts for the intramolecular electrochemical cyclization of *o*-haloaryl compounds containing unsaturated side chains.

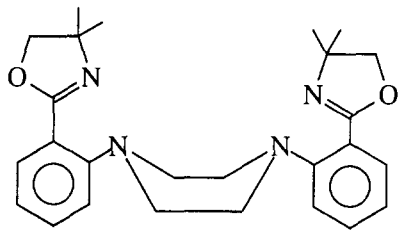
Keywords: Nitrogen ligand; Tetradentate; Nickel catalysis; Intramolecular cyclization

The use of polydentate nitrogen compounds as ligands for organometallic complexes displays an increasing interest in the field of homogeneous catalysis [1]. The range of nitrogen donors is very extensive, with various possibilities of hybridisation and substitution on the nitrogen atom. In particular, complexes associating cyclic polydentate aza-ligands, such as porphyrins or other cyclic polyamines, including cyclam derivatives (cyclam = 1,4,7,11-tetraaza cyclotetradecane) have been widely studied [2]. They may be used selectively in important catalytic reactions [3].

During our previous studies of nickel-catalyzed electrocarboxylation of unsaturated substrates [4], we elucidated the important role of the nitrogen-based ancillary ligand. Moreover, in the electro-reduction of unsaturated aryl halides such as **4a** (Eq. 3), a Ni^{II} complex with 2,2′-bipyridine, was shown to be a catalyst for the protodehalogenation and the cleavage of the oxygen–allyl carbon bond, leading to phenol [5], whereas Ni^{II}-cyclam complexes catalysed the intramolecular cyclisation reaction of the same substrate. Nickel(II) perchlorate complexes of modified cyclam have also been used to catalyze the intramolecular electrochemical cyclization of some bromo- or iodo-containing olefins [6].

We therefore became interested in preparing new polydentate ligands, able to induce intramolecular cyclisation-type reactivity of substrates such as **4a**, and to easily afford chiral analogs for asymmetric catalysis. This led us to undertake the synthesis of tetraaza-ligands containing oxazoline moieties. The use of aminooxazolines has been limited to pyridine-oxazolines or to bis-(oxazolines) [7], and no examples of the use of such compounds as ligands in complexes for electrochemical reactions have been described.

We report here the synthesis of the new nitrogen donor of structure **1** containing oxazoline groups. We compared its use and reactivity in catalytic reactions with cyclam.



1

Compound **1**, is open-chain and is prepared rapidly. Its synthesis is sufficiently flexibile to be used for other derivatives, differing either by the bis-amine or the oxazoline moieties. Such variations are necessary for subtle control of the physical and chemical properties of the desired transition metal complexes. The access to chiral analogs of **1** for use in asymmetric synthesis [8,9] is also an interesting possibility for this molecule.

The synthesis of **1** (Eq. 1) starts from *o*-bromobenzoic acid, by treatment with thionyl chloride, followed

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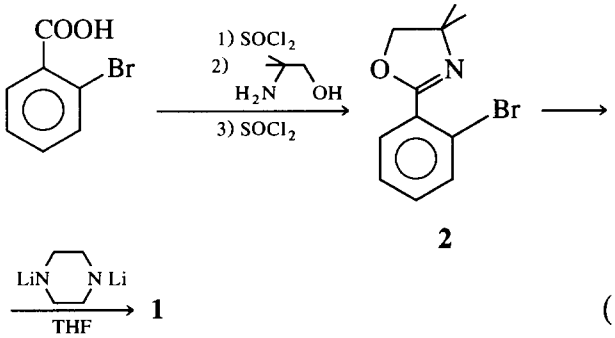
by the addition of 2-amino-2-methylpropan-1-ol and further dehydration with thionyl chloride, according to the method of Meyers et al. [10]. Further treatment of **2** with dilithiopiperazine, following a procedure similar to that described for the reaction of *ortho*-methoxylated aromatic oxazolines with amines [11], led directly to **1** in 64% isolated yield (80% based on recovered **2**) [12].



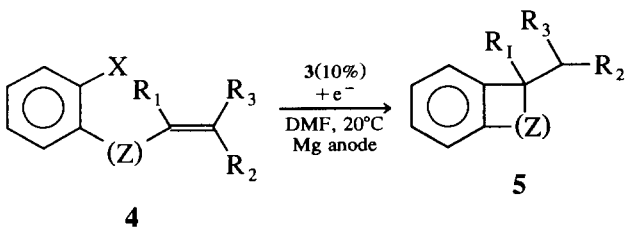
(1)

When **1** was allowed to react with nickel tetrafluoroborate hexahydrate in ethanolic solution, a light-green precipitate was formed upon addition of diethyl ether. The compound is a nickel(II) complex, **3** of type $[Ni(\mathbf{1})]^{2+}$ (Eq. 2). It is diamagnetic and its NMR and IR data are summarised in Ref. [13]. The structure of complex **3** is under investigation. We propose that the tetradentate donor forms a cyclic-type structure, similar to that found in related $[Ni^{II}(cyclam)]^{2+}$ complexes [14].

$$Ni(BF_4)_2 \cdot 6\,H_2O + \mathbf{1} \xrightarrow[40°C,\ 1\ h]{1)\ EtOH} \underset{\mathbf{3}\ 90\%}{[Ni(\mathbf{1})]\,[BF_4]_2} \qquad (2)$$

In the presence of a catalytic amount of **3** (10% molar ratio with respect to the substrate), the electrochemical reduction of a secondary bromide such as 2-bromoheptane in DMF led to 70% of R–R type dimers ($R = C_7H_{15}$). This is comparable to the electroreduction of the same halide in the presence of $[Ni(cyclam)]^{2+}\,2[ClO_4]^-$ or analogous complexes with cyclam derivatives, in which the involvement of Ni^I intermediates and radical R · species have been suggested [15].

We examined the catalytic activity of complex **3** towards intramolecular cyclisation, and in Table 1 we present our results on the reactivity of substituted aryl halides of general structure **4**, which affords bicyclic structures **5** (Eq. 3).



4 **5**

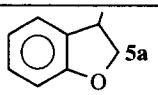
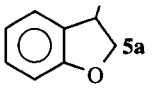
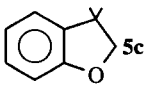
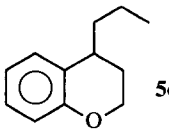
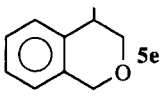
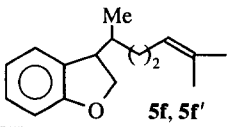
(3)

	X	(Z)	R^1	R^2	R^3
a	Br	$-OCH_2-$	H	H	H
b	I	$-OCH_2-$	H	H	H
c	Cl	$-OCH_2-$	CH_3	H	H
d	Br	$-O(CH_2)_2-$	H	Et	H
e	Br	$-CH_2OCH_2-$	H	H	H
f	Br	$-OCH_2-$	H	CH_3	$(CH_2)_2CH=CMe_2$

The electrochemical cyclizations are carried out at room temperature in DMF, in a single-compartment cell fitted with a sacrificial magnesium anode and a carbon fibre cathode [16] at constant current. The reactions were followed by GC and were stopped when complete consumption of **4** was reached. The faradic consumption was of 2–4 F mol^{-1}. No reaction occurred in the absence of current, and in the absence of the catalyst, the process was non-selective, leading in the case of **4c** to a mixture of phenol, chlorophenol, **5c** and 2-methyl-1-phenoxypropene, resulting from double bond isomerization.

The cyclization becomes selective in the presence of complex **3** (10% with respect to the starting halide).

Table 1
Electrochemical cyclization of **4a–f** catalyzed by **3** [a]

Starting substrate	Product	Yield
4a	 **5a**	90%
4b	 **5a**	90%
4c	 **5c**	77%
4d	 **5d**	68%
4e	 **5e**	52%
4f	 **5f, 5f'**	76%

[a] General electrolysis procedure: A single compartment cell, similar to that described in Ref. [16] with a Mg rod as the anode (diameter 1 cm) and a carbon fibre cathode (apparent surface, 20 cm^2) was used. Freshly distilled DMF (40 ml), $[^nBu_4N][BF_4]$ (5.10^{-4} M), the nickel(II) complex, **3** (0.3 mmol), and substrate **4** (3 mmol) were added. The solution was electrolyzed at 20°C, at constant current of 60 mA (apparent current density 0.3 A dm^{-2}), until the disappearance of **4** (3–6 h). After acidic hydrolysis and ether extraction, the products were purified by column chromatography on silica-gel with pentane/Et_2O mixtures as eluent, and their NMR spectra compared to those of authentic samples.

Thus, allyl ethers **4a–4c** reacted to afford substituted benzofurans in good-to-excellent yields. All three iodo-, bromo- and chloro-derivatives undergo efficient cyclization. The catalytic activation of the aryl carbon–chloride bond in **4c** is worth noting.

The homoallyl ether **4d** could also be cyclized to the benzopyran derivative **5d** in 68% yield. The 2-benzopyran ring compound **5e** was formed upon reaction of benzyl allyl ether **4e**.

The diene ether **4f** was prepared from geranyl chloride in order to study the possibility of a tandem cyclization. However, with **3** as the catalyst, no double cyclization occurred, and two bicyclic diastereomers **5f** and **5f'**, derived from a single cyclization were formed in 76% yield and an approx. 1 : 1 ratio.

In conclusion, this work describes a convenient synthesis of a new donor **1**, able to form mononuclear Ni^{II} complexes such as **3**. The electrochemical reactivity of **3**, towards intramolecular cyclization involving double bonds is enhanced when compared to the reactivity of $[Ni(cyclam)]^{2+}$ [5,6]. In addition, the preparation of **1** is very flexibile. The access to chiral oxazoline analogs and their use in asymmetric synthesis is under investigation. Compound **1** and its derivatives open new and promising perspectives in organometallic catalysis.

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[12] Spectral data for compound **1**: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.63 (d, 2H, J 7.6 Hz,), 7.38 (dd, 2H, J 7.4 and 7.6 Hz), 7.04 (d, 2H, J 8.0 Hz) 7.00 (dd, 2H, J 7.4 and 8 Hz), 4.07 (s, 4H), 3.22 (s, 8H), 1.37 (s, 12H). ^{13}C-NMR ($CDCl_3$, 50.32 MHz): δ 163.3, 151.6, 131.7, 131.5, 122.0, 121.6, 118.2, 79.0, 67.4, 52.0 and 28.4. IR (nujol): 1630, 1600, 1315, 1035 cm^{-1}. White solid, Mp. 178°C.

[13] Spectral data for complex **3**: ^{1}H-NMR (CD_3NO_2, 200 MHz): δ 8.1 (dd, 2H, J 7.5; 1.5 Hz,), 7.9 (td, 2H, J 7.5; 1.5 Hz), 7.8 (dd, 2H, J 7.5; 1 Hz), 7.5 (td 2H, J 7.5; 1 Hz), 4.87 (s, 4H), 3.52 (s, 8H), 1.71 (s, 12H). ^{13}C-NMR (CD_3NO_2 at 57.3 ppm, 50.32 MHz): δ 165.7, 148.8, 133.8, 127.9, 122.2, 118.2, 110.2, 78.5, 60.5, 48.7 and 21.4. IR (KBr): 3233, 3050–2900, 1638, 1577, 1500, 1060 cm^{-1}.

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