

## Pincer Complexes

## Charge Effects in PCP Pincer Complexes of Ni<sup>II</sup> bearing Phosphinite and Imidazol(i)ophosphine Coordinating Jaws: From Synthesis to Catalysis through Bonding Analysis

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This report is dedicated to the memory of our colleague Dr. Guy Lavigne (1947–2015) and to his lifelong passion for organometallic chemistry.

**Abstract:** This contribution reports on a new family of Ni<sup>II</sup> pincer complexes featuring phosphinite and functional imidazolyl arms. The proligands <sup>R</sup>PIMC<sup>H</sup>OP<sup>R'</sup> react at room temperature with Ni<sup>II</sup> precursors to give the corresponding complexes [(<sup>R</sup>PIMCOP<sup>R'</sup>)NiBr], where <sup>R</sup>PIMCOP<sup>R</sup> =  $\kappa^{P}, \kappa^{C}, \kappa^{P}$ -{2-( $R'_2PO$ ),6-( $R_2PC_3H_2N_2$ )C<sub>6</sub>H<sub>3</sub>}, R = iPr, R' = iPr (**3b**, 84%) or Ph (**3c**, 45%). Selective *N*-methylation of the imidazole imine moiety in **3b** by MeOTf (OTf = OSO<sub>2</sub>CF<sub>3</sub>) gave the corresponding imidazoliophosphine [(<sup>Pr</sup>PIMIOCOP<sup>iPr</sup>)NiBr][OTf], **4b**, in 89% yield (<sup>Pr</sup>PIMIOCOP<sup>iPr</sup> =  $\kappa^{P}, \kappa^{C}, \kappa^{P}$ -{2-(*iPr*<sub>2</sub>PO),6-(*i*/Pr<sub>2</sub>PC<sub>4</sub>H<sub>5</sub>N<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>}). Treating **4b** with NaOEt led to the NHC derivative [(NHCCOP<sup>iPr</sup>)NiBr], **5b**, in 47% yield (NHCCOP<sup>iPr</sup> =  $\kappa^{P}, \kappa^{C}, \kappa^{C}$ -{2-(*i*Pr<sub>2</sub>PO),6-( $C_4H_5N_2$ )C<sub>6</sub>H<sub>3</sub>})}. The bromo derivatives

## Introduction

Pincer ligands are considered as privileged platforms for developing practical applications in homogeneous catalysis and functional materials, as well as for exploring fundamental bonding and reactivity patterns.<sup>[1]</sup> Since their introduction nearly 40 years ago,<sup>[2]</sup> research has shown that pincer ligands featuring varying donor moieties, backbones, and metallacycle sizes often lead to unusual bonding/structural features and unique reactivities.<sup>[3]</sup> An important factor that has accelerated the growth of pincer chemistry is the ease with which the

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201502491. **3–5** were then treated with AgOTf in acetonitrile to give the corresponding cationic species  $[({}^{R}PIMCOP^{R})Ni(MeCN)][OTf]$  $[R = Ph, 6a (89\%) \text{ or } iPr, 6b (90\%)], [({}^{R}PIMIOCOP^{R})Ni(MeCN)]$  $[OTf]_{2} [R = Ph, 7a (79\%) \text{ or } iPr, 7b (88\%)], and <math>[(NHCCOP^{R})Ni(MeCN)][OTf] [R = Ph, 8a (85\%) \text{ or } iPr, 8b (84\%)].$  All new complexes have been characterized by NMR and IR spectroscopy, whereas 3b, 3c, 5b, 6b, and 8a were also subjected to X-ray diffraction studies. The acetonitrile adducts 6–8 were further studied by using various theoretical analysis tools. In the presence of excess nitrile and amine, the cationic acetonitrile adducts 6–8 catalyze hydroamination of nitriles to give unsymmetrical amidines with catalytic turnover numbers of up to 95.

 $\kappa^3$  ligand architecture, conformation, and steric/electronic properties can be altered to generate a multitude of chemical entities possessing different physical and chemical properties.

As the central carbyl moiety of ECE pincer ligands is strongly  $\sigma$ -electron donating, particular efforts have been devoted to the study of "balanced" pincers with electron-withdrawing "coordinating jaws", like phosph(in)ite moieties. The objective is to design new, unsymmetrical pincer ligands by judicious combinations of charge-neutral donor moieties, represented by E, and positively charged jaws such as imidazoliophosphine moieties, also regarded as acceptor–donor adducts of phospheniums with N-heterocyclic carbenes (NHCs), [(NHC)R<sub>2</sub>P:]<sup>+</sup>. Our interests in the coordination chemistry of bi-<sup>[4]</sup> or tridentate<sup>[5]</sup> ligands featuring imidazoliophosphine units,<sup>[6]</sup> and in the organonickel chemistry of pincer complexes (Figure 1; e.g., NCN,<sup>[7]</sup> PCP,<sup>[8]</sup> POCOP,<sup>[9]</sup> POCN<sup>[10]</sup>)<sup>[11]</sup> led us to collaborate on the development of a family of unsymmetrical ECE'-type pincer ligands incorporating [(NHC)R<sub>2</sub>P:]<sup>+</sup> and related coordination moieties.

In a previous report, we communicated the initial fruits of our collaborative effort, namely an unprecedented family of Ni<sup>II</sup> pincer complexes featuring a *meta*-phenylene backbone flanked by donor moieties that were either electron-poor (phosphinites, imidazolyl- and imidazoliophosphines) or electron-rich (NHCs), and generated metallacycles of different sizes (5,5 and 5,6).<sup>[12]</sup> The present contribution reports on the results

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**Figure 1.** Various types of Ni<sup>II</sup> pincer complex.

of our follow-up investigations on PIMCOP-, PIMIOCOP-, and NHCCOP-Ni species (Figure 1). The original synthetic methodology has been used to prepare new examples of <sup>R</sup>PIMCOP<sup>R'</sup> proligands (R = iPr; R' = Ph, iPr) and new [(pincer)NiBr] complexes bearing PIMCOP, PIMIOCOP, and NHCCOP ligands. The related mono- and dicationic acetonitrile adducts [(<sup>R</sup>PIMCOP<sup>R'</sup>)Ni(NCMe)] [(OTf)], [(<sup>R</sup>PIMIOCOP<sup>R'</sup>)Ni(NCMe)] [(OTf)]<sub>2</sub> and [(NHCCOP<sup>R'</sup>)Ni(NCMe)][(OTf)]

have also been prepared and characterized. It was anticipated that the cationic character of the latter complexes would enhance the electrophilicity of the nickel center. To test this contention, the C=N stretching frequency,  $\nu$ (C=N), and redox potentials,  $E_p^{ox}$ , of these cationic species were measured to evaluate their aptitude for promoting nucleophilic hydroamination of coordinated nitriles,<sup>[13]</sup> allowing the development of a new catalytic route to

## **Results and Discussion**

#### Syntheses

The title complexes were prepared as outlined in the synthetic sequence shown in Scheme 1. The <sup>R</sup>PIMC<sup>H</sup>OP<sup>R'</sup> proligands **2b** and 2c were prepared similarly to their previously reported Ph analogue <sup>Ph</sup>PIMC<sup>H</sup>OP<sup>Ph</sup>, **2a**,<sup>[12]</sup> by adding two equivalents of chlorophosphines to the doubly deprotonated 3-hydroxyphenylimidazole 1.<sup>[14]</sup> Thus, <sup>iPr</sup>PIMC<sup>H</sup>OP<sup>iPr</sup> 2b was obtained in 70% yield by using 2 equivalents of *i*Pr<sub>2</sub>PCl, whereas sequential addition of *i*Pr<sub>2</sub>PCl and Ph<sub>2</sub>PCl (1 equivalent each) gave the "mixed" <sup>iPr</sup>PIMC<sup>H</sup>OP<sup>Ph</sup> proligand **2c** in 72% yield. Formation of the latter confirmed the anticipated greater nucleophilicity of the lithiated carbon atom of the imidazole ring, which was phosphinylated first. The [(PIMCOP)NiBr] complexes 3b and c were then obtained by direct nickelation of the central C-H bond when the PIMCOP proligands  ${\bf 2\,b}$  and  ${\bf c}$  were treated at RT with a slight excess of  $[Br_2Ni(iPrCN)]_n^{[15]}$  in the presence of NEt<sub>3</sub>.<sup>[16]</sup>



**Scheme 1.** Synthesis of neutral and cationic PIMCOP-derived Ni<sup>II</sup> pincer complexes.

a variety of amidines. Finally, the experimental studies were complemented by extensive theoretical analyses to improve our understanding of the bonding and reactivities in these complexes. Similarly to the synthesis of its previously reported Ph analogue 4a,<sup>[12]</sup> the complex [(<sup>*i*Pr</sup>PIMIOCOP<sup>*i*Pr</sup>)NiBr], 4b, was prepared in 89% yield by *N*-methylation of [(<sup>*P*r</sup>PIMCOP<sup>*i*Pr</sup>)NiBr], 3b, with MeOTf (Scheme 1). Subsequent treatment of 4b with a stoichiometric amount of NaOEt gave [(NHCCOP<sup>*i*Pr</sup>)NiBr], 5b, in 47% yield. A similar reactivity of the Ph analogue 4a has

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been observed with a weaker nucleophile ([Et<sub>4</sub>N][Cl]), giving [(NHCCOP<sup>Ph</sup>)NiX] (X = Cl, Br) **5 a**.<sup>[12]</sup> Finally, all of the bromo derivatives were converted into their corresponding cationic acetonitrile analogues by reaction with a slight excess of AgOTf in acetonitrile (Scheme 1).<sup>[17]</sup>

Formation of the NHCCOP derivatives **5** is thought to arise from the attack of a nucleophile (e.g., EtO<sup>-</sup>) on the phosphenium center [R<sub>2</sub>P:]<sup>+</sup> in the PIMIOCOP complexes **4** (see the canonical forms shown in Scheme 2).<sup>[18]</sup> The relative reactivities of **4a** and **4b** were investigated through NMR spectroscopy, whereby 1 equivalent each of **4a** and **4b** was allowed to compete for 1 equivalent of NaOEt (Scheme 2). The <sup>31</sup>P and <sup>1</sup>H NMR spectra (Figures S1 and S2 in Supporting Information) of the mixture recorded after heating at 50 °C for one hour indicated that **4a** [ $\delta_P$ = +11.1 (d), +147.0 ppm (d); <sup>2</sup>J(P,P)=367 Hz] was totally converted into **5a** [ $\delta_P$ = +144.9 ppm (s)] while **4b** remained unreacted [ $\delta_P$ = +32.6 (d), +184.8 ppm (d); <sup>2</sup>J(P,P)= 309 Hz].<sup>[19]</sup> The greater reactivity of [(<sup>Ph</sup>PIMIOCOP<sup>Ph</sup>)NiBr] **4a** relative to its *i*Pr analogue **4b** is in agreement with the higher electrophilicity of [Ph<sub>2</sub>P:<sup>+</sup>] vs. [*i*Pr<sub>2</sub>P:<sup>+</sup>].

#### Solid-state structural studies

Single crystal X-ray diffraction studies allowed us to establish the solid-state structures of the  $[(P^{P}PIMCOP^{R})NiBr]$  complexes **3b** and **3c**, and of the  $[(NHCCOP^{P})NiBr]$  complex **5b** (Figure 2,

| Su c, and Su S.   |  |  |  |  |   |  |  |
|---|--|--|--|--|---|--|--|
| $\begin{array}{c} & & & & \\ O & & & \\ R'_2 P \longrightarrow Ni \\ P_{11} &   & P_{P12} \\ Br & R_2 \end{array} \qquad \begin{array}{c} O & & \\ O &   & C1 \\ P_1 &   & C7 \\ P_1 &   & C7 \\ Br & R_2 \end{array} $ |  |  |  |  |   |  |  |
| 3a: R= R'= Ph<br>3b: R= R'= /Pr<br>3c: R = /Pr, R' = Ph   |  |  | <b>5a</b> : R' = Ph<br><b>5b</b> : R' = <i>i</i> Pr  |  |   |  |  |
| Ni–C11<br><i>Ni–C1</i>  | Ni—Br  | Ni—P11<br><i>Ni—P1</i>   | Ni—P12<br>Ni—C7  | P11-Ni-P12<br><i>P1-Ni-C7</i>  | C11-Ni-Br<br><i>C1-Ni-Br</i>  |  |  |
| 1.945(2)<br>1.939(3)<br>1.943(2)  | 2.3345(3)<br>2.3414(5)<br>2.3404(5)  | 2.1322(5)<br>2.1339(8)<br>2.1383(7)  | 2.169(2)<br>2.1682(8)<br>2.1985(7)   | 170.30(2)<br>176.60(3)<br>175.90(3)  | 170.68(5)<br>172.06(8)<br>169.54(8)   |  |  |
|   | O<br>R'2P<br>P<br>3a<br>3b<br>3c<br>Ni–C11<br>1.945(2)<br>1.945(2)<br>1.943(2)<br>1.943(2) | $R_{2}P \rightarrow Ni \qquad P_{11} \qquad P_{11$ | $\begin{array}{c} \begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ $ | init 0  Jult 2. $init 0  Jult 2.$ <th>init o J d b. <math>init o J d b.</math> <math>init o J d b.</math></th> | init o J d b. $init o J d b.$ |  |  |

Table 1. Selected bond lengths (Å) and bond angles (°) for complexes

Table 1, and Tables S1 and S2 in Supporting Information);<sup>[20]</sup> these structures can be compared to those of their previously reported all-Ph analogues **3a** and **5a**, respectively.<sup>[12]</sup>

The Ni atom in the PIMCOP complexes is located at the center of a somewhat distorted square-planar environment, with the two P atoms occupying mutually *trans* positions (Figure 2, left and middle). This family of complexes features 5-



Scheme 2. Relative reactivities of [(<sup>R</sup>PIMIOCOP<sup>R</sup>)NiBr][OTf] 4a and 4b towards NaOEt.



Figure 2. Molecular views of the X-ray crystal structures of charge neutral Ni<sup>II</sup> pincer complexes 3b (left), 3c (middle), and 5b (right). Thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

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and 6-membered fused metallacycles and bite angles (P11-Ni-P12) that are much greater than in their POCOP analogues featuring two fused 5-membered metallacycles (ca. 170–176° vs. 164°).<sup>[21]</sup> The bite angles in [(<sup>R</sup>PIMCOP<sup>R</sup>)NiBr] are also influenced by the *P*-substituents, being roughly 6–7° wider in the structures of **3b** and **3c** bearing the bulkier *i*Pr<sub>2</sub>P moieties. Steric factors appear to have less influence over bond lengths, but the Ni–P distances in **3a** and **3b** (R=R': 2.132–2.134 and 2.168–2.169 Å) are significantly shorter than those in **3c** (R  $\neq$  R': 2.138 and 2.199 Å).

A distorted square-planar geometry is also adopted by the [(NHCCOP<sup>R'</sup>)NiBr] complexes **5a** and **b**, and minimal structural variations result from the different P-substituents. The small bite angles (ca. 161–162°) can be attributed to the metallacycle size (5,5) and correlated with the shorter N1-C7 bonds in 5a and 5b relative to the O-P bonds in the analogous POCOP complexes.<sup>[22]</sup> The Ni–P1 distances in **5a** and **5b** (av. 2.147 Å) are longer than those in 3a and 3c (av. 2.133 Å) but remain comparable to the corresponding distance in a typical POCOP structure (2.148 Å).<sup>[13,22]</sup> These observations establish the following order of *trans* influence:  $ArOP(iPr)_2 \approx NHC > 2$ -imidazolyl-PPh<sub>2</sub>. The Ni–CN<sub>2</sub> distances of approximately 1.95 Å in **5**a and 5b are longer than the corresponding distances of approximately 1.90-1.92 Å found in previously reported Ni-NHC complexes.<sup>[23]</sup> Finally, the central Ni–C1 bond lengths are much shorter in the 5,5-complexes 5a and 5b than in the 5,6-complexes 3a-c (1.87 vs. 1.94 Å).

The crystal structures of the cationic complexes **6b** and **8a** (Figure 3) also revealed a somewhat distorted square-planar geometry around the Ni center. The above-noted smaller bite angle P1-Ni-C7 and shorter Ni–C1 bond in NHCCOP complexes are confirmed here. Likewise, the Ni–P1 bond lengths in **6b** (ca. 2.157 Å) and **8a** (ca. 2.166 Å) reflect the superior *trans* influence of the NHC moiety, even though the PR<sub>2</sub> moieties being compared are different. A greater deviation from the ideally linear Ni–NCMe coordination mode is found in **6b** than in **8a**: C1-Ni-N  $\approx$  169° vs. 178°; Ni-N-C  $\approx$  172° vs. 177°. This deviation is likely caused by the steric demand of the inserted *i*Pr<sub>2</sub>P moiety in **6b**.

# Characterization of the proligands and complexes by NMR spectroscopy

The most characteristic NMR features of the <sup>R</sup>PIMCOP<sup>R'</sup> proligands **2b** and **2c** consist of the pair of singlet <sup>31</sup>P resonances for the phosphinite and imidazolophosphine moieties, as well as the <sup>13</sup>C signals for the central C nuclei that are flanked by these moieties [ $\delta_C \approx 118-119$  ppm (dd); <sup>3</sup>J(C,P)  $\approx 7-8$  Hz, <sup>4</sup>J(C,P')  $\approx 3-5$  Hz].<sup>(12)</sup> Upon nickelation, a dramatic <sup>31</sup>P downfield shift occurs, giving rise to doublets of doublets with <sup>2</sup>J(P,P') > 300 Hz, as anticipated for the two inequivalent and mutually *trans* P nuclei.<sup>[24]</sup> The <sup>13</sup>C resonances for the reacting carbon nucleus also moved downfield and turned into pseudo-triplets [ $\delta_C \approx 125$  ppm; <sup>2</sup>J(C,P)  $\approx$  <sup>2</sup>J(C,P')  $\approx 22$  Hz].

Conversion of the PIMCOP complexes **3 a,b** and PIMIOCOP complexes **4 a,b** into their respective cationic acetonitrile adducts **6 a,b** and **7 a,b** has a relatively minor impact on the NMR



**Figure 3.** Molecular views of **6b** (top) and **8a** (bottom). Thermal ellipsoids are drawn at the 50% probability level and the H atoms and the triflate anion have been omitted for clarity. Selected bond lengths (Å) and bond angles (°) for **6b**: Ni–C1 1.944(2), Ni–N 1.882(2), Ni–P1 2.1572(5), Ni–P2 2.2005(5); P1-Ni-P2 175.70(2), C1-Ni-N 168.92(7), Ni-N-C 172.48(15). Selected bond lengths (Å) and bond angles (°) for **8a**: Ni–C1 1.876(4), Ni–N 1.888(4), Ni–P1 2.166(2), Ni–C7 1.943(5); P1-Ni-C7 161.0(2), C1-Ni-N 177.5(2), Ni-N-C 177.3(4).

features, whereas the extent of  $\delta_{31P}$  deshielding upon *N*-methylation depends on the *P*-substituents (by ca. 8 ppm for **3**a  $\rightarrow$ **4**a vs. 21 ppm for **3**b  $\rightarrow$  **4**b). The N<sup>+</sup>–CH<sub>3</sub> substituent of the [(PIMIOCOP)NiX] complexes gives a single <sup>1</sup>H NMR resonance at  $\delta_{H} \approx +3.2$  ppm. Finally, the NHCCOP complexes **5**a,**b** and **8**a,**b** display characteristic <sup>13</sup>C NMR carbene signals at  $\delta_{C}$  $\approx$  172–175 ppm [d; <sup>2</sup>J(C,P) $\approx$  90–110 Hz].

#### IR spectroscopy, cyclic voltammetry, and theoretical studies

In an effort to estimate the electronic density of the Ni center in the title complexes, the oxidation potentials  $E_p^{ox}$  and IR C=N stretching frequencies  $\nu$ (C=N) were measured. Wide-scope computational studies at the density functional theory (DFT) level were also performed on the cationic acetonitrile adducts **6 a, b, 7 a, b, 8 a, b**, and their previously reported POCOP analogues **9 a, b** (Figure 4).<sup>[13,22]</sup> The results that are most pertinent to the present discussion are presented sequentially in the following sections and some of the computational results (including geometry optimization studies, Figures S3–S10 and Tables S3–S8) are provided in the Supporting Information.

**Measured and calculated**  $\nu$ (**C**=**N**): IR stretching frequencies  $\nu$ (**C**=**N**) of coordinated acetonitrile molecules are a priori expected to reflect the overall donor character ( $\sigma$ -donating vs.  $\pi$ -accepting properties) of coligands. It was indeed reported that the (a priori nonbonding) lone pair of a nitrile, which is strong-ly polarized on the nitrogen lone pair, could actually exhibit some antibonding character. Therefore,  $\nu$ (**C**=**N**) values are expected to increase upon  $\sigma$ -donation from the coordinated ace-



Figure 4. Cationic acetonitrile adducts analyzed by DFT studies.

tonitrile to the nickel center in the pincer complexes under study.<sup>[25,26]</sup> Indeed, an increase of 31–46 cm<sup>-1</sup> was observed for the  $\nu$ (C=N) values within the pincer series (Table 2).

We found that calculated and experimental  $\nu$ (C=N) values are comparable, with a shift of 100–120 cm<sup>-1</sup> at the PCM-B3PW91/6-31G\*\* level. In particular, complexes of pincer ligands bearing Ph<sub>2</sub>P moieties (6a, 7a, 8a) exhibit higher  $\nu$ (C= N) values than their *i*Pr<sub>2</sub>P analogues (**6b**, **7b**, **8b**), an observation that could be anticipated from the greater electron-donating character of the *i*Pr substituents, the same trend having been observed for the previously reported complexes [(PO-COP)Ni(NCMe)][OTf].<sup>[13, 17d, 24]</sup> However, the IR data do not correlate with the relative overall electron-donating character of the pincer ligand, as established previously on the basis of electrochemical measurements (NHCCOP > PIMCOP  $\approx$  POCOP > PIMIO-COP).<sup>[12]</sup> For example, both DFT calculations and experimental measurements showed that the  $\nu(C \equiv N)$  value is lower in the PIMCOP adduct 6b than in the NHCCOP adduct 8b (2284 vs. 2296  $\text{cm}^{-1}$ ), whereas the opposite order is a priori expected.

An increase of the  $\nu$ (C $\equiv$ N) resulting from  $\sigma$ -donation of acetonitrile to the nickel center would normally imply a bond order increase or a shortening of the C=N bond. However, the calculated C=N bond length remains close to 1.158 Å over the entire series of the pincer complexes depicted in Figure 4 (see the Supporting Information, Table S6). Similarly, a constant  $C \equiv$ N bond order of about 2.2 is found over the entire series by electron localization function (ELF) topological analysis (see below and Table S7 in the Supporting Information). The  $\nu$ (C=N) values of Table 2 might, therefore, be probing the local electrostatic environment of the CN moiety rather than the electron density of the nickel center. Indeed, the vibrational frequency of nitrile groups has been reported to be very sensitive to their local environment, and nitriles have been used as IR probes of biomolecular structures and dynamics.<sup>[27]</sup> Finally, the  $\nu$ (C=N) values of **6b** and **7b** might also be influenced by the experimentally observed (Figure 3) and computationally confirmed (Table S6) deviation of the Ni-N-CCH<sub>3</sub> angle from 180°, which would decrease the orbital overlap between the Ni<sup>II</sup> center and NCCH<sub>3</sub>.

For the purpose of comparison, a few calculations were performed on theoretical complexes (in the Ph<sub>2</sub>P series) in which the MeCN ligand was replaced by a CO ligand, which is currently used for assessing relative electron densities of metal centers as a function of the overall electron-donating character of coligands.<sup>[28]</sup> The calculated  $\nu$ (C=O) values (Table 2) are consistent with the electrochemical trend of  $E_p^{ox}$ ; they decrease with the electron-richness of the nickel center: <sup>Ph</sup>PIMIOCOP<sup>Ph</sup> > <sup>Ph</sup>PIMCOP<sup>Ph</sup> > <sup>Ph</sup>POCOP<sup>Ph</sup> > NHCCOP<sup>Ph</sup> > <sup>Ph</sup>POCOP<sup>Ph</sup> > <sup>Ph</sup>POCOP<sup></sup>

**Molecular orbital (MO) analysis**: The near-frontier MOs of  $[(pincer)Ni(NCMe)]^+$  complexes (*i*Pr<sub>2</sub>P series in Figure 4) are shown in Figures S5–S8 (see the Supporting Information), and their energy levels are presented in Figure 5. A selection of the more pertinent frontier MOs are depicted in Figure 6 to facilitate the present discussion. Inspection of the MO shapes and energies indicate that those of the POCOP and PIMCOP complexes are similar in shape and quasi-degenerate, but significant differences can be noted in the NHCCOP and PIMIOCOP complexes. Consistent with the respective electron-richness of the pincer ligand, the MO levels are shifted up to higher ener-

| Table 2. Experimental and calculated IR data for acetonitrile adducts and selected CO adducts of cationic pincer Ni complexes. |   |                               |                                    |  |                                |  |
|--|---|-------------------------------|------------------------------------|--|--------------------------------|--|
|  | L = MeCN; $\nu$ (CN) [cm <sup>-1</sup> ] <sup>[a]</sup> |                               |                                    | L=CO; v(CO) [cm <sup>-1</sup> ] <sup>[b]</sup> |                                |  |
| Complexes/L  | Exptl   | $\Delta  u$ (CN) <sup>c</sup> | Calcd                              | $\Delta  u$ (CN) <sup>[c]</sup>                | Calcd                          |  |
| [( <sup>Ph</sup> PIMIOCOP <sup>Ph</sup> )NiL][OTf] <sub>2</sub> 7 a  | 2291  | 38                            | 2408                               | 30   | 2079                           |  |
| [( <sup>iPr</sup> PIMIOCOP <sup>iPr</sup> )NiL][OTf] <sub>2</sub> 7 b  | 2284  | 31                            | 2393                               | 15   |                                |  |
| [( <sup>Ph</sup> PIMCOP <sup>Ph</sup> )NiL][OTf] <b>6 a</b>  | 2287  | 34                            | 2407                               | 29   | 2071                           |  |
| [( <sup>iPr</sup> PIMCOP <sup>iPr</sup> )NiL][OTf] <b>6 b</b>  | 2284  | 31                            | 2395                               | 17   |                                |  |
| [( <sup>Ph</sup> POCOP <sup>Ph</sup> )NiL][OTf] <b>9a</b> <sup>[24]</sup>  | 2297  | 44                            | 2403                               | 25   | 2065                           |  |
| [( <sup>iPr</sup> POCOP <sup>iPr</sup> )NiL][OTf] <b>9b</b> <sup>[17b]</sup>   | 2292  | 39                            | 2397                               | 19   |                                |  |
| [(NHCCOP <sup>Ph</sup> )NiL][OTf] 8 a  | 2299  | 46                            | 2400                               | 22   | 2062                           |  |
| [(NHCCOP <sup>iPr</sup> )NiL][OTf] <b>8 b</b>  | 2296  | 43                            | 2397                               | 19   |                                |  |
| MeCN   | 2253  | 0                             | 2378                               | 0  |                                |  |
| [a] PCM-B3PW91/6-31G** level of ca   | Iculation used for M                                    | eCN adducts (acetonitri       | le solvent, $\varepsilon = 35.688$ | 3); [b] PBE/6-31G** level                      | of calculation used for CO ad- |  |

[a] PCM-B3PW91/6-31G\*\* level of calculation used for MeCN adducts (acetonitrile solvent,  $\varepsilon = 35.688$ ); [b] PBE/6-31G\*\* level of calculation used for CO adducts; [c]  $\nu$ (C=N) difference between the complexes and free acetonitrile.

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**Figure 5.** MO diagrams for the complexes in Figure 4 ( $iPr_2P$  series). Main contributions to the MOs are indicated; *m*-phen and NHC refer to the central *m*-phenylene and the N-heterocyclic carbene moieties, respectively. PCM-B3PW91/6-31G\*\* level of calculation in the acetonitrile continuum ( $\varepsilon = 35.688$ ).



**Figure 6.** Representative frontier MOs of the complexes in Figure 4 (R = iPr). PCM-B3PW91/6-31G\*\* level of calculation in the acetonitrile continuum ( $\varepsilon = 35.688$ ).

gies in the NHCCOP complex, whereas the reverse is observed in the PIMIOCOP complex. Also noteworthy is the changing character of the LUMOs from  $\pi_z^*(CN)$  in the POCOP and PIMCOP systems to  $\pi^*(NHC)$  in the NHCCOP complex and to  $\pi^*(P-C)$  in the PIMIOCOP complex. In contrast, the nature of the HOMO is fairly invariable along the series (Figures 5 and 6). The relative order of the HOMO-*n* is in line with the distorted square-planar geometry of the nickel center. These MO features will be valuable for the analysis of experimental cyclic voltammetry (CV) and electrophilic reactivity results (see below).

**Electrochemical Measurements**: Given that the oxidation potential ( $E_p^{ox}$ ) of a complex can reflect the electronic endowment of its ligands, the title Ni<sup>II</sup> pincer complexes were investigated by CV to establish the relative electron donation from various pincer ligands. The  $E_p^{ox}$  values (Table 3) showed much variation as a function of the pincer ligand: [(NHCCOP)NiBr] (ca. + 0.5 V) < [(PIMCOP)NiBr] (ca. + 0.8 V) < [(PIMIOCOP)NiBr] ( $E_p^{ox} \approx +$  1.0 V). In the POCOP, PIMCOP, and PIMIOCOP series, passing

| _ | CHI          | ΕM   | 151  | K.   |
|---|--------------|------|------|------|
| _ | <b>A</b> Eur | opea | n Jo | urna |
|   | Full         | Pa   | per  |      |

| Table 3. Oxidation potentials (vs. $FeCp_2$ ) of $Ni^{II}$ pincer complexes.^[a] |                           |               |  |  |  |
|--|---------------------------|---------------|--|--|--|
| Complexes  | $E_{\rm p}^{\rm ox}$ [mV] | Reversibility |  |  |  |
| [( <sup>Ph</sup> PIMIOCOP <sup>Ph</sup> )Ni(NCMe)][OTf] <sub>2</sub> 7 a         | 1220                      | quasi         |  |  |  |
| [( <sup>iPr</sup> PIMIOCOP <sup>iPr</sup> )Ni(NCMe)][OTf] <sub>2</sub> 7 b       | 1195                      | no            |  |  |  |
| [( <sup>Ph</sup> PIMIOCOP <sup>Ph</sup> )NiBr][OTf] <b>4a</b>                    | 1120                      | no            |  |  |  |
| [( <sup>iPr</sup> PIMIOCOP <sup>iPr</sup> )NiBr][OTf] <b>4b</b>                  | 1001                      | no            |  |  |  |
| [( <sup>Ph</sup> PIMCOP <sup>Ph</sup> )Ni(NCMe)][OTf] 6 a                        | 1020                      | no            |  |  |  |
| [( <sup>iPr</sup> PIMCOP <sup>iPr</sup> )Ni(NCMe)][OTf] <b>6 b</b>               | 966                       | no            |  |  |  |
| [( <sup>Ph</sup> PIMCOP <sup>Ph</sup> )NiBr] <b>3 a</b>                          | 820                       | no            |  |  |  |
| [( <sup>iPr</sup> PIMCOP <sup>iPr</sup> )NiBr] <b>3 b</b>                        | 862                       | no            |  |  |  |
| [( <sup>iPr</sup> PIMCOP <sup>Ph</sup> )NiBr] <b>3 c</b>                         | 834                       | no            |  |  |  |
| [(NHCCOP <sup>Ph</sup> )Ni(NCMe)][OTf] 8 a                                       | 530                       | no            |  |  |  |
| [(NHCCOP <sup>iPr</sup> )Ni(NCMe)][OTf] <b>8 b</b>                               | 618                       | no            |  |  |  |
| [(NHCCOP <sup>Ph</sup> )NiBr] <b>5 a</b>   | 500                       | quasi         |  |  |  |
| [(NHCCOP <sup>iP</sup> r)NiBr] <b>5 b</b>  | 547                       | quasi         |  |  |  |
| [a] The experiments were carried out at room temperature on solutions            |                           |               |  |  |  |

prepared in dry  $CH_2Cl_2$  containing [ $nBu_4N$ ][ $PF_6$ ] as electrolyte (0.1 M). For complete details of the experimental set-up and conditions, see the Supporting Information.

from a charge-neutral bromo complex to the cationic acetonitrile derivative results in a significant increase of the  $E_p^{ox}$  value (by ca. 100–200 mV); by comparison, ionization has a more muted impact on the oxidation potentials of the NHCCOP complexes, which increased by 30 (**5a/8a**) and 71 mV (**5b/8b**). The influence exerted on the  $E_p^{ox}$  values by the relative donating characters of the *P*-substituents (Ph<sub>2</sub>P < *i*Pr<sub>2</sub>P) varied by as little as 25 mV (**7a/7b**) and as much as 119 mV (**4a/4b**). The highest  $E_p^{ox}$  value was observed for the dicationic complexes [(PIMIOCOP)Ni(NCMe)][OTf]<sub>2</sub> (**7a,b**;  $E_p^{ox} \approx + 1.2$  V), thus reflecting the extreme electron deficiency of PIMIOCOP ligands.

The oxidation potentials of the complexes are correlated with the character of the HOMOs, which involve mainly  $\pi$  orbitals of the *m*-phenylene moiety, whereas the HOMO–n (n = 1–6) present a strong nickel d-orbital character. The relative energy of these HOMOs is found in qualitative agreement with the relative oxidation potentials of the complexes. Furthermore, the experimental oxidation potentials correlate linearly with the energy of the particular HOMO–n with the highest contribution of a Ni d<sub>z<sup>2</sup></sub> orbital (see the Supporting Information, Figure S9), thus corroborating the assumption that the observed redox events are Ni-based, even in the case of irreversible oxidations.

#### Theoretical analysis of the reactivities of pincer-Ni complexes

Although the oxidation properties of the complexes have been correlated with the main features of their HOMOs, the electrophilic reactivities should a priori be correlated with their LUMOs, the features of which vary considerably with the pincer ligand (Figures 5 and 6). In POCOP and PIMCOP complexes where the major contribution to the LUMO is the  $\pi^*$  orbital of the nitrile moiety, interaction with nucleophiles is expected to weaken the C=N bond. In PIMIOCOP complexes in which the main contribution to the LUMO involves the amidi-

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niophosphine  $\pi^*$  orbital (Figure 6),<sup>30</sup> interaction with nucleophiles is expected to weaken the P–C bond.

The chemical reactivity was first investigated by using ELF and AIM (AIM = atoms in molecules) topological analyses and Fukui functions. The results of these studies, including average ELF populations and AIM atomic charges, are provided and described in the Supporting Information (Figure S10). Altogether, these results indicate that regions most susceptible to attack by nucleophiles should be the acetonitrile C<sub>sp</sub> center in POCOP, PIMCOP, and perhaps NHCCOP systems, whereas in PIMIOCOP-based cations nucleophilic attack should occur at the P–CN<sub>2</sub><sup>+</sup> region.

#### Catalytic conversion of nitriles to amidines

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As dinitrogen analogues of carboxylic acids and esters, amidines exhibit particular biological activities and can be used in the synthesis of functional heterocycles.<sup>[31]</sup> Among many possible routes to amidines,<sup>[32]</sup> the most straightforward strategy is the addition of an amine to a nitrile.<sup>[33]</sup> Such additions can be promoted by stoichiometric amounts of Lewis acids,<sup>[34]</sup> but in most cases such additions require harsh conditions.<sup>[35]</sup> Alternatively, nitriles can be converted into amidines in a catalytic fashion by using lanthanide(III) ions.<sup>[36]</sup> For instance, Yb<sup>III</sup>-amide complexes have been shown to catalyze the formation of amidines along with pyrimidine and triazine byproducts.<sup>[37, 38]</sup>

In the course of previous studies on Michael-type hydroalkoxylation and hydroamination of olefins catalyzed by cationic POCOP-Ni complexes (Scheme 3), path A),[17b,24,39] it was discovered that addition of morpholine to 4-cyanostyrene or cinnamonitrile took place at the nitrile moiety, giving the amidine products with catalytic turnover numbers (TONs) of 25 or 35, respectively (Scheme 3, paths B and C).<sup>[13a]</sup> The same reactivity was also evident with nitriles lacking an olefinic moiety, as exemplified by the reaction of morpholine with [(POCOP)-Ni(NCMe)]<sup>+</sup>, from which an acetamidine adduct was isolated (Scheme 3, path D). A report by Arnold and co-workers also showed that the addition of piperidine to acetonitrile is catalyzed, at ambient temperature and with TON  $\approx$  14, by the dicationic "pincer-like" complex  $[\kappa^{P},\kappa^{N},\kappa^{P'}$ related  ${(iPr_2PCH_2CH_2)_2NH}Ni(NCMe)][BF_4]_2$ .<sup>[40]</sup>



Scheme 3. Hydroamination of nitriles promoted by [(POCOP)Ni(NCMe)]<sup>+</sup>.

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Access to the new set of electrophilic PIMCOP- and PIMIO-COP-based pincer complexes **6** and **7** allowed us to screen them for the catalytic hydroamination of nitriles. The benchmark reaction of piperidine with benzonitrile was thus studied under the following conditions: equimolar quantities of piperidine and benzonitrile, no solvent, 50 °C, and 1 mol% of a cationic pincer complex (Table 4). For the sake of comparison, we also screened the catalytic competence of the previously reported cationic adduct [(<sup>Ph</sup>POCOP<sup>Ph</sup>)Ni(NCMe)]<sup>+</sup>, **9a.**<sup>24</sup> Control experiments demonstrated that no hydroamination occurs in the absence of a Ni precursor.



The highest TON values obtained with the PIMIOCOP-based precursors **7a** and **7b** were at first attributed to the increased electrophilic character relative to the PIMCOP analogues **6a** and **6b** (see above). Nevertheless, the very low TON obtained with the <sup>Ph</sup>POCOP<sup>Ph</sup>-based precursor **9a** is at odds with our expectations of the greater electrophilicity of this diphosphinite complex. Likewise, the higher catalytic activity observed with complex **7b** vs. **7a** does not correlate with the greater electrophilicity of the latter, which is both anticipated in view of its less electron-donating *P*-substituents (Ph<sub>2</sub>P vs. *i*Pr<sub>2</sub>P) and also revealed by the more positive oxidation potential of this species.

Optimal reaction conditions were then sought for the hydroamination of benzonitrile with the most competent precursor, complex 7b (Table 5). We first found that the TON values declined significantly when the reaction time was shortened from 67 to 3 h, even when the temperature was raised from 50 to 80°C (Table 5, entry 1). Maintaining this temperature and running the reaction over 21 h resulted in much higher TON values (Table 5, entry 2 VS.

| Table 5. Conditions for the preparation of piperidinobenzamidine frombenzonitrile and piperidine using 7 b as catalyst precursor. <sup>[a]</sup> |                         |               |       |                 |           |     |
|--|-------------------------|---------------|-------|-----------------|-----------|-----|
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$  |                         |               |       |                 |           |     |
| Entry  | Cat. loading<br>[mol %] | <i>T</i> [°C] | t [h] | PhCN/piperidine | Yield [%] | TON |
| 1  | 1                       | 80            | 3     | 1:1             | 13        | 13  |
| 2  | 1                       | 80            | 21    | 1:1             | 49        | 49  |
| 3  | 1                       | 80            | 21    | 1:2             | 68        | 68  |
| 4  | 1                       | 100           | 21    | 1:2             | 72        | 72  |
| 5  | 5                       | 80            | 21    | 1:2             | 80        | 16  |
| 6  | 10                      | 80            | 21    | 1:2             | 68        | 7   |
| [a] Yields and TON values determined by GC-MS analysis of the final mix-   |                         |               |       |                 |           |     |

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Table 4, entry 2 and Table 5, entry 1). Further improvements in TON resulted from using 2 equivalents of piperidine (Table 5, entry 3) and raising the reaction temperature to  $100^{\circ}C$  (entry 4). Finally, increasing the precursor loading from 1% to 5% resulted in the anticipated yield enhancement (to 80%; Table 5, entry 5), but a further increase to a 10% loading led to a yield decrease (entry 6); this unexpected result will be addressed later.

The reaction scope in terms of compatible amine and nitrile substrates was investigated next. As shown in Figure 7, benzonitrile was found to be much more reactive than acetonitrile, and piperidine was found to be a more effective nucleophile than morpholine (TON = 49 vs. 33).

Primary aliphatic amines led to various mixtures of N-monosubstituted or N,N'-disubstituted amidines, depending on the amine/PhCN ratio. For instance, using a 4:1 amine/PhCN ratio with n-hexylamine led to the disubstituted product only (m/



**Figure 7.** Products of nitrile hydroamination reactions carried out at 80 °C for 21 h (with PhCN) or 5 d (with acetonitrile), in a solvent-free manner using 1 mol% of the precursor complex **7 b**, and an amine/RCN ratio of 1:1 (for piperidine and morpholine) or 4:1 (for cyclohexylamine and *n*-hexylamine). Yields were determined by GC-MS with  $n-C_{12}H_{26}$  as internal standard.

z=288; TON=95), whereas cyclohexylamine gave a mixture of mono- and disubstituted products (m/z=201 and 284, respectively; total TON=41). The disubstituted amidines result from a second nucleophilic attack on the coordinated amidine and subsequent elimination of ammonia; it is worth noting that this step occurs in an uncatalyzed manner.<sup>[38]</sup> Finally, PhCN reacted with neither weakly nucleophilic aromatic amines, such as aniline and diphenylamine, nor bulky aliphatic amines, such as  $iPr_2NH$ .

#### **Mechanistic issues**

Two different mechanistic postulates have been put forth for the hydroamination of nitriles catalyzed by lanthanide complexes. Forsberg et al. proposed that hydroaminations catalyzed by Ln<sup>III</sup> ions proceed via an outer-sphere mechanism involving nucleophilic attack of amines on coordinated nitriles.<sup>[36]</sup> This proposal appears to be somewhat incongruent with the fact that amines are more nucleophilic towards lanthanide ions, and they are present in equimolar or even excess quantities in these catalytic settings; these considerations call into question the coordination-activation of nitriles. The authors rationalize this apparent contradiction by proposing that labile binding of amines to Ln<sup>III</sup> allows competitive nitrile binding and activation. The hydroamination reactions catalyzed by Yb amides are believed to proceed via a conceptually different, inner-sphere mechanism involving insertion of R'C=N into the Yb-NR<sub>2</sub> bond, followed by aminolysis of the resulting amidinate Yb–N=C(R')NR<sub>2</sub>.<sup>[37]</sup>

In the search for a mechanism adapted for the Ni-catalyzed hydroamination of nitriles under discussion, we selected as guiding concepts the following known reactivities of Ni<sup>II</sup> species with nitriles and amines: i) Nitriles coordinate very readily to the Ni<sup>II</sup> center in cationic species; ii) cationic adducts of the type [(pincer)Ni(NCMe)]<sup>+</sup> promote Michael-type additions of amines to *N*-coordinated acrylonitrile derivatives.<sup>[13b,39]</sup> Therefore, an outer-sphere mechanism similar to that proposed by Forsberg et al. for Ln<sup>III</sup> catalysts (see above)<sup>[36]</sup> seems plausible in the system under discussion. This postulate is also supported by Fukui index values (see the Supporting Information, Figure S10). We have studied the stoichiometric reactions shown in Scheme 4 to examine whether the hydroamination of nitriles proceeds by direct attack by amines on the coordination-activated nitriles. The results are described below.

Addition of excess piperidine to a CD<sub>3</sub>CN solution of **7b** (Scheme 4, reaction A) led to disappearance of the <sup>31</sup>P doublets of **7b** [ $\delta = +194.2$  and +31.2 ppm; J(P,P) = 250 Hz] and appearance of a broad singlet at  $\delta = 187-188$  ppm, which could be attributed to the cationic adduct [(NHCCOP<sup>iPr</sup>)Ni(amidine)]<sup>+</sup> (**10**-CH<sub>3</sub> or **10**-CD<sub>3</sub>). Consistent with the in situ formation of an NHC species, the <sup>13</sup>C NMR spectrum of the reaction A mixture indeed showed a signal at  $\delta = +173.9$  ppm [ $J(C,P) \approx 100$  Hz] characteristic of a carbene center and comparable to the <sup>13</sup>C signal at  $\delta = 172.9$  ppm [J(C,P) = 93 Hz] attributed to the carbene carbon in **8b**. The proposed formation of NHC species **10** was further supported by the observation that adding an authentic amidine sample to the NHC complex **8b** gave the

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Scheme 4. Formation of amidine complexes 10-R' from cationic acetonitrile adducts 7 b and 8 b. Triflate counterions are omitted for clarity.

same broad  $^{\rm 31}{\rm P}$  singlet at  $\delta\!=\!187\text{--}188\,{\rm ppm}$  (Scheme 4, reaction B).

The hydroamination reaction was then monitored step-bystep by conducting reaction C (Scheme 4). The <sup>31</sup>P NMR spectrum of a RT solution of **7b** in benzonitrile<sup>[41]</sup> showed the appearance of two AX spin systems. One of these resonated at virtually the same chemical shifts as **7**b, thus prompting us to assign it to the corresponding PhCN adduct formed by displacement of MeCN. The second AX spin system consisted of doublets centered at  $\delta = 191.5$  and 14.0 ppm [J(P,P) = 244 Hz], which was tentatively assigned to a cationic adduct arising from the displacement of the MeCN in 7b by residual water.[41] Subsequent addition of piperidine to the sample (1 equivalent with respect to PhCN) led to appearance of the broad singlet at  $\delta = +187-188$  ppm (assigned to **10**-Ph; see above), along with a sharp singlet at  $\delta = +57$  ppm. The latter was attributed to *i*Pr<sub>2</sub>P(O)H, based on our previous observations that hydrolytic oxidation of iPr<sub>2</sub>PCl gives similarly sharp singlets in the 53-55 ppm region of the <sup>31</sup>P NMR spectrum. We postulate that *i*Pr<sub>2</sub>P(O)H arises from a rearrangement of *i*Pr<sub>2</sub>P(OH) generated by hydrolysis of either the phosphenium moiety in **7b** or that of the decomposition byproduct  $iPr_2P(c-N(CH_2)_5)$  resulting from the nucleophilic attack of piperidine on 7 b.

The above observations allow us to conclude that the PI-MIOCOP complexes **7** are dephosphinylated to the NHCCOP analogues at the outset of the catalysis. This assertion is consistent with both the calculated Fukui indices (see the Supporting Information, Figure S10) and previous reports of nucleophile-induced P–C bond cleavage in PIMIOCOP species and other imidazoliophosphanes.<sup>[18a]</sup> As a final argument in support of the proposed scenario, we found that benzonitrile hydroamination proceeds with similar catalytic activities with the precatalysts **8b** and **7b** (TON=55 vs. 49). Kinetic monitoring of

the hydroamination reaction involving the PIMIOCOP precatalyst **7b** revealed no significant induction period (see the Supporting Information, Figure S11), indicating that the initial dephosphinylation of **7** to **8** is very rapid.

An intriguing observation from the above experiments is that, although the catalytic hydroaminations require high temperatures, the stoichiometric conversion of the cationic nitrile adduct 8b into the amidine adducts 10-R proceeds at room temperature. This suggests that the hydroamination catalysis is susceptible to some degree of product inhibition, which can be counteracted by heating to induce substrate uptake and turnover. This scenario is supported by the finding that the

amidine ligand in **10**-Ph (Scheme 4) is resistant to substitution by PhCN: the <sup>31</sup>P NMR spectrum of a mixture of **10**-Ph with excess PhCN and piperidine showed no sign of a new adduct even after it had been heated at 80 °C for over 20 min. The amidine adduct is thus the only observable species during the Ni-catalyzed hydroamination reaction; in other words, this adduct represents the resting state of the catalysis, as illustrated in the proposed mechanism shown in Scheme 5.

The proposed mechanism also provides a rationale for the aforementioned lower activity observed with a 10% loading of the precatalyst **7 b**. Recall that the in situ transformation of the PIMIOCOP adduct **7** to its NHCCOP analogue at the outset of the catalysis would result in the release into the reaction medium of one equivalent of  $R_2PNR''_2$ . The presence of this free ligand in runs using 1% catalyst loadings would have negligible impact on the course of the catalysis, but it would be reasonable to expect an inhibition of catalysis during a catalytic run using a 10% loading of the precatalyst.

## Conclusion

To consider its results in broad strokes, this report illustrates how deeply interactive experimental and theoretical approaches can help address challenges in the three traditionally quite delineated fields of coordination chemistry of new complexes, their spectroscopic and structural characterization, and their use in catalysis. The title complexes were thus extensively characterized by complementary experimental techniques (crystallography, spectroscopy, voltammetry) and DFT modeling (structure optimization; orbital, ELF and AIM analyses; reactivity Fukui indices calculation), and their reactivities in the hydroamination of nitriles were investigated. Beyond their obvious potential developments (generalization of structures and



Scheme 5. Proposed mechanism for catalytic nitrile hydroamination using PIMIOCOP pincer complexes 7 as precatalysts.

tuning of reactivities), these investigations aim to advance our understanding of the interplay between electronic and electrostatic effects in organometallic coordination chemistry and catalysis, in particular by reference to electrostatics-governed enzymatic recognition and transformation processes.

In more concrete terms, the results described in the present study serve to highlight the differences in structural and spectroscopic properties of PIMCOP, PIMIOCOP, and NHCCOP complexes of Ni<sup>II</sup> and the reactivities of their cationic derivatives in the hydroamination of nitriles. IR spectroscopic analysis of the cations based on experimental and computational  $\nu$ (C=N) values has demonstrated how P-substituents and the positive charge on the imidazoliophosphine moieties exert influence on Ni-ligand interactions, in the process shaping the electrophilic character of the complexes. Whereas the  $\nu$ (C $\equiv$ N) values of various cationic adducts followed the counter-intuitive order  $NHCCOP^{Ph}\!>^{Ph}\!POCOP^{Ph}\!>NHCCOP^{iPr}\!>^{iPr}POCOP^{iPr}\!>$  $^{Ph}PIMIOCOP^{Ph} > ^{Ph}PIMCOP^{Ph} > {}^{iPr}PIMIOCOP^{iPr}$  and  ${}^{iPr}PIMCOP^{iPr}$ , the oxidation potentials of both charge-neutral bromo derivatives and cationic adducts followed the intuitively anticipated order PIMIOCOP > PIMCOP > NHCCOP.

In terms of their catalytic activities in hydroamination of benzonitrile, the cationic precatalysts [(PIMIOCOP)Ni(NCCH<sub>3</sub>)] [OTf]<sub>2</sub> proved to be significantly more active than their POCOP and PIMCOP analogues. Interestingly, the more electrophilic Ph<sub>2</sub>P complexes proved to be less active than their *i*Pr<sub>2</sub>P counterparts. Moreover, it was found that the PIMIOCOP complexes are readily converted into NHCCOP analogues during the catalysis, implying that such in situ-generated NHCCOP cationic species have superior catalytic activities in spite of their lower electrophilicities. This unexpected observation can be attributed to the greater thermal stability of the reaction intermediates bearing an NHC moiety. Optimization studies allowed the formation of benzamidines with relatively high catalytic turn-

over numbers (TON = 95 with *n*-hexylamine and 72 with piperidine), but the range of amine substrates active in this reaction remains quite limited. Future studies will be aimed at improving our understanding of how metal–pincer bonding is influenced by ligand features (electrostatic effects and structural architecture), and what factors govern the electrophilicity of the metal center.

## Acknowledgements

The authors are grateful to: Centre National de la Recherche Scientifique (CNRS) for financial support in the form of operating funds and also for a 50% teaching sabbatical to R.C.; NSERC of Canada for a Discovery Grant to D.Z.; Université de Montréal, Centre in Green Chemistry and Catalysis (CGCC) and Fonds de recherche du Québec: Nature et technologies (FQRNT) for graduate fellowships to B.V.; Dr. Michel Simard for his valuable assistance with crystallography. Computational studies were performed by using HPC resources from CALMIP (Grant 2013[0851]) and from GENCI-[CINES/IDRIS] (Grant 2013[085008]). The Direction des Relations Internationales of Université de Montréal and Université Toulouse 3 Paul Sabatier are gratefully acknowledged for the travel grants that made this collaborative project possible.

**Keywords:** electron localization function · Fukui indices · hydroamination · nickel · pincer complexes

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Received: June 26, 2015 Published online on October 9, 2015