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Editor's choice paper

Addition of amines and phenols to acrylonitrile derivatives catalyzed by the POCOP-type pincer complex [{κ^P,κ^C,κ^P-2,6-(*i*-$Pr_2PO)_2C_6H_3$}Ni(NCMe)][OSO_2CF_3]

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ABSTRACT

The pincer-type complex [{κ^P,κ^C,κ^P-2,6-(*i*-$Pr_2PO)_2C_6H_3$}Ni(NCMe)][OSO_2CF_3] (**1**) can serve as a precatalyst for the regioselective, anti-Markovnikov addition of nucleophiles to activated olefins. The catalyzed additions of aliphatic amines to acrylonitrile, methacrylonitrile, and crotonitrile proceed at room temperature and give quantitative yields of products resulting from the formation of C–N bonds. On the other hand, aromatic amines or alcohols are completely inert toward methacrylonitrile and crotonitrile, and much less reactive toward acrylonitrile, requiring added base, heating, and extended reaction times to give good yields. The catalytic reactivities of **1** are thought to arise from the substitutional lability of the coordinated acetonitrile that allows competitive coordination of the nitrile moiety in the olefinic substrates; this binding enhances the electrophilicity of the C=C moiety, rendering them more susceptible to attack by nucleophiles. In some cases, RCN → Ni binding results in double bond isomerization/migration (allyl cyanide) or attack of nucleophiles at the nitrile moiety (cinnamonitrile and 4-cyanostyrene). Reaction of morpholine with **1** at 60 °C led to formation of the amidine derivative **2** that has been characterized by X-ray crystallography.

1. Introduction

Direct addition of N–H bonds of amines and O–H bonds of alcohols to olefins is an attractive, atom-efficient approach for the preparation of substituted amines or ethers since no by-products are formed [1]. Many reports have described olefin hydroamination processes catalyzed by complexes of lanthanides [2], group 4 metals [3], Rh [4], Ir [5], Ni [6], Pd [7], Pt [8], and Cu [9]. Interestingly, a number of reports have also shown that homogeneous, intermolecular hydroamination of styrene by electron-rich anilines can be promoted by acids such as HOTf [10] or even HCl [11], while $PhNH_3B(C_6F_5)_4{\cdot}Et_2O$ promotes both the hydroamination and hydroarylation of styrene and cyclic olefins such as norbornene and *cis*-cyclooctene [12]. Similarly, there are multiple different catalysts for hydroalkoxylation reactions, including strong bases [13] or acids [14], nucleophilic phosphines in the presence of α,β-unsaturated olefins [15], and metal-based catalysts [9,16].

Our group has been interested in development of synthetic routes to pincer complexes of nickel and exploring their reactivities as pre-catalysts for a variety of reactions, including hydroamination and hydroalkoxylation of activated olefins (Michael additions) [17]. In previous reports, we have shown that cationic Ni(II) complexes based on PCP- and POCOP-type pincer ligands serve as competent pre-catalysts for the addition of aliphatic amines and aniline to acrylonitrile and its derivatives [17d,g–i]. For example, the complex [POCOP]Ni(NCCH=CH_2)]$^+$ (POCOP = κ^P,κ^C,κ^P-2,6-{(*i*-$Pr)_2PO\}_2C_6H_3$, Chart 1) promotes the anti-Markovnikov addition of morpholine and cyclohexylamine to acrylonitrile, methacrylonitrile and crotonitrile with turnover numbers (TON) of 80–2000 (room temperature, 5 min–3 h), but addition of aniline to acrylonitrile was less facile (TON = 100–150 at 115 °C over 4–24 h) [17g,i]. The analogous PCP-type complexes (Chart 1) also promote the addition of aniline to acrylonitrile, but the reactivities of these complexes are inferior to those of their POCOP counterparts [17h,i].

As an extension to our previous studies, we have screened the catalytic reactivities of a number of cationic adducts and neutral precursors for the addition of amines and alcohols to activated olefins. The complex [(POCOP)Ni(NCMe)][OSO_2CF_3], **1**, was found to be a practical precatalyst for the purposes of further studies thanks to its ease of synthesis and stability toward air oxidation and hydrolysis. This report describes the catalytic activities of **1** for the addition of aliphatic amines, aniline and its substituted derivatives, substituted phenols, and catechol to acrylonitrile, methacrylonitrile and crotonitrile (Eq. (1)). Also presented is the solid state structure of the amidine adduct **2** that was obtained from the thermal reaction of **1** with morpholine.

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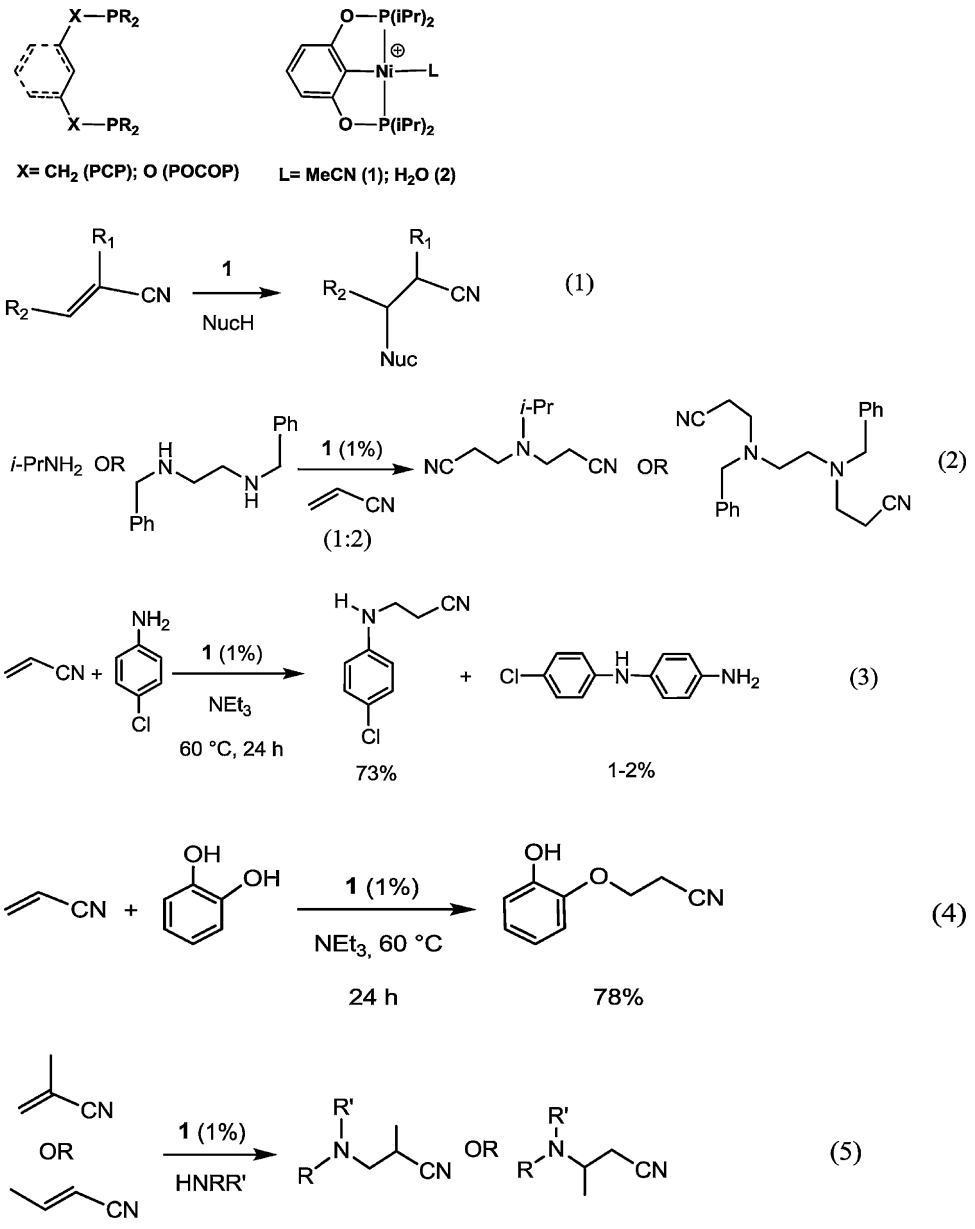


Chart 1.

2. Results and discussion

2.1. Catalytic studies

Various amines and alcohols were screened for their nucleophilicity toward acrylonitrile derivatives and other nitrile functionalized olefins. As expected, aliphatic amines were found to be the most reactive nucleophiles, followed by substituted anilines and phenols; curiously, aliphatic alcohols proved to be completely inert under the reaction conditions employed. Among the olefins examined, acrylonitrile was much more reactive than crotonitrile, methacrylonitrile, and allyl cyanide, while cinnamonitrile and 4-cyano-styrene did not undergo addition at the olefin moiety.

Most catalysis runs were carried out in C_6D_6 using 1% of 1 and a 1:1 ratio of the substrates. The experiments were monitored by NMR, and GC/MS analysis was used to identify the products and to determine conversions/yields. Control experiments showed that non-catalyzed Michael additions to acrylonitrile proceed sluggishly with most aliphatic amines and not at all with aromatic amines or alcohols. For instance, reacting acrylonitrile with aliphatic amines for 24 h at room temperature and in the absence of a catalyst gave poor %yields (or turnover numbers, TON) of the addition product with Et_2NH (25), *i*-$PrNH_2$ (31), and *N,N′*-dibenzyl(ethylenediamine) (5). By comparison, the corresponding Ni-catalyzed reactions proceeded with quantitative yields in 1 h or less (runs 1–3, Table 1; turnover frequency, TOF ~ 100–1000/h). It is worth noting that double addition products were obtained quantitatively when two equivalents of acrylonitrile were reacted with *i*-$PrNH_2$ or *N,N′*-dibenzyl(ethylenediamine) (Eq. (2)).

Catalyzed addition of aromatic amines to acrylonitrile was found to be much less efficient, but the presence in the catalytic mixture of external base such as NEt_3 led to substantial improvements. For instance, addition of aniline and 3-methyl-aniline in the presence of one equivalent of NEt_3 proceeded to completion at room temperature in 4 and 16 h, respectively (runs 4 and 5). As expected, the use of sub-stoichiometric quantities of NEt_3 (0.05–0.1 equiv.) was equally effective in terms of yields, but the catalysis proceeded more slowly. The presence of Me substituents at the *ortho* position

Table 1
Catalytic addition of nucleophiles to acrylonitrile catalyzed by **1**.[a]

Run	Nucleophile	Temp.	Time	Yield (%) or TON	TOF (TON/h)
1	Et_2NH	r.t.	<5 min	100	>1000
2	*i*-$PrNH_2$[b]	r.t.	<5 min	100	>1000
3	$(PhCH_2NH)_2(CH_2CH_2)$[b]	r.t.	1 h	100	100
4	Aniline[c]	r.t.	4 h	100	25
5	3-Methylaniline[c]	r.t.	16 h	100	~6
6	2,5-Dimethylaniline[c]	60 °C	24 h	83	~3
7	2,4,6-Trimethylaniline[c]	60 °C	24 h	56	~2
8	4-Chloroaniline[d]	60 °C	24 h	73	~3
9	4-Nitroaniline[c]	60 °C	24 h	42	1.5
10	Ph_2NH[c]	60 °C	24 h	–	–
11	3-Methylphenol[c]	r.t.	4 h	100	25
12	2-Methylphenol[c]	60 °C	24 h	58	~2
13	2,4,6-Trimethylphenol[c]	60 °C	24 h	69	~3
14	Catechol[c,e]	60 °C	24 h	78	~3
15	4-Phenylphenol[c]	60 °C	24 h	60	2.5
16	Pentafluorophenol[c]	60 °C	24 h	Trace	–

[a] The catalytic tests were conducted in NMR tubes containing 0.5 mL of C_6D_6, 1 mol% of the precatalyst **1**, 0.5 mmol each of acrylonitrile and the nucleophile, and (where needed) one equivalent of NEt_3. The yields are based on GC/MS analyses.
[b] Use of two equivalents of acrylonitrile in this run gave the product of double addition.
[c] One equivalent of NEt_3 used in this run.
[d] Traces of the homocoupling product, (4-Cl-C_6H_4)NH(4-NH_2-C_6H_4), were also obtained from this run.
[e] Only product of single addition formed in this run even though two equivalents of acrylonitrile were used.

on the ring led to reduced activities (runs 6 and 7). Lower yields were also obtained when electron-withdrawing groups such as Cl and NO_2 were present, while the addition was inhibited altogether with Ph_2NH (runs 8–10); the reaction with *p*-chloroaniline gave trace amounts of the homocoupling product (4-Cl-C_6H_4)NH(4-NH_2-C_6H_4) (MW: 208; Eq. (3)).

It was gratifying to find that the addition to acrylonitrile was also possible with alcohols as nucleophiles. Initial tests showed that only phenols were effective nucleophiles, aliphatic alcohols being completely inactive for this reaction. As in the case of additions with anilines, NEt_3 was essential for the hydroaryloxylation of acrylonitrile. Methyl-substituted phenols as well as catechol and 4-phenylphenol underwent the addition reaction under the same conditions as anilines (60 °C, 24 h; runs 11–15), whereas pentafluorophenol was virtually unreactive. Interestingly, only one of the OH moieties of catechol reacted to give 2-(OCH_2CH_2CN)-phenol even when the reaction was run with two equivalents of acrylonitrile (Eq. (4)).

The crucial role of **1** in promoting Michael additions was confirmed for reactions involving methacrylonitrile or crotonitrile, for which control experiments indicated no reactivity in the absence of precatalyst even with aliphatic amines (24 h at room temperature). Thus, the presence of 1% **1** led to quantitative yields for the addition of morpholine, Et_2NH, cyclohexylamine, and *i*-$PrNH_2$ to both methacrylonitrile and crotonitrile in about 10 min at room temperature (Table 2, runs 1–4); the regioselectivity of the addition remains anti-Markovnikov with both methacrylonitrile and crotonitrile (Eq. (5)). On the other hand, the catalyzed addition with aniline (run 5) proceeded quite poorly even at 60 °C, giving 9% yield with methacrylonitrile and no reaction at all with crotonitrile. The alcohols 3-methylphenol and benzyl alcohol were also unreactive (runs 6 and 7).

2.2. Comparison of catalytic reactivities to literature precedents

Most literature reports on transition metal-catalyzed additions of N–H and O–H bonds to activated olefins appear to be focused on the reactivities of acrylates, acrylamides, and α,β-unsaturated ketones-substrates that are not reactive in our system (vide infra). Moreover, there are relatively few reports on Ni-catalyzed additions to acrylonitrile and its derivatives [18]. Nevertheless, the following comparisons to some of the more pertinent literature precedents will help place the present results in the context of this area of study.

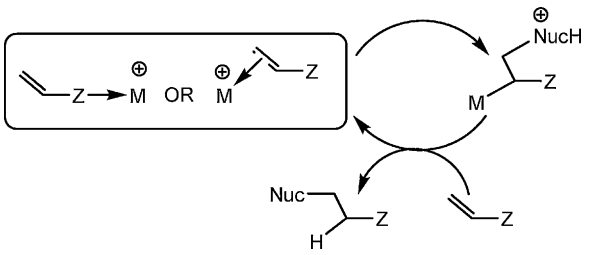
2.2.1. Pd- and Ni-catalyzed hydroaminations

Trogler's group has reported some of the earlier studies on the addition of aniline to acrylonitrile [7a]. Using a system consisting of 10 mol% of $[PhNH_3]BPh_4$ and 2 mol% of the PCP-type pincer complex $\{R_2P(CH_2)_2CH(CH_2)_2PR_2\}$Pd-alkyl (R = *t*-Bu), these workers obtained the product of anti-Markovnikov addition with up to 40–50 TON at 35 °C. It is intriguing to note that the presence of an acid is crucial for this system, whereas in our system addition of anilines was facilitated by an added base. Following Trogler's report, Hartwig's group showed that different combinations of Pd(II) salts (2%) and pincer ligands (2–10%) catalyze the addition of piperidine

Table 2
Addition of nucleophiles to methacrylonitrile and crotonitrile catalyzed by **1**.[a]

Run	Nucleophile	Temp.	Time	Yield (%) or TON	TOF (TON/h)
1	Morpholine	r.t.	10 min	100	~600
2	Diethylamine	r.t.	10 min	100	~600
3	Cyclohexylamine	r.t.	10 min	100	~600
4	Isopropylamine	r.t.	10 min	100	~600
5	Aniline[b,c]	60 °C	24 h	9	~0.4
6	3-Methylphenol[c]	60 °C	24 h	–	–
7	Benzyl alcohol[c]	60 °C	24 h	–	–

[a] The catalytic reactions were performed as indicated for the additions to acrylonitrile. Unless otherwise stated, the yields are the same for the reactions of methacrylonitrile and crotonitrile.
[b] The addition of aniline to methacrylonitrile gave a 9% yield, while no addition took place on crotonitrile.
[c] Reaction yields for these runs were unaffected by the presence of NEt_3.



Scheme 1.

to crotonitrile, methacrylonitrile, and alkyl methacrylates and crotonates at room temperature, whereas addition of aniline required extended periods of heating at 100 °C [7e]. In comparison, our POCOP–Ni system catalyzes the addition of aniline to acrylonitrile at room temperature and shorter reaction times with TON of 100, but is ineffective for the addition of anilines to crotonitrile and methacrylonitrile. Togni's group has studied the catalytic activities of dicationic complexes of Ni(II) ligated by triphosphines for the addition of morpholine, piperidine, aniline, and substituted anilines to crotonitrile, methacrylonitrile, and alkyl acrylates and crotonates [6b,c]. The addition of aniline to crotonitrile and methacrylonitrile in this system proceeds over 24 h at room temperature with 70 and 35 catalytic turnover numbers (TON), respectively, whereas addition of substituted anilines gives lower TON (5–15). The advantages of this system include room temperature hydroamination with aromatic amines and a wider scope of olefins, whereas addition of aliphatic amines seems to be more facile in our system. The reactivities of the above-discussed systems for the addition of alcohols are not known.

2.2.2. Pd-, Ru-, and Cu-catalyzed hydroalkoxylations

Abu-Omar's group has reported Pd(II)-based complexes that promote the addition of a variety of alcohols and aniline to methyl vinyl ketone (5–100 TON at r.t.), but no reactivity is observed with acrylonitrile [16d]. Yi et al. have reported a Ru(II)-catalyzed hydroalkoxylation of acrylonitrile and related derivatives including crotonitrile, methacrylonitrile, 1-cyano-cyclohexene [21]. This system allows high yield addition of aliphatic alcohols under mild reaction conditions (r.t. to 40 °C; 1–24 h), but no examples are given for the addition of phenols. Gunnoe's group has reported that the complexes LCuX (L = *N*-heterocyclic carbine; X = NHPh, OEt, OPh) catalyze the addition of both N–H and O–H bonds to acrylonitrile, crotonitrile, methyl acrylate, cyclohexenone, and methyl vinyl ketone [9]. This system promotes the room temperature addition of Et_2NH, *n*-$PrNH_2$, $PhCH_2NH_2$ and $PhNH_2$ to acrylonitrile with up to 20 TON, but addition to crotonitrile is much more sluggish (80 °C, 40 h, TON ~ 10). Interestingly, addition of PhOH to acrylonitrile requires extended heating (80 °C, 40 h, TON ~ 13), whereas addition of EtOH proceeds at r.t. (TON ~ 19 over 20 h). This system is clearly superior to ours with respect to the reaction of aliphatic alcohols, but our system is more efficient in the addition of aliphatic amines, aniline, and phenols.

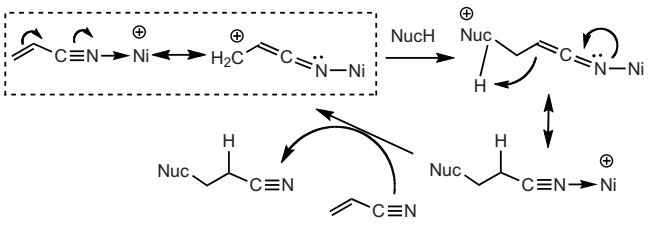
2.3. Mechanistic considerations

The most frequently cited mechanistic proposal for late transition metal-catalyzed Michael-type additions involves outer-sphere attack of an uncoordinated nucleophile on an olefin that is coordinated to the electrophilic metal centre via the C=C moiety or the functional group (COOR, CN, etc.), followed by proton transfer to generate the product (Scheme 1) [7a,16d]. For example, Trogler showed that the major species observed in solution during the Pd-catalyzed addition of aniline to acrylonitrile is the κ^N-acrylonitrile adduct, $[(PCP)Pd \leftarrow NC(CH{=}CH_2)]^+$; these authors suggest, however, that the nitrile binding is fairly labile and allows the formation of minor quantities of the π-bound isomer, which is then attacked by aniline to give the hydroamination product [7a]. Support for a mechanism involving attack of nucleophiles on π-bound olefins also comes from Abu-Omar's studies on the Pd-catalyzed addition of benzyl alcohol to methyl vinyl ketone (MVK) [16d]; interestingly, acrylonitrile was unreactive in this system, because it binds Pd center via its nitrile moiety. In contrast to the above reports, Yi et al. have proposed a mechanism involving a bifunctional Ru(II)-acetamido catalyst that promotes both a κ^N-nitrile binding to an empty coordination site (Lewis acidity) and a heterolytic activation of the alcohol O–H bond moderated by the acetamido moiety (Lewis basicity); the in situ generated alkoxide then adds to the C=C moiety of the substrate that has been activated by the RCN → Ru interaction [21].

A number of observations suggest that hydroamination and hydroaryloxylation reactions promoted by **1** involve attack of nucleophiles on acrylonitrile (or its derivatives) coordinated to the cationic Ni center in **1** through their nitrile moiety. First, we have noted the facile formation of cationic pincer complexes featuring RCN → Ni binding, and a number of these complexes have been isolated and fully characterized [17g,h,j]. Moreover, NMR monitoring of reaction mixtures containing **1**, acrylonitrile, aniline or *m*-cresol, and NEt_3 showed that the only P-containing species observed throughout the catalysis display signals in the same region as authenticated nitrile adducts (i.e., ca. 193–194 ppm); similar observations were made for the analogous reactions with methacrylonitrile (193 ppm) and crotonitrile (194 ppm). In contrast, no reaction was detected between **1** and NEt_3, morpholine, aniline, *m*-cresol, or olefinic substrates that do not undergo hydroamination or hydroaryloxylation in our system (methyl acrylate, methyl methacrylate, 1-hexene, and styrene). We conclude, therefore, that the coordinated acetonitrile moiety in **1** can only be displaced by a substrate possessing a nitrile functionality.

We have also considered but ruled out the viability of other mechanistic scenarios. For instance, the involvement of π-bound olefins was ruled out, because we found no spectroscopic evidence in our system for the presence of even minor quantities of such intermediates; in addition, olefinic substrates lacking a nitrile moiety (e.g., unfunctionalized olefins and acrylates) are inactive in our system. This fact, that in our system the scope of reactive olefins is limited to those cyano olefins that coordinate readily to $[(POCOP)Ni]^+$, also argues against the involvement of a mechanism not requiring olefin coordination. Such a mechanism, involving an attack on uncoordinated olefins by nucleophilic M–NR_2 and M–OR species, has been proposed by Gunnoe for Cu-catalyzed hydroamination and hydroalkoxylation of a range of olefins [9]. It is reasonable to suppose that such a pathway should require the formation of fairly nucleophilic M–NR_2 and M–OR species, whereas we have found little or no support for the formation of neutral species (POCOP)Ni–X (X = NR_2, OAr) under the conditions of the catalytic reactions, as described below.

Monitoring the reaction of the neutral Ni–OSO_2CF_3 precursor with excess morpholine led to partial replacement of the original peak at 186 ppm by a broad new signal at ca. 185 ppm and a sharper signal at ca. 179 ppm; the approximate ratio of these signals was 35:50:5 [19]. A similar experiment with excess aniline led to the broadening of the ^{31}P signal of the precursor and the emergence of a new broad signal at 188 ppm; these two signals were poorly resolved, making their integration unreliable, but the ratio of the two peaks was approximately 1:1. Repeating the latter experiment in the presence of NEt_3 led to the appearance of a weak but sharp signal at 179 ppm (<1% by signal intensity). Our efforts at driving these reactions to completion and isolating the new species have not borne fruit yet, and so we cannot confirm or rule out the formation of neutral anilido derivatives from the



Scheme 2.

reaction of 1 with morpholine or aniline/NEt_3. We propose, tentatively, that these broad signals are due to Ni-amine adducts that form hydrogen bonding type interactions with the triflate anion. It is important to recall, however, that none of these interactions take place in the presence of RCN, the nitrile–Ni interaction being more strongly favourable; as mentioned above, the acetonitrile moiety in **1** is not displaced by anilines or phenols, even in the presence of NEt_3. The combination of these observations and considerations lead us to propose that the role of complex **1** in the hydroamination and hydroaryloxylation of acrylonitrile derivatives is akin to that of a Lewis acid in the Michael-type additions to activated olefins, the dative binding of the nitrile moiety to the cationic Ni center enhancing the electrophilic character of the olefinic moiety, as shown in Scheme 2.

2.4. Nucleophilic attack at the nitrile moiety

Examination of the reactivities of cyano olefins other than acrylonitrile and its derivatives has shown that **1** can promote amination of the nitrile moiety in some cases. For instance, heating morpholine and cinnamonitrile at 60 °C for 24 h in the presence of **1** (1 mol%) gave 34% yield of the amidine product arising from the addition of the N–H bond to the nitrile moiety (Scheme 3). Similarly, reacting 4-cyanostyrene with morpholine at 40 °C and in the presence of 1% **1** led to the corresponding amidine derivative in about 25% yield, as confirmed by GC/MS analyses ($[M-1]^+ = 216$). Neither of these reactions produced products arising from hydroamination of the olefin moiety.

The above observations implied that when the olefinic moiety is insufficiently electrophilic, the nucleophile can react with the nitrile moiety. To confirm this conclusion, we reacted the catalyst precursor, **1**, with morpholine in order to determine if coordination to the cationic Ni center of acetonitrile, which lacks an olefinic moiety, would activate the nitrile moiety toward nucleophilic attack. Addition of one equivalent of morpholine to a 1.25 M C_6D_6 solution of 1 and overnight heating at 60 °C formed a new derivative, as indicated by the disappearance of the original $^{31}P\{^1H\}$ NMR signal for **1** (at 193 ppm) and emergence of a new singlet at 183 ppm; the ^1H NMR spectrum showed the presence of a new N–*H* resonance at ca. 5.4 ppm. Yellow crystals obtained from the NMR sample were subjected to an X-ray diffraction study that allowed us to identify the new product as the anticipated Ni–amidine product, **2** [20].

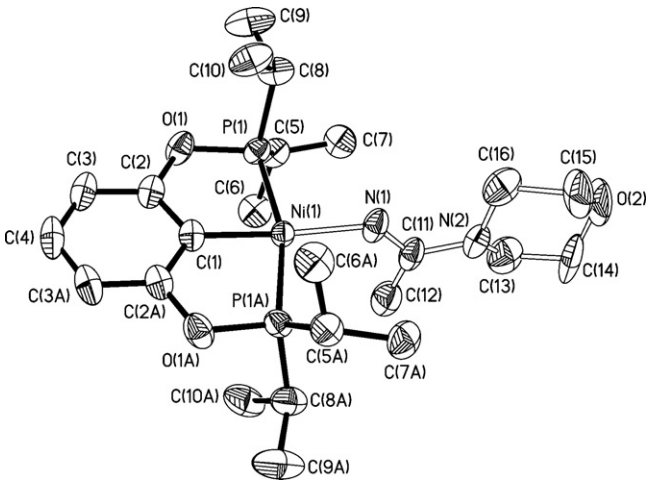
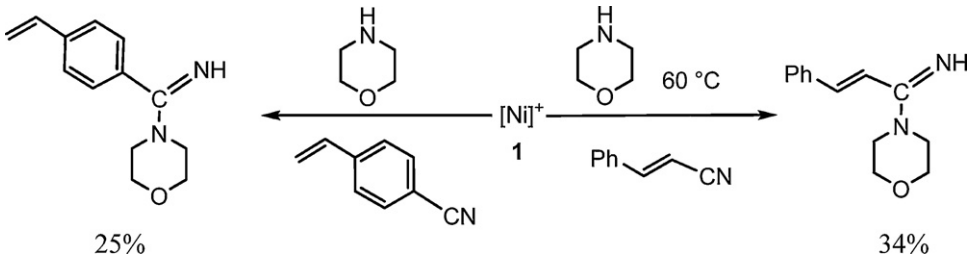


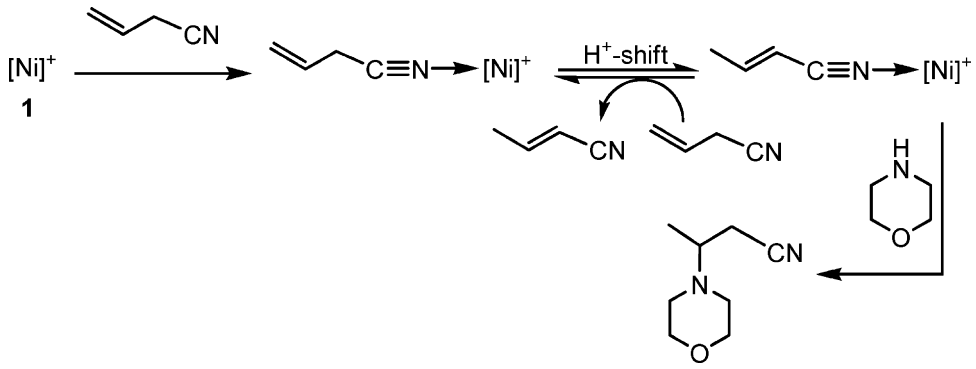
Fig. 1. ORTEP diagram for complex **2**. Thermal ellipsoids are shown at the 50% probability level. The triflate anion was severely disordered (over at least 4 positions) such that no satisfactory solution was found for definitive placement of the atoms involved. Selected bond distances (Å) and angles (°): Ni–C1 = 1.888(3); Ni–P1 = 2.1752(5); Ni–N1 = 1.949(4); N1=C11 = 1.260(7); C11–N2 = 1.417(7); C11–C12 = 1.429(9); C1–Ni–P1 = 81.49(5); C1–Ni–N1 = 173.64(19); P1–Ni–N1 = 97.6(3); Ni–N1–C11 = 130.3(5); N1–C11–N2 = 121.7(6).

The ORTEP diagram and the structural parameters of **2** (Fig. 1) illustrate clearly that the square planar geometry of the Ni center is more or less unchanged on going from **1** to **2**. The Ni–P and Ni–C distances are also quite comparable in these complexes, whereas the Ni–N bond distance is somewhat longer in **2** (1.89 vs. 1.87–1.88 Å) [17g]. The amidine proton could not be located, but the lengthened N1–C19 bond (1.27 Å in **2** vs. the C≡N distance of 1.14 in **1**) as well as the angles Ni–N1–C19 (135°) and N1–C19–N2 (125°) confirm the sp^2 hybridization of N1 and C19 resulting from the conversion of acetonitrile into an amidine. It is worth noting that heating free acetonitrile and morpholine over extended periods of time in the absence of **1** did not result in formation of the corresponding amidine, thus confirming the important activating role of the cationic Ni center in **1**.

Finally, we have also examined briefly the reaction of allyl cyanide with morpholine in the presence of 1% **1**. This reaction gave quantitative yield of the product arising from hydroamination of crotonitrile. To understand this result, we reacted **1** with one equivalent of allyl cyanide alone, which led over one hour to the formation of the crotonitrile derivative; this implies that the N-bound allyl cyanide isomerizes to crotonitrile at room temperature (Scheme 4). On the other hand, a tertiary amine can induce this isomerization even more rapidly (in about 10 min), while the isomerization is virtually instantaneous with a combination of base and **1**. Similar observations have been reported by Yi et al. on the Ru(II)-catalyzed isomerization of allyl cyanide to crotonitrile, followed by nucleophilic attack on coordinated crotonitrile [21]. Moreover, Ni(0)-catalyzed isomerization of allyl cyanide to *cis*- and



Scheme 3.



Scheme 4.

trans-crotonitrile has been reported previously by Jones et al. [22]. These authors propose a mechanism involving π-coordination of allyl cyanide, followed by activation of the allylic C–H bond to give a Ni(II)(allyl)hydride intermediate that eliminates π-bound crotonitrile. Since a similar mechanism operating in our system would require the involvement of highly energetic Ni(IV) intermediates, we postulate that the isomerization of allyl cyanide in our system goes through a concerted H-shift, or a proton transfer facilitated by the base present in the reaction medium.

3. Conclusion

The electrophilic nature of the nickel center in the cationic complex **1** and the lability of the acetonitrile moiety in this complex toward cyano olefins allow the promotion of nucleophilic additions by amines and aromatic alcohols on the C=C moiety of acrylonitrile, methacrylonitrile, and crotonitrile. The requirement for the coordination of a nitrile moiety to nickel limits the scope of these reactions to olefinic substrates bearing a CN functionality. Future studies will aim to develop precursors that can bind carbonyl and nitro functionalities with a view to extending the hydroamination and hydroaryloxylation reactions to a wider range of substrates. On the other hand, in the case of 4-cyanostyrene and cinnamonitrile, the addition takes place on the nitrile moiety to give the corresponding amidines; a similar reaction took place with Ni-bound acetonitrile to give the new amidine adduct **2**. These observations open up new avenues for exploration.

4. Experimental

4.1. General comments

Unless otherwise noted, reagents were used as received from Sigma–Aldrich and were handled in ambient atmosphere. Complex [{κ^P,κ^C,κ^P-2,6-(*i*-$Pr_2PO)_2C_6H_3$}-Ni(NCMe)][OSO_2CF_3] (**1**) was obtained following published preparation **1** was obtained by following a previously reported procedure [17d]. All NMR spectra were recorded at ambient temperature on Bruker AV400 and AV300 instruments. The ^{1}H and ^{13}C NMR spectra were referenced to solvent resonances, as follows: 7.15 and 128.06 ppm for C_6D_5H and C_6D_6, respectively. The $^{31}P\{^1H\}$ NMR spectra were referenced to an external 85% H_3PO_4 sample (0 ppm). The GC/MS analyses were done using a Agilent Technologies 6890 Network GC system equipped with a HP-5MS capillary column and a 5973 MS selective detector.

4.2. Catalytic studies

All catalytic experiments were carried out in NMR tubes containing C_6D_6 solutions of the substrates (0.5 mmol each) and complex **1** (1 mol%). A typical run was conducted as follows: A NMR tube was charged with 0.5 mL of C_6D_6, a 200 μL aliquot of a 25 mM C_6D_6 solution of **1** (0.005 mmol of pre-catalyst), 0.5 mmol each of the substrate (for example, 32 μL of acrylonitrile and 44 μL of morpholine), and 0.5 mmol of triethylamine (when required). The tube was then capped and, when indicated, heated at the desired temperature in an oil bath for the designated time. The progress of the reaction was followed at regular intervals by NMR until the end of the reaction, as signalled by the disappearance of the vinylic protons of the olefinic substrate. Control reactions were performed using the same protocol except that no catalyst and/or triethylamine were introduced. The final reaction mixture was then subjected to a flash filtration through silica gel (Et_2O used as eluent) in order to remove residual nickel particles, and the filtrate was analyzed by GC/MS to identify products and determine the conversion. These analyses usually displayed two peaks, one corresponding to the unreacted nucleophile, and the other to the product. (The MS was kept closed during the first 2 min of the analysis in order to protect the filament and avoid overwhelming the detector with signals due to solvent peak. Thus, all volatile components of the mixtures, including acrylonitrile, were not analyzed.) The MS fragmentation patterns allowed a reliable identification of the species while integration of these two peaks gave the reported yields; the conversions were verified against integration of the vinylic peaks in the ^{1}H NMR spectra.

4.3. Crystal structure determination

The crystallographic data for complex **2** (Table 3) were collected on a Bruker X8 Proteum system with Microstar-H generator, Helios Optic, Kappa goniometer and Platinum-135 detector. Cell refinement and data reduction were done using SAINT [23]. An

Table 3
Details of X-ray diffraction studies on complex **2**.

Formula: $C_{25}H_{43}N_2O_6F_3P_2SNi$	Space group: $P6_522$
M_w (g/mol): 677.35	V (Å^3): 4768.90 (8)
F(0 0 0): 2088	Z: 3
Crystal color and form: yellow blocks	$d_{calcd.}$ (g/cm^3): 1.413
Crystal size (mm): 0.26 × 0.16 × 0.16	θ range (°): 4.31–67.82
T (K): 150	Completeness: 1.00
Wavelength: 1.54178	Collected reflections $R\sigma$: 75,234; 0.0096
Crystal system: hexagonal	Unique reflections R_{int}: 2890; 0.0450
Unit cell	
a (Å): 12.341	μ (mm^{-1}): 2.948
b (Å): 12.341	Abs. correction: multi-scan
c (Å): 36.1550 (4)	$R1(F)$; $wR(F^2)$ [$I > 2\sigma(I)$]: 0.0366; 0.1056
α (°): 90	$R1(F)$; $wR(F^2)$ (all data): 0.367; 0.1056
β (°): 90	GoF(F^2): 1.096
γ (°): 120	Residual electron density: 0.47

empirical absorption correction, based on the multiple measurements of equivalent reflections, was applied using the program SADABS [24]. The space group was confirmed by XPREP routine [25] in the program SHELXTL [26]. The structures were solved by direct-methods and refined by full-matrix least squares and difference Fourier techniques with SHELX-97 [27]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.11.010.

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