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ARTICLE

On the Mechanism of Ni(II)-Promoted Michael-Type Hydroamination of Acrylonitrile and Its Substituted Derivatives †

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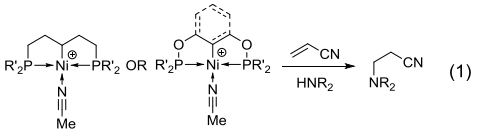
Michael-type hydroamination of acrylonitrile and its substituted derivatives promoted by Ni(II) complexes is believed to proceed via an outer-sphere nucleophilic attack on the cationic adduct of the nitrile-coordinated substrate. As a test for the validity of this mechanistic postulate, we have sought to establish a correlation between the electrophilic character of the Ni(II) center and the degree to which it can activate the substrate toward nucleophilic attack by amines. This has been done by screening the catalytic activities of the cationic acetonitrile adducts [(R-POCOP)Ni(NCCH$_3$)][OSO$_2$CF$_3$] bearing an electron-donating or electron-withdrawing substituent R on the central aromatic ring of the POCOP ligand (R-POCOP= $\kappa^P, \kappa^C, \kappa^P$-2,6-(*i*-Pr$_2$PO)$_2$-4-R-C$_6H_2$; R= OMe (**3**), COOMe (**4**)). The catalytic activities for the addition of primary amines to crotonitrile, methacrylonitrile, and cinnamonitrile were found to depend on the precursor and the amine used, as well as on the reaction time. These studies were complemented by ligand exchange studies that established the relative binding order among the main components of a typical hydroamination mixture (RCN > amine > OSO$_2$CF$_3$), thus supporting the assertion that cationic nitrile adducts constitute the resting state in the catalytic manifold. We have also prepared and characterized the cationic acrylonitrile and cinnamonitrile adducts [(R-POCOP)Ni(NCCH=CHR')][OSO$_2$CF$_3$] (R'= H : R= COOMe (**7**) or OMe (**8**); R'= Ph: R= COOMe (**9**) or OMe (**10**)) as models of the postulated catalytic intermediates in the addition of amines to these substrates. To allow structural comparisons to the nitrile adducts, we have prepared and characterized the ammonia adducts [(R-POCOP)Ni(NH$_3$)][OSO$_2$CF$_3$] (R= H, **11**, and COOMe, **12**). The results of structural, spectroscopic, and reactivity studies carried out on these compounds and their implications for the mechanism of Michael-type hydroamination reactions promoted by the title system have been discussed.

Introduction

Michael additions on acrylonitrile can proceed in an uncatalysed fashion with highly nucleophilic aliphatic amines,[1] but a catalyst is generally required when a wider range of amines is used. A catalyst is also required with all amines for the analogous amination of acrylonitrile's substituted derivatives, including crotonitrile, methacrylonitrile, and cinnamonitrile. The most commonly used catalysts/promoters for these reactions are simple salts or complexes of early and late transition metals.[2-11] Although the mechanisms operating in these systems have not been established unequivocally, two different postulates have been proposed, an outer-sphere mechanism involving cationic adducts that serve to activate the *N*-coordinated nitrile substrate toward attack by the amine nucleophile (**Scheme 1**),[8, 12, 13] and an inner-sphere, insertion mechanism involving amine adducts and amido intermediates (**Scheme 2**).[14-16,]

Our group has shown that cationic Ni complexes featuring PCP- and POCOP-type pincer ligands are competent pre-catalysts for the Michael-type regioselective hydroamination of acrylonitrile and its substituted derivatives (**Equation 1**).[17-20]



A number of studies have suggested that these reactions proceed by an outer-sphere mechanism involving an intermediate featuring the acrylonitrile substrate that, by virtue of being *N*-coordinated to a cationic Ni(II) center, is activated toward an attack by the amine nucleophile.[2, 17, 21] Evidence in support of this proposal includes the isolation and

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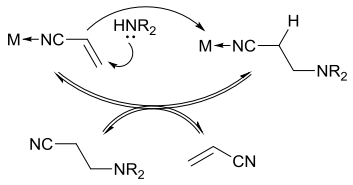
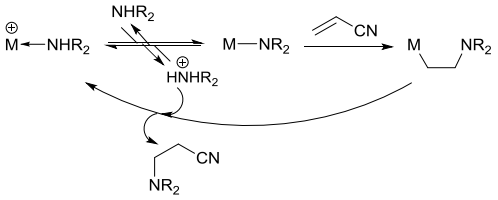
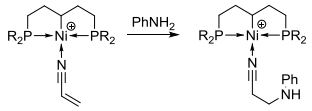


Scheme 1 An outer-sphere mechanism for hydroamination of acrylonitrile catalyzed by electrophilic metal complexes



Scheme 2 An inner-sphere mechanism for hydroamination of acrylonitrile catalyzed by electrophilic metal complexes

structural characterization in a PCP-Ni system of the two postulated cationic adducts, one bearing the acrylonitrile substrate and the other bearing the product of aniline addition to it (**equation 2**).[17]



(2)

The outer-sphere mechanism invoked above would require that factors enhancing the electrophilicity of the Ni centre impart a favorable influence on catalytic activities, and a limited number of investigations have confirmed such a correlation. For instance, the more electrophilic POCOP-based systems display greater activities compared to their PCP counterparts.[17] On the other hand, other variables such as the nature of POCOP ligand backbone (aliphatic vs. aromatic) and *P*-substituents (*i*-Pr vs. Ph) do not appear to exert significant influence on catalytic reactivities. Thus, addition of aniline to acrylonitrile is fairly equally promoted by the aromatic- and aliphatic-backboned POCOP adducts $[(POCOP)Ni(NCMe)]^+$,[18] whereas aromatic-backboned adducts featuring *i*-Pr_2P and Ph_2P moieties led to comparable catalytic activities.[20]

Another potentially favorable factor for the (pincer)Ni(II)-promoted hydroamination of acrylonitrile and its substituted derivatives would be the presence of electron-withdrawing ring-substituents on the central aromatic ring of resorcinol-based POCOP ligands. To date, only one report has examined this issue and the results obtained were counter-intuitive: the cationic Ni adduct bearing a Cl-substituted POCOP ligand, $[(2,6\text{-}(i\text{-}Pr_2O)_2\text{-}3,5\text{-}Cl_2\text{-}C_6H)Ni(NCMe)]^+$, showed a *lower* catalytic activity for hydroamination of acrylonitrile relative to its unsubstituted analogue.[17] It should be mentioned, however, that the weak catalytic performance observed in this case is likely a reflection of the limited thermal stability of this pre-catalyst and cannot disprove the anticipated impact of ring-substituents on catalytic activities.

Having developed practical synthetic routes to new POCOP-based cationic Ni(II) complexes featuring ring-substituents, and having established the relative stabilities and oxidation potentials of these complexes,[22] we set out to examine the catalytic activities of some of these species as a function of the ring substituents. The present report reports the catalytic activities of the cationic complexes [(4-R-POCOP)Ni(NCMe)][OSO_2CF_3] (R= OMe, **3**; CO_2Me, **4**) in the addition of various amines to methacrylonitrile, crotonitrile, and cinnamonitrile. The main objective of these catalytic tests was to examine whether or not the catalytic activities of **3** and **4** correlate with the electrophilicity of each species. We have also examined the spectra, solid state structures, and relative coordinating aptitudes of the different acrylonitrile, cinnamonitrile, and ammonia adducts [(4-R-POCOP)Ni-(NCCH=CHR')][OSO_2CF_3] (R= CO_2Me: R'= H (**7**), Ph (**9**); R= OMe: R'= H (**8**), Ph (**10**)) and [(4-R-POCOP)Ni(NH_3)][OSO_2CF_3] (R= H (**11**), CO_2Me (**12**)).

Results and discussion

Hydroamination tests. We began our studies by screening the catalytic reactivities of cationic acetonitrile adducts bearing an OMe or a CO_2Me substituent on the central aromatic ring of the pincer ligand. The catalytic tests were designed to establish whether the electronic impact of these ring substituents would have the anticipated influence on the hydroamination activities.

Initial results revealed that acrylonitrile is very reactive with a variety of Ni precursors, a fact that did not allow us to differentiate among the various precursors. Moreover, acrylonitrile does undergo uncatalysed Michael addition with some aliphatic amines (e.g., ca. 50% over 24 h at r.t. with morpholine),[18] thus complicating our studies. In contrast, crotonitrile, methacrylonitrile, and cinnamonitrile are unreactive to amines in the absence of a suitable catalyst, proving to be much more challenging substrates for Ni-promoted Michael-type hydroamination reactions.[19] These substrates were, therefore, selected for our studies. Ten primary amine substrates were also selected to cover a wide range of nucleophilic and steric properties: seven aromatic (aniline; 2-X-aniline, X= F, Cl, Br, I; 4-NO_2-aniline; 2,5-dimethylaniline) and three aliphatic (cyclohexylamine, octylamine, and ethanolamine).

The acetonitrile adducts [(4-R-POCOP$^{i\text{-}Pr}$)Ni(NCMe)][OTf] (R= OMe (**3**), CO_2Me (**4**)) were synthesized and purified following previously reported procedures (**Scheme 3**)[22] and used as precursors for our catalytic tests, which were conducted (in triplicate) on THF solutions (total volume ~1 mL) containing one mmol each of the amine and nitrile substrates and NEt_3, plus the precursor Ni complex (0.01 mmol) and dodecane as internal standard (0.1 mmol). The reactions were performed by heating the samples at 50 °C for the designated time (2 or 20 h), and the final mixtures were analyzed by GC/MS; the conversions and yields were determined based on a calibration curve prepared using authentic samples of the

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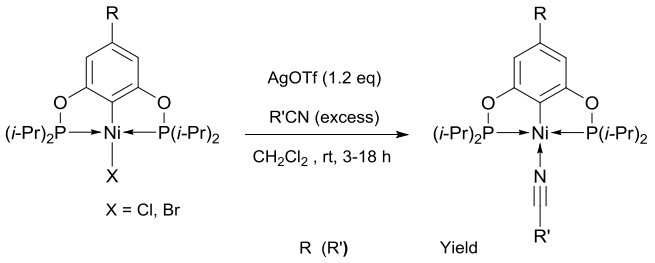


R (R')	Yield	
p-H (-CH_3)	80%	**1**
p-Me (-CH_3)	93%	**2**
p-OMe (-CH_3)	84%	**3**
p-CO_2Me (-CH_3)	81%	**4**
p-Br (-CH_3)	86%	**5**
m,m-tBu_2 (-CH_3)	87%	**6**
p-CO_2Me (-CH=CH_2)	80%	**7**
p-OMe (-CH=CH_2))	98%	**8**
p-CO_2Me (-CH=CH(C_6H_5))	63%	**9**
p-OMe (-CH=CH(C_6H_5))	70%	**10**

Scheme 3 Synthesis of cationic nitrile adducts **7-10** and previously reported complexes **1-6**. [18, 22]

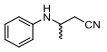
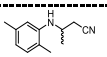
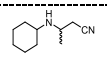
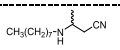
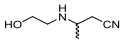
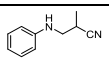
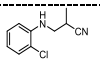
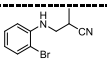
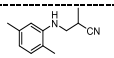
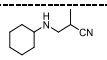
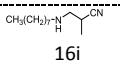
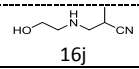
anticipated products. The results of these tests are listed in **Table 1** and graphically plotted in **Figures S28** and **S29** (ESI). (See also **Tables S3-S10** in ESI for more detailed results of all the catalytic runs.) These results lead us to the following general observations.

First, the predominant reactivity observed in nearly all cases consists of mono addition of one amine N-H bond across the double bond moiety of the nitrile substrates, but double N-H addition to give a tertiary amine was observed to a minor extent in the reactions of octylamine (see **Tables S5**, **S6**, **S9**, and **S10** in the ESI). Crotonitrile and methacrylonitrile showed varying activities with all amines except 2-iodoaniline and 4-nitroaniline, whereas cinnamonitrile showed little or no activity with all amines except aniline (*vide infra*).

Second, reaction time appears to play an important role in the relative levels of catalytic activity for the two pre-catalysts examined. Thus, for the catalytic additions to crotonitrile and methacrylonitrile conducted over a short reaction time, precursor **4** proved to be more competent with nearly all aromatic amines aniline, 2-chloroaniline being the exception, whereas precursor **3** was more competent for the addition of aliphatic amines (**Table 1**). In contrast, precursor **3** is the best promoter for addition of nearly all amines when the catalytic reactions are allowed to proceed for 20 h (**Tables S3** vs **S4** and **S7** vs **S8**). A speculative explanation for these counter-intuitive observations involves the relative substitutional labilities of the two (R-POCOP)Ni systems: the stronger binding of the addition product to the Ni centre in the more electrophilic system **4** would hinder the product-substrate exchange equilibrium that we assume to be crucial for catalytic turn-overs; the impact of such a product inhibition would be more pronounced over longer reaction times. It should be emphasized, however, that this and similar conclusions remain to be tested against precise kinetic data that can identify the relative rates of the different steps in the catalytic manifold and the impact of various factors on these steps.[23]

Longer reaction times also appear to improve yields in some cases. For example, reaction of crotonitrile with aniline

Table 1 Single and double addition products for hydroamination reaction of crotonitrile and methacrylonitrile promoted by precursors **3** and **4**. View Article Online DOI: 10.1039/C6DT02105K

Product	Nitrile	[Ni]	TON[a] (yield, %)	TOF[a] [h^{-1}]
 15a	Crotonitrile	**3**	28.6 ± 0.6	14.3 ± 0.3
		4	40 ± 1	20.0 ± 0.7
 15b		**3**	4.9 ± 0.1	2.43 ± 0.03
		4	9 ± 2	4 ± 1
 15c		**3**	2.6 ± 0.5	1.3 ± 0.3
		4	1.3 ± 0.2	0.7 ± 0.1
 15d		**3**	2.0 ± 0.1	1.0 ± 0.1
		4	3.9 ± 0.4	2.0 ± 0.2
 15f		**3**	1.1 ± 0.1	0.56 ± 0.04
		4	4.8 ± 0.3	2.4 ± 0.2
 15h		**3**	36.4 ± 0.6	18.2 ± 0.3
		4	23.9 ± 0.6	11.9 ± 0.3
 15i		**3**	56.1 ± 0.6	28.0 ± 0.3
		4	28.2 ± 0.8	14.1 ± 0.4
 15j		**3**	18 ± 1	9.1 ± 0.7
		4	6.8 ± 0.1	3.4 ± 0.1
 16a	Methacrylonitrile	**3**	21 ± 1	10.6 ± 0.7
		4	35 ± 1 38 ± 2 *	17.5 ± 0.7 19 ± 1 *
 16b		**3**	5.2 ± 0.7	2.6 ± 0.4
		4	7.8 ± 0.4	3.9 ± 0.2
 16c		**3**	3.2 ± 0.3	1.6 ± 0.2
		4	0	0
 16d		**3**	2.4 ± 0.5	1.2 ± 0.2
		4	3.2 ± 0.5	1.6 ± 0.3
 16f		**3**	7 ± 1	3.6 ± 0.5
		4	0.6 ± 0.1	0.30 ± 0.03
 16h		**3**	39 ± 1	19.7 ± 0.6
		4	22.7 ± 0.6	11.3 ± 0.3
 16i		**3**	34.6 ± 0.7	17.3 ± 0.3
		4	12 ± 1	6.1 ± 0.5
 16j		**3**	14.6 ± 0.7	7.3 ± 0.4
		4	0	0

Reaction conditions: Amine (1 mmol), crotonitrile (14a) or methacrylonitrile (14b) (1 mmol), NEt_3 (1 mmol), **3** or **4** (1 mol%), dodecane (10 mol%, internal standard) and THF (500 µL), 50 °C, 2 h. GC/MS yields. Reactions were done in triplicate and the yields are the average of those three experiments. * In this experiment, 5 mmol of amine was used instead of 1 mmol.

in the presence of catalyst **3** yields the mono addition product in ca. 29% over 2 h compared to ca. 48% over 20 h (See **Table S3** and **S4**). However, in other cases we noted that longer reaction times resulted in either no increase in yields or even a slight decrease. For instance, the reaction of crotonitrile with 2-bromoaniline in the presence of precursor **4** gave ca. 4% and 2% yields after 2 h and 20 h, respectively (See **Table S4** in SI for

reaction yields after 20h). Such apparent (and minor) degradations in yields are presumably due to secondary reactions of the products, but the precise reasons for these observations have not been examined.

A final observation relates to the relative reactivities of the nitrile substrates as a function of the substituents on the olefinic moiety: on the basis of the similar hydroamination yields obtained with crotonitrile and methacrylonitrile, it would appear that the electronic/steric impact of the Me group does not vary much as a function of its position (α vs. β relative to the CN moiety), whereas the presence of a Ph group (in cinnamonitrile) leads to a significant loss of reactivity. Indeed, hydroamination of cinnamonitrile occurred only with aniline and in the presence of precursor **4** (22 ± 1 % yield of 3-morpholino-3-phenylpropanenitrile), no reactivity being observed with other amines or in the presence of precursor **3**. It should be emphasized, however, that even this limited reactivity is significant for such a challenging substrate, and attests to the strong activating capacity of precursor **4**.

To sum up, the catalytic reactivities documented in **Table 1** and **Figures S28** and **S29** (ESI) indicate that the activities of the precursors **3** and **4** are time- and amine-dependent, precursor **3** being more efficient for the addition of the more nucleophilic aliphatic amines at all time intervals, and precursor **4** being more efficient for the addition of the less nucleophilic anilines over 2 h. That the more electron-withdrawing CO_2Me substituent results in a greater activation of the more challenging substrates crotonitrile, methacrylonitrile, and particularly the quite inert cinnamonitrile toward nucleophilic attack by the less nucleophilic aniline is consistent with the anticipated substituent effect discussed above. On the other hand, it is not clear why the same effect is not observed for the reactions of the more nucleophilic aliphatic amines.

Cationic acrylonitrile and cinnamonitrile adducts. In the absence of an unambiguous correlation between substituent effects and catalytic Michael-type hydroamination activities, we set out to study the structures and substitutional labilities of the cationic adducts as models of reaction intermediates. Isolation of acrylonitrile adducts allowed us to study the substitutional lability of the nitrile substituent and establish whether amine adducts might be involved in the hydroamination catalytic cycle. In addition, the solid structure of one acrylonitrile adduct was studied by X-ray diffraction analysis. Unfortunately, the analogous studies could not be conducted on the corresponding crotonitrile or methacrylonitrile adducts, because we did not succeed in isolating these derivatives. While it is tempting to conclude that this finding reflects the thermal instability of these adducts and might explain the limited reactivity of these substrates, this assertion is inconsistent with the successful preparation and isolation of cationic adducts with the least reactive substrate, cinnamonitrile. The solid state structures of the two cinnamonitrile adducts bearing the CO_2Me and OMe ring-substituents were investigated to gain insight into its inertness.

The acrylonitrile and cinnamonitrile adducts [(4-R-POCOP$^{i\text{-}Pr}$)Ni(NCH=C(H)R')][OTf] (R= CO_2Me: R'= H (**7**), Ph (**9**); R= OMe: R'= H (**8**), Ph (**10**)) were prepared following the same synthetic route used for accessing the analogous acetonitrile adducts **1**-**6**.[22] Treatment of the charge-neutral halo analogues (R-POCOP$^{i\text{-}Pr}$)NiX (X= Cl, Br)[24,25] with AgOTf and R'C(H)=CHCN for 3 h at rt gave the target complexes **7-10** in 63-98% yields (See **Scheme 3**).

These complexes were then subjected to spectroscopic and X-ray diffraction studies, and the results were compared to data obtained for previously examined analogues in search of evidence demonstrating substrate activation upon RCN→Ni coordination. For example, comparison of IR data for **7-10** to the corresponding data for the previously reported acetonitrile complexes **1**-**6** should allow us to understand how the substituents present on the POCOP central ring and on the substrates can affect the electrophilicity of the nickel center and the substrate-Ni interaction. We have shown earlier[22] that the nature of the backbone substituent can have a significant impact on the nitrile stretching frequency, ν(C≡N), with frequencies of up to 2329 cm^{-1} for the CO_2Me substituted complex **4** and 2297 cm^{-1} for the OMe substituted complex **3**. In a similar manner, it would be interesting to know what is the effect of the nitrile substituent on the ν(C≡N) and how it compares to the closely related complexes reported previously.

Inspection of the IR data shown in **Table 2** leads to the following conclusions. First, we observe large and positive values of Δν(C≡N), implying a significant difference in the ν(C≡N) values for the free and nickel-bound nitrile substrates. Moreover, in all cases both ν(C≡N) and Δν(C≡N) values are greater in the adducts bearing the electron-withdrawing substituent. This observation is consistent with the reasoning that the enhanced electrophilicity of the nickel center in CO_2Me adducts **4**, **7**, and **9** increases the RCN→Ni electron donation, which in turn strengthens the C≡N bond; this follows from the anticipation that net σ-donation from the nitrile lone pair, which has partial anti-bonding character, should reinforce the C≡N bond.[26, 27] It should be noted, however, that while this trend is also observed in the cinnamonitrile analogues **9** and **10**, curiously the difference between the ν(C≡N) values in these complexes is very small: 2244 cm^{-1} vs 2241 cm^{-1}.

Further comparison of the data for various adducts shows greater Δν(C≡N) values for acetonitrile relative to acrylonitrile and cinnamonitrile. For instance, the acetonitrile adducts show Δν(C≡N) values of +41 (**3**) and +77 (**4**), whereas the corresponding acrylonitrile and cinnamonitrile adducts show values of +21 (**8**), +61 (**7**), +23 (**10**), and +26 (**9**). While the precise reason for this discrepancy in the levels of activation of acetonitrile vs acrylonitrile and cinnamonitrile is not known at this stage,[28] this observation is reflected in the previously reported reactivity of acetonitrile adducts with amine nucleophiles (to form amidines).[19, 29]

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Table 2 IR ν(C≡N) data for complexes **1-4** and closely related systems

Complex	ν(C≡N) (cm^{-1})	Δν(C≡N) [nitrile] (cm^{-1})[c]
[(H-POCOP$^{i\text{-}Pr}$)Ni(NCMe)][OSO_2CF_3], **1** [a]	2297 (2292)[b]	+45 (+40)[b]
[(*p*-Me-POCOP$^{i\text{-}Pr}$)Ni(NCMe)][OSO_2CF_3], **2** [a]	2294	+42
[(*p*-OMe-POCOP$^{i\text{-}Pr}$)Ni(NCMe)][OSO_2CF_3], **3** [a]	2293	+41
[(*p*-CO_2Me-POCOP$^{i\text{-}Pr}$)Ni(NCMe)][OSO_2CF_3], **4** [a]	2329	+77
[(*p*-Br-POCOP$^{i\text{-}Pr}$)Ni(NCMe)][OSO_2CF_3], **5** [a]	2302	+50
[(*m,m-t*-Bu_2-POCOP$^{i\text{-}Pr}$)Ni(NCMe)][OSO_2CF_3], **6** [a]	2294	+42
[(*p*-CO_2Me-POCOP$^{i\text{-}Pr}$)Ni(NCCH=CH_2)][OSO_2CF_3], **7**	2291	+61
[(*p*-OMe-POCOP$^{i\text{-}Pr}$)Ni(NCCH=CH_2)][OSO_2CF_3], **8**	2251	+21
[(*p*-CO_2Me-POCOP$^{i\text{-}pr}$)Ni(NCCH=CHPh)][OSO_2CF_3], **9**	2244	+26
[(*p*-OMe-POCOP$^{i\text{-}Pr}$)Ni(NCCH=CHPh)][OSO_2CF_3], **10**	2241	+23
[(H-POCOP^{iPr})Ni(NCCH=CH_2)][OSO_2CF_3] [a]	2257	(+27) [b]
[(H-$POC_{sp3}OP^{iPr}$)Ni(NCCH=CH_2)][OSO_2CF_3] [a]	2252	(+22) [b]

a) Previously reported complexes.[18] b) The ν(CN) values in parentheses were measured using KBr pellets to provide a comparison to the solid-state ATR measurements used in the discussion. c) Δν(CN) is relative to the free nitrile stretching frequency of the nitrile in brackets (Free acetonitrile: 2252 cm^{-1}; Free acrylonitrile: 2230 cm^{-1}; Free cinnamonitrile: 2218 cm^{-1}).

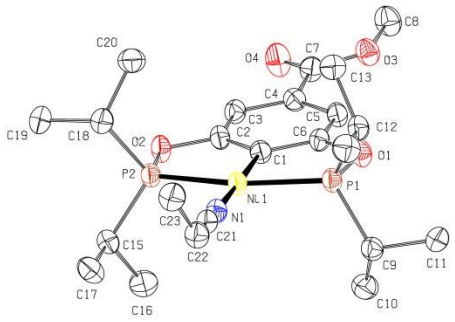

Figure 1 Front view of the molecular diagram for complex **7**. Thermal ellipsoids are shown at the 50% probability level. Hydrogens are omitted for clarity.

Structural analyses of nitrile-bound complexes. The most pertinent structural parameters for the three cationic nitrile adducts complexes subjected to X-ray diffraction studies are listed in **Table 3**, and the front view of the molecular diagrams of adducts **7**, **8** and **10** are shown in **Figures 1** to **3**; the side views of the molecular diagrams for these complexes are shown in **Figures S1-S3**, whereas details of the diffraction studies are given in **Tables S1** and **S2** of the Supporting Information (ESI).

The nickel center in structures **7**, **9**, and **10** adopts a square planar geometry displaying slight distortions from the ideal geometry, most of which are primarily due to the small bite angle of the POCOP ligands: P-Ni-P~163-164°. The displacement of the nickel atom out of the coordination plane (P_1-Ni-P_2-C_{ipso}) is very minor (<0.05(1) Å). We observe close to ideal C_{ipso}-Ni-N angles (ca. 177-179°) in all three complexes, with little or no lifting of the nitrile moiety out of the coordination plane. This contrasts with the parent acetonitrile complexes **2** and **6** where we have observed a significant deviation from the ideal square-planar geometry (C_{ipso}-Ni-N angles of ca. 170-172°).[22] The Ni-P (ca. 2.17 Å) distances in complexes **7**, **9** and **10** are very close to the corresponding distances found in the previously reported complexes **1-6**; however, there are statistically significantly differences in Ni-N distances in these complexes. Overall, the solid state data indicate that changing the nature of the Ni-bound nitrile ligand has a significant effect only on the Ni-N distances, but not on other distances and angles around the coordination plane.

Formation of amine-bound complexes. The above proposed mechanistic schemes for metal-catalyzed hydroamination reactions under discussion invoked the intermediacy of cationic acrylonitrile adducts (outer-sphere mechanism, **Scheme 1**) or amine adducts (inner-sphere mechanism, **Scheme 2**), the latter converting to amido species that might undergo olefin insertion. The observation of thermally stable and isolable acrylonitrile and cinnamonitrile Ni adducts provides indirect support for the validity of the outer-sphere mechanism operating in our systems. In an effort to study the feasibility of the alternative inner-sphere mechanism in our (POCOP)Ni-based systems, we have examined the kinetic accessibility of cationic amine adducts to establish whether they can be viable intermediates in the catalytic cycle, and if so to isolate one or more examples of such adducts and study their structures and reactivities. NMR tube experiments were thus conducted to monitor the reaction of the charge-neutral triflate species, ($^{p\text{-}OMe}$POCOP)Ni(OTf) with excess amine; in the cases where amine adducts could be generated in-situ, they were treated with acrylonitrile to measure the relative binding forces of the two substrates. The results of these tests are summarized below.

In light of its prevalence in our hydroamination studies, aniline was the first amine tested. No color change was observed when 10 equiv of aniline was added to a 0.06 M C_6D_6 solution of the triflate complex ($^{p\text{-}OMe}$POCOP)Ni(OTf), but the ^{31}P NMR spectrum of the mixture showed two broad signals. The broad signal at ca. 186.5 ppm (See **Figure 4a**; $LW_{1/2}$ = 31 Hz) is attributed to ($^{p\text{-}OMe}$POCOP)Ni(OTf), while the other at ca. 189 ppm (See **Figure 4a**; $LW_{1/2}$ = 38 Hz) is believed to arise from the amine-coordinated complex; based on their respective integration values, the major species is the triflate precursor (60:40). The analogous NMR test with the more

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Table 3 Bond distances (Å) and angles (deg.) for complexes **1**-**6** and **7**, **9** and **10**

Complex	Ni-C	Ni-N	N≡C	C=C [b]	Ni-P_1	Ni-P_2	P_1-Ni-P_2	C_1-Ni-N
1 [a]	1.881(2)	1.874(2)	1.140(3)		2.1683(7)	2.1704(7)	164.38(3)	175.8(1)
2 [a]	1.879(3)	1.875(2)	1.142(4)		2.1693(8)	2.1687(7)	163.52(3)	171.7(1)
3 [a]	1.884(2)	1.881(2)	1.135(3)		2.1784(5)	2.1747(5)	163.16(2)	176.84(7)
4 [a]	1.880(2)	1.879(2)	1.138(2)		2.1698(4)	2.1748(4)	164.45(1)	178.43(6)
5 [a]	1.879(3)	1.871(3)	1.145(4)		2.1685(9)	2.171(2)	164.44(4)	176.6(2)
6 [a]	1.890(2)	1.875(2)	1.140(2)		2.1785(5)	2.1640(4)	163.79(2)	170.35(6)
7	1.877(2)	1.873(2)	1.147(3)	1.319(3)	2.1798(5)	2.1777(5)	164.10(2)	176.62(8)
9	1.878(2)	1.867(2)	1.140(2)	1.333(3)	2.1801(4)	2.1758(5)	164.49(2)	177.14(7)
10	1.881(2)	1.864(2)	1.149(3)	1.316(4)	2.1709(6)	2.1740(6)	163.57(2)	178.59(9)

a) Previously reported complexes [18, 22] b) Nitrile moiety alkene bond distances

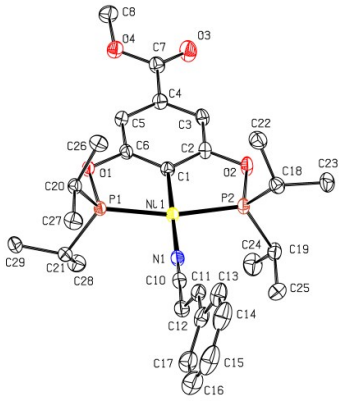

Figure 2 Front view of the molecular diagram for complex **9**. Thermal ellipsoids are shown at the 50% probability level. Hydrogens are omitted for clarity.

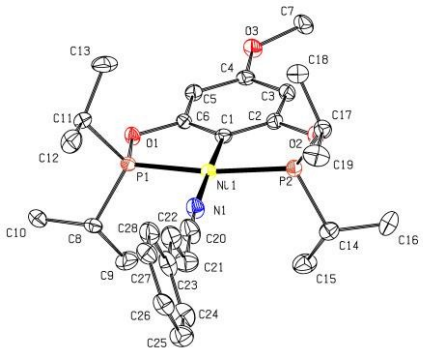

Figure 3 Front view of the molecular diagram for complex **10**. Thermal ellipsoids are shown at the 50% probability level. Hydrogens are omitted for clarity.

nucleophilic cyclohexylamine showed a complete conversion of the triflate complex and emergence of a new major species showing a ^{31}P NMR signal at ca. 188.7 ppm (see **Figure 4b**; $LW_{1/2}$ = 5.4 Hz); a minor species is also present in this mixture (at ca. 190 ppm). Complete conversion of the triflate complex was also observed with piperidine (at ca. 188 ppm), but in this case we observed additional peaks in the upfield region of 50-70 ppm associated with decomposition products arising from hydrolysis or oxidation of the phosphinite moieties.

Finally, we were surprised to find that morpholine, whose nucleophilicity should be similar to that of piperidine and cyclohexylamine, reacted quite differently than its counterparts, displacing the triflate moiety only partially (~20%). The ^{31}P NMR spectrum of this mixture showed two new signals, the major one (accounting for ~18 % of the *P*-containing species) representing the morpholine adduct and the minor peak remaining unidentified. The above observations indicate that cyclohexylamine and piperidine act as stronger nucleophiles in displacing the triflate moiety, whereas the substitution reaction appears to be incomplete with aniline and morpholine.

While the relative binding aptitudes of amines and the triflate anion are interesting to note, a more important question in the context of the hydroamination mechanism is whether the amine substrates can compete with nitrile substrates for binding to the cationic Ni center. To answer this question, we reacted the in-situ generated amine adducts with acrylonitrile and monitored the ligand substitution reaction by ^{31}P NMR spectroscopy. Results of these tests showed that even a small amount of acrylonitrile (less than half the equiv of amines) led to a complete and instantaneous suppression of the signals for amine adducts and the sharp signal at ca. 195 ppm for the corresponding acrylonitrile adduct emerged in every case. This observation confirms the much greater binding aptitude of nitrile substrates and rules out scenarios involving the generation of amine adducts under the normal condition of the hydroamination catalysis wherein the amine and RCN substrates are normally present in a 1:1 ratio.

Isolation of amine adducts. Although the above results discounted the possibility that amine adducts might form during the hydroamination catalysis in our system, we were nevertheless interested in isolating such species and examining their structures and reactivities. Unfortunately, none of the amine adducts discussed above furnished isolable products, but an ammonia adduct was obtained serendipitously from the reaction of (R-POCOP$^{i\text{-Pr}}$)Ni(OTf) (R= H, CO_2Me) with tris(trimethylsilyl)amine ($N(SiMe_3)_3$); the same material was also isolated from the reaction of the triflate precursor with NH_4OH. These reactions and the complete characterization of

the products [(R-POCOP$^{i\text{-Pr}}$)Ni(NH_3)][OTf] (R = H (**11**), CO_2Me (**12**)) are described below.

The reaction of (H-POCOP$^{i\text{-Pr}}$)Ni(OTf) with excess $N(SiMe_3)_3$ in relatively dry THF (~40 ppm H_2O) led to the disappearance of the ^{31}P NMR signal for the starting material and a new signal emerged at 189 ppm. X-ray diffraction studies conducted on a crystalline solid obtained from this sample revealed the formation of the ammonia adduct **11** (**Figure 5**); this species presumably arises from the hydrolysis of the N-Si bonds in the corresponding $N(SiMe_3)_3$ adduct. This hydrolysis scenario was supported by noting that adding one equiv of $N(SiMe_3)_3$ and only three equiv of water to the mixture of the triflate precursor gave the corresponding ammonia adduct with 71% yield over 2 h. We obtained the ammonia adducts **11** and **12** in 85% and 90% yields, respectively, by direct reaction of 1-10 equiv of NH_4OH with (R-POCOP$^{i\text{-Pr}}$)Ni-OTf (R = H, OMe). It should be added that a black oily residue was also formed in these reactions, pointing to possible decomposition of complex

Structural analyses of complexes **11** and **12** (see **Table 4**) showed that they are globally quite similar to analogous cationic complexes **1-10** in terms of most bond distances and angles around the nickel atom (see **Table 3**), the main exception being the Ni-N distances which are longer in the ammonia adducts (ca. 1.96 vs. 1.86-1.88 Å). Another important difference is the presence in complexes **11** and **12** of hydrogen bonding between a H atom in the NH_3 moiety and the O atom of the triflate moiety, with distances of 2.2(1) Å for **11** and 2.1(1) Å for **12**. The positions of the hydrogen atoms on the ammonia nitrogen atom were located using electron density.

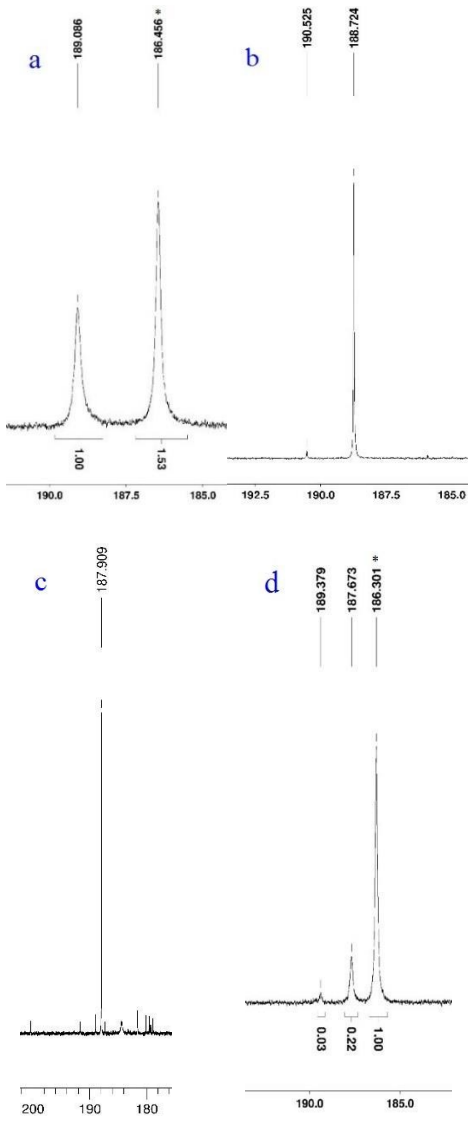

Figure 4 ^{31}P NMR (162 MHz, C_6D_6, rt) spectrums from the treatment of ($^{p\text{-OMe}}$POCOP)Ni-(OTf) with 10 equiv of: aniline (a), cyclohexylamine (b), piperidine (c), and morpholine (d). Peaks marked with a star symbol (*) are due to the precursor complex.

Table 4 Bond distances (Å) and angles (deg.) for complexes **11** and **12**

	11	**12**
Ni-C	1.894(2)	1.890(2)
Ni-N	1.961(2)	1.962(2)
Ni-P1	2.1862(4)	2.1873(5)
Ni-P2	2.1850(4)	2.1807(5)
P1-Ni-P2	162.96(2)	163.37(2)
C1-Ni-N	177.01(6)	177.70(7)

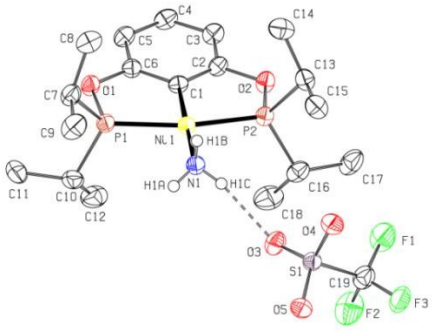

Figure 5 Molecular diagram for complex **11**. Thermal ellipsoids are shown at the 50% probability level. Hydrogens are omitted for clarity

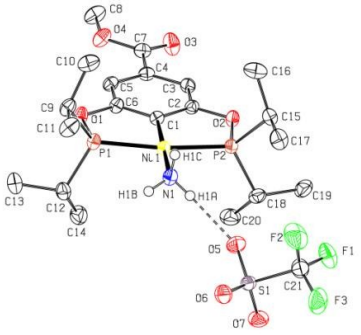

Figure 6 Molecular diagram for complex **12**. Thermal ellipsoids are shown at the 50% probability level. Hydrogens are omitted for clarity

The-above discussed direct pathway to the ammonia adduct is very interesting as it requires a very inexpensive and readily available nucleophile. Since it was shown previously that POCOP pincer complexes decompose in basic media,[30] it is significant that the fragile P- O linkage of the POCOP ligands survives the basic aqueous conditions of the reaction with NH_4OH. The formation of this adduct also implies that ammonia is a much stronger ligand compared to water, and the latter is in turn stronger than the triflate moiety as reported in a previous study.[20]

As a final test for the feasibility of the inner-sphere mechanism, we treated the ammonia adducts with NaH in an effort to form the postulated charge-neutral Ni-amido derivatives via deprotonation; these reactions failed to generate the target Ni-NH_2 species, leading instead to the decomposition of the starting materials, presumably because of secondary reactions at the relatively fragile P-O linkage.[30] Finally, addition of excess acetonitrile to the ammonia adducts **11** and **12** at r.t. resulted in significant broadening of the original ^{31}P NMR signal of the ammonia adduct, giving $LW_{1/2}$ of 127 Hz with 10 equiv of MeCN and 187 Hz with 50 equiv. These observations imply that ammonia is a highly competitive nucleophile for binding to the Ni center.

Conclusion

This study has generated a number of findings in support of the outer-sphere reaction mechanism postulated for the Ni(II)-promoted Michael-type hydroamination of acrylonitrile and its substituted derivatives. For instance, ligand binding studies showed that the cationic, nitrile-coordinated adducts of the substrates are the dominant species under the conditions of the catalytic reactions (1:1 mixture of amines and nitrile substrates); this observation is consistent with the idea that the key role of the Ni(II) center in the catalytic cycle is to activate the substrate toward nucleophilic attack by amines.[31] Indeed, cationic adducts of crotonitrile and methacrylonitrile could be isolated and structurally characterized. The catalytic tests undertaken also showed that addition of aniline to crotonitrile and methacrylonitrile over a short time period (2 h) proceed with higher yields in the presence of pre-catalyst **4**, the more electrophilic of the two cationic acetonitrile adducts tested. Moreover, this same pre-catalyst was the only one that could promote the addition of aniline to cinnamonitrile, the least reactive Michael acceptor examined.

On the other hand, some of the observations from our catalytic tests appear to be inconsistent with the main elements of the outer-sphere proposal. For instance, for the addition of the more nucleophilic, aliphatic amines onto crotonitrile and methacrylonitrile, the greater catalytic activities were observed with complex **3**, the *less* electrophilic of the two pre-catalysts investigated, regardless of the time period over which the catalytic reactions were monitored. This finding does not correlate well with a mechanism in which activation of the nitrile-coordinated substrate plays an important role in determining reactivities.[32] Moreover, allowing a longer reaction time resulted in a reversal of catalytic activities for the addition of aniline: complex **3** led to higher yields when the reactions were allowed to run over 20 h.

Finally, the structural analyses of the substrate adducts **7**, **9**, and **10** revealed no concrete structural evidence for the anticipated activation of the nitrile-coordinated acrylonitrile or cinnamonitrile substrate. These observations suggest that even if the outer-sphere postulate fairly represents the "true" mechanism of action in this system, there are many kinetic subtleties that must be understood in order to rationalize all observations. We have speculated that one such subtlety is that the stronger nitrile-Ni binding anticipated with the more electrophilic precursor **4** can result in a stronger binding of the addition product; such a product inhibition factor would, in turn, hinder the product-substrate exchange equilibrium that is crucial for turnover in the envisaged catalytic cycle.

The somewhat ambiguous nature of the above results prompted us to isolate and study amine adducts that are postulated to be involved in the alternative, inner-sphere mechanism for the title reactions. Although ligand exchange studies showed that certain amines have sufficiently strong binding capacities to generate observable amine adducts, we were unable to isolate thermally stable adducts of the amines that are active in hydroamination reactions with the nitrile substrates in question. However, two new cationic ammonia adducts were isolated, which allowed us to study the structures of these rare complexes. Finally, preliminary ligand exchange studies showed that ammonia-Ni interaction is sufficiently robust so as not result in displacement of the NH_3 moiety by large excess of acetonitrile.

Future studies will aim to examine more closely the kinetics of the Michael-type hydroamination of acrylonitrile with the objective of establishing the relative importance of the various steps in the postulated reaction mechanism, including coordination-activation of the nitrile substrate, nucleophilic attack by amines, H^+-transfer, as well as product inhibition. Of outmost importance will be to identify unequivocally which, if any, of these steps is the rate-determining event in the catalytic process.

Experimental section

General methods

Unless otherwise indicated, all manipulations were carried out under a nitrogen atmosphere using standard Schlenk and glovebox techniques. The solvents were dried by passage over activated alumina contained in MBRAUN-SPS systems and analyzed by a Coulorimetric Karl Fischer titrator to acceptable water content. Triethylamine was dried by distillation over CaH_2. The following reagents and NMR solvents were purchased from Sigma-Aldrich and used without further purification: nickel powder, bromine, $ClP(i\text{-}Pr)_2$, methyl 3,5-dihydroxybenzoate, silver trifluoromethanesulfonate, C_6D_6 and $CDCl_3$. 5-methoxyresorcinol was purchased from Chemsavers and used as received.

NMR spectra were recorded using Bruker AVII400 and AV500 spectrometers. Chemical shift values are reported in ppm (δ) and referenced internally to the residual solvent signals (^{1}H and ^{13}C: 7.26 and 77.16 ppm for $CDCl_3$; 7.16 and 128.06 ppm for C_6D_6) or externally (^{31}P, H_3PO_4 in D_2O, δ = 0). Coupling constants are reported in Hz. Due to either insufficiently concentrated samples or an insufficient number of scans collected, we were unable to ^{13}C signals for some quaternary carbons. In the case of the ^{13}C signal for the triflate moiety, a similar observation has been reported previosuly in closely related complexes.[18] The IR spectra were recorded on a Bruker Alpha-P FTIR (4000-400 cm^{-1}). The elemental analyses were performed by the Laboratoire d'Analyse Élémentaire, Département de Chimie, Université de Montréal. Synthesis and characterization of complexes **1**-**6** as well as the triflate complex (**1-OTf**) have been reported elsewhere.[18, 22] Synthesis of the neutral bromo or chloro precursors were done following reported procedures.[18, 24]

Ligand exchange reactions with the charge-neutral triflate complex and different amines and acrylonitrile were probed as follows. To an NMR tube containing a 0.086 M solution of the charge-neutral triflate complex (prepared following a procedure published elsewhere[20]) was added 10 equiv of the target amine. The ^{31}P NMR spectrum was recorded following a vigorous shaking of the sample tube to ensure complete mixing. To the same solution was added 3.0 equiv of acrylonitrile and another ^{31}P NMR spectrum was recorded after more vigorous shaking.

Catalytic tests were performed following this general procedure. In a sealable vial was placed the amine and nitrile substrates (1 mmol each), NEt_3 (1 mmol), the internal standard (dodecane, 0.1 mmol), and 0.5 mL of a 0.02 M solution of the Ni precursor (**3** or **4**) in THF, and the resulting mixture was heated at 50 °C for the designated time. A small aliquot of the final mixture was diluted with acetone (~100x) and analyzed by GC/MS. The conversion and yield were determined based on a calibration curve prepared using authentic samples of the anticipated products.

[(2,6-(*i*-Pr$_2$OP)$_2$4-(CO$_2$CH$_3$)C$_6$H$_2$)Ni(NCCHCH$_2$)][OSO$_2$CF$_3$] (7). To a Schlenk flask containing the charge-neutral chloro complex **(2,6-(*i*Pr$_2$OP)$_2$-4-(CO$_2$Me)C$_6$H$_2$)NiCl** [24] (114 mg, 0.230 mmol, 1.00 equiv) in dichloromethane (15 mL) was added silver triflate (71 mg, 0.28 mmol, 1.2 equiv) and acrylonitrile (5 mL) at rt. The solution was then agitated for 3 h and filtered to remove the insoluble silver salts. Evaporation of the filtrate gave the desired product as a yellow solid (125 mg, 80%). Single crystals suitable for diffraction studies were obtained from slow evaporation of a concentrated THF solution of the complex.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (q, J_{HH} = 7, 12H, P(CHC(C$\underline{\boldsymbol{H_3}}$)$_2$)$_2$), 1.42 (q, J_{HH} = 7, 12H, P(CHC(C$\underline{\boldsymbol{H_3}}$)$_2$)$_2$), 2.57 (sept, J_{HH} = 6, 4H, P(C$\underline{\boldsymbol{H}}$C(CH$_3$)$_2$)$_4$), 3.86 (s, 3H, CO$_2C\underline{\boldsymbol{H_3}}$), 6.15 (dd, J_{HH} = 12; 18, 1H, NCC$\underline{\boldsymbol{H}}$=CH$_2$), 6.33 (d, J_{HH} = 12, 1H, NCCH=C$\underline{\boldsymbol{H}}$H), 6.42 (d, J_{HH} = 18, 1H, NCCH=CH$\underline{\boldsymbol{H}}$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 16.86 (s, 4C, P(CH(C$\underline{\boldsymbol{H}}_3$)$_2$)$_2$), 17.60 (t, J_{PC} = 3, 4C, P(CH(C$\underline{\boldsymbol{H}}_3$)$_2$)$_2$), 28.68 (t, J_{PC} = 11, 4C, P(C$\underline{\boldsymbol{H}}$(CH$_3$)$_2$)$_4$), 52.4 (s, 1C, C$_{Ar}$-CO$_2C\underline{\boldsymbol{H}}_3$), 107.10 (t, J_{PC} = 6, 2C, C$\underline{\boldsymbol{_{Ar}}}$H), 107.33 (s, 1C, Ni-C$\underline{\boldsymbol{_{ipso}}}$), 133.18 (s, 1C, C$\underline{\boldsymbol{_{Ar}}}CO_2CH_3$), 141.38 (s, 1C, NCCH=C$\underline{\boldsymbol{H}}_2$), 166.27 (s, 1C, C$_{Ar}C\underline{\boldsymbol{O}}_2CH_3$), 168.94 (t, J_{PC} = 9, 2C, (C$\underline{\boldsymbol{_{Ar}}}$-OP)$_2$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ 192.2 (s). ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ -77.97 (s). Elemental analysis was not satisfactory for this complex, because it proved difficult to remove all traces of solvents.

[(2,6-(*i*-Pr$_2$OP)$_2$4-(OCH$_3$)C$_6$H$_2$)Ni(NCCHCH$_2$)][OSO$_2$CF$_3$] (8). The procedure described above for the preparation of **7** was used for this synthesis, using **(2,6-(*i*Pr$_2$OP)$_2$-4-(OMe)C$_6$H$_2$)NiCl**[24] (199 mg, 0.430 mmol, 1.00 equiv) as starting material. The desired product was obtained as a yellow solid (271 mg, 98%).

^{1}H NMR (500 MHz, C_6D_6) δ 1.15 (q, J_{HH} = 8, 12H, P(CHC(C$\underline{\boldsymbol{H_3}}$)$_2$)$_2$), 1.36 (q, J_{HH} = 9, 12H, P(CHC(C$\underline{\boldsymbol{H_3}}$)$_2$)$_2$), 2.41 (sept, J_{HH} = 8, 4H, P(C$\underline{\boldsymbol{H}}$C(CH$_3$)$_2$)$_4$), 3.18 (s, 3H, OC$\underline{\boldsymbol{H_3}}$), 5.61 (s(br), 1H, NCCH=C$\underline{\boldsymbol{H}}$H), 5.70 (s(br), 1H, NCC$\underline{\boldsymbol{H}}$=CH$_2$), 6.00 (d(br), J_{HH} = 23, 1H, NCCH=CH$\underline{\boldsymbol{H}}$). 6.19 (s, 2H, (C$_{Ar}\underline{\boldsymbol{H}}$)$_2$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6) δ 16.71 (s, 4C, P(CH(C$\underline{\boldsymbol{H}}_3$)$_2$)$_2$), 17.58 (t, J_{PC} = 3, 4C, P(CH(C$\underline{\boldsymbol{H}}_3$)$_2$)$_2$), 28.58 (t, J_{PC} = 11, 4C, P(C$\underline{\boldsymbol{H}}$(CH$_3$)$_2$)$_4$), 55.11 (s, 1C, C$_{Ar}O\underline{\boldsymbol{C}}H_3$), 93.50 (vt, $^vJ_{PC}$ = 8, 2C, (C$\underline{\boldsymbol{_{Ar}}}H_{meta}$)$_2$), 107.28 (s, 1C, Ni-C$\underline{\boldsymbol{_{ipso}}}$), 140.61 (s, 1C, NCCH=C$\underline{\boldsymbol{H}}_2$), 163.79 (s, 1C, C$\underline{\boldsymbol{_{Ar}}}OCH_3$), 170.00 (t, J_{PC} = 9, 2C, (C$\underline{\boldsymbol{_{Ar}}}$-OP)$_2$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ 194.9 (s). ^{19}F{^{1}H} NMR (376 MHz, C_6D_6) δ -77.48 (s). Elemental analysis was not satisfactory for this complex, because it proved difficult to remove all traces of solvents

[(2,6-(*i*-Pr$_2$OP)$_2$4-(CO$_2$CH$_3$)C$_6$H$_2$)Ni(NCCH=CHPh)][OSO$_2$CF$_3$] (9). To a Schlenk flask containing the charge-neutral chloro complex **(2,6-(*i*Pr$_2$OP)$_2$-4-(CO$_2$Me)C$_6$H$_2$)NiCl**[24] (268 mg, 0.540 mmol, 1.00 equiv) in dichloromethane (15 mL) was added silver triflate (167 mg, 0.650 mmol, 1.20 equiv) and cinnamonitrile (682 µL, 5.43 mmol, 10.0 equiv) at rt. The solution was then agitated overnight and filtered to remove the insoluble silver salts. Single crystals suitable for x-ray diffraction were obtained by slow evaporation in air of the dichloromethane solution. The crystals obtained were washed with cold hexanes and crushed, giving a yellow-orange powder (252 mg, 63%).

^{1}H NMR (400 MHz, C_6D_6) δ 1.08 (q, J_{HH} = 8, 12H, P(CHC(C$\underline{\boldsymbol{H_3}}$)$_2$)$_2$), 1.33 (q, J_{HH} = 8, 12H, P(CHC(C$\underline{\boldsymbol{H_3}}$)$_2$)$_2$), 2.36 (sept, J_{HH} = 8, 4H, P(C$\underline{\boldsymbol{H}}$C(CH$_3$)$_2$)$_4$), 3.43 (s, 3H, CO$_2C\underline{\boldsymbol{H_3}}$), 6.65-7.04 (m(br), 7H, NCC$\underline{\boldsymbol{H}}$=C$\underline{\boldsymbol{H}}$(C$_6\underline{\boldsymbol{H_5}}$)), 7.38 (s, 2H, (C$_{Ar}\underline{\boldsymbol{H}}$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 16.87 (s, 4C, P(CH(C$\underline{\boldsymbol{H}}_3$)$_2$)$_2$), 17.69 (t, J_{PC} = 3, 4C, P(CH(C$\underline{\boldsymbol{H}}_3$)$_2$)$_2$), 28.80 (t, J_{PC} = 12, 4C, P(C$\underline{\boldsymbol{H}}$(CH$_3$)$_2$)$_4$), 52.45 (s, 1C, C$_{Ar}CO_2C\underline{\boldsymbol{H}}_3$), 96.09 (s, 1C, NC$\underline{\boldsymbol{C}}$H=CH(C$_6H_5$)), 107.24 (s, 2C, C$\underline{\boldsymbol{_{Ar}}}H_{meta}$) 127.62 (s, 2C, NCCH=CH(C$\underline{\boldsymbol{_{ortho}}}C_4H_5$)), 129.23 (s, 2C, NCCH=CH(C$\underline{\boldsymbol{_{meta}}}C_4H_5$)), 131.51 (s, 1C, NCCH=CH(C$\underline{\boldsymbol{_{para}}}C_5H_5$)), 133.51 (s, 1C, NCCH=CH(C$\underline{\boldsymbol{_{ipso}}}C_5H_5$)), 151.41 (s, 1C, NC$\underline{\boldsymbol{C}}$H=CH(C$_6H_5$)), 166.27 (s, 1C, C$_{Ar}\underline{\boldsymbol{C}}O_2CH_3$), 168.94 (t, J_{PC} = 9, 2C, (C$\underline{\boldsymbol{_{Ar}}}$-OP)$_2$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 194.27 (s). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -77.98 (s). Elemental analysis was not satisfactory for this complex, because it proved difficult to remove all traces of solvents

[(2,6-(*i*-Pr$_2$OP)$_2$4-(OCH$_3$)C$_6$H$_2$)Ni(NCCH=CHPh)][OSO$_2$CF$_3$] (10). The same procedure described above for the preparation of **9** was used for this synthesis, using **(2,6-(*i*Pr$_2$OP)$_2$-4-**

(OMe)C$_6$H$_2$)NiBr [25] (500 mg, 0.980 mmol, 1.00 equiv) and furnished a yellow-orange powder (486 mg, 70 %).

^{1}H NMR (400 MHz, C_6D_6) δ 1.18 (q, J_{HH} = 8, 12H, P(CHC(C***H*****$_3$**)$_2$)$_2$), 1.38 (q, J_{HH} = 8, 12H, P(CHC(C***H*****$_3$**)$_2$)$_2$), 2.46 (sept, J_{HH} = 8, 4H, P(C***H***C(CH$_3$)$_2$)$_4$), 3.18 (s, 3H, OC***H*****$_3$**), 6.02 (s, 2H, C$_{Ar}$-***H*****$_{meta}$**), 6.35 (s(br), 1H, NCC***H***=CH(C$_6$H$_5$)), 7.05 (s(br), 3H, NCCH=C***H***(C$_6$(***H*****$_{ortho}$**)$_2$H$_3$)), 7.53 (m(br), 3H, NCCH=CH(C$_6$H$_2$(***H*****$_{meta}$**)$_2$***H*****$_{para}$**)). ^{13}C NMR (101 MHz, $CDCl_3$) δ 16.87 (s, 4C, P(CH(***C***H$_3$)$_2$)$_2$), 17.66 (s, 4C, P(CH(***C***H$_3$)$_2$)$_2$), 28.64 (t, J_{PC} = 12, 4C, P(***C***H(CH$_3$)$_2$)$_4$), 55.68 (s, 1C, C$_{Ar}$O***C***H$_3$), 93.24 (t, J_{PC} = 7, 1C, ***C*****$_{Ar}$**H$_{meta}$), 95.360 (s, 1C, NC***C***H=CH(C$_6$H$_5$)), 113.05 (t, J_{PC} = 21, 1C, N***C***CH=CH(C$_6$H$_5$)) 128.15 (s, 2C, NCCH=CH(***C*****$_{ortho}$**C$_4$H$_5$)), 129.22 (s, 2C, NCCH=CH(***C*****$_{meta}$**C$_4$H$_5$)), 131.94 (s, 1C, NCCH=CH(***C*****$_{para}$**C$_5$H$_5$)), 133.27 (s, 1C, NCCH=CH(***C*****$_{ipso}$**C$_5$H$_5$)), 163.55 (s, 1C, ***C*****$_{Ar}$**OCH$_3$), 169.28(t, J_{PC} = 9, 2C, (***C*****$_{Ar}$**-OP)$_2$). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ 194.37 (s). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$) δ -78.13 (s). Anal. calcd. for $C_{38}H_{47}F_3N_2NiO_6P_2S$ (837.5): C, 54.50; H, 5.66; N, 3.34; S: 3.83. Found: C, 55.04; H, 5.81; N, 3.50; S, 3.37.

[(2,6-(*i*Pr$_2$OP)$_2$C$_6$H$_3$)Ni(NH$_3$)][OSO$_2$CF$_3$] (11). **Procedure 1.** To a Schlenk flask containing the charge-neutral triflate complex **(2,6-(*i*Pr$_2$OP)$_2$C$_6$H$_3$)Ni(OSO$_2$CF$_3$)** (**1-OTf**) (975 mg, 1.78 mmol, 1.00 equiv) was added tris(trimethylsillyl)amine (415 mg, 1.78 mmol, 1.00 equiv) and water (96 µL, 5.3 mmol, 3.0 equiv) at rt. The solution was then agitated for 2 h and the resulting insoluble, black oily residue was removed. Evaporation of the solution gave the desired product as a yellow solid (715 mg, 71 %). Single crystals suitable for x-ray diffraction were obtained by a slow evaporation in air of an acetone solution.

Procedure 2. To a Schlenk flask containing the charge-neutral bromo complex **(2,6-(*i*Pr$_2$OP)$_2$C$_6$H$_3$)NiBr** (240 mg, 0.500 mmol, 1.00 equiv) in THF (15 mL) was added NH_4OH (38.9 µL, 1.00 mmol, 2.00 equiv) and AgOTf (154 mg, 0.600 mmol, 1.20 equiv) at rt. The solution was then agitated for 2 h, filtered to remove the AgBr salts, and the organic phase separated. Evaporation of the solution gave the desired product as a yellow solid (254 mg, 90 %).

^{1}H NMR (400 MHz, C_6D_6): δ 1.10 (q, J_{HH} = 7, 12H, P(CHC(C***H*****$_3$**)$_2$)$_2$), 1.32 (q, J_{HH} = 8, 12H, P(CHC(C***H*****$_3$**)$_2$)$_2$), 2.34 (sept, J_{HH} = 7, 4H, P(C***H***C(CH$_3$)$_2$)$_4$), 2.96 (s(br), 3H, N***H*****$_3$**), 6.46 (d, J_{HH} = 8, 2H, C$_{Ar}$-***H*****$_{meta}$**), 6.80 (t, J_{HH} = 8, 1H, C$_{Ar}$-***H*****$_{para}$**). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 16.80 (s, 4C, P(CH(***C***H$_3$)$_2$)$_2$), 17.77 (t, J_{PC} = 3, 4C, P(CH(***C***H$_3$)$_2$)$_2$), 28.21 (t, J_{PC} = 11, 4C, P(***C***H(CH$_3$)$_2$)$_4$), 105.73 (t, J_{PC} = 6, 2C, (***C*****$_{Ar}$**-H$_{meta}$)$_2$), 130.25 (s, 1C, ***C*****$_{Ar}$**-H$_{para}$), 168.90 (t, J_{PC} = 9, 2C, (***C*****$_{Ar}$**-OP)$_2$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ 189.42 (s). ^{19}F {^{1}H} NMR (376 MHz, C_6D_6) δ -77.97 (s). Anal. calcd. for $C_{19}H_{34}F_3NNiO_5P_2S$ (566.18): C, 40.31; H, 6.05; N, 2.47; S: 5.66. Found: C, 40.95; H, 6.11; N, 2.18; S, 5.13.

[(2,6-(*i*Pr$_2$OP)$_2$-4-(CO$_2$CH$_3$)C$_6$H$_2$)Ni(NH$_3$)][OSO$_2$CF$_3$] (12). The **procedure 2** described above for the preparation of **11** was used for this synthesis using **(2,6-(*i*Pr$_2$OP)$_2$-4-(CO$_2$Me)C$_6$H$_2$)NiBr** [25] (215 mg, 0.400 mmol, 1.00 equiv). The desired product was obtained as a yellow solid (211 mg, 85 %). Crystals suitable for x-ray diffraction were obtained by slow evaporation from a concentrated acetone solution.

^{1}H NMR (500 MHz, C_6D_6): δ 1.06 (q, J_{HH} = 7, 12H, P(CHC(C***H*****$_3$**)$_2$)$_2$), 1.28 (q, J_{HH} = 8, 12H, P(CHC(C***H*****$_3$**)$_2$)$_2$), 2.31 (sept, J_{HH} = 7, 4H, P(C***H***C(CH$_3$)$_2$)$_4$), 3.00 (s(br), 3H, N***H*****$_3$**), 3.43 (s, 3H, OC***H*****$_3$**) 7.42 (s, 2H, C$_{Ar}$-***H*****$_{meta}$**). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 16.46 (s, 4C, P(CH(***C***H$_3$)$_2$)$_2$), 17.62 (s, 4C, P(CH(***C***H$_3$)$_2$)$_2$), 28.40 (t, J_{PC} = 11, 4C, P(***C***H(CH$_3$)$_2$)$_4$), 51.72 (s, 1C, O***C***H$_3$) 107.05 (t, J_{PC} = 6, 2C, ***C*****$_{Ar}$**-H$_{meta}$), 131.41 (s, 1C, ***C*****$_{ipso}$**-Ni), 133.29 (s, 1C, ***C*****$_{Ar}$**CO$_2$CH$_3$) 166.13 (s, 1C, C$_{Ar}$***C***O$_2$CH$_3$), 168.90 (t, J_{PC} = 9, 2C, ***C*****$_{Ar}$**-OP). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6) δ 190.94 (s). ^{19}F {^{1}H} NMR (376 MHz, C_6D_6) δ -78.03 (s). Anal. calcd. for $C_{21}H_{36}F_3N_1Ni_1O_7P_2S_1$ (624.22): C, 40.41; H, 5.81; N, 2.24; S: 5.14. Found: C, 40.26; H, 5.87; N, 2.16; S, 4.92.

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32 Our working hypothesis has been, and remains, that the attack of the amine on the olefin is rate-limiting. However, a reviewer of our manuscript has pointed out correctly that our observations to date do not substantiate this hypothesis; therefore, the rate-limiting step in this process should be considered unknown.

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On the Mechanism of Ni(II)-Promoted Michael-Type Hydroamination of Acrylonitrile and Its Substituted Derivatives

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Monocationic Ni(II) complexes featuring variously substituted POCOP-type pincer ligands promote the addition of primary amines to crotonitrile, methacrylonitrile, and cinnamonitrile.