Application of chelating diphosphine ligands in the nickel-catalysed hydrocyanation of alk-l-enes and ω-unsaturated fatty acid esters

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The hydrocyanation of alk-l-enes and ω-unsaturated fatty acid esters using zerovalent nickel complexes yields the corresponding nitriles and cyanoesters, which can be useful starting materials in organic synthesis.

The nickel-catalysed addition of HCN to butadiene, known as the DuPont ADN Process, is the most important hydrocyanation reaction today at an industrial scale.[1] Many investigations have been made to understand its mechanism and to improve activity and selectivity.[2] A major problem still arises from the formation of inactive nickel cyanides when the zero-valent metal centre is exposed to an excess of HCN.

Recently we reported the successful application of diphosphines in the hydrocyanation of styrene.[3] These newly developed Xantphos ligands[4] have large bite angles and rigid backbones (Fig. 1). It is likely that they enhance the final reductive elimination step in the catalytic cycle by supporting a tetrahedral geometry. Dicyano nickel(II) species with a square-planar geometry affording P–Ni–P angles of about 90° are disfavoured. Moreover, the Xantphos ligands allow a large excess of HCN by providing more stable Ni[0] complexes compared to monodentates due to the chelate effect.

Although the first homogeneously catalysed hydrocyanation of linear alkenes was published by Arthur and Pratt[6] in 1954, only a few more examples representing this class of substrates can be found in the literature.[7] Nevertheless alkyl nitriles are valuable intermediates for the synthesis of amides, amines, carboxylic acids and esters.

Using n-octenes as starting materials, Keim et al. have found in earlier work that, irrespective of the position of the double bond, the anti-Markovnikov product 1-cyanooctane is formed with 80% regioselectivity.[8] However, in order to avoid fast deactivation of the catalyst, the monodentate phosphite ligands like $P(OC_6H_4Me$-$p)_3$ had to be employed in ratios (relative to Ni) > ca. 15 to 1. Recent efforts were made with diphosphites in the hydrocyanation of butadiene[9] and with diphosphinites in the hydrocyanation of vinylarenes.[10]

We report here the catalytic hydrocyanation of long-chain substrates having a non-conjugated double bond with Ni[0] complexes. This work represents the first successful hydrocyanation of alk-l-enes and ω-unsaturated fatty acid esters applying chelating diphosphines, with a ligand to metal ratio of only 1.05 [eqn. (1)].‡ These systems were shown to be stable

$$\text{(1)}$$
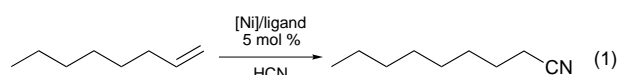
against an excess of HCN up to 1000 in a batch reaction. $AlCl_3$ was added to the reaction mixtures as a cocatalyst. The role of the Lewis acid is to activate the catalyst precursor when non-conjugated alkenes are used as substrates.[11]

The use of diphosphines with large bite angles induces yields that are comparable to those obtained with the commercial ortho-tolylphosphite system in the hydrocyanation of oct-1-ene (Table 1, entries 1–4). The hydrocyanation of dec-1-ene with the same catalysts leads to similar results. Ligands with electron-withdrawing substituents on the phosphorus atom give rise to more stable Ni[0] complexes, since back-donation of d electrons from the metal is favoured in this case. For that reason the Thixantphos ligand was derivatised by introducing trifluoromethyl groups at the meta positions in the PPh moiety (Fig. 1). Increased yields and excellent selectivities with this system clearly indicate a higher complex stability and better performance of the catalyst (Table 1, entry 4).

When dealing with monodentate phosphite ligands in hydrocyanation catalysis the Tolman angle θ is the important factor,[12] whereas with bidentate ligands the bite angle is decisive. The use of common diphosphine ligands with bite angles between 78 and 98° like dppe, dppp, dppb or binap in the hydrocyanation of styrene results in almost no conversion.[3] We observed the same behaviour in the hydrocyanation of substrates dealt with in the present communication. Best activities are obtained with bite angles around 109°.

Table 1 Nickel-catalysed hydrocyanation of oct-1-ene and methyl dec-9-enoate[a]

| Entry | Ligand | Oct-1-ene | | Methyl 9-dec-1-enoate |
		Yield[b] (%)	Selectivity[c] (%)	yield[b] (%)
1	DPEphos	36	82	13
2	Thixantphos	42	91	10
3[d]	$P(OC_6H_4Me)_3$	51	82	33
4	CF_3-Thixantphos	51	96	36

[a] Reaction conditions: $Ni:AlCl_3:ligand:substrate:HCN = 1:1:1.05:20:25$, 333 K, 16 h. [b] Yields are based on the substrate and were determined by temperature-controlled gas chromatography with added standard compounds. [c] Selectivity = chemical yield of nitriles / conversion (substrate). [d] Ligand to nickel ratio = 20.
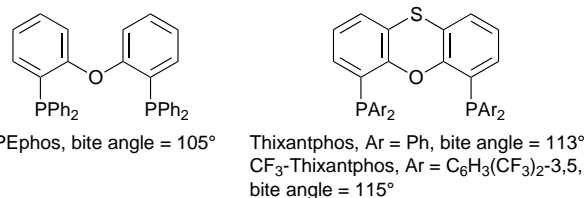


Fig. 1 Xantphos type ligands. Bite angles were calculated using molecular mechanics.† The natural bite angle is defined as the preferred chelation angle determined only by ligand backbone constraints and not by metal valence angles.[5]

DPEphos, bite angle = 105°

Thixantphos, Ar = Ph, bite angle = 113°
CF_3-Thixantphos, Ar = $C_6H_3(CF_3)_2$-3,5, bite angle = 115°

Table 2 Regioselectivity[a] towards the terminal nitriles obtained in the hydrocyanation of oct-1-ene and methyl dec-9-enoate

Ligand	Oct-1-ene	Methyl 9-dec-1-enoate
DPEphos	29	39
Thixantphos	84	75
P(OC$_6$H$_4$Me-p)$_3$	82	77

[a] Regioselectivity is defined as the % of linear nitrile.

Hydrocyanation of functionalised alkenes leads to interesting chemical building blocks. Reaction of ω-unsaturated fatty acid esters with HCN gives the corresponding cyanoesters [eqn. (2),

$$\text{(2)}$$
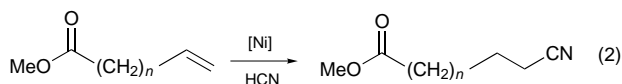
$n = 7–11$]. The substrate acid esters are readily available from natural resources.[13] To the best of our knowledge this is the first example of a catalytic hydrocyanation using this class of substrates.

For methyl dec-9-enoate the obtained yields and selectivities are similar to the unfunctionalised alkenic substrates (Table 1, entries 1–4). The presence of the ester group does not inhibit the catalytic reaction. However, with fatty acid esters containing a longer chain, such as methyl undec-10-enoate or methyl tetradec-13-enoate, the yields decrease slightly.

The Xantphos type diphosphines DPEphos and Thixantphos have almost identical electronic properties but different bite angles. Moreover, for DPEphos, the S-bridge in the backbone is missing which makes the ligand flexible. These characteristics influence the regioselectivity towards the nitrile products (Table 2). We suggest that the more rigid ligand backbones disfavour conformational changes in the metal complexes formed. With Thixantphos the observed linearity reaches 84%.

The formation of branched nitriles mainly takes place when the double bond of the starting unsaturated substrate is isomerised *via* an intermediate nickel hydride species to give an internal alkene. Usually, isomerisation and β-elimination of a thermodynamically favoured internal alkene (k_2) is much faster than hydrocyanation (k_1) (Scheme 1). Thus another approach to explain the difference in regioselectivity with DPEphos and Thixantphos is a kinetic one. The more rigid a ligand is, the more favoured is hydrocyanation (k_1).
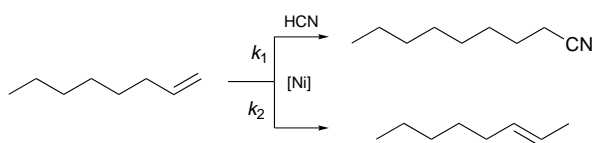
Scheme 1

The results reported here clearly indicate the unique properties of the Xantphos type diphosphine ligands possessing large bite angles in hydrocyanation reactions. Effective nickel-catalysed hydrocyanation of long-chain unsaturated substrates can be achieved. The regioselectivity can be controlled by providing a rigid ligand backbone.

Footnotes and References

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