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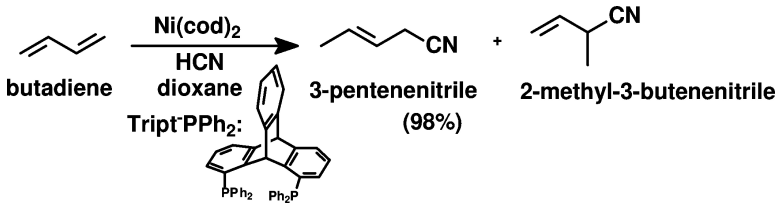

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Highly Selective Hydrocyanation of Butadiene toward 3-Pentenenitrile

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In 1971 DuPont started the production of adiponitrile (ADN) as an intermediate in the production of Nylon(6,6).[1] This process is so far the only example of a large-scale industrial application of an alkene hydrocyanation. Originally it was developed using a monodentate phosphite-based zerovalent nickel catalyst.[2] The process consists of three steps. The hydrocyanation of butadiene leads to a mixture of 2-methyl-3-butenenitrile (2M3BN) and 3-pentenenitrile (3PN), obtained in varying ratio (typically 2:3) depending on the ligand employed. In a second step the branched 2M3BN is isomerized to the desired linear 3PN. The last step is the hydrocyanation of 3PN to ADN, requiring a Lewis acid cocatalyst such as $AlCl_3$.

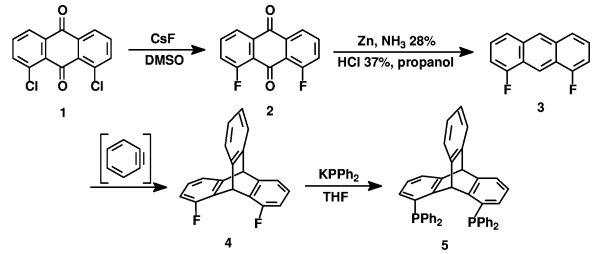
Many efforts have been made to improve the performance of the nickel catalysts. An important step was the replacement of monodentate ligands by bidentate π-acceptor ligands that lead to higher conversion and selectivity for 3PN up to 70%.[3] A higher selectivity has been claimed only in a patent for bis(diphenylphosphino)ferrocene (DPPF) as ligand used in large excess.[4] Large bite angle ligands, based on a rigid xanthene backbone (e.g., sixantphos or thixantphos) were proven to enhance the Ni(0)-catalyst performance in hydrocyanation.[5] It was proposed that these ligands improve the reductive elimination of the product and stabilize the active Ni-species while suppressing the formation of inactive dicyano Ni(II)-complexes.

Triptycene-based bidentate ligands, first described by Hofmann at al.,[6] possess both a very rigid backbone and a large bite angle. So far, these systems were described only in the patent literature with examples of Rh-catalyzed hydroformylation reactions.[6,7] In more recent publications different mono- and dinuclear metal complexes with a variety of bite angles and geometries were investigated.[8]

As part of our continuing interest in this field,[9] we now describe the use of a triptycene-based diphosphine ligand in the hydrocyanation of butadiene, resulting in unprecedented high selectivities to 3PN of up to 98%. A new route toward the ligand tript-PPh_2 (**5**) (Scheme 1) has been devised, giving considerably higher yields than the reported[6,7] method; 1,8-dichloroanthraquinone (**1**) was converted into the difluoro compound (**2**) and subsequently reduced to 1,8-difluoroanthracene (**3**) with Zn dust[10,11] (Scheme 1). The triptycene moiety (**4**) was obtained by reaction of the corresponding anthracene with benzyne, generated in situ from anthranilic acid. Nucleophilic substitution of the fluoro groups with potassium diphenylphosphide gave ligand (**5**) in 20% overall yield.

Reaction of (**5**) with (cod)$PtCl_2$ and Ni(cod)$_2$, respectively, led to the corresponding complexes (**5**)$PtCl_2$ (**6**) and (**5**)Ni(cod) (**7**). The pale-yellow compound **6** was characterized by means of ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy as well as by elemental analysis.

Scheme 1. Synthesis of Triptycene-Based Ligands



The ^{31}P NMR spectrum of **6** shows a singlet at $\delta = 0.42$ ppm with platinum satellites ($^1J_{Pt-P} = 3761$ Hz), suggesting that the ligand is coordinated in a cis fashion.[8c] This was confirmed by determining the X-ray crystal structure (see Supporting Information). The complex (**5**)Ni(cod) (**7**) displays a singlet at $\delta = 25.82$ ppm in the ^{31}P NMR spectrum. No formation of bischelate complexes[5,12] was detected by NMR spectroscopy even with an excess of the ligand added to the solution of **7**. The formation of inactive bischelates is strongly related to the bulk of the ligand; the rigid and bulky triptycene ligand apparently leads to exclusive monochelate formation.

The hydrocyanation of butadiene using complex **7** with acetonecyanohydrine (ACH) as HCN source was carried out in toluene and in dioxane. The reaction in toluene is slow (Table 1, entry 1) and gives normal selectivity to 3PN (65%), comparable to results with the best performing diphosphite ligands reported.[3]

Most strikingly the reaction in dioxane gives excellent selectivity toward 3PN (98%) and a conversion of up to 87% (Table 1, entries 2,3), attributed to the higher solubility of gaseous butadiene in polar solvents.[13] Solvent effects in hydrocyanation have been reported earlier, especially in asymmetric catalysis, where higher ee values were obtained in apolar solvents in the reaction of MVN (6-methoxy-2-vinyl-naphthalene).[14] Addition of an excess of ligand slowed down the reaction but still leads to high product linearity (entry 4). An excess of ACH leads to lower conversion and lower product linearity (entry 5). The high concentration of ACH probably deactivates the catalyst by formation of dicyano Ni(II)-species (see Supporting Information). At low catalyst loading, the conversion to nitriles decreases as expected, but 3PN is still formed in 90% selectivity (Table 1, entry 6).

Subsequently the reaction was performed with free HCN as a dioxane solution under syringe pump dosation. Full conversion of butadiene to nitriles was achieved also at lower catalyst loading (Table 2, entries 1,2), while the product linearity decreases. Additional experiments under various HCN concentrations were performed (Table 2) to understand the origin of the high selectivity toward 3PN. As anticipated from the results in Table 1, high HCN concentrations lead to low conversion, most likely due to the formation of inactive (**5**)Ni(CN)$_2$ species, and to moderate selectivi-

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Table 1. Butadiene Hydrocyanation in Dioxane with ACH as HCN Source[a]

entry	ratio S/Ni	ratio (**5**)/Ni	ratio ACH/butadiene	conversion (%)	3PN (%)	time (h)
1[b]	125	1.0	1.2	48	65	5
2	125	1.0	1.2	59	97.6	3
3	125	1.0	1.2	85	94.8	5
4	125	2.0	1.2	62	92	5
5	125	1.0	3.0	21	70.5	5
6	600	1.0	1.2	20	90.0	3

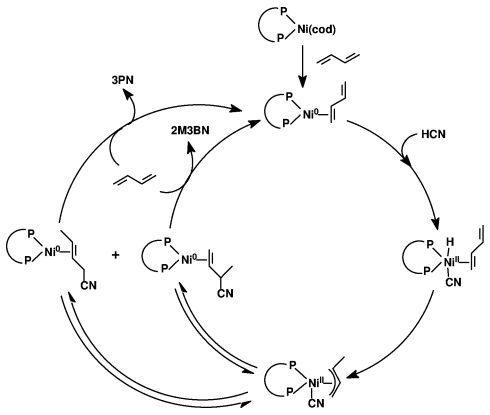
[a] Conditions: 0.018 mmol $Ni(cod)_2$, acetonecyanohydrine (ACH) as HCN source, 90 °C, 2 mL of dioxane. [b] Reaction performed in toluene (2 mL).

Table 2. Butadiene Hydrocyanation in Dioxane with HCN Dosation and Direct Addition[a]

entry	ratio S/Ni	ratio (**5**)/Ni	conversion (%)	2M3BN (%)	3PN (%)	time (h)
1[b]	125	1.0	100	2.4	93.3	5
2[b]	300	1.0	100	25.6	73.3	5
3[c]	125	1.0	9	58.5	41.5	0.5

[a] Conditions: 0.018 mmol $Ni(cod)_2$, HCN excess, 90 °C, 2 mL of dioxane. [b] Slow HCN dosation (excess) as dioxane solution (13 μmol/min). [c] Direct addition of excess HCN.

Scheme 2. Proposed Cycle for Butadiene Hydrocyanation and 2M3BN Isomerization



ties. Indeed, direct addition of an excess of HCN deactivates the catalyst and lowers the selectivity to 3PN (Table 2, entry 3). Traces (<2%) of product isomers, 2M2BN and 2PN, were detected in case of full conversion of butadiene to nitriles (Table 2, entry 1 and 2).

These results indicate that in fact two independent processes are responsible for the high linearity observed with this catalyst: the hydrocyanation of butadiene giving the usual mixture of branched (2M3BN) and linear (3PN) product, and the isomerization of 2M3BN toward 3PN (Scheme 2).[15]

This means that (**5**)Ni(0)(cod) must also be an efficient isomerization catalyst. Under conditions of HCN starvation the isomerization reaction plays a dominant role: 2M3BN undergoes oxidative addition to the Ni(0) species, leading to a high selectivity of 3PN after reductive elimination. On the other hand, with an excess or fast addition of HCN, oxidative addition of HCN dominates, resulting in the hydrocyanation of butadiene giving rise to the usual linear to branched mixture and ultimately deactivating the catalyst after complete conversion of butadiene.

To test this hypothesis, we performed the isomerization of 2M3BN in absence of HCN, applying the (**5**)Ni(cod) complex. Indeed, this complex is able to isomerize 2M3BN to 3PN very efficiently, giving selectivities of 97% within 30 min. For different catalyst loadings the isomerization was followed in time (see Supporting Information). Careful adjustment of HCN dosation to the rate of hydrocyanation and isomerization could indeed lead to an improved one-step process for 3PN. For comparison we applied typical diphosphite and diphosphine ligands under identical conditions (see Supporting Information). These hydrocyanation reactions led to a low selectivity for 3PN. Moreover, these systems show a lower activity in the isomerization of 2M3BN to 3PN, which is in agreement with the proposed catalytic cycle.

In conclusion, we developed an improved route for a triptycene-based diphosphine. The coordination behavior of this ligand toward Pt(II) and Ni(0) was investigated and the X-ray crystal structure of the complex *cis*-(**5**)$PtCl_2$ was determined. The (**5**)Ni(cod) complex was applied in the hydrocyanation of butadiene, showing excellent selectivities of up to 98% toward 3PN. Low HCN concentrations achieved by controlled dosation guarantee both high conversion and high selectivity, avoiding catalyst deactivation in this one-step procedure. Thus, robust hydrocyanation catalyst systems with additional isomerization activity could be the key toward process intensification.

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Supporting Information Available: A listing of all experimental procedures, cif file, and the crystal data for complex **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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