Effect of the Bite Angle of Diphosphine Ligands on Activity and Selectivity in the Nickel-catalysed Hydrocyanation of Styrene

Mirko Kranenburg,[a] Paul C. J. Kamer,[a] Piet W. N. M. van Leeuwen,*[a] Dieter Vogt[b] and Wilhelm Keim[b]

[a] *J. H. van't Hoff Research Institute, Department of Inorganic Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands*

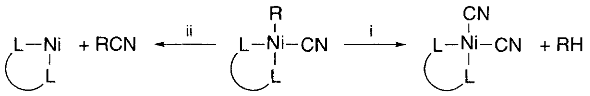
[b] *Institut für Technische Chemie und Petrolchemie, Rheinisch-Westfälischen Technische Hochschule, Worringer Weg 1, D-52074 Aachen, Germany*

The application of diphosphines with large bite angles (β_n = 101–109°) in nickel catalysts leads to successful, regioselective hydrocyanation of styrene.

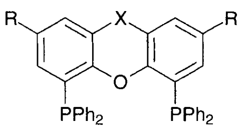
Nickel catalysts modified with arylphosphite ligands are applied for the hydrocyanation of butadiene on a commercial scale.[1,2] Phosphine ligands, however, have so far led to catalysts with hardly any activity.[1,3–5] The explanation is straightforward; the reductive elimination of the alkyl cyanide is rate determining[6–9] and thus proceeds faster when phosphites or phosphinites are employed. Secondly, a derailment of the catalytic reaction occurs *via* a side-reaction with HCN, which leads to completely inactive $L_nNi(CN)_2$ species. In order to suppress this side-reaction the concentration of HCN is kept low in the catalytic process. Thirdly, the diphosphines used so far all favour a bite angle of *ca.* 90°, *i.e.* they stabilise the divalent species and retard the reductive elimination even further. It occurred to us that ligands favouring bite angles of *ca.* 110° would (*a*) destabilise the square-planar nickel(II) species, and (*b*) stabilise tetrahedral nickel(0) complexes, thus enhancing the reductive elimination and the overall catalysis.[10]

Recently we developed a series of new diphosphines having such bite angles (Fig. 1).[11]

Hydrocyanation of styrene using nickel catalysts containing these ligands as catalyst components (Scheme 2) resulted in remarkable yields and selectivity, especially when compared to common diphosphines (see Table 1).† The use of DPEphos, the ligand in our series with the smallest β_n of 101°, induced a yield (based on HCN) of 35–41%, which is modest but still a significant enhancement when compared to PPh_3 or $Ph_2P(CH_2)_nPPh_2$ (n = 2–4). When the bite angle is increased further to 105–106°, using Sixantphos or Thixantphos, the yields increased up to 95%. When Xantphos, with a calculated bite angle of 109°, was applied, the yield was slightly lower, 75%. The reaction mixture is not fully homogeneous in this case; an orange precipitate was formed. Application of DBFphos, with a β_n of 131°, resulted in virtually no yield. The reaction mixture was pale yellow and a whitish yellow precipitate was formed, indicating the formation of nickel cyanides.



Scheme 1 *Reagents and conditions*: i, HCN; ii, reductive elimination



	X	R	$\beta_n{}^{a,b}$/ °
DPEphos	H,H	H	101
Sixantphos	$SiMe_2$	H	105
Thixantphos	S	Me	106
Xantphos	CMe_2	H	109
DBFphos	Bond	H	131

Fig. 1 Structure and chelational features of the ligands. (*a*) Calculated using molecular mechanics (CAChe WorkSystem),[12] with a P–Ni bond length of 2.33 Å and a P–Ni–P angle bending force constant of 0 mdyne Å rad^{-2}. (*b*) The natural bite angle (β_n) is defined as the preferred chelation angle determined only by ligand backbone constraints and not by metal valence angles.[13]

For comparison, we tested several well known common diphosphines as catalyst components for comparison under identical conditions (see Table 1). Yields of nitriles were 0–11% (based on HCN) and large amounts of a yellowish precipitate were observed, presumably nickel cyanides. We ascribe this to the stabilisation of the intermediate square-planar nickel(II) species by the phosphines, which upon exposure to an excess of HCN leads to formation of inactive nickel dicyanides.

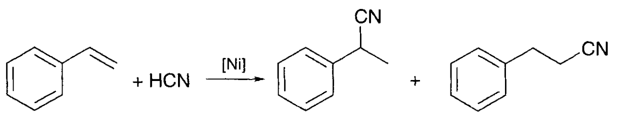
For styrene as a substrate, the branched nitrile is strongly favoured over the linear one. This regioselectivity is attributed to stabilisation of the branched alkyl intermediate by a η^3-benzyl interaction of the nickel.[2] The selectivity induced by the ligands with large bite angles (up to 99%) is significantly higher than those obtained with the common diphosphines (up to 95%) and the commercial *ortho*-tolylphosphite system (91%),[14] and comparable to that of the new diphosphinites for enantioselective hydrocyanation reported recently.[15]

The results reported here clearly indicate that effective nickel–phosphine catalysed hydrocyanation can be achieved when the phosphines enhance the reductive elimination step by supporting a tetrahedral geometry. Diphosphine ligands with bite angles of *ca.* 106° allow very high conversion and

Table 1 Nickel catalysed hydrocyanation of styrene using diphosphine ligands[a]

Ligand	$\beta_n{}^{b,c}$/°	Yield[d] (%)	(%) Branched product
DPEphos	101	35–41	88–91
Sixantphos	105	94–95	97–98
Thixantphos	106	69–92	96–98
Xantphos	109	27–75	96–99
DBFphos	131	0.7	83
PPh_3	—	0	—
$Ph_2P(CH_2)_2PPh_2$	78	< 1	*ca.* 40
$Ph_2P(CH_2)_3PPh_2$	87	4–11	*ca.* 90
$Ph_2P(CH_2)_4PPh_2$	98	3–8	92–95
BINAP[e]	85	4	29

[a] *Reaction conditions*: styrene/Ni = 28.5, HCN/Ni = 17.5, [Ni] = 73.3 mmol dm^{-3}, T = 333 K, t = 18 h. [b] The natural bite angle (β_n) is defined as the preferred chelation angle determined only by ligand backbone constraints and not by metal valence angles.[13] [c] For computational details, see legend to Fig. 1. [d] Yields are based on HCN. Maximum yields based on styrene are 61%. [e] BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl.



Scheme 2 Reaction scheme for the hydrocyanation of styrene

selectivity in the hydrocyanation of styrene. The optimal bite angle is 105–106°, while either a slight increase to 109° or a decrease to 101° already results in a significant drop in activity.

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Footnote

† In a typical experiment, 2.0 cm^3 of a bright yellow 73.3 mmol dm^{-3} solution of Ni(cod)$_2$ (cod = cycloocta-1-5-diene) in toluene (90.147 mmol) was added to a Schlenk vessel containing a stirring bar and 1.2 equiv. of ligand. The reaction mixture turned red immediately, and was stirred for 2 h to ensure complete formation of the catalyst. Styrene (0.336 cm^3, 433 mg, 4.15 mmol) was added, and the reaction mixture was stirred for another 30 min. The reaction mixture was then cooled to *ca.* 243 K, and liquid HCN (0.100 cm^3, 2.58 mmol) was added at once, and the Schlenk vessel was placed in a thermostatted heating bath at 333 K. After 18 h, the stopper was removed to allow the evolution of HCN (which was possibly still present) from the reaction mixture. The reaction mixture was analysed with temperature-controlled gas chromatography. Owing to the excess of styrene, a maximum conversion of 61% based on styrene can be achieved.

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