

### Preliminary communication

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## CATALYTIC ASYMMETRIC HYDROCYANATION OF NORBORNENE USING CHIRAL BIPHOSPHINEPALLADIUM COMPLEXES \*

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### Summary

Addition of HCN to norbornene is catalysed by Pd(BPPM)<sub>2</sub> or Pd(BINAP)<sub>2</sub> complexes to give the corresponding nitrile in 20 and 40% enantiomeric purity, respectively. Optical yields using Pd(DIOP)<sub>2</sub> are lower than originally surmised.

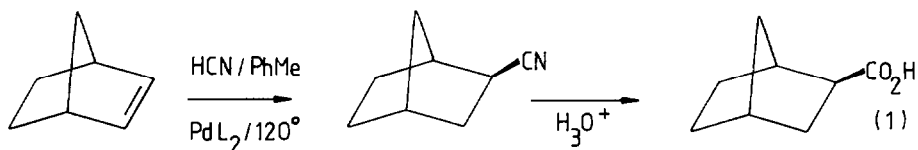
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A short series of papers has described the catalytic asymmetric addition of hydrogen cyanide to simple alkenes using chiral nickel(0) or palladium(0) biphosphine complexes [1-3]. Little attention has been paid to the evaluation of different biphosphines, although it is well established in chiral catalysis that, for example, chelate ring size markedly influences reactivity. In addition there have been relatively few mechanistic investigations, and little is known about the nature of the true catalytic intermediates in these reactions. The corresponding nickel phosphite catalysed hydrocyanation of alkenes has been thoroughly investigated, and provides some general guidelines for the related palladium catalysed reaction [4-6].

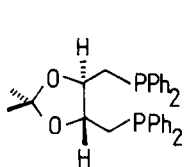
The addition of HCN to norbornene is catalysed by bis(4,5-bis[diphenyl]phosphinomethyl)-2,2-dimethyl-1,3-dioxolan)palladium(0), [Pd(DIOP)<sub>2</sub>], to give the *exo*-nitrile stereoselectively (eq. 1). The product enantiomeric purity has been deduced by measuring the rotation of the corresponding *exo*-2-norbornanecarboxylic acid obtained by acid hydrolysis. The enantiomerically pure (-) acid has an optical rotation  $[\alpha]_D^{20} -27.8$  (*c* 1, EtOH) [7] and not  $[\alpha]_D^{20} -10.7$  as had been originally surmised [1-3]. Product enantiomeric purities based on the correct chiroptical data are given in Table 1, and compare results obtained using DIOP, **1**, BPPM, **2**, and BINAP, **3**. Independent confirmation of the enantiomeric purity of *exo*-acid has been obtained by derivatising it with (*S*)-methyl mandelate [8], under non-racemising conditions, to give the diastereomeric esters **4a** and **4b**. Proton NMR integration of the separated anisochronous resonances due to the mandelate H<sub>a</sub> ( $\Delta\delta$  0.01 ppm, C<sub>6</sub>D<sub>6</sub>) and bridgehead norbornyl protons, H<sub>b</sub>, ( $\Delta\delta$  0.33 ppm) gives values in close agreement with the chiroptical data (Table 1).

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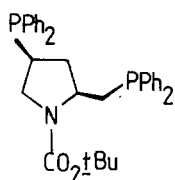
\* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday.



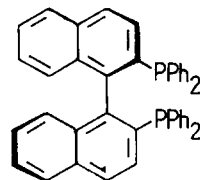
(L = 1-3)



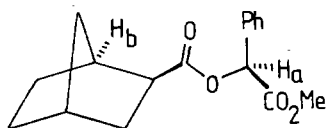
(1)



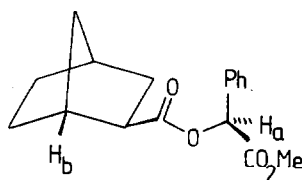
(2)



(3)



(4a)



(4b)

The hydrocyanation reactions were typically carried out in benzene, at 120 °C in the presence of excess phosphine and norbornene. An optical yield of 40% was obtained using palladium (BINAP)<sub>2</sub>, while Pd(BPPM)<sub>2</sub> gave lower product enantiomeric purity (20%), but a higher chemical yield. The lowest product enantiomeric purities (10%) were obtained using Pd(DIOP)<sub>2</sub>, and the value obtained was the same in benzene as in tetrahydrofuran. The palladium(0) catalyst used was either generated in situ by treating bis(dibenzylideneacetone)palladium(0) with an excess of the chiral biphosphine, or by using an isolated complex. For example, reaction of *SS*-BPPM with PdCl<sub>2</sub>(PhCN)<sub>2</sub> in dichloromethane gave BPPMPdCl<sub>2</sub> quantitatively ([α]<sub>D</sub><sup>20</sup> -72.3 (c 0.8, CHCl<sub>3</sub>)). Reduction of this colourless complex with a 5 M excess of sodium borohydride in ethanol in the presence of BPPM yielded the bright yellow complex (BPPM)<sub>2</sub>Pd ([α]<sub>D</sub><sup>20</sup> -30.5 (c 0.6, CHCl<sub>3</sub>)). Similar optical and chemical yields were obtained using the 'in situ' generated or isolated Pd(BPPM)<sub>2</sub> catalyst.

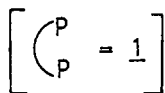
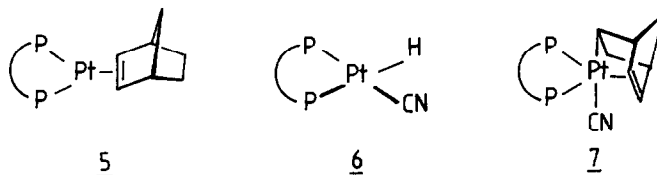
TABLE 1

PdL<sub>2</sub> CATALYSED HYDROCYANATION OF NORBORNENE IN BENZENE<sup>d</sup>

PdL <sub>2</sub> catalyst	Reaction temperature (°C)	Yield of <sup>e</sup> nitrile (%)	Enantiomeric <sup>a</sup> purity (±1%)
R DIOP	120	60	10 R <sup>f</sup>
S DIOP	80	94	13 S <sup>b</sup>
SS BPPM	120	68	20 R <sup>f</sup>
R BINAP	120	6	40 R
R DIOP <sup>c</sup>	120	86	9 R
SS BPPM	80	13	25 R

<sup>a</sup> Refers to the purity of the (1*R*,2*R*,4*S*)-*exo*-2 cyanonorbornane. <sup>b</sup> i.e. the (1*S*,2*S*,4*R*)-enantiomer. <sup>c</sup> In tetrahydrofuran as solvent. <sup>d</sup> Typically using an in situ catalyst generated from Pd(dibenzylideneacetone)<sub>2</sub>, (0.02 mmol), phosphine (0.20 mmol), HCN (14 mmol) and norbornene (28 mmol). <sup>e</sup> Refers to the isolated yield of pure distilled nitrile. <sup>f</sup> Values obtained by <sup>1</sup>H NMR and chiroptical methods were identical.

Some preliminary solution NMR results, pertaining to the mechanism of this reaction have been obtained. The coordinated ethene group in DIOPPt(C<sub>2</sub>H<sub>4</sub>) is readily displaced by various η<sup>2</sup> donors [9], and the study of more kinetically inert platinum analogues of reactive palladium complexes has been often advocated [10]. Reaction of PtDIOP(C<sub>2</sub>H<sub>4</sub>) with norbornene in toluene gave the norbornene complex **5** clearly (*J*(PtP) 3414 Hz, δ(P) + 15.8 ppm), and in the absence of excess alkene, **5** reacted with excess HCN to generate one major species, which could also be formed directly from PtDIOP(C<sub>2</sub>H<sub>4</sub>) with excess HCN (δ(P(1)) 11.5, *J*(PtP(1)) 2840 Hz; (δ(P(2)) 9.69, *J*(P(1)P(2)) 17 Hz). The spectroscopic data are in accord with hydrido cyanide (**6**), in which P(2) is *trans* to a hydride and P(1) *trans* to a cyano group [11,12]. This intermediate reacts slowly with displaced norbornene to give a complex series of products. It may therefore be regarded as a simple model pro-catalyst for alkene hydrocyanation. Reaction of DIOPPt(C<sub>2</sub>H<sub>4</sub>) with norbornadiene gives DIOPPt(nbd) (*J*(PtP) 3251 Hz, δ(P) 14.6 ppm) and exposure of this complex to HCN at 298 K gives a major species (δ(P(1)) 1.47 ppm, *J*(PtP(1)) 1240 Hz; δ(P(2)) 1.27 ppm, *J*(PtP(2)) 1238 Hz, *J*(P(1)P(2)) 5 Hz) which may be five or six coordinate. It may involve a σ-alkyl, π-olefin coordinated norbornadiene, **7**, as defined for several complexes of palladium and platinum in which nucleophilic attack on one bound olefin has occurred [13]. The fact that hydrocyanation of norbornene and norbornadiene give quite different optical yields (10*R* vs 7*S*) [3]



with Pd(DIOP)<sub>2</sub> may be related to their different catalytic reaction pathways, perhaps involving similar intermediates to those detected in this simple model study.

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