

TITLE

Preparation of Triarylborane

FIELD OF THE INVENTION

This invention relates to the preparation of triarylborane from nickel complexes of the formula:
5 $\text{Ni}(\text{NC}(\text{CH}_2)_4\text{CN})_2(\text{NCBAr}_3)_2$ where Ar is phenyl or phenyl substituted with an alkyl group having 1 to 4 carbon atoms where the alkyl group may contain one or more fluorine atoms. These nickel complexes may be contained in
10 catalytic residue formed during the alkene hydrocyanation (for example butadiene hydrocyanation) using organophosphorous nickel complexes as catalysts and triarylborane as catalytic promoters.

BACKGROUND OF THE INVENTION

15 King et al. U.S. patent 3,798,256 discloses the hydrocyanation of 3-pentenitrile to produce adiponitrile using nickel complexes as catalysts and organic boron compounds as promoters. Such hydrocyanation reactions produce catalyst residues which are primarily
20 $\text{Ni}(\text{NCR})_4(\text{NCBAr}_3)_2$ hereinafter referred to as NCBCs. Shook U.S. Patent 4,082,811 discloses treating such residues with ammonium hydroxide to precipitate the amine adduct of triarylborane. The triarylborane can be recovered from the adduct by treatment with metal hydroxide--see Shook
25 U.S. Patent 4,134,923.

The present invention is a direct method of recovery of the triarylborane promoter from the catalyst residue.

SUMMARY OF THE INVENTION

30 The present invention is a process for the manufacture of a triarylborane having the formula: BAr_3 where Ar is phenyl or phenyl substituted with an alkyl group having 1 to 4 carbon atoms where the alkyl group may contain one or more fluorine atoms, which comprises
35 heating a complex of the formula: $\text{Ni}(\text{NC}(\text{CH}_2)_4\text{CN})_2(\text{NCBAr}_3)_2$ where Ar is as above, in an inert atmosphere at a pressure less than atmospheric to a temperature in the range of 120 degrees C to 300 degrees C; thus forming a vapor containing the triarylborane, and condensing triarylborane

from the vapor. In a preferred embodiment of the process an inert gas stream moves the vapor containing triarylborane to a zone where the triarylborane is condensed.

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DESCRIPTION OF THE DRAWING

The drawing is a diagrammatic cross-sectional view of an apparatus suitable for use in carrying out the process of the invention.

DETAILED DESCRIPTION OF THE INVENTION

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In one embodiment of the invention, the catalyst residue or NCBC is placed in a conventional sublimation apparatus and then heated under an inert atmosphere such as nitrogen or argon, or, preferably, under reduced pressure to decompose the catalyst residue or NCBC and release BAR_3 and RCN. BAR_3 and RCN solidify on the sublimer cold finger. Temperatures ranging from 120°C to 300°C may be used, 170°C to 230°C is preferred. Pressures ranging from 0 to 760 torr may be used, .001 to 40 torr is preferred.

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In a second embodiment of the invention, the catalyst residue or NCBC is placed in a tube and then heated, preferably under reduced pressure, while a stream of an inert carrier gas, such as nitrogen or argon, is passed over the catalyst residue or NCBC and through a cold trap. BAR_3 and RCN released during this process are swept into the trap by the carrier gas and condensed onto the surface of the trap.

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The catalyst residue is obtained from alkene, preferably 3-pentenitrile (3PN), hydrocyanations carried out in the presence of the active Ni catalyst $\text{Ni}[\text{P}(\text{OR})_3]_4$ and a triarylborane promoter of the formula BAR_3 , where R is an aryl radical having up to 18 carbon atoms and Ar is an aryl radical having up to 10 carbon atoms, preferably BPh_3 (Ph=phenyl). Typical Ni catalysts of this type include $\text{Ni}[\text{P}(\text{OC}_6\text{H}_5)_3]_4$, $\text{Ni}[\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{CH}_3)]_4$, $\text{Ni}[\text{P}(\text{O}-m\text{-C}_6\text{H}_4\text{CH}_3)_3]_4$, and $\text{Ni}[\text{P}(\text{O}-m\&p\text{-C}_6\text{H}_4\text{CH}_3)_3]_4$. The amount of promoter used can generally be varied from about 1:16 to 50:1 mole ratio of promoter to catalyst. A detailed description of the formation of catalyst residue is found

in U.S. Patent 4,082,811 .

NCBC's can be prepared as described in Cone U.S. Pat. No. 4,394,321.

Examples

5 In the following examples, unless stated otherwise, all operations were carried out under a nitrogen atmosphere using a drybox or standard Schlenk techniques. Exposure of triphenylboron to air or moisture typically leads to the formation of diphenylboron
10 derivatives. ADN-NCBC refers to the NCBC derived from adiponitrile (ADN), specifically $\text{Ni}(\text{NC}(\text{CH}_2)_4\text{CN})_2(\text{NCBPh}_3)_2$. Elemental analyses for the catalyst residue and ADN-NCBC were as follows. Ni Catalyst residue: C, 72.96; H, 5.66; N, 10.53. ADN-NCBC: C, 72.14; H, 5.70; N, 11.71; Ni, 6.56;
15 B, 4.26.

Example 1

0.158 g (0.195 mmol) of ADN-NCBC was placed in a sublimier equipped with a dry ice cold finger and then heated at 150°C at 0.004 torr for 15 minutes, whereupon a
20 white solid began to form on the cold finger. The temperature was increased to 190°C for 30 minutes and then, finally, 200°C for 4 hours. The apparatus was cooled to room temperature and the white solids collected from the cold finger. Yield 0.133 g. ^1H NMR spectroscopic
25 analysis of these solids indicated a 1.5:1 mix of ADN to BPh_3 , and a small amount of a diphenylboron derivative. Yield of BPh_3 = 83%.

Example 2

2.0 g of Ni catalyst residue was heated to 210°C
30 at about 0.004 torr in a sublimier equipped with a dry ice cold finger. After 1 day the the temperature was increased to about 230°C for several hours. After cooling the apparatus to room temperature, 1.192 g of a white solid was collected from the cold finger and analyzed by ^1H NMR
35 spectroscopy. The sample contained a mixture of BPh_3 and adiponitrile in a ratio of 1.0:1.1, and a small amount of a diphenylboron derivative. Yield of BPh_3 = 71%.

Example 3

5.0 g of Ni catalyst residue was placed in a

ceramic boat 1, inside a glass tube 2, as shown the figure. The pressure inside the system was reduced to about 20 torr while a nitrogen stream 4, was passed over the catalyst residue at a rate of about 200 ml/min. The tube was heated at 190°C for about 5 hours and the volatile products collected in the dry ice trap 3. 3.4 g of a pale yellow solid was collected from the trap. 1H NMR spectroscopic analysis of the product indicated a mixture of BPh₃ and ADN that was 65% by weight BPh₃.

Hydrocyanation Performance Of BPh₃ Obtained from Degraded Catalyst.

Evaluation of the material containing triphenylboron recovered from degraded hydrocyanation catalyst in the manner described above for hydrocyanation activity was performed in a single-stage, 22-ml glass continuous stirred-tank reactor. U.S. Patent 4,874,884, which is incorporated herein by reference, describes the use of continuous stirred-tank reactor to evaluate promoter performance. The steady-state conditions for the continuous hydrocyanation were as follows:

Reaction rate = 1.0×10^{-4} moles ADN / liter-second

20% conversion of 3PN

0.1 moles of Ni(TTP)₄ catalyst / mole HCN fed

(where TTP refers to tritolyphosphite) 0.12 moles of TTP / mole HCN fed

0.0065 moles of BPh₃ / mole HCN fed

Temperature = 40°C

The reactor was initially charged with a 3PN solution containing 24 wt.% Ni(TTP)₄ catalyst, 6.3 % TTP, and 0.28 % BPh₃. The steady-state conditions were achieved by pumping the following solutions in a continuous fashion for 41 hours:

Reagent	Feed Rate
25 wt.% HCN in 3PN	0.88 g/hr.
2.24 % BPh ₃ in 3PN	0.57 g/hr.
35 % TTP in 3PN	0.66 g/hr.
51 % Ni(TTP) ₄ , 3.7 % TTP in 3PN	2.39 g/hr.
3PN	0.80 g/hr.

The BPh₃ promoter solution was made with 52.0 g 3PN and 2.1 g of sublimed material, recovered from degraded Ni catalyst in the manner described in Example 2. Analysis of the solution by liquid chromatography showed
 5 that the solution contained 2.24 wt.% BPh₃.

The reactor product was collected from the reactor overflow for analysis by gas chromatography. The reaction of a given promoter can be characterized by the yields and selectivities shown below. The results shown are averaged
 10 over samples taken at 17 to 41 hours from the inception of continuous flow. As a comparison, the results are also shown for a continuous hydrocyanation under the same conditions, except for the use of BPh₃ purchased on the commercial market as the promoter.

15	Recovered BPh ₃	Purchased	BPh ₃
	ADN Yield	92.6 %	92.9 %
	Linearity	96.2 %	96.3 %
	2PN Yield	3.7 %	3.6 %
	VN Yield	0.04 %	0.04 %

20 Definitions:

Conversion = moles reacted / moles fed

VN = Valeronitrile

2PN = 2-Pentenitrile

MGN = Methylglutaronitrile

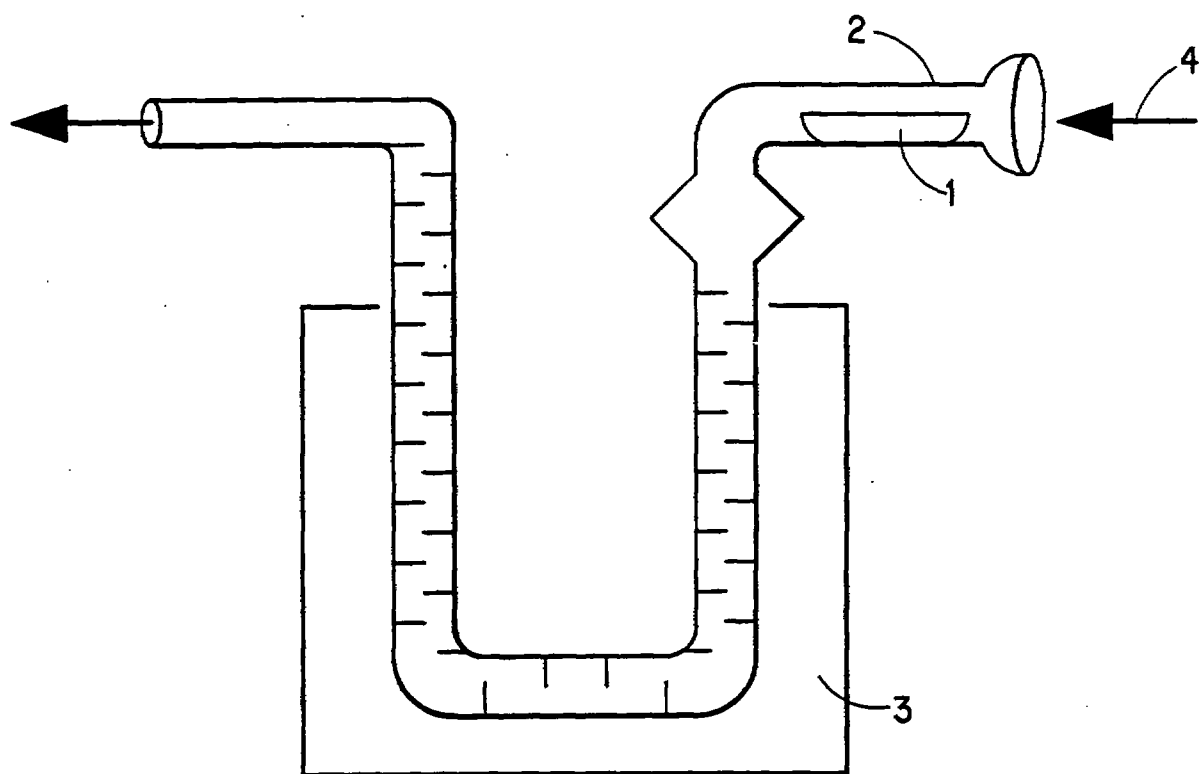
25 ESN = Ethylsuccinonitrile

ADN (2PN/VN) Yield = moles ADN (2PN/VN) produced
 moles 3PN reacted

Linearity = moles ADN / moles ADN + MGN + ESN.

WHAT IS CLAIMED IS:

1. A process for the manufacture of a triarylborane having the formula: BAr_3 where Ar is phenyl
5 or phenyl substituted with an alkyl group having 1 to 4 carbon atoms where the alkyl group may be fluorinated, which comprises heating a complex of the formula:
 $Ni(NC(CH_2)_4CN)_2(NCBAr_3)_2$ where Ar is as previously defined, in an inert atmosphere at a pressure less than
10 atmospheric to a temperature in the range of 120 degrees C to 300 degrees C; thus forming a vapor containing the triarylborane, and condensing triarylborane from the vapor.
2. The process of claim 1 in which an inert gas
15 stream moves the vapor containing triarylborane to a zone where the triarylborane is condensed.
3. The process of claim 1 in which the complex is contained in catalyst residue.
4. The process of claim 1 in which Ar is phenyl.



FIGURE



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(21) International Application Number: PCT/US95/07127 (22) International Filing Date: 19 June 1995 (19.06.95) (30) Priority Data: 08/264,275 23 June 1994 (23.06.94) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: CASALNUOVO, Albert, Loren; 208 Dakota Avenue, Wilmington, DE 19803-3218 (US). FOO, Thomas; Apartment 2-A-3, 402 Foulk Road, Wilmington, DE 19803-3936 (US). (74) Agents: HANDLEY, Earl, L. et al.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: CN, JP, KR, MX, SG, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.
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