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Chemical Synthesis with Metal Atoms. Cyclodimerization of Norbornadiene via Nickela-cyclopentane Intermediates.

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### Summary

The catalytic cyclodimerization of norbornadiene by reaction with nickel atoms has been re-investigated. Nickela-cyclopentane derivatives are formed in the presence of  $\alpha, \alpha'$ -dipyridyl,  $\alpha, \alpha'$ -dipyridyl-*exo-trans-endo*-3-nickela-pentacyclo[9.2.1.1<sup>5,8</sup>.0<sup>2,10</sup>.0<sup>4,9</sup>]-pentadeca-6,12-diene being the major component. By contrast, the catalytic dimerization leads predominantly to the *exo-trans-exo* isomer of pentacyclo[8.2.1.1<sup>4,7</sup>.0<sup>2,9</sup>.0<sup>3,8</sup>] tetradeca-5,11-diene. A norbornadiene cyclotrimer of *exo-trans-exo-trans-exo* structure is subsequently formed.

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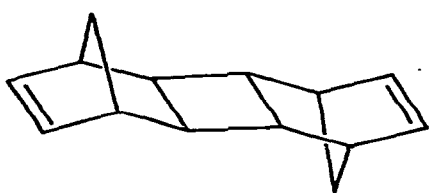
## Introduction

Our interest in metal-assisted olefin coupling *via* bis-(olefin)metal complexes and metalla-cyclopentanes<sup>1-3</sup> led us to re-investigate the reaction of nickel atoms with norbornadiene, which was reported by Skell *et al.*<sup>4</sup> to yield predominantly the *exo-trans-exo* cyclodimer 1. On the other hand, Binger *et al.*<sup>5</sup> obtained the nickela-cyclopentane derivative 4 with *exo-trans-endo* geometry from the reaction of (1,5-cyclooctadiene) ( $\alpha, \alpha'$ -dipyridyl)nickel with norbornadiene. Reductive elimination of the metal gave the corresponding *exo-trans-endo* norbornadiene cyclodimer 2 along with traces of other isomers.

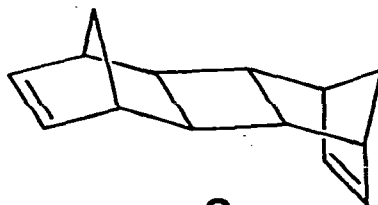
## Results and discussion

Norbornadiene, when co-condensed with nickel atoms at liquid nitrogen temperature and subsequently allowed to warm up to room temperature, was catalytically cyclodimerized to yield pentacyclo[8.2.1.1<sup>4,7</sup>.0<sup>2,9</sup>.0<sup>3,8</sup>]tetradeca-5,11-diene.

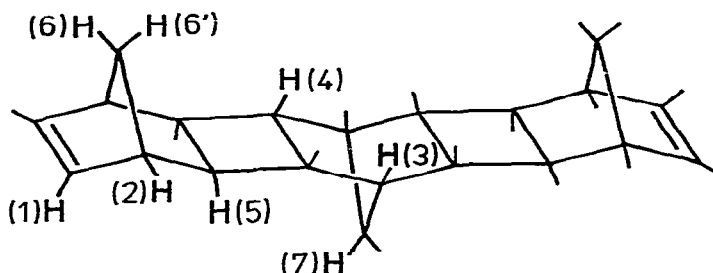
The *exo-trans-exo* (1) and *exo-trans-endo* (2) isomers were obtained in the ratio *ca.* 13:1 and identified on the basis of the <sup>1</sup>H n.m.r. spectra<sup>6</sup>. In addition to small amounts of other cyclodimer isomers, several cyclotrimers were formed among which the *exo-trans-exo-trans-exo*-octacyclo[14.2.1.-1<sup>4,13</sup>.1<sup>7,10</sup>.0<sup>2,15</sup>.0<sup>3,14</sup>.0<sup>5,12</sup>.0<sup>6,11</sup>]heneicoso-8,17-diene (3) was the major component. The <sup>1</sup>H n.m.r. spectrum of 3 indicates the symmetry of the molecule, and comparison with the spectra of the cyclodimers<sup>6</sup> led to the detailed structural assignment.



1



2



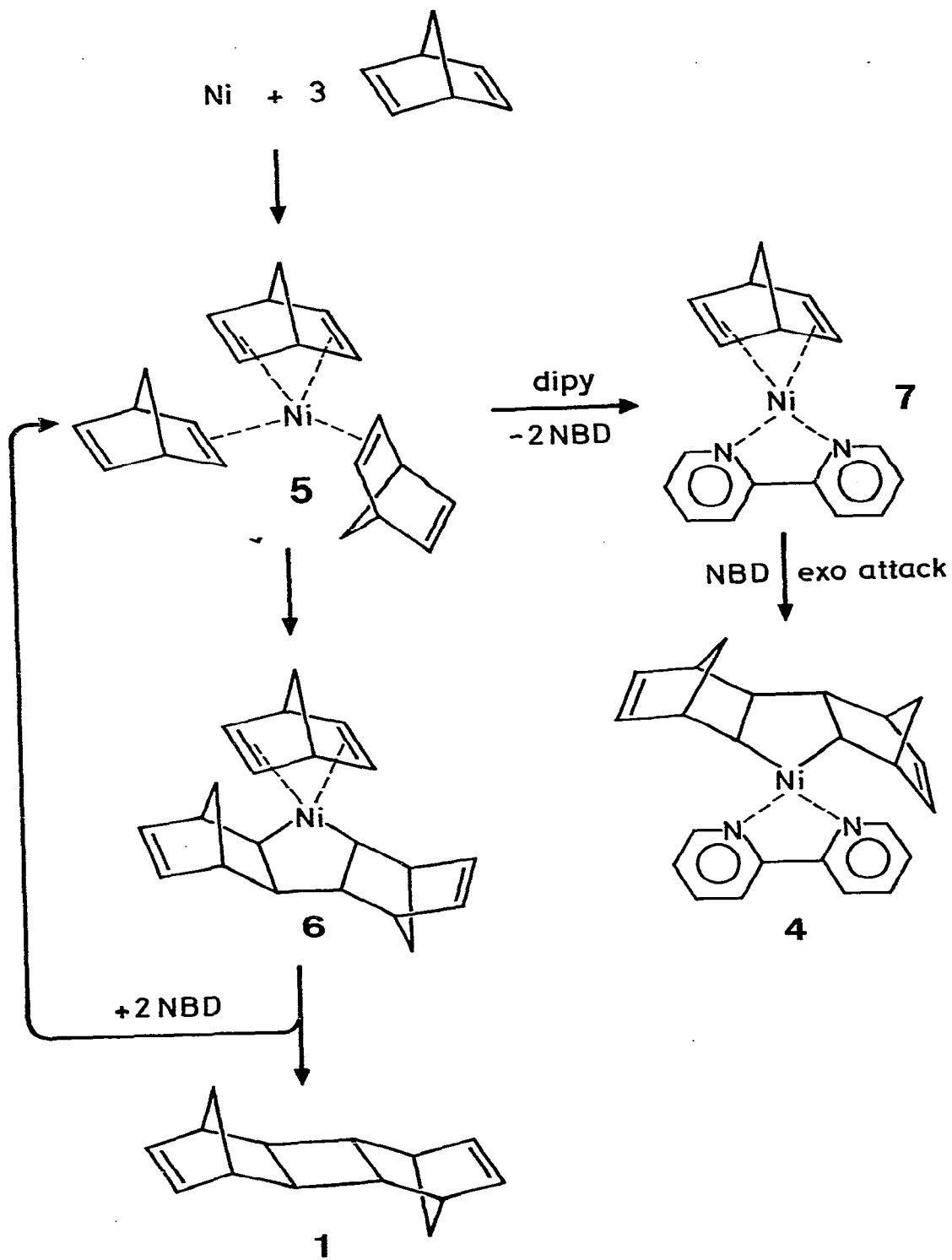
3

H	(1)	(2)	(3)	(4)	(5)	(6)	(6')	(7)	$J(6,6')=8\text{Hz}$
$\delta$	5.83	2.56	1.90	1.37	1.28	1.19	1.73	1.72	

(in  $\text{CCl}_4/\text{C}_6\text{D}_6 \sim 3:1$ )

The catalytic species in the norbornadiene/nickel system proved to be highly active. For example 0.65 mol of norbornadiene was completely consumed in the presence of 0.01 mol of nickel within 3.5 h. During this time the temperature of the reaction mixture rose gradually to 50-60°C without external heating. At this point the system was still catalytically active, and an additional 2.3 mol of norbornadiene was subsequently dimerized over a period of 18.5 h. This total turnover number of ca. 300 in the above reaction does not appear to be the upper limit. UV-vis irradiation did not significantly affect the catalysis, except that the formation of dimer and trimer isomers as by-products increased slightly.

After a similar co-condensation of nickel atoms and norbornadiene in a toluene matrix the mixture was warmed to -78°C.



Upon addition of  $\alpha,\alpha'$ -dipyridyl the brown toluene solution immediately turned dark green. After warming up to room temperature ( $\alpha,\alpha'$ -dipyridyl)-3-nickela-pentacyclo[9.2.1.1<sup>5,8</sup>.0<sup>2,10</sup>.0<sup>4,9</sup>]pentadeca-6,12-diene was isolated as a dark green solid. The complex was shown, by comparison of the <sup>1</sup>H n.m.r. spectrum with that of an authentic sample<sup>7</sup>, to have the *exo-trans-endo* structure 4, contaminated with a small amount of the *exo-trans-exo* isomer. Oxidative degradation of complex 4 with air or thermal decomposition yielded norbornadiene dimers, predominantly the *exo-trans-endo* isomer 2, in agreement with the results of Binger *et al.*<sup>5,7</sup>.

Obviously the isolated dipyridyl stabilized complex does not represent the intermediate in the major pathway of the catalytic cycle, which might be explained in the following simplified scheme. Coordination of the metal occurs preferentially at the less hindered *exo* side of norbornadiene<sup>6</sup> whereas chelated *endo*- $\eta^4$ -coordinated norbornadiene should be thermodynamically favoured. A plausible intermediate based on these considerations is str.5, which represents both of these coordination modes. Retention of the more stable (*endo*- $\eta^4$ -norbornadiene)-nickel moiety throughout the catalytic cycle would account for the preferential formation of the *exo-trans-exo* cyclodimer. The proposed metalla-cycle intermediate 6 parallels the norbornadiene derived *exo-trans-exo* irido-cycle reported by Osborn *et al.*<sup>8</sup>. Upon addition of dipyridyl, on the other hand, the *exo*- $\eta^2$ -norbornadiene ligands should be preferentially displaced leading to 7. Subsequent attack of a second norbornadiene would occur from its *exo* side, and finally result in formation of the *exo-trans-endo* nickela-cycle 4. Thus, the above-mentioned discrepancy can be understood in terms of the straight forward ordering of norbornadiene complex stabilities. Note-

worthy, the dimerization of norbornadiene catalyzed by 4 at 90°C<sup>5</sup> yields predominantly<sup>7</sup> the *exo-trans-exo* cyclodimer 1, i.e. *exo* coordination is favoured in the catalytic cycle after the original metalla-cycle is lost. Not surprisingly in view of the high temperature, the stereospecificity is reduced to some extent. Although the yields of the other cyclodimers increase at the expense of 2, the latter is still the major product.<sup>7</sup> These observations should aid in the explanation of the stereochemistry of other norbornadiene dimerization reactions and point out again that species trapped from catalytic reactions are not necessarily involved in the catalytic cycle.

### Experimental

Metal evaporation was performed as described previously<sup>9</sup> using resistive heating. Handling and work-up of metal complexes were carried out under argon. <sup>1</sup>H n.m.r. and mass spectra were recorded using Bruker WH 270 and Varian MAT CH 5 spectrometers, respectively. Elemental analysis was performed by Dornis & Kolbe, Mülheim a.d. Ruhr.

Nickel powder (99.8 %) was purchased from Ventron/Alfa Products, norbornadiene (99.8 %, Merck) was used as received, and analytical grade solvents were distilled from LiAlH<sub>4</sub> under argon.

### Reaction of nickel atoms with neat norbornadiene

Norbornadiene (100 ml) and nickel (according to the geometry of the evaporation vessel 30 % of the metal can be estimated to be lost to the non-cooled parts of the apparatus; thus 0.55 g (9.5 mmol) of the evaporated metal was available for chemical

reactions) were co-condensed onto the liquid nitrogen cooled walls of the evaporation vessel during 20 min ( $\leq 4 \times 10^{-5}$  torr; alumina crucible in a tungsten coil; 95 A, 14 V). After removal of the liquid nitrogen from the cooling jacket, a fraction of the molten reaction mixture (60 g norbornadiene, 0.65 mol) were collected and allowed to warm up to room temperature. The reddish-brown mixture was stirred for 3.5 h until it became solid; without external heating the temperature increased and was kept at  $\leq 60^{\circ}\text{C}$  by occasional cooling. Additional norbornadiene (214.4 g, 2.33 mol) was introduced, and stirring continued at  $\leq 60^{\circ}\text{C}$  for 18.5 h. A sample of the solid reaction mixture (275 g) was dissolved in benzene and analyzed by gas chromatography (Varian 1400, 50 m glass capillary column, silicon fluor phase SF 96,  $90 \rightarrow 230^{\circ}\text{C}$ ,  $4^{\circ}\text{C}/\text{min}$ , carrier gas  $\text{H}_2$  0.7 bar, FID): 1 (80.5 %), 2 (6.7 %), other cyclodimers (0.5 %), 3 (10.6 %), and other cyclotrimers (1.3 %). - Samples of 1, 2, and 3 were isolated by the following procedure. Dissolution of the reaction mixture in n-hexane gave a turbid solution which was filtered and cooled to  $-70^{\circ}\text{C}$  whereupon fine white crystals of 3 precipitated, m.p.  $210^{\circ}\text{C}$ . The mass spectrum of 3 indicated contamination with a small amount of norbornadiene tetramer and showed the molecular ion of 3 ( $m/e$  276) and other prominent peaks at  $m/e$  210, 197, 181, 169, 157, 144, 129, 117, 105, 91, 79, 66, 53, 39, and 27. The mother liquor was evaporated to dryness. Attempts to separate the products by column chromatography (silica gel 0.04-0.06 mm Merck 60; ether, benzene or hexane-benzene) were unsuccessful. Preparative gas chromatography (Hupe & Busch APG 402, modified version <sup>10</sup>; 0.5 ml per cycle; column 9 m,  $\phi$  10 mm, XE 60 10 % on chromosorb P,  $140^{\circ}\text{C}$ , 3.7 bar  $\text{N}_2$ , 230 ml/min) afforded 1 (purity 99.4 %) and 2 (purity 71.9 %).

Preparation of complex **4** from co-condensed nickel atoms and norbornadiene by reaction with  $\alpha,\alpha'$ -dipyridyl

Norbornadiene (50 ml) and nickel (1.24 g; 0.87 g estimated to be available for the reaction, 0.015 mol) were co-condensed in a toluene matrix (200 ml) during 45 min. After warming up to  $-78^{\circ}\text{C}$   $\alpha,\alpha'$ -dipyridyl (1.5 g) was added, and the reaction mixture was allowed to warm up to room temperature. The solution was passed through a 3 x 9 cm column of Florisil (Merck), and the absorbed green band was eluted with ether. Evaporation of the solvent gave a dark green solid material which, according to the  $^1\text{H}$  n.m.r. spectrum, contained some  $\alpha,\alpha'$ -dipyridyl in addition to the *exo-trans-endo* complex **4**<sup>7</sup> and a trace amount of the *exo-trans-exo* complex<sup>7</sup>. The yield of the complexes was calculated from the  $^1\text{H}$  n.m.r. spectrum to be 8.6 %. - From an analogous experiment a sample of **4** was purified by sublimation of  $\alpha,\alpha'$ -dipyridyl and norbornadiene dimers, chromatography and recrystallization of the residue from toluene/hexane. Elemental analysis: Found C, 71.56; H, 6.05; N, 7.21; Ni, 15.15.  $\text{C}_{24}\text{H}_{24}\text{N}_2\text{Ni}$  requires C, 72.21; H, 6.06; N, 7.02; Ni, 14.72 %. The mass spectrum shows the molecular ion [ $m/e$  398(Ni<sub>1</sub>)] and other prominent peaks at 358, 242 (P - dipy), 214 [(dipy)Ni], 184 P - Ni-dipy), 156(dipy), 128, 117, 91, 78, 66, 51, and 39.

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