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METALLACYCLOALKANES

II *. REACTIONS OF α,α'-BIPYRIDYL-5-NICKELA-3,3,7,7-TETRAMETHYL-*trans*-TRICYCLO[4.1.0.0^{2,4}]HEPTANE

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Summary

The title compound (II) underwent reductive elimination on treatment with maleic anhydride, tetracyanoethylene or triphenylphosphite to give 3,3,6,6-tetramethyl-*trans*-tricyclo[3.1.0.0^{2,4}]hexane (III). With triphenylphosphite bi(2,2-dimethylcyclopropyl) (V) and 1-(2,2-dimethylcyclopropyl)-3-methyl-1,3-butadiene (VI) were also formed. Acidolysis of II with either HCl, malonic acid or methanol gave V. An intermediate complex α,α'-bipyridyl(phenoxy)-3-nickel-1,1'-bi(2,2'-dimethylcyclopropyl) (VIII) was isolated by reaction of II with phenol. Methylene dibromide reacts with II to give III and 3,3,7,7-tetramethyl-*trans*-tricyclo[4.1.0.0^{2,4}]heptane (IV). With triethylaluminum and II complete exchange of the alkyl groups occurred and V was released on hydrolysis. Trifluoroborane diethyl ether and II gave 3,3,6,6-tetramethylcyclohexa-1,4-diene in a rearrangement-displacement reaction. The cyclodimerisation of 3,3-dimethylcyclopropene (I) to III catalysed by II and the fact that II can be recovered from the reaction mixture provides strong evidence for the intermediacy of metallacyclopentanes in these transition-metal-catalysed [2π + 2π] cyclo-additions.

Introduction

3,3-Dimethylcyclopropene (I) is smoothly cyclodimerised at room temperature to 3,3,6,6-tetramethyl-*trans*-tricyclo[3.1.0.0^{2,4}]hexane (III) by catalytic amounts of phosphane-modified nickel(0) complexes [2]. With α,α'-bipyridyl-(1,5-cyclooctadiene)nickel(0), however, under the same conditions a stoichio-

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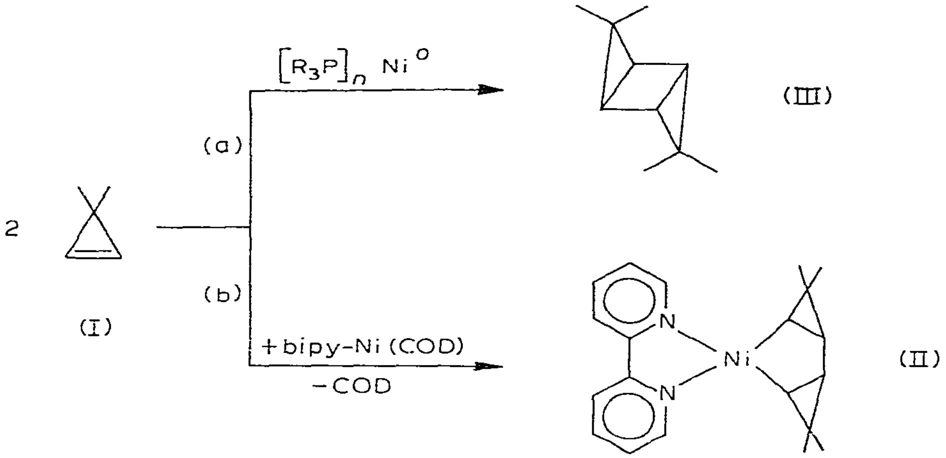
[*] For part 1 see ref. 1.

metric reaction takes place to give α,α′-bipyridyl-5-nickela-3,3,7,7-tetramethyl-*trans*-tricyclo[4.1.0.$0^{2,4}$]heptane (II) in high yield [1] (eq.1). This latter reac-



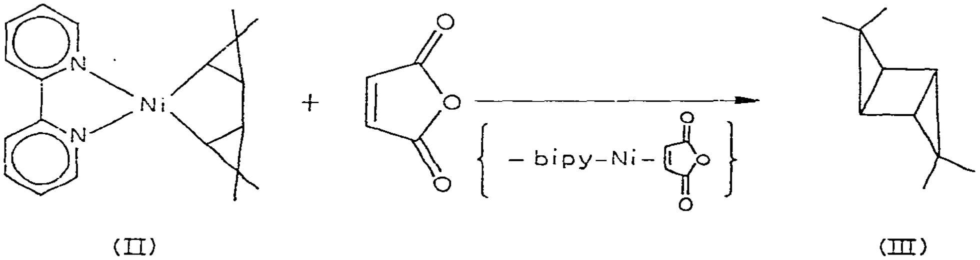
(1)

tion is one of the few examples which are known where two monoolefins undergo oxidative cyclo-coupling to a transition-metal centre forming an isolable metallacyclopentane derivative [3a—d]. The formation of II according to eq. 1b also suggests that analogous metallacyclopentanes are intermediates in the transition-metal-catalysed cyclodimerisation [2] (eq. 1a) or cyclotrimerisation [4] of I. A main objection to this hypothesis is that the hitherto isolated metallacyclopentanes are inactive as catalysts for these reactions [5].

With this in mind, we investigated the reductive eliminations occurring at II with π-acceptor olefins or I itself to give the cyclodimer III (preliminary report see lit. 3b). The reactions of II with Lewis acids, Lewis bases and dibromomethane are also described.

Reactions of compound II

It is well established that α,α′-bipyridyldialkylnickel compounds react with π-acceptors, e.g. methylacrylate, acrylonitrile, maleic anhydride, etc., under mild conditions to give α,α′-bipyridyl(olefin)nickel(0) complexes and the coupling product of the two alkyl ligands [6]. We found that II reacts with maleic anhydride or tetracyanoethylene at 25° C releasing III in yields of 96 and 60%, respectively.

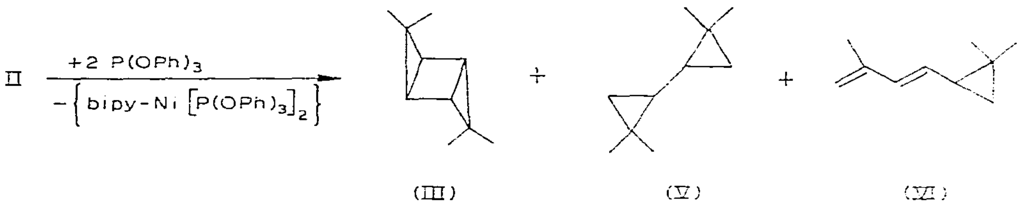


(2)

Methylacrylate or acrylonitrile do not react under the same conditions;

heating results in polymerisation of these olefins and III is not detected among the reaction products.

Also triphenylphosphine, triphenylphosphite or carbon monoxide do not react with II at room temperature. At 60° C, however, triphenylphosphite displaces the hydrocarbon function of II in a slow reaction to give a mixture of three hydrocarbons. Besides the normal reductive cyclo-coupling product III (3% yield) bi(2,2'-dimethylcyclopropyl) (V) and 1-(2,2-dimethylcyclopropyl)-3-methyl-1,3-butadiene (VI) are obtained in 6 and 15% yield, respectively.



(3)

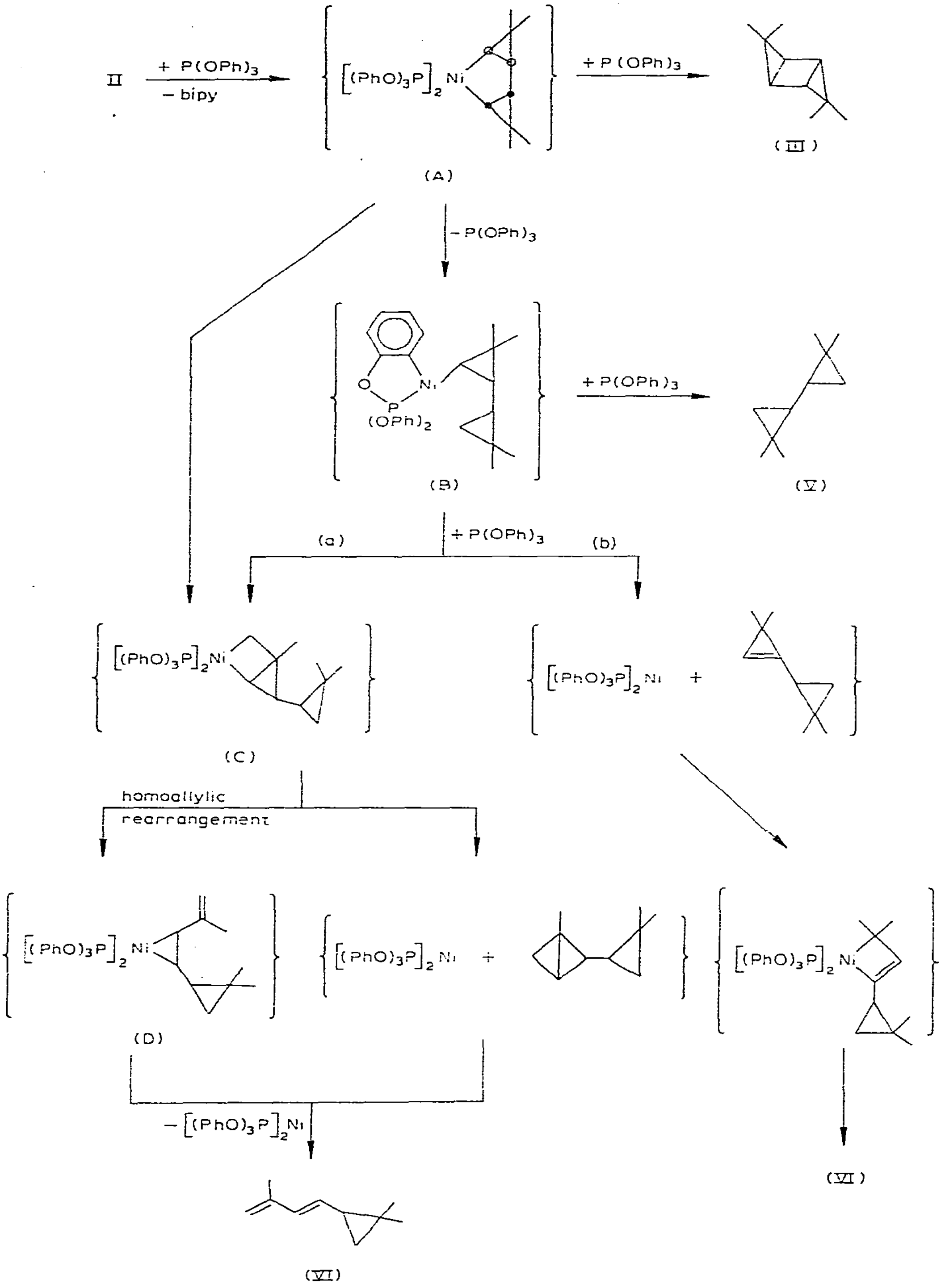
The formation of V and especially VI cannot be explained on the basis of the isolated hydrocarbons alone. Therefore a speculative pathway is outlined in Scheme 1. We assume an initial displacement of α,α'-bipyridyl from II by the phosphite ligands to give A followed by an *ortho*-metallation of an aromatic ring and hydrogen transfer forming a 3-nickel-1,1'-bi(2,2'-dimethylcyclopropyl) species(B). V may be generated from B by a second *ortho*-metallation/hydrogen transfer step. At least two possibilities exist to explain the formation of VI from B outlined in Scheme 1 as pathway a and b. Although pathway a involves an unprecedented γ-hydrogen elimination it is considered a more plausible alternative to the β-hydrogen elimination in B (way b) as this β-hydrogen is directed away from nickel whereas the γ-hydrogen of one methyl group is directed toward the metal.

II reacts with dibromomethane readily at room temperature to give III and the cyclopentane derivative IV in 10 and 47% yield, respectively. As shown in Scheme 2 two related mechanisms appear to be responsible for the formation of III and IV. Nickel complexes of type E also seem to be important in the preparation of cycloalkanes from α,ω-dibromoalkanes, $Ni(COD)_2$ and α,α'-bipyridyl [8].

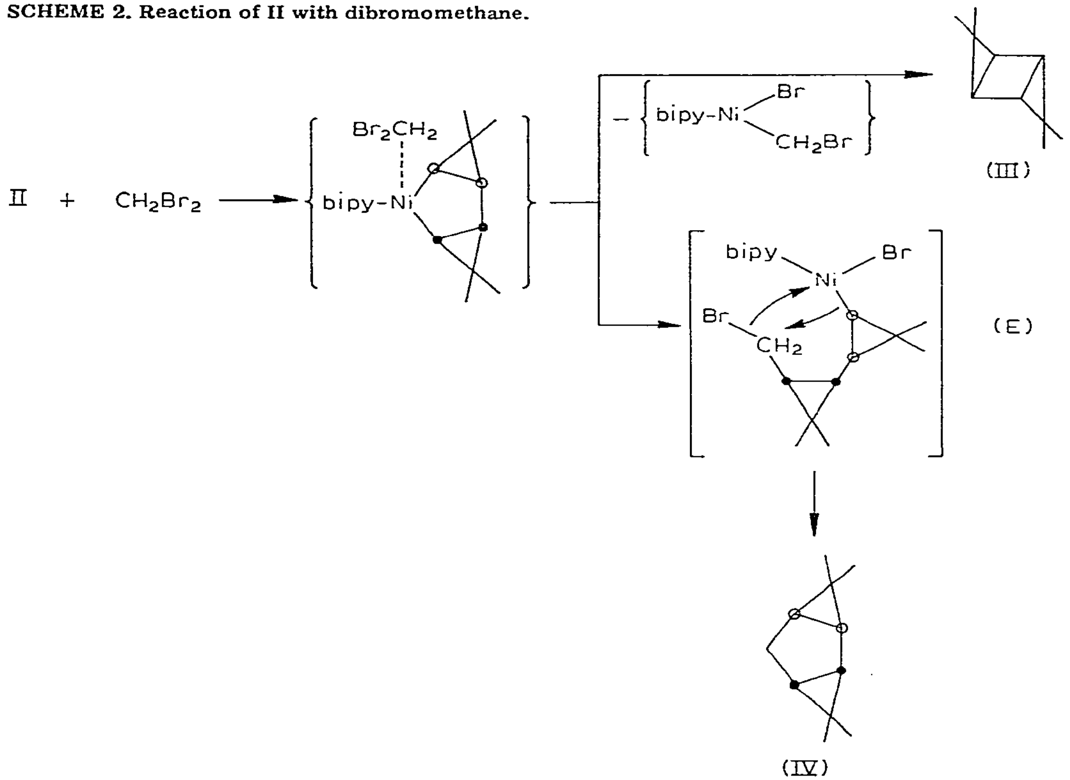
To study the behaviour of a cyclopentanenickel species, free of stabilising ligands, we tried to displace α,α'-bipyridyl from II by treatment with strong Lewis acids, such as triethylaluminium or trifluoroborane diethyl ether. These reactions should follow an analogous path as the interaction of these Lewis acids with α,α'-bipyridyldimethylnickel, where mainly methane and ethane are formed in the course of the decomposition of dimethylnickel [9]. Therefore III or bi(2,2-dimethylcyclopropyl) (V) is expected to be eliminated from II.

Triethylaluminium reacts with II rapidly at room temperature in a molar ratio of 2/1. Nickel is deposited and two mol equivalents of a mixture of ethane (70%) and ethylene (30%) are evolved. After distillation of the reaction mixture no trace of the hydrocarbon ligand could be detected in the distillate. This is found as V in 82% yield after addition of ethanol to the residue and usual workup. It is therefore apparent that the $C_{10}H_{16}$ group has been bonded to aluminium. Obviously the most rapid reaction between II and triethylaluminium

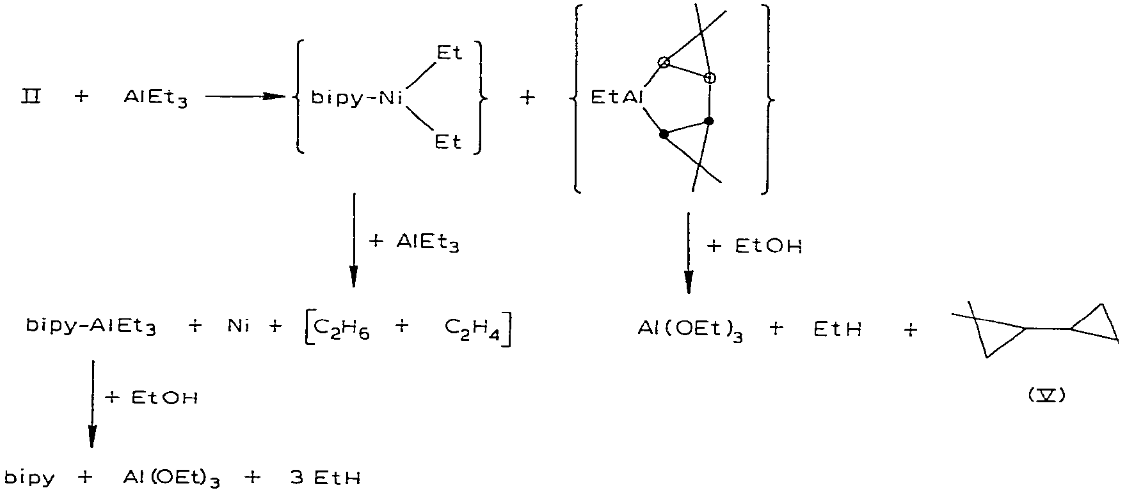
SCHEME 1. Possible formation of III, V and VI from II and triphenylphosphite.



SCHEME 2. Reaction of II with dibromomethane.



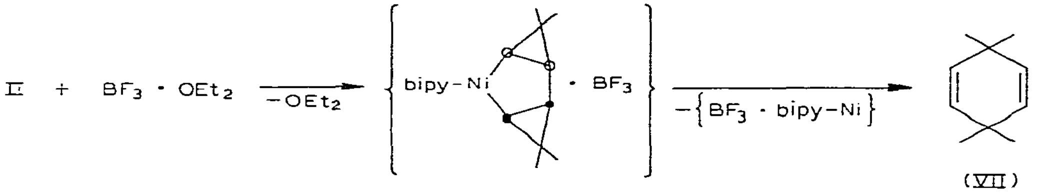
SCHEME 3. Reaction of triethylaluminium with II.



is a nearly quantitative exchange of the alkyl groups (see Scheme 3).

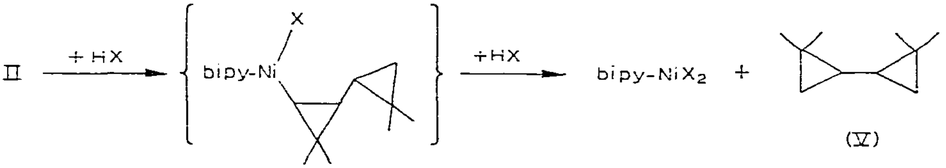
Although aluminacyclopentanes are known [10] the experimental data do not allow comment as to whether the $C_{10}H_8$ group is bonded to one or to two aluminium atoms.

Treatment of II with an excess of trifluoroborane diethyl ether at 25°C leads to only a slight change in appearance of the initially dark green suspension after several days. Nevertheless, during this time a reaction has occurred as is shown by the formation of 3,3,6,6-tetramethyl-1,4-cyclohexadiene (VII) in 68% yield. Trifluoroborane diethyl ether apparently does not displace α,α'-bipyridyl from II as no metallic nickel is deposited during the reaction; this indicates that VII is not a decomposition product of a ligand-free nickelacyclopentane species. Since bipyridyl(1,5-cyclooctadiene)nickel as well as trifluoroborane diethyl ether [10] or a mixture of both failed to rearrange pure III to VII under the same conditions it is likely that both rearrangement and elimination to VII occur at the metal (eq. 4). The combination of reactions 1b and 4 has the characteristics of olefin metathesis.



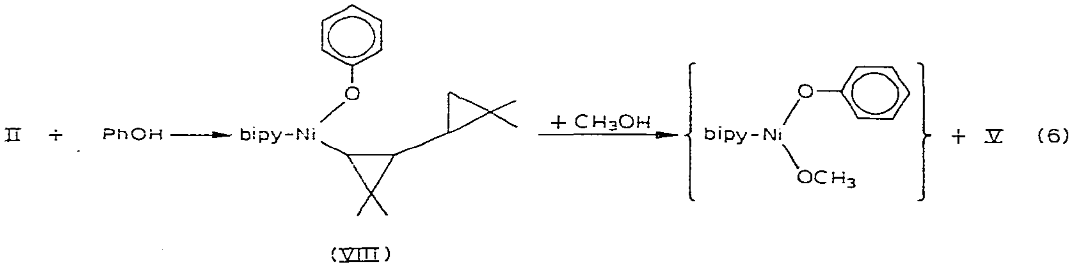
(4)

In analogy to the reaction of α,α'-bipyridyldiethylnickel with ethanol [12, 13] II reacts with compounds having an acidic hydrogen. These acidolyses occur smoothly at room temperature with e.g. an ether solution of hydrogen chloride, methanol or with malonic acid; however, under these conditions ethanol does not react. Bi(2,2-dimethylcyclopropyl) (V) is formed as the only product in high yields. A colour change from dark green to red and back to green again in all these reactions indicates a two-step mechanism as shown in eq. 5. This formulation was substantiated by isolation of the nickel complex VIII in 77% yield from the reaction between II and phenol.



(5)

(X = Cl ; OCH_3 ; $O_2CCH_2CO_2H$)



(6)

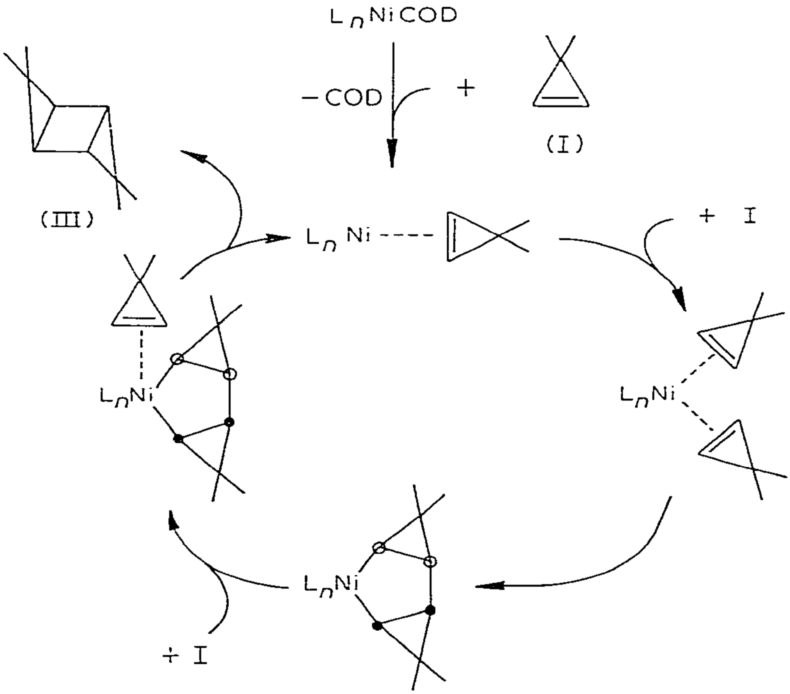
The isolated pure VIII is deep red and crystalline. It decomposes on heating to 100° C in an inert atmosphere. The analytical data (see Experimental) are in full agreement with the postulated structure. It reacts smoothly with methanol at 25° C giving V in ca. 70% yield (eq. 6).

II as intermediate in the catalytic cyclodimerisation of I

Formation of II from α,α'-bipyridyl(1,5-cyclooctadiene)nickel and I (eq. 1b) and its reductive elimination to III by activated olefins (eq. 2) indicate that metallacycles analogous to II can be important in the catalysed cyclooligomerisation of I. Strong evidence for the intermediacy of metallacyclopentanes like II in the catalytic cyclodimerisation is now furnished by the displacement of III from II by I. In this reaction II is regenerated (see Scheme 4, L_n = bipy). Thus, in the presence of the stabilised nickelacyclopentane II (1 mol %) I undergoes a 70% conversion to oligomers after 3 h at 90° C, 27% being the cyclodimer III representing a turnover of about 9. Further, the cyclotrimer hexamethyl-*trans*-tris-σ-homobenzene is formed in 6% yield together with an oily non-distillable dark green residue from which it was not possible to isolate II in a pure form. When this catalysis is carried out at 50° C after 3 h about three catalytic cycles to cyclodimer III have occurred. II can be isolated in ca. 40% yield from the reaction mixture.

On the basis of these observations we propose the catalytic cycle shown in Scheme 4 for the nickel-catalysed formation of III from I. A significant feature of this cycle is that the substrate behaves as an activator for the displacement of III from the metallacyclopentane. This is indicated by the observation that no III was displaced from II when II was heated alone in toluene for 24 h under the conditions of the catalytic reaction.

SCHEME 4. The proposed course of the catalytic cyclodimerisation of I.



Isolation and identification of the reaction products

In the above described reactions of the title compound II with the exception of complex VIII we isolated and characterised only the hydrocarbon parts III—VII of the products. Since these hydrocarbons were found as diluted solutions and in small amounts, their purifications were achieved by preparative GLC *. For comparison we had in hand larger amounts of III from the catalytic cyclodimerisation of I [2] and VII from the thermal rearrangement of III [14].

The hydrocarbons III-VII were characterised by physical methods. The molecular weights were determined by mass spectroscopy. The spectra are reported in the experimental part. Unambiguous proof of their structures was achieved mainly by their ^{1}H NMR spectra. These are given in Table 1. The ^{13}C NMR spectra of III, V and VI are in full agreement with these structures (see Experimental).

III is a fully symmetric molecule. Therefore no coupling between the ring protons is observed in its ^{1}H NMR spectrum. In the ^{1}H NMR spectrum of IV no coupling is found between the ring protons 4 and 4'. This indicates an angle of nearly 90° between these two protons and therefore the *trans*-configuration of IV.

Experimental

General

All manipulations involving nickel complexes were carried out in oxygen-free, rigorously dried solvents under an atmosphere of high purity argon.

IR spectra of nickel complexes were measured in KBr discs with a Perkin—Elmer—521 spectrophotometer **. ^{1}H NMR spectra were obtained on Varian Associates A60 and HA100 spectrometers, or taken in the FT mode on Bruker WP60 and WH90 spectrometers. ^{13}C NMR spectra were measured with a Varian XL 100 spectrometer operating at 25.2 MHz in the FT mode; multiplicity of signals was determined from single-frequency off-resonance decoupling. Mass spectra (MS) of hydrocarbons and nickel complexes were measured on Varian CH4 and CH5 spectrometers, respectively; the former was used for GC/MS combination measurements. Reported MS spectra include the parent molecular ion with all peaks of intensity >10%. GC determinations were made with a Varian Aerograph Series 1400 gas chromatograph using a 100 meter glass capillary column coated with a squalane stationary phase. The column was maintained at 70° C with a helium gas flow at 1.5 bar. Preparative GC separations were achieved with a Hewlett—Packard F&M gas chromatograph using a silicon SF-96 Chromosorb-coated stationary phase 3 m packed column maintained at 100° C with a helium gas flow rate of 75 ml per minute. Microanalytical data for C, H and N were provided by Dornis und Kolbe, 4330 Mülheim a.d. Ruhr, W. Germany, and for Ni at these laboratories by X-ray fluorescence.

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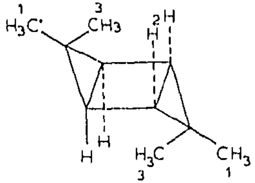
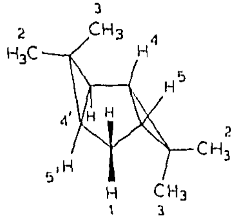
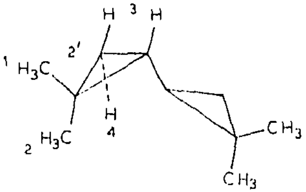
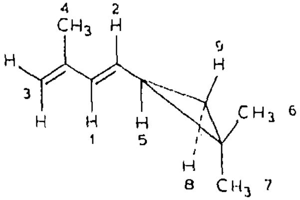
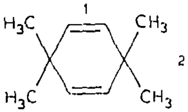
** NMR, IR and mass spectra were recorded at the Max-Planck-Institut für Kohlenforschung, 4330 Mülheim a.d. Ruhr, by Drs. E.G. Hoffmann, K. Seevogel, R.J. Mynott and D. Henneberg, respectively; the GC determinations were done by Dr. G. Schomburg and the Ni determinations were carried out by Dr. C. Krüger and K.H. Claus at the same institute.

TABLE 1. ^{1}H NMR DATA OF THE ISOLATED HYDROCARBONS III–VII

Assignment		Chemical shift [a] (τ, ppm), multiplicity and coupling constants (^{1}H—^{1}H) (Hz)
	(III)	1: 8.88 (s, 6H); 2: 9.00 (s, 4H); 3: 9.21 (s, 6H)
	(IV)	1: 8.37 (t, $J_{1,5}$ 3.4 Hz, 2H); 2: 9.03 (s, 6H); 3: 9.18 (s, 6H); 4: 9.19 (d, $J_{4,5}$ 6.5 Hz, 2H); 5: 9.47 (dt, $J_{4,5}$ 6.5 Hz, $J_{1,5}$ 3.4 Hz, 2H)
	(V)	1: 9.03 (s, 6H); 2: 9.08 (s, 6H); 3: 9.71 (s, W 3 Hz, 4H); 4: 10.10 (s, W 4 Hz, 2H)
	(VI)	1: 3.89 (d, $J_{1,2}$ 15.5 Hz, 1H); 2: 4.72 (dd, $J_{1,2}$ 15.5 Hz, $J_{2,5}$ 8.5 Hz, 1H); 3: 5.26 (s, W 6 Hz, 2H); 4: 8.30 (s, 3H); 5: 8.83 (ddd, $J_{2,5} = J_{5,8} = 8.5$ Hz; $J_{5,9}$ 5.5 Hz, 1H); 6: 9.02 (s, 3H); 7: 9.03 (s, 3H); 8: 9.42 (dd, $J_{5,8}$ 8.5 Hz, $J_{8,9}$ 4 Hz, 1H); 9: 9.72 (t, $J_{5,9}$ 5.5 Hz, $J_{8,9}$ 4 Hz, 1H)
	(VII)	1: 4.71 (s, 4H); 2: 9.10 (s, 12H)

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[a] 100 MHz spectra of CCl_4 solutions relative to C_6H_6.

Reagents

Published procedures were used to prepare α,α′-bipyridyl-5-nickela-3,3,7,7-tetramethyl-*trans*-tricyclo[4.1.0.0^{2,4}]heptane [1] and 3,3-dimethylcyclopropene [15]. Methylacrylate, acrylonitrile, dibromomethane (Merck-Schuchardt) triethyl aluminium (Schering AG), and $BF_3 \cdot Et_2O$ (BASF) were distilled and stored under argon before use. α,α′-Bipyridyl (Merck AG), malonic acid, and tetracyanoethylene (Merck-Schuchardt) were stored under argon without further purification. Maleic anhydride (Merck-Schuchardt) was vacuum distilled, recrystallized from rigorously dried ether and stored under argon.

Reactions of α,α′-bipyridyl-5-nickela-3,3,7-7-tetramethyl-trans-tricyclo-[4.1.0.0^{2,4}]heptane (II)

With maleic anhydride. To a mixture of II (0.81 g, 2.3 mmol) and maleic anhydride (1.1 g, 10.9 mmol) was added toluene (2 ml). There was a rapid colour change from green to red-brown, accompanied by a slight increase in temperature. The mixture was stirred for 2 h at room temperature and the volatile material (2.1 g) collected at −196°C by distillation under vacuum (10^{-3} Torr, 25°C) (GC: 85.2% toluene, 14.6% III (0.30 g, 96.5% yield)].

Characterisation of III (after separation by preparative GC): MS (70 eV): *m/e* 136 (M^+, rel. int. 3%); 121 (100), 106 (14); 105 (47); 93 (39); 91 (42); 79 (44); 77 (33); 67 (10); 55 (11); 53 (11); 43 (14); 41 (29); 39 (23); 29 (12); 28 (20); 27 (21). ^{13}C NMR (C_6D_6 solution, ref. TMS): δ 16.13 (q); 23.34 (q); 28.83 (d); 35.90 ppm (s). ^1H NMR: see Table 1.

With tetracyanoethylene. To a mixture of II (0.53 g, 1.5 mmol) and tetracyanoethylene (1.12 g, 8.7 mmol) was added toluene (2.5 ml). The mixture was stirred at 23°C for 16 h. There was a gradual colour change from deep green to brown-red. The volatile material (2.53 g) was collected at −196°C by distillation at 23°C under vacuum (0.5 Torr) (GC: 94.8% toluene and 5.0% III (0.13 g, 63.7% yield)).

With methylacrylate, acrylonitrile, triphenylphosphine or carbon monoxide. To II was added a 15-fold excess of neat methylacrylate, acrylonitrile, or triphenylphosphine in toluene. The green suspension was stirred for 24 h at 25°C with no observable change in appearance. GC examination of the material volatile at 25°C and 0.5 Torr showed no presence of displaced hydrocarbons from II. Under the same conditions, a toluene solution of II was stirred for 24 h under an atmosphere of CO. No uptake of gas was observed.

With triphenylphosphite. To a stirred suspension of II (1.1 g, 3.2 mmol) in toluene (ca. 3 ml) was added triphenylphosphite (6 ml, ca. 20 mmol) at 25°C. No change in the dark-green colour was observed after 20 h. The mixture was then heated to 60°C and over 1 h the suspension acquired an olive-green colour. The volatile material (2.45 g) was collected under vacuum (10^{-3} Torr, 25°C) at −196°C (GC: 94.9% toluene, 1.1% V (0.2 mmol, 6.1% yield), 0.5% III (0.1 mmol, 3.0% yield), 2.6% VI (0.5 mmol, 14.5% yield)).

Characterisation of V (after purification by preparative GC). MS (70 eV): *m/e* 138 (M^+, rel. int. 3%); 95 (100); 82 (68); 81 (46); 79 (10); 69 (29); 67 (67); 55 (37); 53 (17); 42 (29); 41 (80); 40 (29); 27 (16); 25 (22). ^{13}C NMR (CCl_4 solution, C_6D_6 lock, TMS reference): δ 15.8 (s); 20.6 (apparent t); 20.9 (q); 24.7 (apparent d); 27.3 ppm (q). ^1H NMR: see Table 1.

Characterisation of VI (after purification by preparative GC). MS (70 eV): *m/e* 136 (M^+, rel. int. 25%); 121 (15); 107 (10); 105 (11); 94 (10); 93 (100); 92 (13); 91 (31); 80 (21); 79 (33); 77 (31); 55 (11); 53 (11); 43 (14); 41 (28); 39 (14); 29 (13). ^{1}H NMR: see Table 1.

With dibromomethane. At room temperature dibromomethane (3.5 ml, 50 mmol) was added to a suspension of II (1.96 g, 5.6 mmol) in toluene (4 ml) in one aliquot. An exothermic reaction ensued and the reaction temperature was maintained below +60° C by cooling in an ice bath. The colour of the suspension changed from dark green to pale yellow. The volatile material (8.61 g) was collected at —196° C by distillation under vacuum (0.5 Torr) at +60° C (GC: 68.2% dibromomethane, 26.3% toluene, 0.87% III (0.075 g, 9.8% yield), 4.12% IV (0.35 g, 46.5% yield)). A pale yellow, dry powder (2.3 g) remained.

Characterisation of IV (after purification by preparative GC): MS (70 eV): *m/e* 150 (M^+, rel. int. 14%); 31 (44); 107 (100); 105 (17); 93 (93); 91 (63); 79 (30); 77 (34); 67 (13); 65 (13); 55 (13); 53 (13); 43 (59); 41 (49); 39 (35); 29 (14); 27 (21). ^{1}H NMR: see Table 1.

With triethylaluminium. To a deep green solution of II (0.43 g, 1.23 mmol) in toluene (5 ml) was added dropwise triethylaluminium (0.34 ml, 2.46 mmol) in toluene (3 ml). The colour of the solution darkened to give a black-green suspension with evolution of 57 *N* ml (2.5 mmol) of gas (GC: 68.1% C_2H_6 (1.70 mmol), 28.3% C_2H_4 (0.71 mmol)). From the residue, pure (GC) toluene (6.55 g) was collected at —196° C by distillation under vacuum (0.5 Torr) at 25° C. Ethanol (5 ml) was added dropwise to the oily residue, heat was generated and 106 *N* ml of gas was evolved (GC: 99.5% C_2H_6 (4.7 mmol)). From the residue, volatile material (2.20 g) was collected at —196° C by distillation under vacuum (0.5 Torr, 25° C) (GC: 91.7% EtOH, 1.1% toluene, 6.5% V (0.14 g, 82.5% yield)).

With boron trifluoride etherate. To a suspension of II (0.87 g, 2.48 mmol) in diethyl ether (ca. 2 ml) at —80° C was added $BF_3 \cdot Et_2O$ (0.66 ml, ca. 5 mmol). The dark green mixture was allowed to warm to room temperature and stirred for 8 days with no observable change in appearance. Volatile material (1.4 g) was collected at —196° C by distillation under vacuum (10^{-3} Torr, 25—30° C), a green-brown oily residue remained (1.13 g). The distillate was washed with 3 *N* NaOH (3 × 5 ml) and dried over Na_2SO_4 to give a colourless solution (0.8 g) (GC: 68.74% Et_2O, 27.7% VII (1.63 mmol, 65.7% yield)).

Characterisation of VII (after separation by preparative GC). MS (70 eV): *m/e* 136 (M^+, rel. int. 11%); 122 (9); 121 (100). ^{1}H NMR: see Table 1.

With malonic acid. To a mixture of II (1.38 g, 3.9 mmol) and malonic acid (2.24 g, 19.7 mmol) at —80° C was added toluene (ca. 10 ml). The resultant dark green suspension was allowed to warm to room temperature during which time an orange suspension was formed. The suspension was stirred at 25° C for 3 h and volatile material (7.95 g) collected at —196° C by distillation under vacuum (0.5 Torr, 25° C) (GC: 95.12% toluene, 4.75% V (0.38 g, 70% yield)). A pale orange solid (3.99 g) remained.

With hydrogen chloride. To a suspension of II (0.80 g, 2.3 mmol) in diethyl ether (ca. 2 ml) was added dropwise a solution of HCl in ether (12 ml, 0.42 molar, 5.0 mmol). During the addition of 6 ml (2.5 mmol) the colour of the suspension changed from green to red. Further addition of 6 ml (2.5 mmol) resulted in the formation of a pale green suspension. The volatile material (9.63 g) was collected at —196° C by distillation under vacuum (10^{-3} Torr, 25° C), washed with 2 × 5 ml 3 *N* NaOH solution and dried over anhydrous Na_2SO_4 (GC: 96.65% Et_2O, 3.04% V (0.29 g, 91.4% yield)). A pale green powder (0.66 g) remained.

With methanol. To II (1.20 g, 3.4 mmol) was added methanol (5 ml). The resultant green suspension was stirred at 25° C. After ca. 10 min the colour had changed to red, and during a further 3 h this colour changed to give again a green suspension. The volatile material (4.31 g) was collected at —196° C by distillation under vacuum (10^{-3} Torr, 20° C) (GC: 91.8% MeOH. 8.1% V (0.35 g, 73.5% yield)). A dark-green, oily residue (1.32 g) remained.

With ethanol. To II (0.88 g, 2.5 mmol) was added ethanol (ca. 2 ml). The resultant green suspension was stirred at room temperature for 3 days with no observable change in appearance. Volatile material (1.5 g) was collected at —196° C by distillation under vacuum (10^{-3} Torr, 25° C) (GC: 97.01% EtOH, 1.21% V (0.018 g, 5.2% yield). II (by ^1H NMR, 0.88 g) remained as dark green solid.

With phenol. To a suspension of II (3.33 g, 9.5 mmol) in diethyl ether (10 ml) at room temperature was added dropwise a solution of phenol (1.80 g, 19.2 mmol) in diethyl ether (10 ml). The green suspension slowly changed colour to deep red-violet. After 2 h a deep red microcrystalline solid was separated by filtration, washed with diethyl ether (2 × 5 ml) and dried under vacuum (10^{-3} Torr, 25° C) to yield VIII (3.24 g, 76.7% yield) Mp. 100—110° C (decomp.). Anal. Found: C, 69.90; H, 6.76; N, 6.26; Ni, 12.9. $C_{26}H_{30}N_2NiO$ calcd.: C, 70.14; H, 6.79; N, 6.29; O, 3.59; Ni, 13.19%. MS (70 eV): highest *m/e* 156 (100%) ($dipy^+$). ^1H NMR (THF-d_8 solution, 80 MHz): τ 0.32 ppm (d, *J* 5.5 Hz, 1 H); 0.77 (d, *J* 5.5 Hz, 1 H); 1.40 (m, 4 H); 2.0 (m, 2 H); 2.34 (d, *J* 7 Hz, 2 H); 2.61 (d, *J* 7 Hz, 2 H); 3.21 (t, *J* 7 Hz, 1 H); 8.70 (s, 3 H); (8.95 u. 9.03 (s + m, 8 H); 9.42 (s, 3 H); 10.03 (m, 3 H). ^{13}C NMR (C_6D_6 solution): δ 170.6 (s); 153.0 (d); 148.7 (d); 137.1 (d); 135.3 (d); 129.0 (d) (coincident with solvent signal); 125.4 (d); 124.8 (d); 122.3 (d) (3 overlapping peaks); 120.0 (d); 118.9 (d); 113.9 (d); 32.1; 30.7 (d); 28.0 (d); 27.6 (d); 24.2 (q); 23.6 (s); 22.8 (t); 21.8 (q); 21.6 (q); 16.9 (s) ppm.

Reaction of VIII with methanol

To VIII (0.34 g, 0.76 mmol) was added methanol (3 ml). The resultant red solution was stirred at room temperature for 4 h by which time the colour had changed to green. Volatile material (2.43 g) was collected at —196° C by distillation under vacuum (10^{-3} Torr, 25° C) (GC: 96.93% MeOH, 2.98% V (0.073 g, 69.0% yield)].

Catalytic cyclodimerisation of I by II

(a) At 50° C: A dark green solution of II (1.08 g, 3.08 mmol) in toluene (ca. 10 ml) was introduced into an autoclave. The vessel was cooled to —78° C and I (15 ml, ca. 176 mmol) added. The mixture was shaken at 50° C for 3 h after which time the autoclave was opened, the contents transferred with washing (3 × 5 ml toluene) into a glass flask and the volatile material (31.1 g) collected at —196° C by distillation under vacuum (10^{-3} Torr, 25° C) (GC: 16.0% I

(4.99 g, 73.4 mmol); 79.2% toluene; 3.8% III (1.17 g, 17.2 mmol 279% yield based on II). A dark green, oily residue (2.30 g) was left. To this was added toluene (10 ml) and warmed to 90° C; on cooling to —30° C microcrystals were deposited. These were filtered and washed with pentane to give II (^{1}H NMR, 0.42 g, 38.9% recovery).

(b) At 90° C: A mixture of II (0.82 g, 2.6 mmol), I (12 g, 176 mmol) and toluene (10 ml) was shaken in a 200 ml V2A autoclave at 90° C for 3 h. The dark green contents were transferred with washing (2 × 5 ml toluene) into a glass flask and all volatiles distilled off (17.6 g; b.p. until 30° C/0.1 Torr; GC: 81.4% toluene and 18.2% III (3.2 g, 26.7%). Sublimation of the residue yielded hexamethyl-*trans*-σ-homobenzene (0.5 g, 6% yield); 5.4 g of an oily, dark green material remained.

References

1 P. Binger, M.J. Doyle, J. McMeeking, C. Krüger and Yi-Hung Tsay, J. Organometal. Chem., 135 (1977) 405.
2 P. Binger and J. McMeeking, Angew. Chem. Intern. Edit., 13 (1974) 466.
3 (a) J.X. McDermott, M.E. Wilson and G.M. Whitesides, J. Amer. Chem. Soc., 98 (1976) 6529 and ref. therein; (b) M.J. Doyle, J. McMeeking and P. Binger, J. Chem. Soc., Chem. Commun., (1976) 376; (c) J.J. McLain, C.D. Wood and R.R. Schrock, J. Amer. Chem. Soc., 99 (1977) 3519; (d) R.H. Grubbs and A. Miyashita, J. Chem. Soc., Chem. Commun., (1977) 864.
4 P. Binger, G. Schroth and J. McMeeking, Angew. Chem. Intern. Edit., 13 (1974) 465.
5 F.D. Mango, Coord. Chem. Rev., 15 (1975) 109.
6 T. Yamamoto, A. Yamamoto and S. Ikeda, J. Amer. Chem. Soc., 93 (1971) 3350.
7 J. Halpern in I. Wender and P. Pino (Eds.) Organic Syntheses via Metal Carbonyls, Vol. 2, 1977, p. 705; and ref. cited therein.
8 Sh. Takahashi, Y. Suzuki and N. Hagihara, Chem. Lett., (1974) 1363.
9 K. Fischer, K. Jonas, P. Misbach, R. Stabba and G. Wilke, Angew. Chem. Intern. Edit., 12 (1973) 943.
10 R. Köster and G. Benedikt, Angew. Chem., 74 (1962) 589.
11 P. Binger and H. Schäfer, Tetrahedron Lett., (1975) 4673.
12 G. Wilke and G. Herrmann, Angew. Chem. Intern. Edit., 5 (1966) 581.
13 T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji and S. Ikeda, J. Amer. Chem. Soc., 88 (1966) 5198.
14 P. Binger, unpublished.
15 P. Binger, Synthesis, (1974) 190.