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METALLACYCLOALKANES

I. PREPARATION AND CHARACTERISATION 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

Oxidative addition of 2 molecules of 3,3-dimethylcyclopropene (I) to α,α'-bipyridyl(1,5-cyclooctadiene)nickel(0) (III) gave the title compound (IV) in over 90% yield. Complex IV was characterized by mass, ^{1}H NMR and ^{13}C NMR spectroscopy. Its structure was determined by X-ray diffraction (a 13.7081(2), b 14.638(2), c 9.5139(1) Å, β 110.82(1)°, $C2/c$, R = 0.05 for 1614 reflections).

Introduction

Strained-ring olefins, such as 3,3-dimethylcyclopropene (I) [1], methylenecyclopropane [2] or norbornadiene [3] undergo cyclodimerisation in the presence of catalytic quantities of certain transition metal species. For example, 3,3-dimethylcyclopropene (I) is preferentially converted to the cyclic dimer *trans*-3,3,6,6-tetramethyltricyclo[3.1.0.0^{2,4}]hexane (II) under the influence of phosphane modified nickel(0) catalysts [1]. Analogous palladium(0) catalysts, however, induce cyclotrimerisation of I to form hexamethyl-*trans*-σ-homobenzene [1].

Two mechanisms may be considered for these catalysed cycloadditions: a concerted, "forbidden-to-allowed" process or a nonconcerted pathway, involving metallacyclic intermediates [4]. To distinguish between these two possibilities, we attempted to isolate such metallacycloalkanes, and were able to make nickelacyclopentane derivatives by oxidative addition of the above-mentioned strained ring olefins to α,α'-dipyridyl(1,5-cyclooctadiene)-nickel(0) (III). In contrast to an iridiacyclopentane derivative obtained analogously [5], the new nickelacyclopentanes are active catalysts for the cyclodimerisation of these

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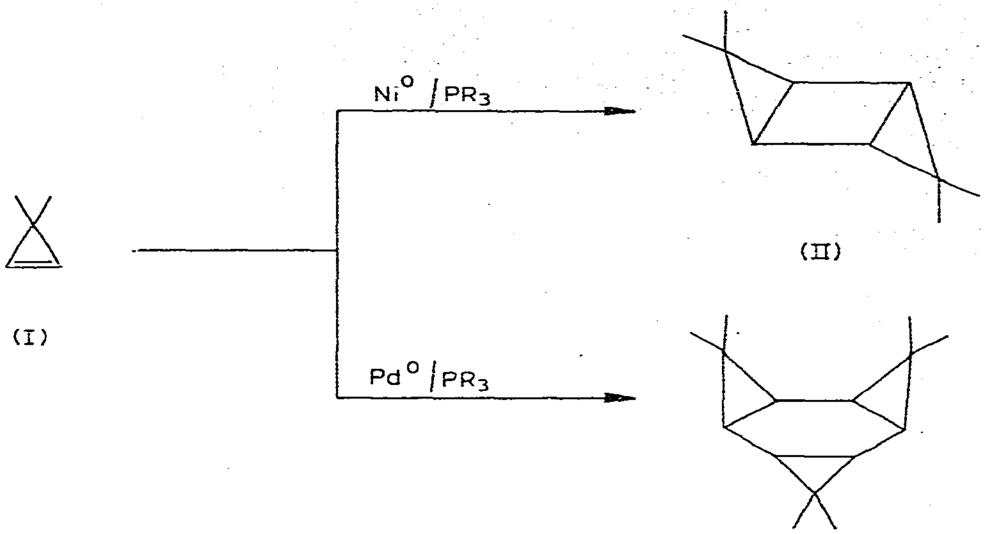
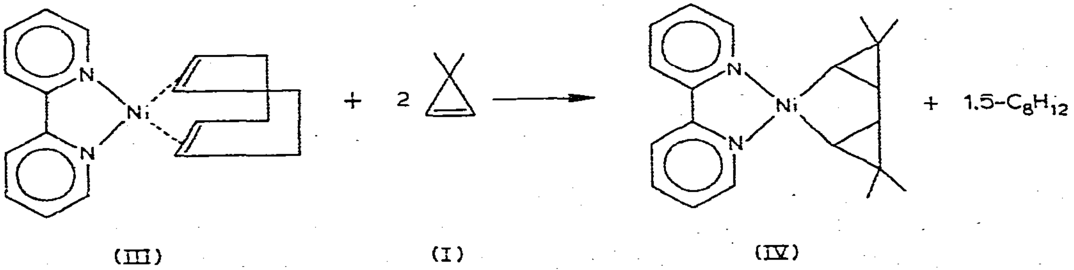
* X-ray analysis.



strained-ring olefins [6]. This result supports a stepwise mechanism for the catalytic reaction. Following a preliminary communication [6] we are now presenting the detailed results, and describe below the preparation and characterisation of α,α'-bipyridyl-5-nickela-3,3,7,7-tetramethyl-*trans*-tricyclo[4.1.0.0^{2,4}]heptane (IV).

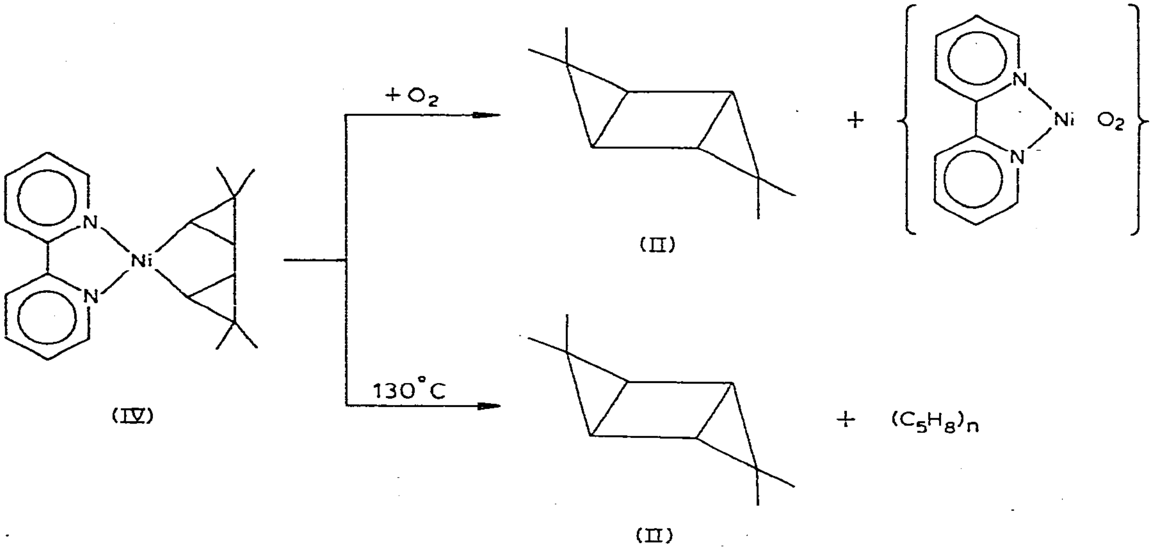
Results

α,α'-Bipyridyl(1,5-cyclooctadiene)nickel(0) (III), which is easily prepared from di-1,5-cyclooctadienenickel(0) and α,α'-bipyridyl [7] reacts readily with an excess of I to give the dark green, crystalline α,α'-bipyridyl-5-nickela-3,3,7,7-tetramethyl-*trans*-tricyclo[4.1.0.0^{2,4}]heptane (IV). In diethyl ether, reaction is observed at ca. —70°C when the deep violet suspension darkens; on warming to room temperature a deep-green solution is obtained from which crystals of IV may be isolated in ca. 92% yield.



IV is only slightly air sensitive in the solid state and may be exposed to air for several minutes before any decomposition is observed. In solution, however, the intense green colour rapidly turns to brown on exposure to air, and the cyclodimer (II) is produced in about 80% yield. The same reductive coupling of σ-bonded alkyl groups has been observed in the reaction between α,α'-bipyridylethylnickel and oxygen [8], where butane and an α,α'-bipyridylnickel—oxygen complex is formed.

Complex IV is very stable thermally for an alkylnickel derivative containing a β-hydrogen atom [9]. It decomposes slowly at temperatures above 130°C with the formation of undistillable material and of II in approximately 30% yield. Its stability is thus considerably greater than that of the corresponding α,α'-bipyridyldiethylnickel complex, which decomposes fairly rapidly at 110°C [9]. A similar difference in thermal stability has recently been described between diphosphinediethylplatinum complexes and diphosphineplatinacyclopentanes [10]. In both cases the relatively rigid five-membered metallacycle does not permit a planar M—C—C—H moiety, which seems to be optimal for a metal-hydride elimination.



The characterisation of IV has been achieved by physical methods. The reactions of IV will be described in a subsequent paper [11].

The molecular weight, determined by mass spectroscopy, is 350 (for ^{58}Ni). The ^{1}H NMR spectrum is shown in Fig. 1, ^{1}H and the corresponding ^{13}C NMR data are given in Table 1. Single frequency selective decoupling was used to ascertain the relationship between ^{1}H and ^{13}C signals. Both spectra are consistent with the given structure. The methyl group resonances were assigned from the expected steric γ-shift in the ^{13}C spectrum, and assignment of ring positions was made on the basis of comparison with ^{13}C NMR data of analogous compounds *.

To test the latter assignment we employed a method used by Yamamoto [13] in which variable temperature ^{1}H NMR measurements of the analogous bipyNiEt$_2$ complex in coordinating solvents revealed a larger change in chemical shift for the methylene protons than for the methyl protons. In an analogous experiment with IV in acetone-d_6 (Fig. 2) both signals are shifted to approximately the same degree, and so no light is thrown on this problem.

The observed pattern for the ring protons can be explained by a coupling of 6.6 Hz between protons 6 and 7, of 1.9 Hz between protons 6 and 7′ and no

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* For a detailed discussion of the ^{1}H and ^{13}C NMR spectra see ref. 12.

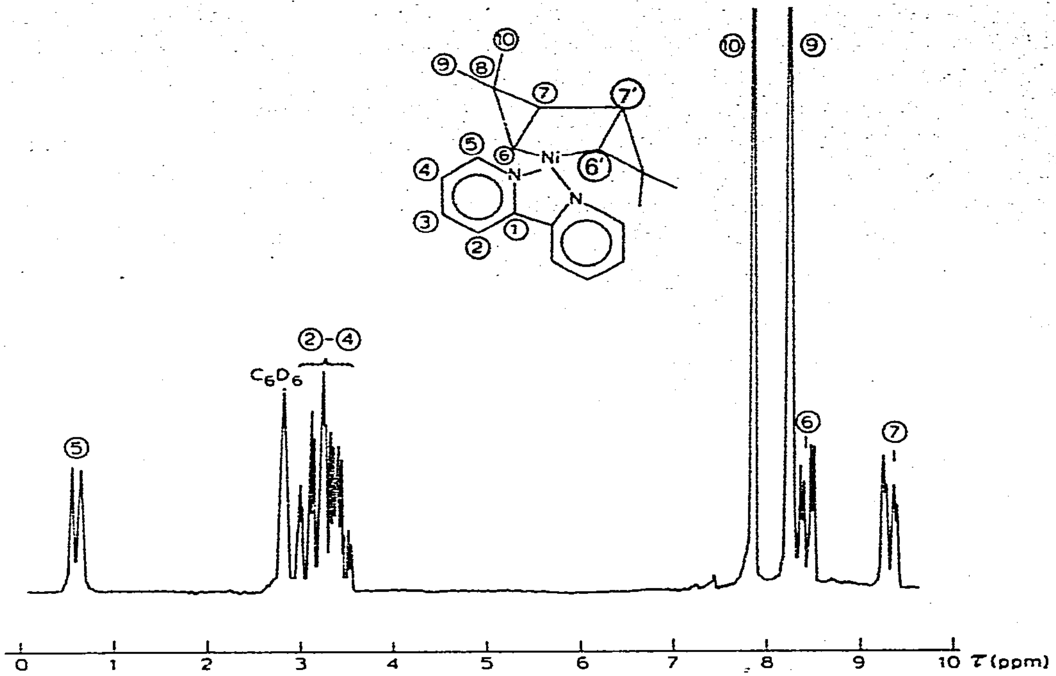

Fig. 1. 60 MHz ^1H NMR spectrum of IV in benzene-d_6.

resolvable coupling between protons 6 and 6′ or 7 and 7′. This latter observation is consistent with a dihedral angle of ca. 90° between protons 7 and 7′, and shows the cyclopropane rings to be *trans*.

An unambiguous proof for the structure of IV was obtained by an X-ray analysis. Experimental details are given in Tab. 2. The structure was solved by the heavy atom technique, the nickel atom being located at a special position at x

TABLE 1

^1H AND ^{13}C NMR DATA FOR [bipyNi($C_{10}H_{16}$)] (IV)

Assignment	Chemical shift [a]		Coupling Constant
	^1H (τ, ppm)	^{13}C (δ, ppm) [b]	$J(^1H—^1H)$ (Hz)
1	—	153.8(3)s	
2		125.9(0)d	
3	3.25m	133.6(7)d	
4		120.0(4)d	
5	0.62d	149.6(6)d	$J_{1,2}$ 5.6
6 [c]	8.47dd	33.6(4)d	$J_{6,7}$ 6.6
7 [c]	9.34dd	37.0(9)d	$J_{6',7}$ 1.9
8		23.1(1)s	
9 [c]	8.29s	30.5(4)q	
10 [c]	7.90s	24.7(6)q	

[a] In C_6D_6 relative to $(CH_3)_4Si$. [b] Multiplicity determined by single frequency off-resonance decoupling.
[c] Assignment is tentative.

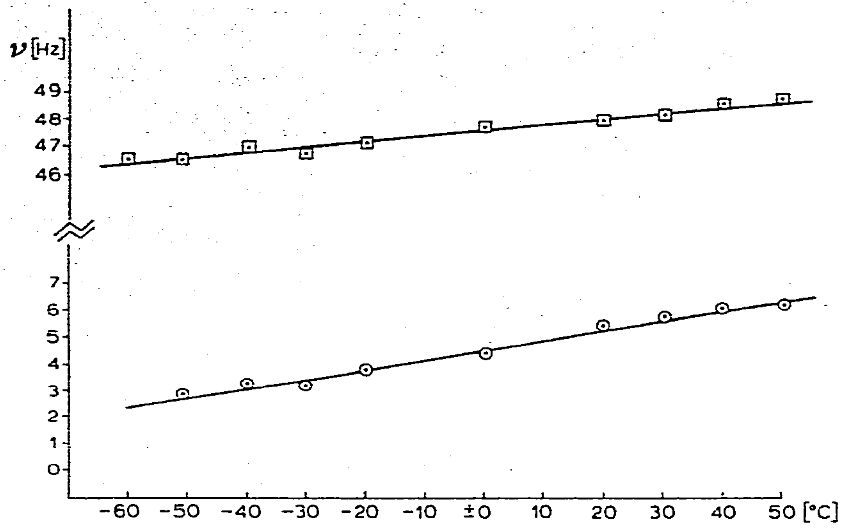

Fig. 2. Temperature dependence of the chemical shifts of the ring-proton signals 6 (—⊡—⊡—) and 7 (—⊙—⊙—) in IV (solvent: acetone-d_6, reference: TMS).

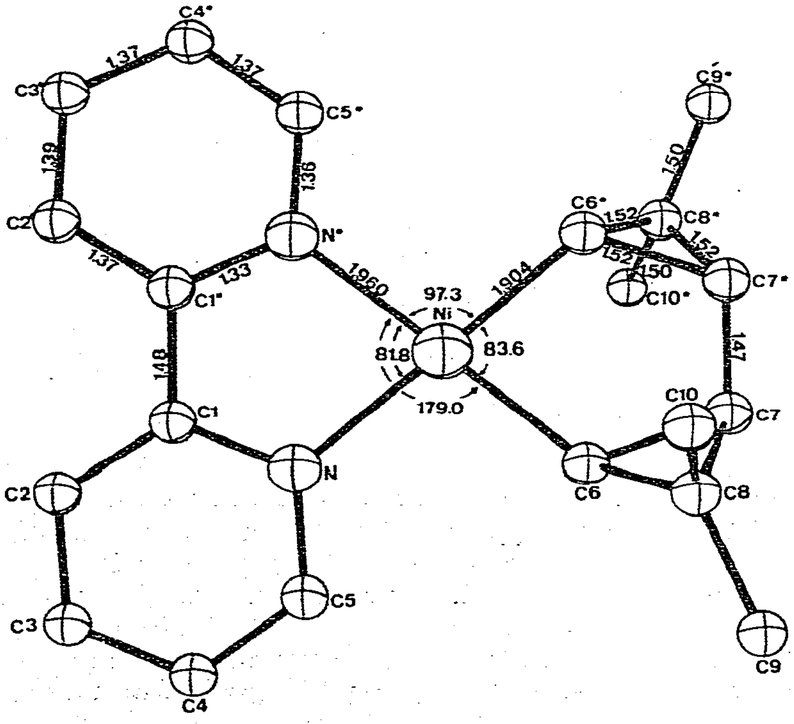

Fig. 3.

TABLE 2

EXPERIMENTAL DETAILS OF THE X-RAY STRUCTURAL ANALYSIS

Crystal data	
a 13.7081(2) Å	Space group: $C2/c$ (Cc)
b 14.638(2) Å	Nonius CAD-4 Diffractometer
c 9.5139(1) Å	λ (Mo-$K_{\overline{\alpha}}$) 0.71069 Å
β 110.82(1)°	Graphite monochromator
V 1784.5 Å^3	Data collected: hkl, $\bar{h}kl$, $h\bar{k}l$, $\bar{h}\bar{k}l$
$Z=4$	2973 reflections, averaged to give
d_{calc} 1.32 g/cm^3	1614 unique reflections, of which
	758 were considered unobserved
	($I/\sigma(I) \leqslant 2.0$)

TABLE 3a

FINAL ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS (×10^4)

Atom	x	y	z
Ni	0(1)	1870(1)	2500(1)
N	726(4)	858(3)	3800(5)
C(1)	416(5)	28(4)	3254(7)
C(2)	837(7)	−751(5)	4028(9)
C(3)	1618(7)	−693(6)	5444(9)
C(4)	1923(5)	158(6)	6026(8)
C(5)	1474(5)	911(5)	5200(7)
C(6)	724(5)	2839(4)	3780(6)
C(7)	424(6)	3807(5)	3234(7)
C(8)	231(6)	3463(4)	4617(6)
C(9)	929(10)	3844(8)	6094(9)
C(10)	−870(8)	3306(7)	4534(11)
H(2)	644(58)	−1272(60)	3593(80)
H(3)	1786(56)	−1220(61)	6007(74)
H(4)	2394(73)	203(58)	6832(99)
H(5)	1670(51)	1521(49)	5633(66)
H(6)	1433(52)	2734(44)	4309(63)
H(7)	1000(68)	4276(68)	3487(86)
H(9A)	1692(64)	3899(58)	6244(78)
H(9B)	655(93)	4283(99)	6330(99)
H(9C)	1003(99)	3349(86)	6756(99)
H(10A)	−834(76)	2938(66)	5307(99)
H(10B)	−1060(70)	3847(72)	4593(94)
H(10C)	−1357(65)	3002(52)	3660(84)

= 0, z = 0.25. The structure was refined anisotropically by full matrix least squares techniques to a final R-value of R = 0.050 (R_w = 0.059). In this refinement, isotropic hydrogen atoms as located in a difference Fourier synthesis were included *. The molecule possesses rigorous crystallographic symmetry 2, the twofold axis passing through the connecting C—C linkage of the dipyridyl and the second ligand, as well as nickel (see Fig. 3). The geometry of nickel is exactly planar. The dipyridyl ligand is located in this coordination plane, which also

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* For details of data collection and computing procedure see ref. 14.

TABLE 3b

FINAL THERMAL PARAMETERS ($\times 10^3$)

Atom	$U_{1,1}$	$U_{2,2}$	$U_{3,3}$	$U_{1,2}$	$U_{1,3}$	$U_{2,3}$
Ni	38	40	34	0	3	0
N	40	48	43	−7	10	0
C(1)	48	42	50	8	19	8
C(2)	77	43	67	7	22	13
C(3)	69	67	74	13	15	39
C(4)	41	81	52	−9	−5	30
C(5)	48	58	48	−5	6	3
C(6)	40	42	40	−3	−3	−6
C(7)	60	42	46	−5	14	−3
C(8)	68	45	36	−1	15	−3
C(9)	99	77	46	−15	7	−11
C(10)	89	56	65	0	38	5
H(2)	58					
H(3)	59					
H(4)	78					
H(5)	40					
H(6)	40					
H(7)	87					
H(9A)	59					
H(9B)	123					
H(9C)	137					
H(10A)	91					
H(10B)	78					
H(10C)	60					

TABLE 4

BOND DISTANCES (Å) AND BOND ANGLES (°) WITH THEIR STANDARD DEVIATIONS

Ni—N	1.960(5)	N*—Ni—N	81.8(2)
Ni—C(6)	1.904(7)	N*—Ni—C(6)	179.0(3)
N—C(1)	1.331(9)	N—Ni—C(6)	97.3(3)
N—C(5)	1.364(8)	C(6)—Ni—C(6)*	83.6(3)
C(1)—C(1)*	1.483(10)	Ni—N—C(1)	115.0(4)
C(1)—C(2)	1.372(11)	Ni—N—C(5)	127.6(5)
C(2)—C(3)	1.394(13)	C(1)—N—C(5)	117.3(6)
C(3)—C(4)	1.369(14)	N—C(1)—C(1)*	114.1(6)
C(4)—C(5)	1.368(12)	N—C(1)—C(2)	122.4(7)
C(6)—C(7)	1.516(10)	C(1)*—C(1)—C(2)	123.5(7)
C(6)—C(8)	1.520(10)	C(1)—C(2)—C(3)	120.0(8)
C(7)—C(7)*	1.468(10)	C(2)—C(3)—C(4)	117.8(9)
C(7)—C(8)	1.517(10)	C(3)—C(4)—C(5)	119.5(8)
C(8)—C(9)	1.499(11)	C(4)—C(5)—N	122.9(7)
C(8)—C(10)	1.503(14)	Ni—C(6)—C(7)	117.5(5)
		Ni—C(6)—C(8)	123.8(5)
		C(7)—C(6)—C(8)	59.9(5)
		C(6)—C(7)—C(8)	60.2(5)
		C(6)—C(7)—C(7)*	110.7(6)
		C(8)—C(7)—C(7)*	120.2(7)
		C(6)—C(8)—C(7)	59.9(5)
		C(7)—C(8)—C(9)	116.1(7)
		C(7)—C(8)—C(10)	119.2(7)
		C(6)—C(8)—C(9)	117.4(8)
		C(6)—C(8)—C(10)	120.4(7)
		C(9)—C(8)—C(10)	113.7(8)

contains the carbon atoms (C(6) and C(7)) of the nickelacyclopentane system. The maximum deviation from planarity of this system is ±0.027 Å. The cyclopropane rings (C(6)C(7)C(8)) are bent 115.9° from the plane of this ring (NiC(6)C(7)C(6)* C(7)*). While the C—C-distances in the cyclopropyl rings are equidistant (1.52 Å), the connecting bond C(7)—C(7)* is considerably shorter (1.47 Å). This feature has been observed in related compounds [15], and may be due in part to a conjugative effect induced by the unsaturated character of the two adjacent cyclopropyl groups. This effects causes also a significant shortening of the σ-Ni—C bond (1.904(1) Å), which in related square planar α,α'-bipyridylnickel compounds is 1.95 Å [16]. Distances and angles within the rings of the α,α'-bipyridyl ligand are as found in the non-complexed, centrosymmetric moiety, which has both nitrogen atoms *trans* to each other [17]. A list of positional and thermal parameters is given in Table 3. Bond distances and bond angles are given in Table 4.

Experimental

General

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

^{1}H NMR (60 MHz) and ^{13}C NMR (25.2 MHz) spectra were recorded in the F.T. mode on Bruker WP60 and Varian XL-100 spectrometers respectively *. IR spectra were recorded on a Perkin—Elmer-521 spectrophotometer with KBr discs. The mass spectra were obtained on an Atlas-CH5 spectrometer. 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. Microanalytical data for C, H and N were provided by Dornis und Kolbe, 4330 Mülheim-Ruhr, W. Germany, and for Ni in our laboratories by X-ray fluorescence.

Reagents

Published procedures were used to prepare I [18], and di-1,5-cyclooctadienenickel [19]. 1,5-Cyclooctadiene (Chem. Werke Hüls AG), was distilled and stored under argon. α,α'-Bipyridyl (Merck AG), was stored under argon and used without further purification.

Preparation of α,α'-bipyridyl(1,5-cyclooctadiene)nickel (III) [20]

To a mixture of di-1,5-cyclooctadienenickel (16.3 g, 59.1 mmol) and α,α'-bipyridyl (9.3 g, 59.6 mmol) was added diethyl ether (50 ml). The yellow colour of the suspension changed rapidly to deep violet. The suspension was stirred for 5 h at 25°C and the solid was separated, washed with cold diethyl ether (2 × 20 ml) and dried under vacuum (10^{-3} torr) to give the dark violet microcrystalline complex III (16.8 g, 87.9%). Anal. Found: C, 66.92; H, 6.57; N, 8.68; Ni, 17.50. $C_{18}H_{20}N_2Ni$ calcd.: C, 66.92; H, 6.24; N, 8.67; Ni, 18.17%. ^{1}H NMR **

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* NMR, IR and mass spectra were recorded at the Max-Planck-Institut für Kohlenforschung, 4330-Mülheim-Ruhr by Drs. E.G. Hoffmann, K. Seevogel and D. Henneberg, respectively; the GC determinations were done by Dr. G. Schomburg of the same institute.

** ^{1}H NMR and ^{13}C NMR data are compatible with symmetrical bis-bonding of 1,5-cyclooctadiene to nickel; this is at variance with ^{1}H NMR data reported in ref. 20.

(C_6D_6 solution) τ (ppm) —0.15 (d, 2H, J 5.6 Hz); 3.0—2.5 (m, 8H); 6.10 (s, 4H); 7.2 (m, 4H); 8.0 (m, 4H). ^{13}C NMR (C_6D_6 solution) σ (ppm) 31.8 (methylenic); 82.1 (olefinic); 122.1, 122.3, 124.8, 150.4 (bipyridyl-quarternal carbon not observed). IR ν(C=C): 1532 cm^{-1}.

Preparation of α,α'-bipyridyl-5-nickela-3,3,7,7-tetramethyl-trans-tricyclo-[4.1.0.0^{2,4}]heptane (IV)

To a violet suspension of α,α'-bipyridyl(1,5-cyclooctadiene)nickel (3.1 g, 9.6 mmol) in diethyl ether (10 ml) was added I (4 ml, ca. 47 mmol) at —78°C. The mixture was allowed to warm slowly to room temperature with stirring. The suspension darkened and gradually became deep green. After stirring at room temperature for 1 h, the suspension was cooled to —30°C for 2 h. The solid material was then separated, washed with cold diethyl ether (3 × 5 ml) and dried under vacuum (10^{-3} torr, 25°C) to yield the dark green crystalline complex IV (3.1 g, 92% yield). Anal. Found: C, 67.84; H, 6.78; N, 8.28; Ni, 16.3. $C_{20}H_{24}N_2Ni$ calcd.: C, 68.41; H, 6.89; N, 7.98; Ni, 16.72%. IR: ν(C—H) 2980—2810, ν(bipy) 1311, 755 cm^{-1}. Mass spectrum (70 eV, 150°C): *m/e* (principal peaks for only ^{58}Ni) 350 (M^+, rel. int. 2%); 214 (bipyNi$^+$, 100); 156 (bipy$^+$, 14).

Decomposition of α,α'-bipyridyl-5-nickela-3,3,7,7-tetramethyltricyclo[4.1.0.0^{2,4}]-heptane (IV)

(a) With dioxygen. A flask containing a dark green suspension of IV (1.06 g, 3.02 mmol) in toluene (4 ml) was partially evacuated and filled with oxygen. A mildly exothermic reaction ensued and the colour changed to dark brown. After two hours volatile material (5.37 g) was collected at —196°C by distillation under vacuum (10^{-3} torr, 25°C) [GC: II, 5.9% (77.1% yield) and 93.6% toluene]. A brown solid (0.9 g) remained.

(b) With heat. Complex IV (1.53 g, 4.35 mmol) was heated under vacuum (0.5 torr) and volatile material was trapped at —196°C. At 130°C the surface became grey-green. After 3 h traces of volatile material in the trap were washed out with toluene (ca. 1.5 ml, combined weight 1.27 g) [GC: toluene, 99.45%; II, 0.35% (0.7% yield)]. The residue was then heated up to 200°C. In the range 130—160°C, the material darkened. After 3 h a small quantity (0.2 g) of volatile material was found in the —196°C trap [GC: II, 95.92% (32.4% yield)].

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