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BIS(TRIPHENYLPHOSPHINE)-5-NICKELA-3,3,7,7-TETRAMETHYL-*trans*-TRICYCLO[4.1.0.0^{2,4}]HEPTANE

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Summary

The oxidative addition of 3,3-dimethylcyclopropene (DMCP) to the nickel complexes $(Ph_3P)_3Ni$ and $(\pi\text{-}C_2H_4)Ni(PPh_3)_2$ resulting in the formation of bis(triphenylphosphine)-5-nickela-3,3,7,7-tetramethyl-*trans*-tricyclo[4.1.0.0^{2,4}]heptane has been carried out. The NMR (^{1}H and ^{31}P-{^{1}H}) spectra, the reactivity and some of the catalytic properties of this complex in the cyclodimerization of DMCP have been studied.

Introduction

In recent years the chemistry of metallacycloalkanes has advanced extensively. These compounds have been proposed as intermediates in the dimerization and metathesis of olefins catalyzed by transition metals [1]. In some cases they have been isolated and characterized by their spectra. Thus, the first nickelacycloalkanes stabilized by 2,2′-bipyridyl were prepared by the reaction of (2,2′-bipyridyl)(cycloocta-1,5-diene)nickel with either methylenecyclopropane [2,3] or DMCP [2,4]. Simultaneously, phosphine complexes of nickelacyclopentane, generated by treatment of $(R_3P)_2NiCl_2$ with 1,4-dilithiobutane at low temperature, were described [5]. However, no nickelacyclopentanes with triphenylphosphine and DMCP ligands have been known until now.

The present paper deals with the synthesis and investigation of the reactivity and some of the catalytic properties of the novel complex containing nickel in the five-membered ring.

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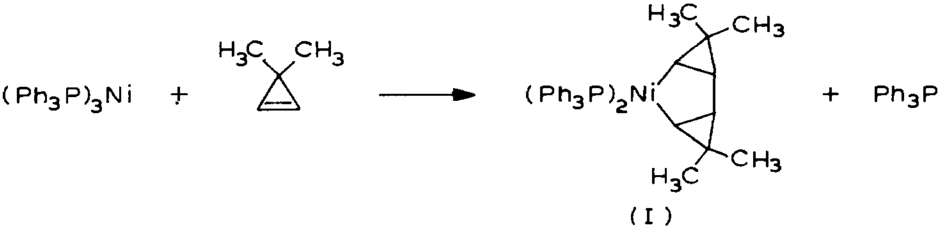
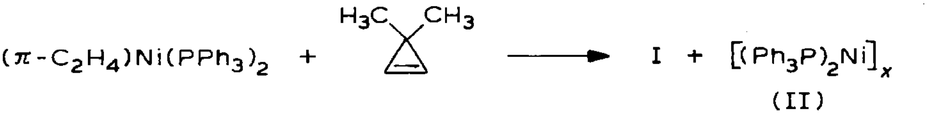
Results and discussion

Such a nickelacyclopentane has been synthesized by the oxidative addition of DMCP to zero-valent nickel complexes containing triphenylphosphine ligands. It was found that treating tris(triphenylphosphine)nickel with a four-fold excess of DMCP in toluene at room temperature leads to bis(triphenylphosphine)-5-nickela-3,3,7,7-tetramethyl-*trans*-tricyclo[4.1.0.0^{2,4}]heptane (I) (50%):



(1)

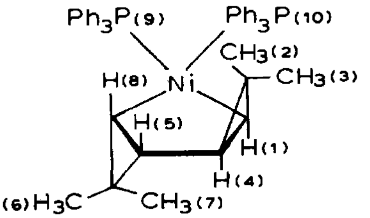
The reaction of the other nickel complex, (π-C_2H_4)Ni(PPh_3)$_2$, with DMCP proceeds in a more complicated manner:



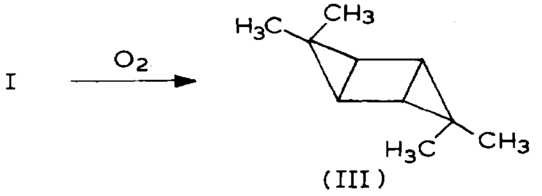
(2)

In this case, a very unstable red-brown product (II) is formed along with complex I. We succeeded in separating I from II by making use of the small difference in solubility of these compounds in benzene and ether. This procedure is accompanied by a great loss of I and II. The yield of I is twice as small as that in reaction (1) and amounts to only 20–25%.

The ^{1}H NMR spectrum of I (recorded in C_6D_6) contains two equally intensive singlet signals at δ 2.20 and 0.98 ppm corresponding to the methyl protons 3(6) and 2(7), respectively, together with a multiplet for the phenyl ring protons of the PPh_3 ligands at δ 7.40–7.90 (*o*-Ph) and 6.90–7.20 (m, *p*-Ph) ppm. Protons 4(5) and 1(8) appear as a doublet and a doublet of triplets at δ 1.51 and 0.53 ppm J(H(1)–H(4)) = J(H(5)–H(8)) = 6.2 Hz; J(H(1)–P(9)) = J(H(8)–P(10)) = 21.6 Hz; J(H(1)–P(10)) = J(H(8)–P(9)) = 6.2 Hz), respectively. The ratio of integrated intensities of these signals corresponds to the proposed structure for I. A similar ^{1}H NMR spectrum was described for (2,2′-bipyridyl)-5-nickela-3,3,7,7-tetramethyl-*trans*-tricyclo-[4.1.0.0^{2,4}]heptane in ref. 4. In the ^{31}P-{^{1}H} NMR spectrum of complex I (recorded in toluene at −60°C), a narrow singlet is observed at δ 32.03 ppm, which indicates the equivalence of the phosphorus atoms in this compound.

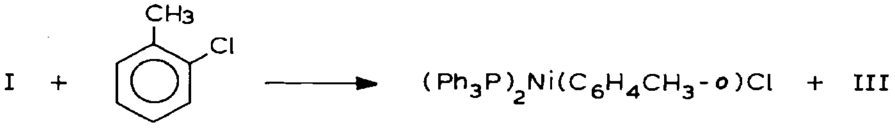


The novel complex I is a pale-yellow, crystalline substance, moderately soluble in aromatic hydrocarbons and poorly soluble in ether and petroleum ether. Contrary to bis(triphenylphosphine)nickelacyclopentane [5], which is unstable at room temperature, complex I decomposes only on heating to 150°C. However, complex I and in particular its solutions are sensitive to atmospheric oxygen and decompose with the liberation of 3,3,6,6-tetramethyl-*trans*-tricyclo[3.1.0.0^{2,4}]hexane (III), detected by GLC [11].



(3)

The formation of cyclic dimer III is also observed in the reaction of I with *o*-chlorotoluene:



(4)

A large excess of *o*-chlorotoluene and heating at 60°C for 10 h are required for the latter reaction to occur. In this case, *o*-tolylbis(triphenylphosphine)nickel chloride (40%) and III are formed.

The reductive elimination from I induced by *trans*-stilbene affords the expected (π-*trans*-stilbene)bis(triphenylphosphine)nickel (IV) and III in low yield whereas the interaction of II with *trans*-stilbene results in complex IV in a quantitative yield.

In contrast to I, elucidation of the structure of II causes considerable difficulties. The ^1H NMR spectrum of II (recorded in C_6D_6) contains a complicated multiplet at δ 7.04–7.87 ppm assigned to the phenyl ring protons of the PPh_3 ligands and no signals in the range of aliphatic protons. In the $^{31}P\text{-}\{^1H\}$ NMR spectrum of II (recorded in toluene at −80°C), a broad signal with the centre at δ 23.60 ppm ($\Delta\nu$ 100 Hz) is observed. The broadening of the signal seems to be due to exchange processes with participation of the PPh_3 ligand.

Therefore, the spectral data show compound II to involve only coordinated PPh_3. Complex II is likely to be similar to $[Pt(PPh_3)_2]_3$ described earlier, which is formed from $[Pt(PPh_3)_2]$ [6].

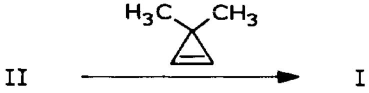
In addition, the catalytic properties of isolated complexes I and II in the cyclodimerization of DMCP were investigated.

Previous experiments have shown that in the absence of a catalyst the thermally induced cyclodimerization of DMCP proceeds above 40°C with the formation of only dimer III (Table 1, Nos. 1-3). In the presence of complex I or II, apart from the main product III a negligible admixture (1–3.5%) of a trimer is formed, which seems to be 3,3,6,6,9,9-hexamethyl-*cis,cis,trans*-tetracyclo[6.1.0.0^{2,4}.0^{5,7}]nonane [7] (Table 1, Nos. 4–7).

Regardless of the nature of the solvent used, complexes I and II revealed a high initial catalytic activity: at 20°C in benzene it corresponds to 230 and 250 catalytic cycles in 1 h upon 1 g-atom of nickel and in ether it amounts to 180 and 140 cycles, respectively (Table 1, Nos. 4–7).

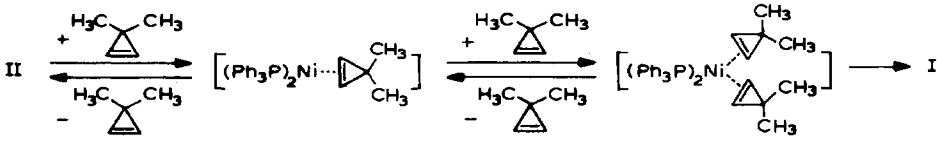
Observation of the reaction course allowed us to propose the mutual transitions of complexes I and II in the reaction considered. The electronic spectra of reaction mixtures containing DMCP and I or II and also those of complex I or II alone are in agreement with such an assumption. These spectra were recorded in pentane in the range 190–850 nm *.

In the spectrum of I a strong absorption band with a border at 315 nm is observed. Besides this band, the spectrum of II contains an absorption maximum at ca. 370 nm and a shoulder at 536 nm. Addition of DMCP to a pentane solution of II causes the electronic spectrum of II to change sharply, becoming similar to that of I. The spectral changes observed are likely due to the following reaction:



(5)

The following intermediate stages can be suggested for this process: initially, reversible π-binding of the first and then that of the second molecule of the substrate with II occur, which are accompanied by the following coupling of the DMCP molecules in the coordinate sphere of nickel and by the formation of nickelacyclopentane I:



(6)

Finally, regardless of whether complex I or II is used as the catalyst, the identity

TABLE 1

COMPARATIVE CATALYTIC ACTIVITY OF COMPLEXES I AND II IN THE CYCLODIMERIZATION OF DMCP ([Ni] 1.8 mg-atom/l; [DMCP] 1.55 mol/l; τ 3 h)

No.	Catalyst	Solvent	Temperature (°C)	Conversion (%)	Activity [a] (mol DMCP/h g-atom Ni)	Selectivity (%)	
						Dimer	Trimer
1	–	benzene	20	0	–	–	–
2	–	benzene	40	20	–	100.0	0
3	–	benzene	60	91	–	100.0	0
4	I	benzene	20	38	230	96.5	3.5
5	I	ether	20	24	180	98.5	1.5
6	II	benzene	20	39	250	97.0	3.0
7	II	ether	20	22	140	99.0	1.0

[a] Initial activity is given for the first hour of the catalyst work.

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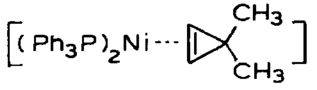
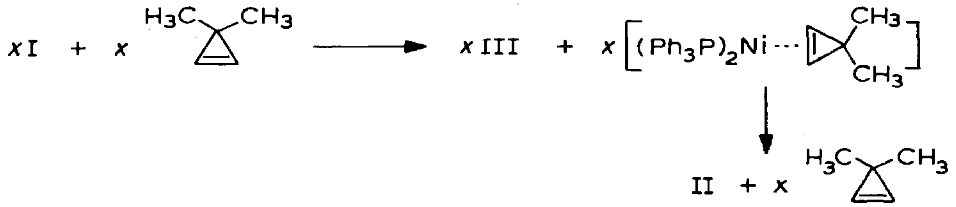
* The authors thank Dr. I.V. Elev for help in recording and discussion of the electronic spectra.

of the electronic spectra of the reaction mixtures with that of II is observed when the conversion of DMCP is close to 100%. Such a transition of I into II at the final stage of the reaction is likely to occur through the unstable intermediate



and to be accompanied by the reductive elimination of III from I under the influence of an equimolar amount of DMCP.



(7)

Additional information on the mutual transitions of complexes I and II was obtained by direct experiments using ^{31}P NMR spectroscopy. Thus, treatment of I with a toluene solution of DMCP (molar ratio I/DMCP 1/40) led to the disappearance of the ^{31}P NMR signal of I at δ 32.03 ppm in 24 h and to the appearance of a signal at δ 24.2 ppm assigned to II. On the other hand, on treating a suspension of II with a toluene solution of DMCP (Ni/DMCP $\approx$ 1/4), a yellow crystalline solid was isolated. The ^{31}P NMR spectrum of this compound contained a signal at δ 32.03 ppm corresponding to I.

The mutual transition of I and II found in the catalytic cyclodimerization of DMCP allows the above-mentioned inversion of initial catalytic activity of these complexes to be explained satisfactorily with regards to their solubility in benzene and ether (Table 1). The greater decrease of the activity of II compared to I with the change of solvent is obviously due to inhibition of the transition of II into I in ether in comparison with benzene.

Detailed investigation of the catalytic cyclodimerization of DMCP in the presence of complexes I and II, carried out for the first time, has enabled us to reveal the following previously unknown peculiarities of the cyclic stepwise reaction path: (1) the formation of complex II upon reductive elimination of III from I under the influence of DMCP; (2) the transition of I into II at the final stage of the reaction when the conversion of DMCP is close to 100%.

Experimental

The ^{1}H NMR spectra were recorded with a Bruker WP-200 SY spectrometer at 22°C. Deuterobenzene was used as the solvent for all the samples. The chemical shifts are given with respect to residual benzene (7.25 ppm). The ^{31}P-$\{^{1}H\}$ NMR spectra were measured on a Bruker HX-90 spectrometer (with 85% H_3PO_4 as external standard). The UV-VIS spectra were obtained in pentane on a Hitachi M-340 spectrophotometer in the range 190–850 nm.

GLC analysis was performed on a Biochrom-1 chromatograph equipped with a flame-ionizing detector, using a 1.5 m × 3 mm column, with 5% SE-30/Chezasorb AW-HMDS as filler and helium as carrier gas and with a temperature program ranging from 50 to 250°C.

Tris(triphenylphosphine)nickel was prepared according to the method [8] reported for tetrakis(triphenylphosphine)nickel using three equivalents of PPh_3.

(π-Ethylene)bis(triphenylphosphine)nickel and 3,3-dimethylcyclopropene were synthesized as described in refs. 9 and 10, respectively.

All the experiments were carried out under an argon atmosphere using absolute solvents which were distilled under argon prior to use.

1. *Bis(triphenylphosphine)-5-nickela-3,3,7,7-tetramethyl-trans-tricyclo[4.1.0.0^{2,4}]heptane (complex I)*

(a) A toluene solution of DMCP (7.7 mmol) was added dropwise to a suspension of $(Ph_3P)_3Ni$ (1.9 mmol) in toluene (10 ml) at −20°C. The dark-brown solution obtained was kept at 22°C for 20 h. It was then filtered, evaporated to dryness, and treated with ether. The resulting pale-yellow precipitate was filtered off, washed with ether, and dried in a vacuum to yield complex I (0.70 g, 50%), m.p. 152–153°C (from benzene/ether). (Found: C, 77.52; H, 6.46. $C_{46}H_{46}NiP_2$ calcd.: C, 76.79; H, 6.44%).

(b) A toluene solution of DMCP (13.6 mmol) was added to a suspension of $(\pi\text{-}C_2H_4)Ni(PPh_3)_2$ (3.2 mmol) in toluene at −20°C. The reaction mixture was stirred for 2 h at −20°C and then evaporated to dryness. The oily residue was treated with ether and cooled to −78°C. After 12 h the resulting precipitate was filtered off and washed with a small amount of benzene and ether. 0.46 g (20%) of complex I was obtained, m.p. 152–153°C (from benzene/ether).

The ether mother liquor was evaporated to minimal volume; the red-brown precipitate formed was filtered off, washed with pentane, and dried in a vacuum. 0.55 g of $[(Ph_3P)_2Ni]_x$ (complex II) was obtained, m.p. 138–140°C (from benzene/ether).

2. *Reactions of complex I*

(a) With air oxygen. A suspension of I (0.02 g) in benzene (0.57 g) was kept in air for 6 h. GLC analysis showed the solution to contain dimer III.

(b) With o-chlorotoluene. *o*-Chlorotoluene (24.0 mmol) was added to the suspension of I (1.2 mmol) in toluene (3 ml). The mixture was heated for 10 h at 60°C. The obtained solution containing dimer III (GLC) was filtered, evaporated to minimal volume, and treated with ether. The yellow precipitate formed was filtered off, washed with ether, and dried in a vacuum. 0.35 g (41%) of $(Ph_3P)_2Ni(C_6H_4CH_3\text{-}o)Cl$ was obtained. This complex was identified by comparing its IR spectrum with that of a known sample [12].

(c) With trans-stilbene. A benzene solution of *trans*-stilbene (3.6 mmol) was added to I (1.2 mmol) at 22°C. The reaction mixture was kept at room temperature for 2 days. According to GLC data it contained III. It was then almost evaporated to dryness and the residue was treated with ether. The precipitate formed was filtered off, washed with ether, and dried in a vacuum. 0.52 g of a yellow substance was obtained. According to the ^1H NMR spectrum it was a mixture of the starting complex I and (π-*trans*-stilbene)bis(triphenylphosphine)nickel [13].

3. *(π-trans-Stilbene)bis(triphenylphosphine)nickel*

A benzene solution of *trans*-stilbene (0.50 g) was added to a benzene solution of II (0.53 g). The reaction was carried out as described in the previous experiment to give complex IV (0.20 g). The ^1H NMR spectrum of IV was in agreement with that reported earlier [13].

4. 3,3,6,6-Tetramethyl-trans-tricyclo[3.1.0.0^{2,4}]hexane (III)

(a) A common procedure of the catalytic experiment: In a thermostatted glass reactor equipped with a magnetic stirrer, 0.009 mmol of the nickel complex, 5 ml of a 1.55 *M* DMCP solution in the corresponding solvent, and 0.2 ml of n-hexane as a GLC standard were placed. Sample taking and GLC analysis of the catalysed products were carried out 30 min after the beginning of the reaction and then every hour during the reaction. The initial reaction rate was determined by plotting the DMCP conversion at $\tau = 0$.

(b) Compound III was isolated in experiments 5 and 7 (Table 1). The ether solution containing III (GLC) was poured into cold water, the ether layer was then separated, and the aqueous one was extracted with ether. The combined ether extracts were dried over K_2CO_3, and ether was removed. The ^1H NMR and mass spectra of III are in good agreement with literature data [11].

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