On the interaction of a nickel(0) complex with mono- and di-bromo derivatives of cyclopropane. Novel η^3-allylnickel complexes

T.A. Peganova, L.S. Isaeva *, P.V. Petrovskii and D.N. Kravtsov

A.N. Nesmeyanov Institute of Organoelement Compounds U.S.S.R. Academy of Sciences, Vavilov St., 28, Moscow, V-334 (U.S.S.R.)
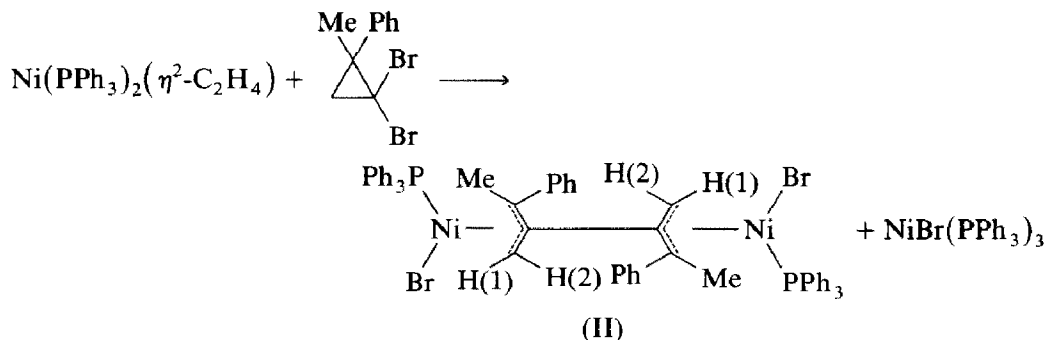
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Abstract

The interaction of (η^2-ethylene)bis(triphenylphosphine)nickel(0) with 1-bromo-2-methyl-2-phenyl- and 1,1,-dibromo-2-methyl-2-phenyl-cyclopropane has been studied. These reactions were expected to proceed with opening of the three-membered ring and to lead to the formation of novel nickel η^3-allyl complexes: bromo(η^3-1-methyl-1-phenylallyl)triphenylphosphinenickel (I) and dibromo[2,2'-bis(η^3-1-methyl-1-phenylallyl)]bis(triphenylphosphine)dinickel (II), respectively. The structures of complexes I and II are discussed on the basis of ^{1}H and ^{31}P{^{1}H} NMR spectra. The novel cationic complex bis(acetonitrile)[2,2'-bis(η^3-1-methyl-1-phenyl-allyl]bis(triphenylphosphine)dinickel bis(tetrafluoroborate) has been synthesized by replacing the halide ligand in compound II by acetonitrile in the presence of TlBF$_4$ and characterized by ^{1}H and ^{31}P, ^{13}C NMR spectral data.

Introduction

Nickel compounds containing a Ni–C σ-bond are often synthesized using the reactions of oxidative addition of aryl-, vinyl-, benzyl-, as well as perfluoro- and polychloroalkyl halides to zero-valent nickel complexes [1–5]. However, in the literature there is no information on the interaction of nickel(0) complexes with bromo derivatives of cyclopropane. Only in ref. 6 is there a mention of the reaction of bromocyclopropane with palladium chloride, leading to the formation of a palladium complex with an η^3-allyl structure. The aim of the present work was to investigate the interaction of (η^2-ethylene)bis(triphenylphosphine)nickel(0) with 1-bromo-2-methyl-2-phenyl- and 1,1-dibromo-2-methyl-2-phenylcyclopropane.

Results and discussion

It has been established that in the reaction of $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$ with an excess of 1-bromo-2-methyl-2-phenylcyclopropane at room temperature the novel nickel complex bromo(η^3-1-methyl-1-phenylallyl)triphenylphosphinenickel (I) (yield 50%) is formed.

$$Ni(PPh_3)_2(\eta^2\text{-}C_2H_4) + \underset{Br}{\overset{Me\quad Ph}{\triangle}} \longrightarrow \underset{Br\quad Me}{\overset{Ph_3P\quad H(1)\quad H(2)}{Ni-H(3)}} + Ni(PPh_3)_3$$

(I)

The η^3-allyl complex I is probably formed as a result of oxidative addition of a cyclopropane monobromo derivative to the nickel(0) complex with the formation of a labile nickel σ-cyclopropyl compound, which is the transformed into the more stable complex I with opening of the three-membered ring.

Compound I is a crystalline red substance, which is moderately soluble in toluene, poorly soluble in ether and petroleum ether, and sensitivite to atmospheric oxygen. Solvents such as chloroform and acetonitrile decompose it even in argon.

The structure of complex I has been established on the basis of elemental analysis and ^{1}H and ^{31}P NMR spectral data. In the ^{1}H NME spectrum of this compound (recorded in C_6D_6), together with multiplet signals from the phenyl protons in the range δ 6.90–7.90 ppm, a narrow singlet signal from protons of the η^3-allyl ligand methyl substituent at δ 2.18 ppm is observed. The allyl protons appear as three multiplets characteristic of an AMX three-spin system: $\delta(H(1))$ 2.01 ppm, $\delta(H(2))$ 2.13 ppm, $\delta(H(3))$ 4.98 ppm ($^2J(H(1)\text{-}H(2))$ 2.4 Hz, $^3J(H(2)\text{-}H(3))$ 8.3 Hz, $^3J(H(1)\text{-}H(3))$ 13.5 Hz). The relative integral intensities of all the above signals agree with the assumed structure of complex I. A similar ^{1}H NMR spectrum has been described for chloro(η^3-1-methylallyl)triphenylphosphinenickel [7].

The ^{31}P\{^{1}H\} NMR spectrum of compound I (recorded in C_6D_6) contains one narrow singlet signal at δ 28.88 ppm.

Together with compound I, $Ni(PPh_3)_3$ was isolated from the mother liquor of the above reaction. It was identified by comparing the ^{1}H and ^{31}P\{^{1}H\} NMR spectral parameters with those of an independently prepared sample. Moreover, when the benzene solution of $Ni(PPh_3)_3$ obtained was treated with trans-stilbene, (η^2-trans-stilbene)bis(triphenylphosphine)nickel was formed [8]. It should be noted that previously we also observed the formation of phosphinenickel(0) complexes $[Ni(PPh_3)_2]_x$ in reactions of (η^2-ethylene)bis(triphenylphosphine)nickel with three-membered carbon rings [9].

The course of the reaction of $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$ with 1,1-dibromo-2-methyl-2-phenylcyclopropane in benzene at room temperature is expected to be more complicated, the composition of the products formed depending on the ratio between the initial reagents. Thus, with a $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$ to dibromocyclopropane ratio of 2/1 the main products of the reaction are the binuclear nickel η^3-allyl complex dibromo[2,2'-bis(η^3-1-methyl-1-phenylallyl)]bis(triphenylphosphine)dinickel (II) and the univalent nickel complex $NiBr(PPh_3)_3$ [10].

$$\text{Ni}(PPh_3)_2\big(\eta^2\text{-}C_2H_4\big) + \quad \overset{\displaystyle Me\;Ph}{\underset{\displaystyle Br}{\triangle}}\!\!\!\overset{Br}{} \longrightarrow$$

$$\underset{Br\;\;H(1)\;\;\;\;H(2)\;Ph}{\overset{Ph_3P\;\;\;Me\;\;\;\;Ph\;\;H(2)\;\;\;\;\;H(1)\;\;Br}{Ni \text{—} \Big\rangle\!\!=\!\!=\!\!\Big\langle\text{—} Ni}} \quad + \text{NiBr}(PPh_3)_3$$

(II)

In the course of this reaction, the same unusual oxidative addition of dibromo-cyclopropane to the nickel(0) complex seems to take place, as in the case of the cyclopropane monobromo derivative, with the formation of a nickel complex with a 2-bromo-substituted η^3-allyl ligand. This is then transformed into the binuclear η^3-allyl complex II by the splitting of bromine under the action of the nickel(0) compound and the coupling of η^3-allyl fragments.

The same mixture of complexes II and NiBr(PPh$_3$)$_3$ has been obtained in the reaction of equimolar quantities of Ni(PPh$_3$)$_2$(η^2-C$_2$H$_4$) and 1,1-dibromo-2-methyl-2-phenylcyclopropane, carried out for 20 min. However, if the reaction mixture is kept for 24 h it is possible to isolate compound II and NiBr$_2$(PPh$_3$)$_2$ [11]. The same mixture of products is formed in the interaction of Ni(PPh$_3$)$_2$(η^2-C$_2$H$_4$) with a two-fold excess of dibromocyclopropane. In this case, NiBr(PPh$_3$)$_3$ seems to be formed initially and then interacts with the excess dibromocyclopropane to give NiBr$_2$(PPh$_3$)$_2$. Indeed, when NiBr(PPh$_3$)$_3$ is treated with 1,1-dibromo-2-methyl-2-phenylcyclopropane, NiBr$_2$(PPh$_3$)$_2$ is formed in high yield.

The binuclear complex II, obtained for the first time, is a crystalline brick-red substance, which is readily soluble in halogen-containing hydrocarbons, moderately soluble in benzene, and poorly soluble in ether, petroleum ether and acetonitrile. It has a high thermal stability; in the solid state, it is also oxidatively stable.

The structure of II has been established on the basis of elemental analysis and ^{1}H and ^{31}P NMR spectral data. The ^{1}H NMR spectrum of complex II (recorded in C$_6$D$_6$) contains, together with a complicated multiplet signal from the phenyl protons of the triphenylphosphine ligand and from the proton of the η^3-allyl ligand phenyl substituent in the range δ 6.90–7.90 ppm, a doublet signal from the protons of the η^3-allyl ligand methyl group at δ 2.34 ppm (J(H–P) 4.6 Hz) and two triplet signals from the η^3-allyl ligand terminal protons at δ 2.89 ppm (J(H–P) 4.4 Hz, ^2J(H(1)–H(2)) 3.6 Hz) and 3.87 ppm (J(H–P) 3.6 Hz, ^2J(H(1)–H(2) 3.6 Hz). Comparison of the spectrum of II with those of similar allylnickel complexes [12] allows the latter two signals to be assigned to the η^3-allyl ligand H(1) and H(2) protons, respectively.

When analysing the integral intensities of the above-mentioned signals, it appeared that the number of aromatic protons was almost twice as high as that assumed for complex II. Besides, one can see a very broad signal with the centre at δ 2.52 ppm ($\Delta\nu$ 50 Hz) in the spectrum. Proceeding from this, it can be assumed that along with the η^3-allyl form the solution of compound II probably contains another structural form undergoing dynamic transformations. The ^{31}P $\{^1$H$\}$ NMR spectral data of compound II (recorded in C$_6$D$_6$) do not contradict this assumption. In this spectrum, in addition to a narrow singlet signal at δ 26.74 ppm ($\Delta\nu$ 1.9 Hz),

(III)
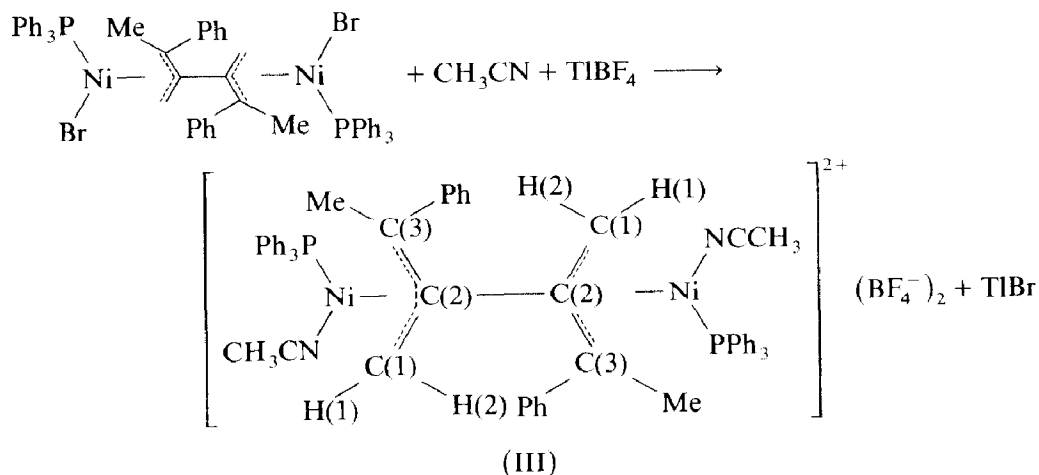
a broadened signal at δ 26.74 ppm ($\Delta\nu$ 40 Hz) is present. In [13], dynamic transformation of the η^3-allyl structure into a butadiene one was detected in a solution of the binuclear η^3-allyl iron complex by ^1H NMR spectroscopy.

To confirm the structure of complex II, we chose a reaction that proceeds with retention of the binuclear η^3-allyl structure. This reaction consists in replacement of the coordinated halide ligand by a neutral one in the presence of a non-coordinating anion. Thus, the action of acetonitrile on complex II in the presence of TlBF$_4$ at room temperature leads to rapid disappearance of the initial nickel complex and the precipitation of TlBr. From the mother liquor the novel cationic binuclear nickel complex bis(acetonitrile)[2,2'-bis(η^3-1-methyl-1-phenylallyl)]bis(triphenylphosphine)dinickel bis(tetrafluoroborate) (III) was isolated in a quantitative yield:

Compound III is an orange crystalline substance, which is readily soluble in polar solvents and has a high thermal and oxidative stability.

The ^1H NMR spectrum of III (recorded in CDCl$_3$) is similar to that of complex

(J(H–P) 4 Hz) from the protons of the η^3-allyl ligand methyl substituent, a singlet signal at δ 2.10 ppm from the protons of the acetonitrile ligand methyl group and two triplet signals at δ 3.27 ppm (J(H–P) 4.8 Hz, J(H(1)–H(2)) 4.8 Hz) and 3.57 ppm (J(H–P) 4.8 Hz, J(H(1)–H(2)) 4.8 Hz) assigned to the H(1) and H(2) protons of the η^3-allyl ligand. In contrast to the spectrum of compound II, in the spectrum of III the ratio of integral intensities of the above signals is 20/1/1/3/3, which corresponds exactly to the η^3-allyl structure assumed for III.

The $^{31}P\{^1H\}$ NMR spectrum of complex III (recorded in CDCl$_3$), having only one narrow singlet signal at δ 28.36 ppm, also indicates the presence of only one structural form in the solution of compound III.

The $^{13}C\{^1H\}$ NMR spectrum of III (recorded in CH$_3$NO$_2$) shows signals from the phenyl carbon atoms in the range δ 128.7–138.2 ppm, together with singlet signals from the methyl group carbon atom of the acetonitrile ligand at δ 2.98 ppm and one of the allyl ligand at δ 23.70 ppm, as well as singlet signals from the carbon atoms of the η^3-allyl ligand at δ 54.02 and 66.29 ppm, assigned to C(1) and C(3),

respectively, and a doublet signal from C(2) at δ 109.36 ppm (J 12.5 Hz). The CN group carbon atom of the acetonitrile ligand appears as a singlet at 120.64 ppm. It should be noted that the spectral data confirm the η^3-allyl structure for complex III and correlate well with those of known η^3-allyl nickel complexes [14].

Consequently, the data obtained demonstrate the first example of the formation of an η^3-allyl system as a result of cleavage of the cyclopropane ring of halogen-substituted cyclopropane under the action of nickel(0) complexes.

Experimental

^{1}H NMR spectra were recorded with a Bruker WP 200 SY spectrometer (200.13 MHz) at 25°C. Chemical shifts are given with respect to residual benzene (7.25 ppm) or residual chloroform (7.15 ppm) and are recalculated relative to TMS. The ^{31}P{^{1}H} NMR spectra were also recorded with a Bruker WP 200 SY instrument (81.01 MHz) at 25°C and with 85% H_3PO_4 as external standard. The ^{13}C{^{1}H} NMR spectra were recorded with a Bruker WP 200 SY spectrometer (50.31 MHz) at 25°C. Chemical shifts are given with respect to CH_3NO_2 (63.11 ppm.).

(η^2-Ethylene)bis(triphenylphosphine)nickel was obtained according to ref. 4. 1,1-Dibromo-2-methyl-2-phenylcyclopropane was synthesized as described in ref. 15, with subsequent reduction resulting in 1-bromo-2-methyl-2-phenylcyclopropane [15].

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

Bromo(η³-1-methyl-1-phenylallyl)triphenylphosphinenickel (I)

A solution of 1-bromo-2-methyl-2-phenylcyclopropane (12.70 mmol) in benzene (8 ml) was added to a suspension of Ni(PPh$_3$)$_2$(η^2-C$_2$H$_4$) (4.04 mmol) in benzene (12 ml). The resulting red-brown solution was kept at 22°C for 24 h and then evaporated to minimum volume. The precipitate formed after addition of ether was filtered off, washed with ether and dried in vacuum to give 1.08 g (50%) of complex I, m.p. 172–174°C (dec.) (from benzene/ether). Anal. Found: C, 63.31. H, 4.93; Br, 14.80; P, 5.82. C$_{28}$H$_{26}$BrNiP calcd.: C, 63.20; H, 4.93; Br, 15.02; P, 5.82%. The combined mother liquor and washing solutions were evaporated to minimum volume and treated with a small quantity of ether. The dark cherry coloured residue was filtered off, washed with a small quantity of ether, and dried in vacuum to give 0.84 g (24%) of Ni(PPh$_3$)$_3$; ^{31}P{^{1}H} NMR (C$_6$D$_6$): 25.58 (br. s.) ppm. The ^{31}P{^{1}H} NMR spectrum of the independently prepared Ni(PPh$_3$)$_3$ [16], recorded under the same conditions, shows a signal at δ 25.24 ppm.

Dibromo[2,2'-bis(η³-1-methyl-1-phenylallyl)]bis(triphenylphosphine)dinickel (II)

(a) A solution of 1,1-dibromo-2-methyl-2-phenylcyclopropane (3.26 mmol) in benzene (8 ml) was added to a suspension of Ni(PPh$_3$)$_2$(η^2-C$_2$H$_4$) (6.48 mmol) in benzene (12 ml). The mixture was stirred at room temperature for 5 h and kept overnight. The yellow precipitate was filtered off, washed with small quantities of benzene and ether, and dried in vacuum; 2.16 g of NiBr(PPh$_3$)$_3$ was obtained. The filtrate was evaporated to minimum volume. The precipitate was filtered off, washed with benzene and ether, and dried in vacuum. NiBr(PPh$_3$)$_3$ (0.43 g) was additionally obtained. The total yield of NiBr(PPh$_3$)$_3$ was 2.59 g (43%), m.p. 157–159°C (dec.)

(from benzene/ether 2/3). (Lit. [10] m.p. 160–162°C (dec.)). The mother liquor was treated with a small quantity of ether. After 2 h, the brick-red precipitate was filtered off, washed with ether and dried in vacuum to give 1.38 g (40%) of complex II, m.p. 209–210°C (dec.) (from benzene). Anal. Found: C, 64.34; H, 4.76; Br, 14.79; P, 5.72. $C_{56}H_{50}Br_2Ni_2P_2$ calcd.: C, 63.32; H, 4.74; Br, 15.05; P, 5.83 %.

(b) A solution of 1,1-dibromo-2-methyl-2-phenylcyclopropane (8.50 mmol) in benzene (15 ml) was added to a suspension of $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$ (4.25 mmol) in benzene (15 ml). The dark brown solution was kept at room temperature for 24 h, and the reaction mixture was then evaporated in vacuum. The oily residue was treated with ether. The precipitate formed, consisting of two substances, was filtered off, washed with ether, and dried in vacuum. Its weight was 2.54 g. It was then washed with CH_3CN. 0.85 g (38%) of complex II remained undissolved on the filter. The acetonitrile solution was evaporated to dryness. A few drops of glacial acetic acid were added to the oily residue. The precipitate formed was filtered off, carefully washed with ether, and dried in vacuum to give 0.86 g (27%) of green $Ni(PPh_3)_2Br_2$, m.p. 220–222°C (dec.) (from glacial CH_3COOH). Lit. data: m.p. 222–225°C (dec.) [11].

(c) As a result of the interaction of $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$ (3.83 mmol) and 1,1-dibromo-2-methyl-2-phenylcyclopropane (3.83 mmol) in benzene for 20 min, 1.20 g (34%) of $NiBr(PPh_3)_3$ and 0.68 g (34%) of complex II were isolated.

(d) The reaction of $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$ (4.81 mmol) and 1,1-dibromo-2-methyl-2-phenylcyclopropane (4.83 mmol) carried out in benzene for 24 h yielded 0.99 g (39%) of complex II and 0.97 g (27%) of $NiBr_2(PPh_3)_2$.

Bis(acetonitrile)[2,2′-bis(η³-1-methyl-1-phenylallyl)]bis(triphenylphosphine)dinickel bis(tetrafluoroborate) (III)

A mixture of complex II (1.13 mmol) and $TlBF_4$ (2.50 mmol) in acetonitrile (20 ml) was stirred at room temperature. After 3 h the precipitate of TlBr was filtered off; the filtrate was evaporated to minimum volume and treated with ether. The precipitate formed was filtered off, washed with ether, and dried in vacuum to give 1.28 g (98%) of complex III, m.p. 205–207°C (dec.) (from acetone). Anal. Found: C, 61.64; H, 5.09; F, 12.61; P, 5.10. $C_{60}H_{56}B_2F_8N_2Ni_2P_2$ calcd: C, 62.23; H, 4.87; F, 13.12; P, 5.35%.

Acknowledgement

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