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Novel olefin nickel(0) complexes of the methyl derivatives of methylenecyclopropane and cyclopropene

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Abstract

The interaction of phosphine nickel complexes $Ni(PPh_3)_3$ and $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$ with methyl derivatives of methylenecyclopropane and cyclopropene has been studied. The novel olefin complexes: (η^2-2,2-dimethyl-1-methylenecyclopropane)bis(triphenylphosphine)nickel, (η^2-1,3,3-trimethylcyclopropene)bis(triphenylphosphine)nickel and (η^2-tetramethylcyclopropene)bis(triphenylphosphine)nickel have been prepared. The structure of the compounds obtained is discussed on the basis of the ^1H and $^{31}P\{^1H\}$ NMR spectra. Comparative studies of the reactivities of the resulting complexes in the substitution reactions of η^2-olefin ligands are described.

Introduction

It has been shown that the interaction between phosphine complexes of nickel(0) and methylenecyclopropane (MCP) and 3,3-dimethylcyclopropene (DMCP) results in (η^2-methylenecyclopropane)bis(triphenylphosphine)nickel [1] and bis(triphenylphosphine)5-nickela-3,3,7,7-tetramethyl-*trans*-tricyclo [4.1.0.0^{2,4}] heptane [2] which are regarded as possible intermediates in catalytic transformations of three-membered carbocycles in the presence of nickel(0) complexes [3].

Here we report on a study on the interaction of phosphine complexes of nickel(0) with the methyl derivatives of methylenecyclopropane, as well as with 1,3,3-trimethyl- and tetramethylcyclopropene. Preliminary information on this work has appeared [4,5].

Results and discussion

It has been found that (η^2-ethylene)bis(triphenylphosphine)nickel or tris(triphenylphosphine)nickel react with 2,2-dimethyl-1-methylenecyclopropane as readily as with MCP [1] at 22°C in benzene to give (η^2-2,2-dimethyl-1-methylenecyclopro-

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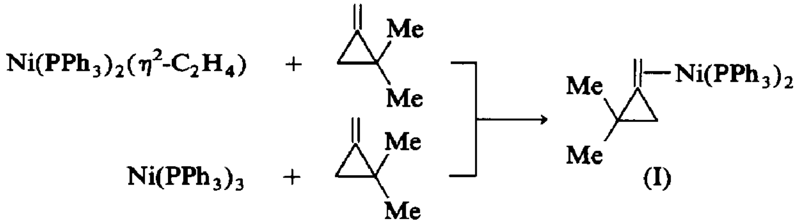
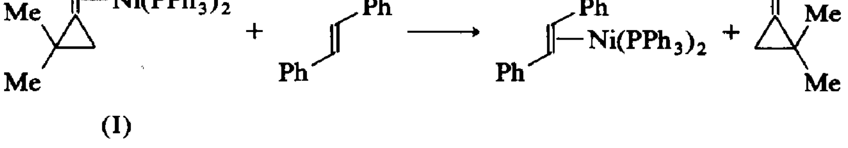
pane)bis(triphenylphosphine)nickel (I) in high yield:



It should be noted that the olefin complex I is formed in the reaction of tris(triphenylphosphine)nickel with 2,2-dimethyl-1-methylenecyclopropane only if the molar concentration of 2,2-dimethyl-1-methylenecyclopropane in the reaction mixture exceeds 3 *M*.

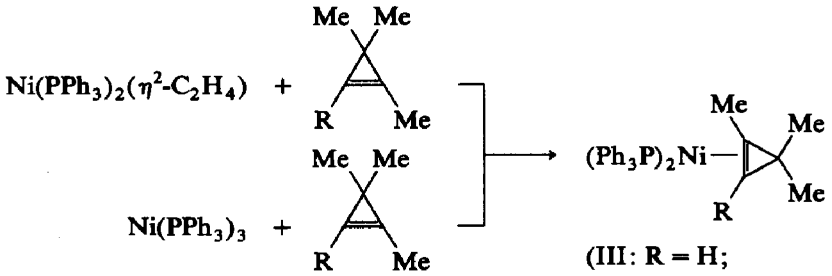
Complex I is a yellow crystalline substance, moderately soluble in benzene, poorly soluble in ether, sensitive to the action of air, and decomposes upon heating above 100 ° C. The ^{1}H NMR spectrum of complex I exhibits two singlet signals of equal integral intensity at δ 1.13 and 1.55 ppm which are assigned to the protons of the methyl groups. Olefin protons give signals typical of the AB spin system (δ 2.51; 2.35 ppm, ^2J(H–H) 2.8 Hz), their low-field components are broadened owing to spin–spin interaction with the less screened proton of the cyclopropane ring. Thus upon complexation there is an upfield shift of the signals from the olefin ligand protons of approximately 2.8–3.0 ppm relative to the corresponding signals from the protons of non-coordinated 2,2-dimethyl-1-methylenecyclopropane [6]. The protons of the cyclopropane ring are also non-equivalent and appear as two signals with the centres at 0.98 and 0.88 ppm, the latter is observed as a quadruplet (^2J(H–H) = J(P(1)–H) = J(P(2)–H) = 3.0 Hz). The signal from the cyclopropane proton at 0.98 ppm is broadened owing to the interaction with the less screened olefin proton (^4J(H–H) 1.5 Hz). The protons of the phenyl rings of triphenylphosphine ligands are revealed as two multiplet signals in the range δ 6.90–7.90 ppm.

In the ^{31}P{^{1}H} NMR spectrum of compound I, only one narrow singlet, at 32.88 ppm, is observed which is probably attributable to the fast rotation (on the NMR time scale) of the methylenecyclopropane ligand around the Ni–ligand bond. The spectral data indicates that I is a structural analogue of the previously synthesized (η^2-methylenecyclopropane)bis(triphenylphosphine)nickel (II) [1]. In compound I as well as in II, the substitution of the methylenecyclopropane ligand to form (η^2-*trans*-stilbene)bis(triphenylphosphine)nickel occurs readily under the action of *trans*-stilbene:



2,2-Dimethyl-1-methylenecyclopropane which is liberated is detected in solution by GLC and ^{1}H NMR spectroscopy.

Unexpected results that indicate the formation of new olefin complexes (η^2-1,3,3-trimethylcyclopropene)bis(triphenylphosphine)nickel (III) and (η^2-tetramethylcyclopropene)bis(triphenylphosphine)nickel (IV) were obtained during our study of the interaction of (η^2-ethylene)bis(triphenylphosphine)nickel or tris(triphenylphosphine)nickel with 1,3,3-trimethyl- and tetramethylcyclopropene:



(III: R = H;
(IV: R = Me)

The reactions proceed in benzene at 22° C. Compounds III and IV are formed in 80–90% yields.

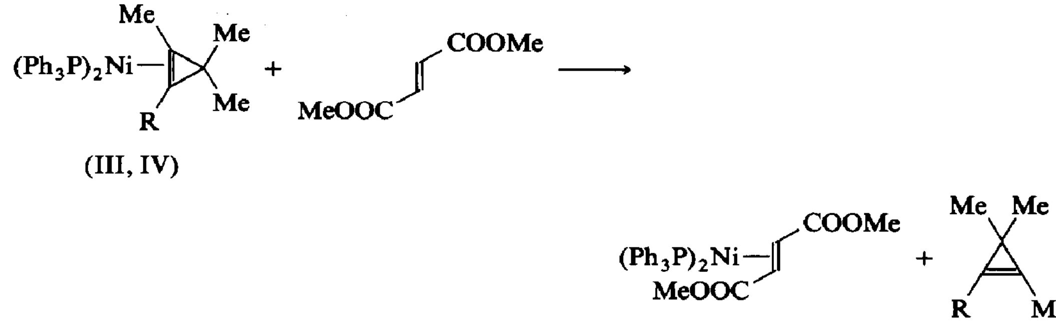
In contrast, the reactions of DMCP with the same nickel compounds, described previously [2,7] yield the nickelacyclopentane derivatives. It appears that the presence of the methyl substituents at the double bond of cyclopropene creates some steric hindrance which inhibits the formation of the nickelacyclopentane structure.

The structure of complexes III and IV was established from their ^1H and ^{31}P NMR spectra as well as from their chemical behaviour. In the ^1H NMR spectrum of compound III there are three signals from the protons of the cyclopropene ligand methyl groups; two are singlets at δ 1.36 and 2.18 ppm and one is a doublet at δ 1.79 ppm, J(P–H) 5.6 Hz. The proton at the double bond of the coordinated cyclopropene, which in the spectrum, gives rise to a doublet of doublets, centred at 2.55 ppm with J(P(1)–H) 12.1 Hz, J(P(2)–H) 2.8 Hz. It should be noted that in compound III the signal from the proton at the double bond is shifted by 4 ppm towards high field as compared with the corresponding signal from the proton of free 1,3,3-trimethylcyclopropene [8].

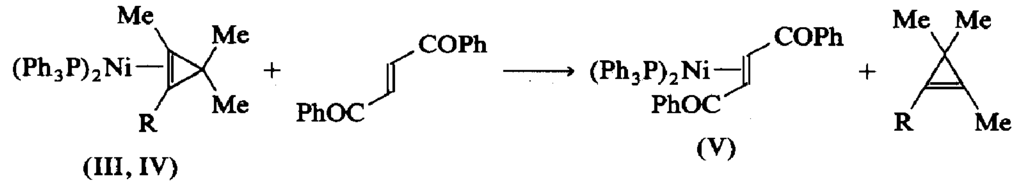
The ^1H NMR spectrum of compound IV also shows the three signals from the protons of the cyclopropene ligand methyl groups. These singlets, at δ 1.27, 1.48 and 2.40 ppm, have an intensity ratio of 1 : 2 : 1. In the spectra of III and IV, the signals from the phenyl protons of the triphenylphosphine ligands appear as two multiplets in the range δ 6.90–7.90 ppm.

An examination of the $^{31}P\{^1H\}$ NMR spectra of complexes III and IV has shown that the spectrum of III contains the quadruplet signal typical for an AB spin system (δ_A 36.99, δ_B 37.75 ppm, J_{AB} 30.4 Hz), and the spectrum of IV contains one singlet signal at δ 36.24 ppm. These data indicate that the phosphorus atoms are equivalent in IV but not in III, which is consistent with the supposed trigonal structure of these compounds.

Similar to the known olefin complexes of nickel(0), compounds III and IV are yellow crystalline substances, sensitive to the atmospheric oxygen but in contrast to $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$ for example, these compounds are stable towards the action of vinyltrimethylsilane, *trans*-stilbene and triphenylphosphine [9,10]. However, they readily undergo replacement of the cyclopropene ligand by olefins having electron-accepting groups, such as the dimethyl ester of fumaric acid or *trans*-1,2-dibenzoylethylene. Thus the reactions of III and IV with dimethylfumarate proceed under mild conditions in benzene solution at 22° C, to give (η^2-dimethylfumarate)bis(triphenylphosphine)nickel in a quantitative yield:



Similarly, III and IV react with *trans*-1,2-dibenzoylethylene to form (η^2-*trans*-1,2-dibenzoylethylene)bis(triphenylphosphine)nickel (V) in 74 and 73% yields, respectively:

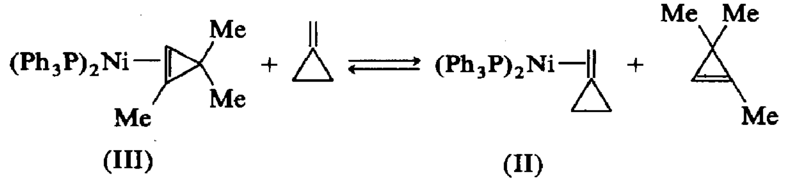


The olefin complex V is novel. It is a dark-blue crystalline substance, sensitive to the action of the atmospheric oxygen, soluble in aromatic hydrocarbons, and poorly soluble in ether and pentane. The structure of this compound was determined on form its NMR spectral data. The $^{31}P\{^1H\}$ NMR spectrum of complex V shows one narrow singlet signal at δ 34.3 ppm which indicates the equivalence of the phosphorus atoms in this compound. The presence of one singlet of the olefin protons at 5.30 ppm in the ^1H NMR spectrum of V confirms their chemical equivalence and, consequently, the η^2-coordination of *trans*-1,2-dibenzoylethylene with the nickel atom. Similar features are observed in the ^1H NMR spectrum of the tetracarbonyl complex of iron-containing η^2-coordinated 1,2-dibenzoylethylene [11].

The reactions of complexes III and IV with dimethylfumarate and *trans*-1,2-dibenzoylethylene can be regarded as chemical evidence of the η^2-olefin structure of these compounds. Similar η^2 coordination is quite typical for methyl-substituted cyclopropene complexes of Pt^0 [12].

Further comparative studies of the reactivities of the cyclopropene complexes synthesized, III and IV, permitted us to establish not only the similarities, but also the differences in their chemical behaviour.

It has been found that trimethylcyclopropene complex III reacts reversibly with a five-fold excess of MCP to give compound II (50% yield):

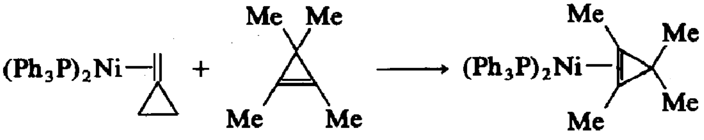


So when II is treated with an excess of 1,3,3-trimethylcyclopropene the reaction can be shifted to the left and III can again be obtained in 80% yield.

In contrast, the tetramethylcyclopropene complex IV fails to react even with an 18-fold excess of MCP.

Such a difference in the behaviour of III and IV with respect to MCP appears to be due to the difference in the steric requirements of the cyclopropene ligands in these compounds.

It is noteworthy that the reaction of II with an excess of tetramethylcyclopropene gives IV in high yield:



(II) (IV)

Consequently, in terms of reactivity the methylenecyclopropane complex II differs substantially from the cyclopropene complexes III and IV. A qualitative comparison of the reactivity of olefin complexes II, III and IV shows that firstly, the reactivity of IV in the replacement of the olefin ligand is lower than that of III, probably because of steric factors, and secondly, the reactivity of III is lower than that of II, because II does undergo reaction with *trans*-stilbene [1], vinyltrimethyl- [5], and tetravinylsilane [1].

Experimental

The ^1H NMR spectra were recorded with a Bruker WP 200 SY spectrometer (200.13 MHz) at 25 °C. Deuterobenzene was the solvent in all cases. The chemical shifts are given with respect to residual benzene (7.25 ppm), and recalculated with respect to TMS. The $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker WP 200 SY (81.01 MHz), in deuterobenzene solution at 25 °C, and 85% H_3PO_4 as external standard.

GLC analysis of the mixtures containing 2,2-dimethylmethylenecyclopropane and 1,3,3-trimethylcyclopropene was performed on a Tsvet 104 chromatograph equipped with a flame-ionization detector in a stream of N_2, a 3 m × 2 mm column with 5% SE-30 on Chromatone N-AW. The mixtures containing tetramethylcyclopropene were chromatographed on Chrom 41 instrument equipped with a flame-ionization detector in a stream of N_2, in a glass 2.5 m × 3 mm column using 4.25% OV-101 and 0.75% OV-17 as a liquid phase on Chromosorb HP W/AW treated with dimethyldichlorosilane.

(η^2-Ethylene)bis(triphenylphosphine)nickel [13] and tris(triphenylphosphine)nickel [14] were prepared by published procedures. 1,3,3-Trimethylcyclopropene was synthesized as described previously [15], and then isomerized to 2,2-dimethylmethylenecyclopropane [16]. Tetramethylcyclopropene was obtained by methylation of 1,3,3-trimethylcyclopropene [8].

All the experiments involving the nickel complexes were carried out under argon in absolute solvents which had been distilled under argon immediately before.

(η^2-2,2-Dimethyl-1-methylenecyclopropane)bis(triphenylphosphine)nickel (I)

(a) A solution of 2,2-dimethyl-1-methylenecyclopropane (12.00 mmol) in benzene (12 ml) was added to a suspension of $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$ (4.63 mmol) in 20 ml of benzene. The mixture was kept at 22 °C for 20 h. The resulting yellow-brown solution was evaporated in vacuum to minimal volume and treated with ether. The yellow precipitate that formed was filtered off, washed with a small amount of benzene and ether, and dried in vacuum to give 2.70 g (88%) of complex I m.p. 100–125 °C (dec.) (from benzene/ether). Anal. Found: C, 75.81; H, 6.02. $C_{42}H_{40}NiP_2$ calcd.: C, 75.81; H, 6.06%.

(b) A solution of 2,2-dimethyl-1-methylenecyclopropane (9.00 mmol) in benzene (3 ml) was added gradually to $Ni(PPh_3)_3$ (1.90 mmol). The reaction mixture immediately changed from red-brown to yellow. After 45 minutes the mixture was treated with 5 ml of ether, the resulting precipitate was filtered off, then carefully washed with ether, and dried in vacuum to give 1.03 g (82%) of complex I.

(η^2-*trans-Stilbene)bis(triphenylphosphine)nickel*

A solution of *trans*-stilbene (3.66 mmol) in benzene (5 ml) was added to a suspension of complex I (1.22 mmol) in benzene (10 ml). The mixture was stirred at 22 °C for 20 h. The resulting dark-red solution was evaporated to dryness in vacuum. The distillate that was collected at −78 °C contained 2,2-dimethyl-1-methylenecyclopropane by GLC and ^{1}H NMR spectroscopy. Ether was added to the dry residue. The resulting precipitate was filtered off, washed with ether, and dried in vacuum to give 0.88 g (94%) of (η^2-*trans*-stilbene)bis(triphenylphosphine)nickel; its ^{1}H NMR spectrum is identical with that described previously [1].

(η^2-*1,3,3-Trimethylcyclopropene)bis(triphenylphosphine)nickel (III)*

(a) A solution of 1,3,3-trimethylcyclopropene (10.64 mmol in benzene (7 ml) was added to a suspension of $Ni(PPh_3)_3$ (2.99 mmol) in 15 ml of benzene at 22 °C. In this case the precipitate dissolved and the solution colour changed from dark red to yellow. After 20 h the mixture was evaporated to dryness and a small amount of ether and pentane was added to the residue. The resulting yellow precipitate was filtered off, washed with pentane, and dried in vacuum to give 1.78 g (89%) of III, m.p. 105–120 °C (dec.) (from ether/pentane). Anal. Found: C, 75.21; H, 6.00. $C_{42}H_{40}NiP_2$ calcd.: C, 75.81, H, 6.06%.

(b) A solution of 1,3,3-trimethylcyclopropene (12.50 mmol) in benzene (10 ml) was added to a suspension of $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$ (4.05 mmol) in 20 ml of benzene. The mixture was stirred for 5 h and left to stand overnight at 22 °C. After work-up of the mixture as described above, 2.14 g (80%) of III was isolated.

(c) A solution of 1,3,3-trimethylcyclopropene (9.16 mmol) in benzene (4 ml) was added to complex II (1.80 mmol). The resulting suspension was stirred for 4 h at 22 °C until the initial complex had completely dissolved. 0.88 g (73%) of complex III was isolated after the had been worked up as described above.

(η^2-*Tetramethylcyclopropene)bis(triphenylphosphine)nickel (IV)*

(a) A solution of tetramethylcyclopropene (21.06 mmol) in benzene (6 ml) was added to $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$ (7.13 mmol). The mixture was stirred for 3 h at 22 °C and left to stand overnight. The resulting yellow-brown solution was evaporated to dryness. The oily residue was dissolved in a minimal amount of ether and the solution was treated with pentane. The yellow precipitate that formed after two hours of standing was filtered off, washed twice with a small amount of pentane, and dried in vacuum to give 4.01 g (83%) of complex IV, m.p. 142–146 °C (dec.) (from ether/pentane). Anal. Found: C, 76.09; H, 6.20; P, 9.42. $C_{43}H_{42}NiP_2$ calcd.: C, 76.01; H, 6.23; P, 9.12%.

(b) A solution of tetramethylcyclopropene (13.75 mmol) in benzene solution (5 ml) was added to $Ni(PPh_3)_3$ (3.00 mmol). The resulting dark-red suspension was stirred for 2 h at 22° C. After work up of yellow-brown solution as described above, 1.80 g (88%) of compound IV was isolated.

(c) A solution of tetramethylcyclopropene (15.85 mmol) in benzene (3.8 ml) was added to complex II (1.96 mmol). The resulting suspension was stirred for 10 h at 22° C until the initial complex had completely dissolved. Then the reaction mixture was evaporated to dryness. The oily residue was worked up as described above, to give 1.08 g (81%) of compound IV.

(η^2-Dimethylfumarate)bis(triphenylphosphine)nickel

(a) A solution of dimethylfumarate (2.01 mmol) in benzene (15 ml) was added to complex III (2.01 mmol) and a gradual change in the colour of the mixture from yellow to red was observed. The mixture was left to stand overnight at 22° C, then evaporated to dryness. The GLC analysis data and the ^{1}H NMR spectrum indicate that the distillate contained 1,3,3-trimethylcyclopropene. A small amount of ether was added to the oily residue. The resulting red precipitate was filtered off, washed with ether, and dried in vacuum to give 1.05 g (83%) of (η^2-dimethylfumarate)bis (triphenylphosphine)nickel; its ^{1}H NMR spectrum is identical with that described previously [17].

(b) A solution of dimethylfumarate (1.30 mmol) in benzene (10 ml) was added to complex IV (1.30 mmol). The resulting mixture was left to stand for 20 h at 22° C. The red solution that formed was evaporated to dryness. The GLC data showed the distillate to contain tetramethylcyclopropene. The oily residue was worked up as described above to give 0.78 g (95%) of (η^2-dimethylfumarate)bis(triphenylphosphine)nickel.

*(η^2-*Trans*-1,2-dibenzoylethylene)bis(triphenylphosphine)nickel (V)*

(a) A solution of *trans*-1,2-dibenzoylethylene (3.00 mmol) in benzene (7 ml) was added to the a solution of complex IV (2.70 mmol) in benzene (10 ml) at 22° C and the mixture turned from dark brown to a deep lilac. After 2 h the mixture was evaporated to the minimal volume and treated with a small amount of ether. The resulting dark blue precipitate was filtered off, washed with ether, and dried in vacuum. 1.62 g (73%) of complex V was obtained, m.p. 195–197° C (dec.) (from benzene). Anal. Found: C, 76.06; H, 5.36; P, 7.39. $C_{52}H_{42}NiO_2P_2$ calcd.: C, 76.21; H, 5.17; P, 7.56%. The GLC data, showed the distillate of the reaction mixture to contain tetramethylcyclopropene.

(b) Similarly, 0.95 g (74%) of complex V was obtained from the reaction of complex III (1.56 mmol) with *trans*-1,2-dibenzoylethylene (1.75 mmol). GLC showed the distillate of the reaction mixture to contain 1,3,3-trimethylcyclopropene.

(η^2-Methylenecyclopropane)bis(triphenylphosphine)nickel (II)

A solution of MCP (12.00 mmol) in toluene (4 ml) was added to complex III (2.30 mmol). After 20 min a yellow precipitate started to form. The mixture was stirred for 2 h at 22° C. The precipitate was filtered off, washed with ether, and dried in vacuum, to give 0.72 g (49%) of complex II; its ^{1}H NMR spectrum is identical to that described previously [1]. GLC showed the mother solution to contain 1,3,3-trimethylcyclopropene.

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