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CATIONIC π-ALLYLIC COMPLEXES

II *. CATIONIC π-ALLYLIC COMPLEXES OF NICKEL(II) FROM ALLYLOXYTRIS(DIMETHYLAMINO)PHOSPHONIUM SALTS **

D. NEIBECKER *** and B. CASTRO *

Laboratoire de Chimie Organique II, ERA No. 558 CNRS, Université de Nancy I, Case Officielle 140, 54037 Nancy Cédex (France)

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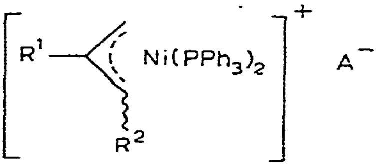
Summary

In a preliminary communication, we described the preparation of air stable cationic π-allylic complexes of nickel(II) of the type:



The reaction of allyloxytris(dimethylamino)phosphonium salts with tetracarbonylnickel which afforded these salts is in detail described.

Introduction

Recently there has been increasing interest in cationic complexes of transition metals. Their reactivities, either in synthesis or in catalysis are often greater than those of neutral complexes. Cationic π-allylic complexes are catalysts or precursors of catalysts for many reactions (codimerization butadiene/ethylene [2], telomerization of butadiene [3]). There are essentially three types of preparation

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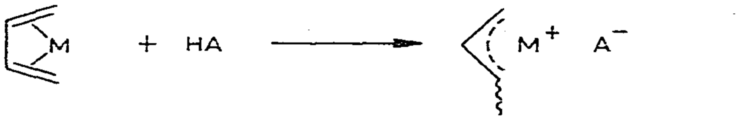
[*] For Part I see ref. 1.

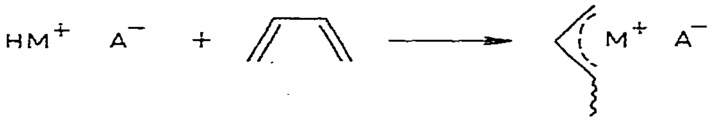
[**] In the text we use "oxyphosphonium" for "oxytris(dimethylamino)phosphonium".

[***] Present adress: Institut de Recherches sur la catalyes, 79, bld du 11 Novembre 1918, 69626 Villeurbanne Cédex (France).

of these complexes which are summarized in eqns. 1—3.



(1)



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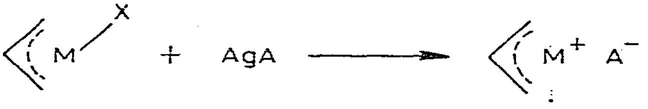
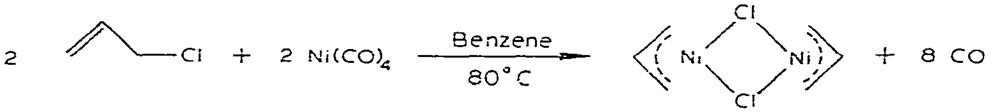


(3)

The range of products obtainable by reactions 1 and 2 is limited. Reaction 3 is more versatile but more expensive. Up to now, cationic π-allylic complexes could be obtained by only two routes, neither of which are general [2,4,5] *. The difficulty is to avoid the presence of halogen ions in the reaction mixture which give rise to formation of neutral complexes [6] (eq. 4).



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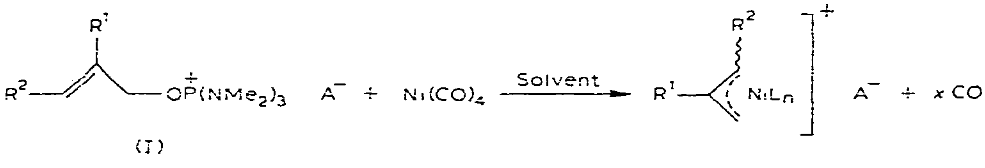
It occurred to us that the use of allyloxyphosphonium salts would avoid such difficulties; cationic π-allylic complexes would be obtained in one step, the decomposition of oxyphosphonium salts affording a neutral species, viz. hexamethylphosphoramide (HMPA) (eq. 5).



(5)

R^1 = H, Me, Ph ; R^2 = H, Me

A = ClO_4 , PF_6 , BF_4

L = CO, HMPA, solvent ;

n = 2, 3

Results

Choice of the solvent: optimal conditions

An excess of tetracarbonylnickel (2 equivalents) is added to a solution or a suspension of allyloxyphosphonium salts I (1 equivalent) in the selected solvent. A reaction occurs which is characterized by a change of colour of the reaction mixture and evolution of carbon monoxide. As soon as gas evolution ceases,

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* For a detailed review of nickel complexes and their applications see ref. 5.

TABLE 1

INFLUENCE OF SOLVENT ON REACTION 5

Solvent	t (h)	T (°C)	"ρ"
C_6H_{12}	7	40	0.75
C_6H_6	1	40	0.75
$(C_2H_5)_2O$	3	room temp.	0.75
HMPA	0.5	room temp.	0.9
CH_3CN	0.25	room temp.	0.93
C_6H_6/CH_3CN [a]	1	room temp.	0.96

[a] Suspension in benzene with 2 equivalents of acetonitrile for one equivalent of salt I.

the excess of tetracarbonylnickel is removed by evaporation under reduced pressure.

We first used benzene as solvent, since this is commonly used in the synthesis of π-allylic neutral complexes. The product is a red oily material, insoluble in benzene. The IR spectrum exhibits two absorptions at 2060 and 2090 cm^{-1} in accordance with formation of $[\pi\text{-allylNi(CO)}_2]^+$ which was postulated by Green in 1964 [7] but never isolated [8]. However, we were unable to characterize this product because any attempts to dissolve or crystallize it, led only to decomposition.

Using *N,N*-dimethylformamide (DMF), in which the starting salt is soluble, affords a green solution characteristic of Ni^{2+} ions. The reaction probably follows the same route as the reaction of allylic halides with tetracarbonylnickel, yielding hexadienes and nickel salts [9,10,15].

To avoid these difficulties we started a systematic study of the influence of solvent on reaction 5.

We have postulated that this reaction could be explained by a simple mechanism only if the yield in nickel "ρ" * was equal or close to unity. Using the experimental procedure described above, we obtained the results shown in Table 1. The important features of the results are as follows. (i) The yield of nickel complex increases with the polarity and the "coordination efficiency" of the solvent. (ii) In polar solvents the reaction is fast and proceeds at room temperature. (iii) The yield in nickel increases from 0.75 in benzene to 0.96 when the reaction is carried out in benzene/acetonitrile; acetonitrile functions not only as solvent but participates in the reaction, and appears to be the optimal solvent for these reactions.

Reactions in acetonitrile: characterization of products

The achievement of yields close to 1 is in agreement with the formation of 1/1 adducts of the type II. However it is not possible to isolate such a compound in a pure state as the solution contains (among other by-products) some HMPA. Any attempts to purify them always give rise to a partial decomposition. The products were characterized as follows:

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* The yield "ρ" is defined as the ratio of the number of moles of nickel remaining in the reaction mixture after removal of excess of $Ni(CO)_4$ over the number of moles of allyloxyphosphonium salt introduced.

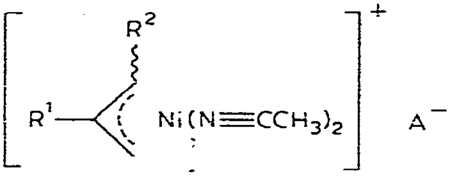
The IR spectrum shows no absorption corresponding to a double bond or to coordinated carbon monoxide, but two bands at 2280 and 2310 cm^{-1} characteristic of acetonitrile bound to a metal through the nitrogen lone-pair [11].

The volume of evolved carbon monoxide is 3.7 mole per mole of consumes salt, in good agreement with the theoretical value 4.

The ^1H NMR spectrum of the products of a reaction in deuteriated acetonitrile in the case R^1 = Ph; R^2 = H is presented in Fig. 1, and is particularly simple. Two singlets at δ 3.73 and 2.51 ppm (downfield from TMS) are attributed respectively to *syn* and *anti* hydrogens [12].

The ^{13}C NMR spectrum (broadband decoupling) of products obtained in the case R^1 = Me; R^2 = H shows the equivalence of carbons 1 and 3 at δ 57.8 ppm and a broad signal is observed at δ 118.6 ppm for the carbon of the cyano group of acetonitrile (Fig. 2) [13].

These results indicate that the allyl group is rigidly bound to nickel at the temperature of observation and that acetonitrile is exchanging rapidly at that temperature [2,14]. These results suggest structure III in solution.



(III)

The formation of complexes III is accompanied by formation of hexadienes produced in less than 8% yield from the starting salt. Hexadienes can be formed

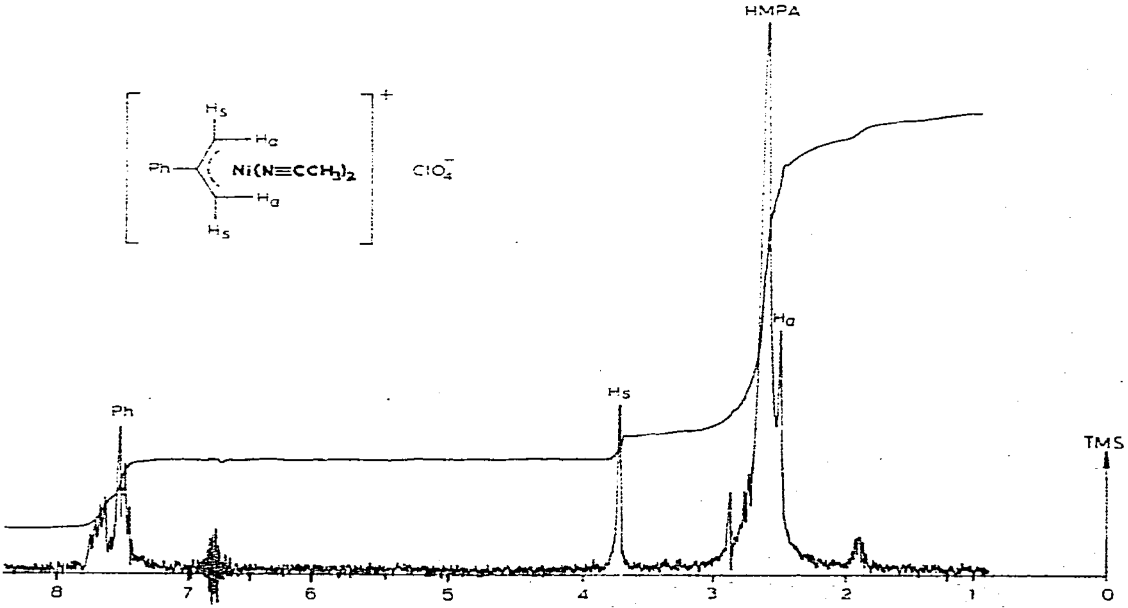


Fig. 1. ^1H NMR spectrum of the products of a reaction in deuteriated acetonitrile (R^1 = Ph; R^2 = H).

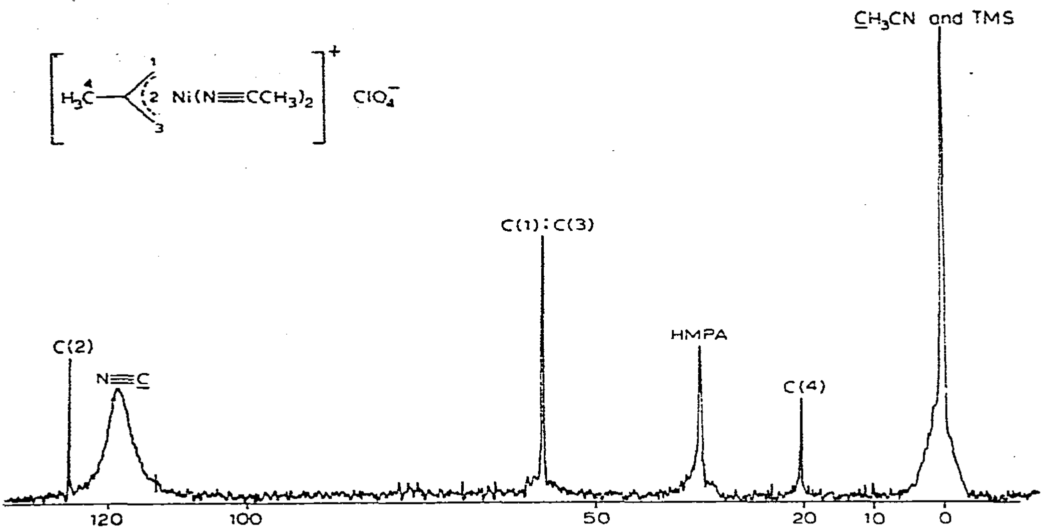
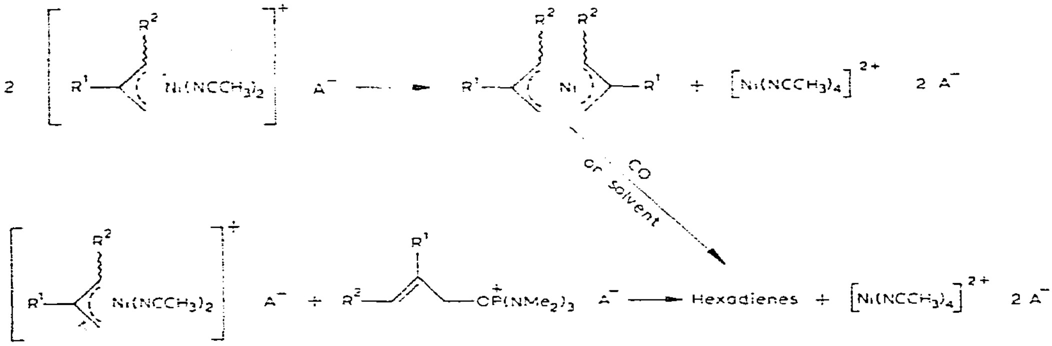


Fig. 2. ^{13}C NMR spectrum of the products obtained when R^1 = Me; R^2 = H.

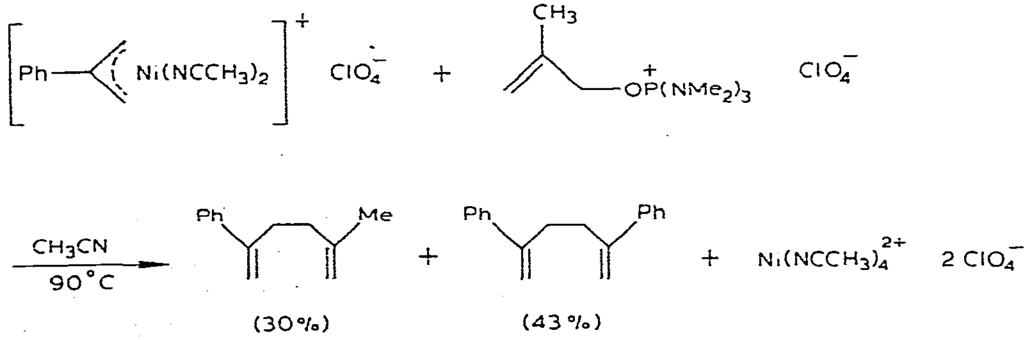
by two routes (eqns. 6,7). Reaction 6 is similar to the dissociation of bis(π-allyl-



(6)

(7)

halonickel) described by Corey [15]. In our case a bis(π-allyl)nickel is formed and reacts further with carbon monoxide or with solvent to give the hexadienes [16]. Reaction 7 is a reaction between the starting salt and the complex formed. We have investigated the feasibility of these two reactions. The addition of one equivalent of salt I (R^1 = CH_3; R^2 = H) to a solution of complex III (R^1 = Ph; R^2 = H) in acetonitrile at 90°C gives 2,5-diphenyl-1,5-hexadiene (43%) and 2-phenyl-5-methyl-1,5-hexadiene (30%) (eq. 8).

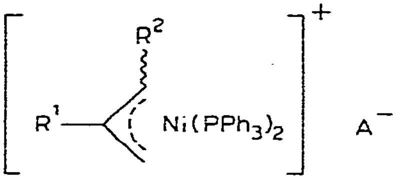


(8)

The isolation of 2,5-diphenyl-1,5-hexadiene is in accordance with reaction 6, while formation of 2-phenyl-5-methyl-1,5-hexadiene is in agreement with reaction 7.

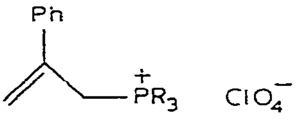
Reactions of complexes of type III

We have previously described [1] the isolation of air stable cationic π-allylic complexes formulated as:



by addition of an ethereal solution of triphenylphosphine to a solution of III in acetonitrile.

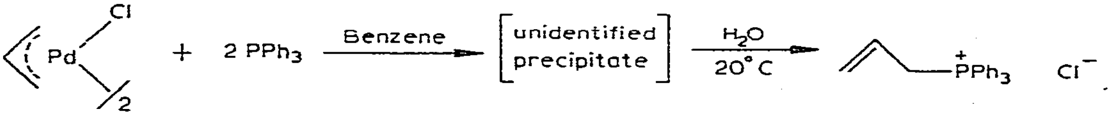
Similarly we have used tributyl- or tricyclohexyl-phosphine instead of triphenylphosphine in the case of complex III (R^1 = Ph; R^2 = H), but no change is observed. No reaction is observed on introducing water and exposing the reaction mixture to the atmosphere, except for a very slow appearance of a green colour in the aqueous phase and a decrease of the red colour of the organic layer. At the same time a precipitate appears at the interface water/diethyl oxide. The products have been identified by ^{1}H NMR spectroscopy as 2-phenylallylphosphonium salts IV.



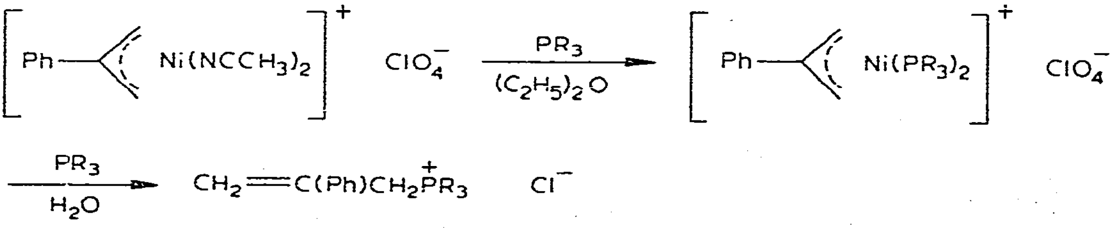
(IVa) R = $n\text{-}C_4H_9$

(IVb) R = C_6H_{11}

These results are similar to those of Hüttel and König [17] who obtained related compounds by treatment of bis(π-allylhalopalladium) with an excess of triphenylphosphine (eq. 9).



From the results with triphenylphosphine, we propose the reaction path 10.



(IV)

We are now studying the reactions of complexes III with electrophilic and nucleophilic reagents. Our preparation is a clear improvement over previous methods, and allows the introduction of a large number of ligands in the coordination sphere of nickel.

The involvement of cationic π-allylic species in catalytic reactions has also prompted us to investigate the activity of these compounds in homogeneous catalytis, and the results will be reported in the near future.

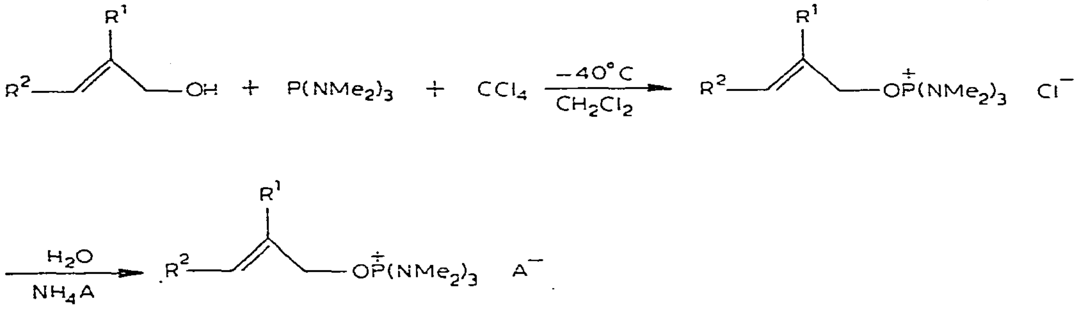
Experimental

General

All the complexes prepared are air-sensitive and all manipulations were carried out under arogn. Tetracarbonylnickel is very inflammable and extremely toxic *; it must be handle in a well ventiled hood. Tetracarbonylnickel (Fluka Company) was filtered immediately before use. IR spectra were recorded on a Perkin—Elmer model 457 spectrophotometer and ^{1}H and ^{13}C NMR spectra on a Bruker HX 90 spectrometer. Chemical shifts are given in δ (ppm) downfield to tetramethylsilane as internal standard.

Preparation of allyloxyphosphonium salts

These salts were prepared by a published method [19] starting from alcohols (eq. 11) (Table 2). The NMR spectra and analytical results are in agreement with structure I.



(I)

Optimisation of the reaction: yield in nickel

10^{-3} mole of allyloxyphosphonium salt.are added to 5—10 cm^3 of the solvent. Reactions were carried out as specified in Table 1. After removal of the excess of tetracarbonylnickel and most of the solvent, the products were decomposed by addition of concentrated nitric acid. The mixture was diluted with water and the pH adjusted to 4—5 by addition of aqueous sodium hydroxide. The green solution of nickel(II) salt was then titrated against EDTA/Murexide.

Reactions in acetonitrile

These reactions have been described above and in ref. 1. They are carried out

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* For toxicity see ref. 18.

TABLE 2

YIELD AND MELTING POINTS OF COMPOUNDS I

R^1	R^2	A	Yield (%)	M.p. (°C)
H	H	ClO_4	91	240 (dec)
H	H	PF_6	95	260 (dec)
H	Me	ClO_4	64	115 (dec)
H	Me	PF_6	68	146 (dec)
Me	H	ClO_4	80	170 (dec)
Me	H	PF_6	96	200 (dec)
Me	H	BF_4	89	131
Ph	H	ClO_4	75	149
Ph	H	PF_6	70	120

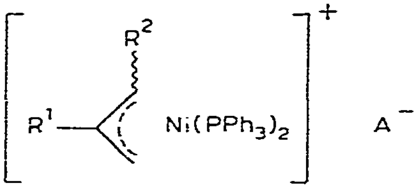
with 10^{-2} mole of allyloxyphosphonium salt dissolved in 20 cm^3 oxygen-free acetonitrile. The evolution of carbon monoxide was monitored by a manometer.

Reaction 8

Complex III (R^1 = Ph; R^2 = H) was prepared following the general procedure from 3.96 g (10^{-2} mole) of phenylallyloxyphosphonium perchlorate dissolved in 20 cm^3 acetonitrile. A solution of 3.36 g (10^{-2} mole) of methallyloxyphosphonium perchlorate in acetonitrile was added and the mixture refluxed for 5 hours until a green colour appeared. Acidic hydrolysis followed by extraction with ether gave a crude product which was chromatographed on silica gel. Elution with petroleum ether gave successively 0.515 g (30%) of 2-phenyl-5-methyl-1,5-hexadiene and 0.800 g (43%) of 2,5-diphneyl-1,5-hexadiene. The NMR spectra of these compounds were in agreement with the proposed structures.

Reactions of complexes III with phosphines

Triphenylphosphine. Complexes III were prepared in acetonitrile as described above. Addition of an etheral solution of 4 × 10^{-2} mole of triphenylphosphine caused precipitation of the complexes:



Tributyl and tricyclohexylphosphine. Complex III (R^1 = Ph; R^2 = H) was obtained analogously from 10^{-2} mole (3.96 g) of phenylallyloxyphosphonium perchlorate. After removal of the excess of tetracarbonylnickel, 4 × 10^{-2} mole of phosphine in solution in 100 cm^3 diethyloxide were added and the solution stirred for 24 h. After addition of water, the mixture was poured into a separatory funnel. The white solid material which appeared at the ether/water interface was extracted with dichloromethane after separation of the organic layer. The usual work-up gave 3.2 g (76.5%) of phenylallyltri-n-butylphosphonium perchlorate (IVa) and 2.77 g (55.8%) of phenylallyltricyclohexylphosphonium perchlorate (IVb).

The NMR spectra and analytical results were in good agreement with the proposed structures.

Acknowledgement

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Bibliography

1 B. Castro and D. Neibecker, J. Organometal. Chem., 85 (1975) C39.
2 C.A. Tolman, J. Amer. Chem. Soc., 92 (1970) 6777.
3 D. Commereuc and Y. Chauvin, Bull. Soc. Chim. Fr., (1974) 652.
4 C. Vitulli, P. Pertici, C. Agami and L. Porri, J. Organometal. Chem., 84 (1975) 399.
5 P.W. Jolly and G. Wilke, The organic chemistry of Nickel, Vol. I and II, Academic, New York, 1974—1975.
6 E.O. Fischer and B. Bürger, Chem. Ber., 94 (1961) 2409.
7 M.L.H. Green and P.L.I. Nagy, Advan. Organometal. Chem., 2 (1964) 359.
8 E.W. Abel and S.P. Tyfield, Advan. Organometal. Chem., 8 (1970) 158.
9 I.G. Farbenind, Chem. Abstr., 41 (1945) 6576a.
10 I.D. Webb and G.T. Borcherdt, J. Amer. Chem. Soc., 73 (1951) 2654.
11 R.B. King, J. Organometal. Chem., 8 (1967) 139 and 151; R.H. Reimann and E. Singleton, J. Organometal. Chem., 59 (1973) C24
12 P.W.N.M. Van Leeuwen, A.P. Praat and M. Van Diepen, J. Organometal. Chem., 29 (1971) 433 and refs. therein.
13 B.E. Mann, R. Pietropolo and B.L. Shaw, J. Chem. Soc. Dalt. Trans., 22 (1973) 2390; J. Chem. Soc. Chem. Commun., (1971) 790; L.A. Churl yaeva, M.I. Lobach, G.P. Kondratenkov and V.A. Kormer, J. Organometal. Chem., 39 (1972) C23.
14 D.L. Tibbets and T.L. Brown, J. Amer. Chem. Soc., 92 (1970) 3031.
15 E.J. Corey, M.F. Semmelhack and L.S. Hegedus, J. Amer. Chem. Soc., 90 (1968) 2416, 2417.
16 P. Heimbach, P.W. Jolly and G. Wilke, Advan. Organometal. Chem., 8 (1970) 29.
17 R. Hüttel and C. König, Amer. Chem. Soc. Div. Petr. Chem. Prep., 14 (1969) B35.
18 Ref. 5, vol. I, 24.
19 B. Castro and C. Selve, Bull. Soc. Chim. Fr., (1971) 4308.