

EVIDENCE FOR π -ALLYLIC NICKEL COMPLEXES AS INTERMEDIATES IN THE REACTIONS OF NICKELCENE WITH ALLYLIC CHLORIDES

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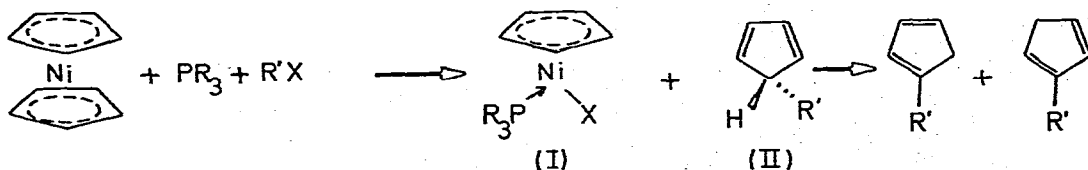
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Summary

Reactions of *trans*-1-chloro-2-butene and of 3-chloro-1-butene with nickelocene give mixtures of (1-methyl-2-propenyl)-, (*trans*-2-butenyl)-, and (*cis*-2-butenyl)-cyclopentadienes. The reaction between π -crotyl- π -cyclopentadienylnickel and 5-chlorocyclopentadiene yields identical products. In the presence of tetrachloromethane, 5-(trichloromethyl)cyclopentadiene is formed. Mechanisms involving oxidative addition and π -allylic nickel complexes are discussed.

Introduction

Nickelocene reacts with hydrogen halides [1,2], allylic halides [3] and tetrahalogenomethanes [2] in the presence of phosphines or phosphites to give a π -cyclopentadienylnickel halide (I) and a cyclopentadiene (II) [1,4]. With an excess of phosphine, complex I reacts further to give $[(C_5H_5)Ni(PR_3)_2]^+X^-$ [3]. The initially formed 5-substituted cyclopentadienes usually rearrange to give mixtures of 1- and 2-substituted cyclopentadienes [5].



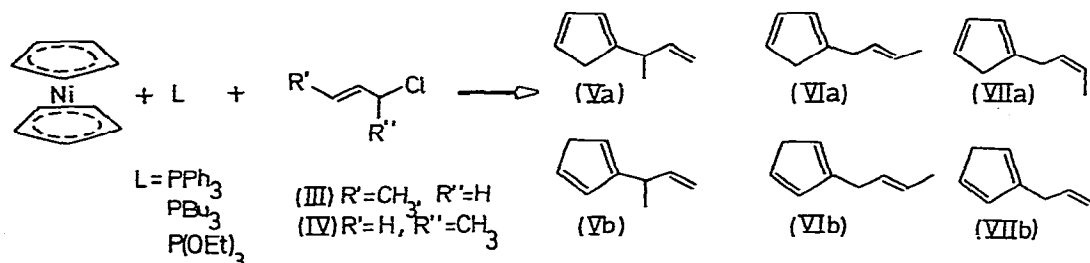
It is known that 3-bromopropene [4], octachlorocycloheptatriene [6], hexachlorocyclopentadiene [7] and triphenylmethyl chloride [8] react with nickelocene to give substituted cyclopentadienes even in the absence of phosphines.

It has been suggested [2,9] that the first step in the reactions with phosphines or phosphites is the coordination of the ligand to the nickel atom with subsequent π - σ rearrangement of one of the cyclopentadienyl rings. Since few de-

tails of these reactions are known, we have performed a series of experiments to acquire additional mechanistic information.

Results

The reactions of nickelocene with *trans*-1-chloro-2-butene (III) and with 3-chloro-1-butene (IV) in the presence of triphenylphosphine, tributylphosphine or triethyl phosphite were studied in tetrahydrofuran. In these reactions (1-methyl-2-propenyl)cyclopentadiene (Va and b), (*trans*-2-butenyl)cyclopentadiene (VIa and b) and (*cis*-2-butenyl)cyclopentadiene (VIIa and b) are formed in the same relative amounts from both *trans*-1-chloro-2-butene and from 3-chloro-1-butene. The ligands have only a minor influence on the isomeric distribution. The relative and total yields of the isomers as determined by gas-liquid chromatography (GLC) are shown in Table 1.



The butenyl chlorides are not isomerized during the reactions, since when an excess of *trans*-1-chloro-2-butene is used, no *cis*-1-chloro-2-butene or 3-chloro-1-butene is found in the reaction mixture. No bialkyls are formed in the reactions.

When either of the butenyl chlorides, III–IV, are allowed to react with lithium cyclopentadienide, totally different isomeric distributions of the butenylcyclopentadienes are observed. *trans*-1-Chloro-2-butene yields ca. 5% of V and 95% of VI and 3-chloro-1-butene forms ca. 85% of V and 15% of VI.

We have also investigated the reaction of 5-chlorocyclopentadiene [10] with

TABLE 1

RELATIVE AND TOTAL YIELDS OF BUTENYLCYCLOPENTADIENES FORMED FROM NICKELOCENE, BUTENYL CHLORIDES AND A PHOSPHINE OR PHOSPHITE

The yields are means of duplicate experiments. The largest differences in the relative and total yields are 3% and 10%, respectively.

Butenyl chloride	L	Relative yields of			Total yields (%)
		Va, b	VIa, b	VIIa, b	
III ^a	PPh ₃	41	49	10	89
IV ^a	PPh ₃	40	50	10	42
IV ^b	PPh ₃	42	48	10	90
III ^a	PBu ₃	43	53	4	80
IV ^a	PBu ₃	42	55	3	80
III ^a	P(OEt) ₃	45	46	9	86
IV ^a	P(OEt) ₃	45	48	7	75

^a Reaction conditions: 5 h at 20°C, 1 h at 65°C. ^b Reaction conditions: 15 h at 20°C, 2 h at 65°C.

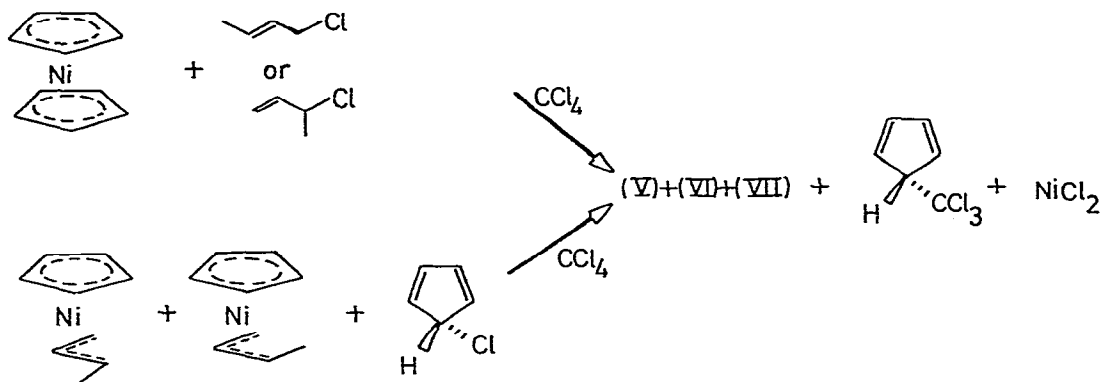
TABLE 2

RELATIVE AND TOTAL YIELDS OF BUTENYLCYCLOPENTADIENES AND YIELDS OF 5-(TRICHLOROMETHYL)CYCLOPENTADIENE FORMED FROM NICKELOCENE, BUTENYL CHLORIDES AND TETRACHLOROMETHANE AND FROM π -CROTYL- π -CYCLOPENTADIENYLNICKEL, 5-CHLOROCYCLOPENTADIENE AND TETRACHLOROMETHANE

The yields are means of duplicate experiments. The largest differences in the relative and total yields are 5% and 12%, respectively. The yields given for 5-(trichloromethyl)cyclopentadiene were calculated by determining the amounts of 6,6-dipiperidinofulvene formed when the reaction mixtures were added to piperidine.

Reaction	Relative yields of			Total yields (%)	Yields of $C_5H_5CCl_3$ (%)
	Va, b	VIa, b	VIIa, b		
$(C_5H_5)_2Ni + III$	44	40	16	40	58
$(C_5H_5)_2Ni + IV$	44	40	16	41	65
$(C_5H_5)(C_4H_7)Ni + C_5H_5Cl$	44	42	14	75	65

π -crotyl- π -cyclopentadienylnickel, which, according to its NMR spectrum, consists of approximately equal amounts of the *syn* and *anti* isomers*. In the preparation of 5-chlorocyclopentadiene, the highest yield was obtained when tetrachloromethane was used as a solvent. When the tetrachloromethane solution of 5-chlorocyclopentadiene is allowed to react with π -crotyl- π -cyclopentadienylnickel, the butenylcyclopentadienes V—VII are formed along with nickel chloride and, unexpectedly, 5-(trichloromethyl)cyclopentadiene. For comparison, the reactions of nickelocene with tetrachloromethane and *trans*-1-chloro-2-butene or 3-chloro-1-butene were investigated. In these reactions the butenylcyclopentadienes V—VII are formed along with nickel chloride and, also in these cases, 5-(trichloromethyl)cyclopentadiene. Furthermore, the relative yields of isomers V—VII are the same starting from either compound III or IV and also the same as in the reaction of π -crotyl- π -cyclopentadienylnickel, 5-chlorocyclopentadiene and tetrachloromethane (Table 2).

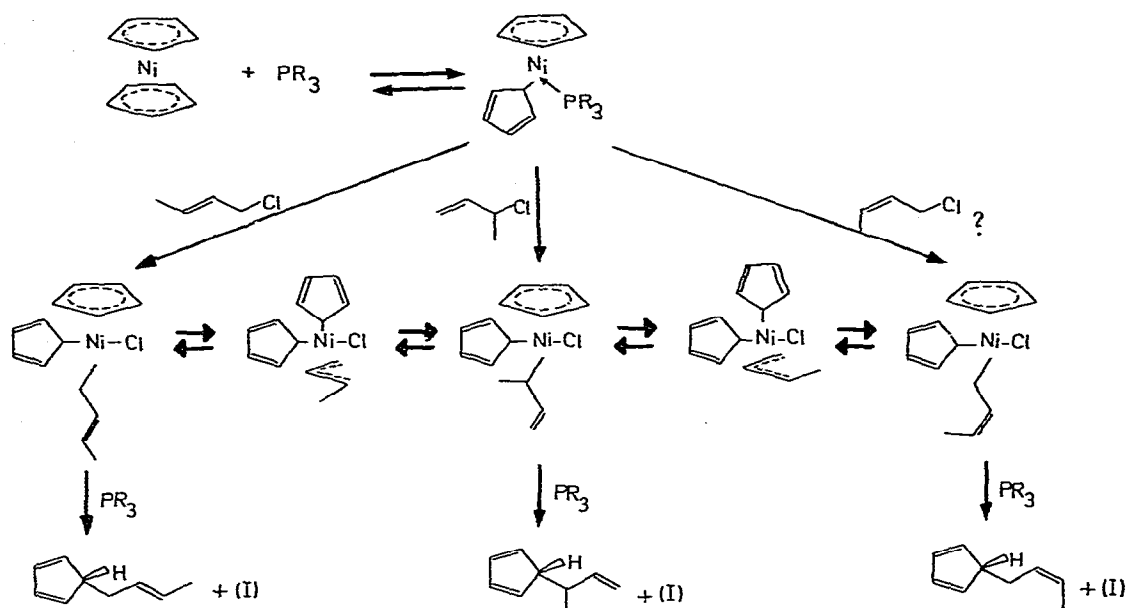


* This complex has earlier been prepared by another method [11].

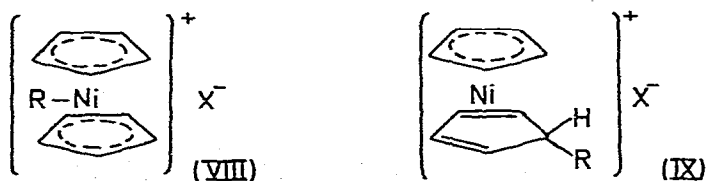
Discussion

One possible path for the reaction of nickelocene with allylic halides is a nucleophilic displacement by a cyclopentadienyl ligand at the allylic halide. However, in view of our results, such a mechanism does not seem probable since one would not expect *trans*-1-chloro-2-butene and 3-chloro-1-butene both to give the same relative amounts of butenylcyclopentadienes. Furthermore, no *cis-trans* isomerization would be expected [12]. Instead the results may be explained by the intermediacy of π -allylic nickel complexes, a possible reaction mechanism being the oxidative addition of the allylic halide to nickel followed by reductive elimination of the butenylcyclopentadienes and the formation of complex I (Scheme 1).

SCHEME I

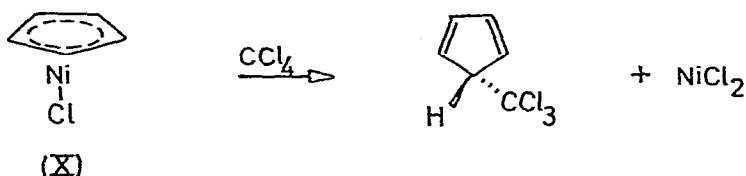


Some questions could be raised about the structures of the complexes shown in Scheme 1. It is, of course, not known whether the cyclopentadienyl rings are bonded to the nickel by σ or π bonds. In the scheme they have simply been drawn in such a way that the nickel atom has a maximum of 18 electrons. In the reaction of nickelocene with triphenylmethyl chloride, Werner and co-workers have suggested that the first step is one-electron transfer from nickelocene to give a radical pair which collapses to an ionic complex (VIII) [8], which then rearranges to complex IX before elimination of the substituted cyclopentadiene.



A similar mechanism could also explain the results of our reactions. Complex VIII is similar to the σ - and π -allylic nickel complexes shown in Scheme 1, the difference being that complex VIII is ionic. In both cases, the result is the formation of a nickel(IV) complex via a formal oxidative addition. In our reactions, the intermediate formation of a complex analogous to IX may also be more probable than a direct reductive elimination, since it has been shown that protonation of nickelocene, probably at the nickel atom, ultimately gives complex IX ($R = H$) [13].

A mechanism involving π -allylic nickel complexes is further supported by the results from the reactions of nickelocene with tetrachloromethane and *trans*-1-chloro-2-butene or 3-chloro-1-butene, as well as the results of the reaction of π -crotyl- π -cyclopentadienylnickel with tetrachloromethane and 5-chlorocyclopentadiene. In both cases, the same σ -allylic and π -allylic nickel complexes could be formed. Reductive elimination would yield, instead of complex I, complex X, which could then react with a second allylic halide or with tetrachloromethane to give a butenylcyclopentadiene or 5-(trichloromethyl)cyclopentadiene and nickel chloride.



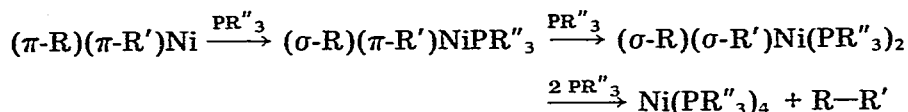
Complex X has previously been postulated by Werner and co-workers, and they have suggested an alternative structure, a dimer where the nickel atom would have noble gas configuration [14]. They have also isolated an analogous ionic complex, $(C_5H_5)Ni^+BF_4^-$ [13]. A similar complex has also been postulated as an intermediate in the reactions of nickelocene with thiols [15].

It is clear that 5-(trichloromethyl)cyclopentadiene is not formed by the direct reaction of nickelocene with tetrachloromethane, since a mixture of these compounds does not react under the conditions used for the reactions with the butenyl chlorides. We have previously shown, however, that 5-(trichloromethyl)cyclopentadiene is formed from nickelocene, tetrachloromethane and triphenylphosphine [4]. Starting with π -crotyl- π -cyclopentadienylnickel and tetrachloromethane, 5-(trichloromethyl)cyclopentadiene is formed, but the yield (17%) is much lower than in the reaction with 5-chlorocyclopentadiene. 5-(Trichloromethyl)cyclopentadiene is also formed from π -cyclopentadienyl-[5-(trichloromethyl)cyclopentadiene]cobalt and various acceptor ligands [16].

π -Cyclopentadienyl- σ -cyclopentadienyl(triphenylphosphine)nickel is a d^8 18-electron complex. If triphenylphosphine is lost, a 16-electron complex is formed, and such complexes are known to undergo oxidative addition reactions. However, only metals below and to the left of nickel in the periodic table easily undergo these reactions [17], and the number of known nickel(IV) compounds is limited. Mechanisms similar to the one we suggest have, however, been proposed. Bis(π -allyl)nickel and bis(π -allyl)nickel bromide undergo analogous coupling reactions with various halides in coordinating, polar solvents like dimethyl formamide (DMF) [18,19]. For the reactions of the latter complex, it has been

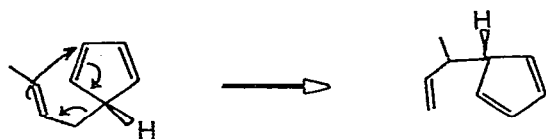
suggested that the first step is the coordination of one solvent molecule to nickel and breaking of the dimer structure followed by the coordination of a second solvent molecule with subsequent π - σ conversion of the allyl ligand and oxidative addition of the halide to the nickel atom. Recently, however, it has been claimed that this reaction involves radicals [20].

Further similarities between nickelocene [21], π -allyl- π -cyclopentadienyl-nickel [22] and bis(π -allyl)nickel [18] are found in the reactions of these complexes with phosphines or phosphites to give nickel(0) complexes and coupling products. For all of these complexes the following mechanism seems to be valid (the π - σ conversions of the cyclopentadienyl and allyl ligands have been proved for the analogous reactions with π -allyl- π -cyclopentadienylpalladium complexes [23]).



(R, R' = cyclopentadienyl, allyl)

The pure butenylcyclopentadienes are not isomerized upon standing at room temperature or when mixed with nickelocene or π -cyclopentadienyl(triphenylphosphine)nickel chloride under the reaction conditions. The isolated butenylcyclopentadienes consist almost exclusively of the 1- and 2-substituted isomers. The 5-substituted isomers could possibly undergo Cope rearrangements to give an equilibrium mixture of the isomers. However, we have excluded this possibility, mainly because these rearrangements should give identical mixtures in all reactions, and also because, although slow, the rearrangement should be observed with the isolated products. Furthermore, in the reaction of π -(1,1,2-trimethylallyl)- π -cyclopentadienylpalladium with phosphines or phosphites, it has been shown that no such isomerization takes place [23].



Experimental

Gas chromatography was performed on a Pye 104 instrument. NMR spectra were recorded on a Jeol MH 100 spectrometer and on a Varian EM 360 spectrometer (TMS internal standard), infrared spectra on a Perkin-Elmer 421 spectrometer, ultraviolet spectra with a Beckman DK 2 instrument and mass spectra on an LKB 9000 instrument.

All reactions were performed under purified nitrogen. Tetrahydrofuran (THF) was freshly distilled from potassium and benzophenone. Nickelocene was prepared from sodium cyclopentadienide and hexaamminenickel(II) chloride [24].

Commercial samples of *trans*-1-chloro-2-butene and 3-chloro-1-butene were used. *trans*-1-Chloro-2-butene contained ca. 7% of 3-chloro-1-butene and ca. 10%

of the *cis* isomer, and 3-chloro-1-butene contained ca. 3% of *trans*-1-chloro-2-butene. The isomers were purified by preparative GLC using a 3 m $\times$ 19 mm column of 15% β,β' -oxydipropionitrile on Chromosorb P at 40°C [25]. The reactions with triphenylphosphine and tributylphosphine were run with the purified compounds and the results were identical with those obtained using the unpurified compounds. For the large scale reactions described below, the unpurified compounds were used.

All yields were determined by the use of an internal standard (mesitylene) from peak areas (peak height $\times$ peak width at 0.5 peak height).

General procedure for the reactions of nickelocene with trans-1-chloro-2-butene and 3-chloro-1-butene

Nickelocene (5 mmol) was dissolved in THF (15 ml) and the butenyl chloride (5.5 mmol) in THF (10 ml) and the phosphine or phosphite (5 mmol) in THF (10 ml) were added. The mixture was stirred at room temperature for 5 h, most of the solvent was distilled at atmospheric pressure during 1 h, and the residue along with some remaining solvent was vacuum distilled (at room temperature, 0.3 mmHg) to a cold trap at -78°C . A prolonged reaction time (15 h at 20°C and 2 h at 65°C) was used to complete the reaction of 3-chloro-1-butene with nickelocene and triphenylphosphine. The mixture of butenylcyclopentadienes was analysed by gas chromatography using a 2.7 m $\times$ 6 mm column of 1% SF 96 on Chromosorb W at 60°C . The relative response factor was determined only for one isomer and was assumed to be equal for the other isomers. The remaining butenyl chlorides were analysed on a 2.7 m $\times$ 6 mm column of 15% β,β' -oxydipropionitrile on Chromosorb P at 40°C .

The reactions without phosphine or phosphite were performed in the following way: nickelocene (1 mmol) was dissolved in THF (10 ml) and the butenyl chloride (2.2 mmol) in CCl_4 (5 ml) was added. The reaction mixture was stirred overnight, the nickel chloride was filtered off and the solution was added to piperidine (5 mmol) in THF (5 ml) with stirring. After 1 h the piperidinium chloride was removed by filtration and the butenylcyclopentadienes were analysed as described above. Evaporation of the solvents and of the volatile products gave a residue which was almost pure 6,6-dipiperidinofulvene, the yield of which was determined by NMR integration using a known amount of mesitylene as a standard.

The butenylcyclopentadienes were isolated by preparative GLC at 65°C using the same column as for the purification of the butenyl chlorides. All three isomers had UV maxima at 260 nm in CCl_4 . The IR spectrum (CCl_4) of compound V shows a weak band at 1830 cm^{-1} and that of compound VI a band at 970 cm^{-1} . The NMR spectra (CCl_4) of the isomers show the vinylic protons in the cyclopentadienyl rings at δ 5.8–6.3. The methylene protons in the rings appear in compound V at δ 2.78 and 2.86 and in compounds VI and VII at δ 2.74 and 2.84. The other absorptions of compound V are found at δ 1.23 (d, $J = 6.5\text{ Hz}$, 3H), 3.16 (m, 1H), 4.9 (m, 2H) and 5.66 (m, 1H), those of compound VI at δ 1.65 (m, 3H), 2.98 (m, 2H) and 5.40 (m, 2H) and those of compound VII at δ 1.64 (m, 3H), 3.04 (m, 2H) and 5.40 (m, 2H).

Lithium cyclopentadienide and trans-1-chloro-2-butene or 3-chloro-1-butene

Lithium cyclopentadienide was prepared from cyclopentadiene and butyl-

lithium in THF and reacted with *trans*-1-chloro-2-butene and with 3-chloro-1-butene under the same conditions as nickelocene and phosphines.

π -Crotyl- π -cyclopentadienylnickel and 5-chlorocyclopentadiene

π -Crotyl- π -cyclopentadienylnickel was prepared from crotylmagnesium chloride and nickelocene analogously to π -allyl- π -cyclopentadienylnickel [26]. After distillation at 50°C, 0.3 mmHg to a cold trap at -78°C, 60–70% of the complex was obtained. Traces of THF always remained after distillation. The NMR spectrum (benzene-*d*₆) showed absorptions at δ 0.65 (d, *J* = 7, 3H), 1.07 (d, *J* = 7, 3H), 1.11 (d, *J* = 12, 1H), 1.91 (d, *J* = 12, 1H), 2.26 (m, 1H), 2.51 (d, *J* = 7, 1H), 2.90 (d, *J* = 7, 1H), ca. 5.1 (m, 2H), 5.28 (s, 10H), and a peak hidden under the low field THF multiplet at δ 3.6. The yield of the complex was determined by NMR integration using a known amount of mesitylene as a standard.

5-Chlorocyclopentadiene was prepared from *N*-chlorosuccinimide and thallium cyclopentadienide (10% excess) in tetrachloromethane [10]. The highest yield (ca. 50%) was obtained after 20 min at 0°C, whereafter the thallium salts and unreacted *N*-chlorosuccinimide were removed by filtration. The solution was kept at 0°C or below while the concentration of 5-chlorocyclopentadiene was determined by NMR with a known amount of mesitylene. In a typical experiment 5-chlorocyclopentadiene (0.8 mmol) in CCl₄ (10 ml) was added to π -crotyl- π -cyclopentadienylnickel (0.8 mmol) in THF (10 ml) at 0°C, the reaction mixture was stirred for 3 h, and the nickel chloride was filtered off. 5-(Trichloromethyl)-cyclopentadiene was transformed to 6,6-dipiperidinofulvene as described above, the butenylcyclopentadienes analysed by GLC, and the yield of 6,6-dipiperidinofulvene determined by NMR.

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