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# THE THERMAL FORMATION OF BIALKYLS FROM ALKYLMETALS

## II *. SOME REACTIONS OF NEOPHYLNICKEL COMPLEXES

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## Summary

Neophylnickel complexes have been generated from neophylmagnesium chloride and nickel chloride or complexes between nickel chloride and various ligands such as phosphines and bipyridine. *t*-Butylbenzene and the product from reductive elimination, bineophyl, are always formed but the relative amounts vary markedly with the reaction conditions. Minor products which indicate transmetallation processes, e.g. 1(2-t-butyl)phenyl-2-methyl-2-phenyl propane and 2,2'-di-t-butylbiphenyl, are formed. Carbene and carbyne intermediates may also be produced in the absence of coordinating ligands, as indicated by the formation of the olefin $PhMe_2CCH{=}CHCMe_2Ph$ and the acetylene $PhMe_2CC{\equiv}CCMe_2Ph$. When ethene and carbon monoxide were present as ligands, the insertion products $PhMe_2CCH_2CH{=}CH_2$, $PhMe_2CCH_2COCH_2CMe_2Ph$ and $PhMe_2CCH_2COCOCH_2CMe_2Ph$ respectively, were detected. None of the reactions appear to have appreciable radical character. Products which indicate radical intermediates are formed only in side reactions which probably involve the Grignard reagent rather than a nickel complex.

Since the reductive elimination reaction is probably concerted, an attempt is made to use orbital interactions to rationalize the factors governing reductive elimination.

## Introduction

Alkyl transition metal compounds are intermediates in a large number of catalytic reactions. Their properties have therefore been extensively studied [1] and many aspects of their chemistry have been clarified in recent years. We have been particularly interested in carbon—carbon bond formation [2,3], since this reaction has great potential in synthetic chemistry.

*(Continued on p. 100)*

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* Part 1: ref. 3.

TABLE 1

REACTIONS OF COMPOUNDS 1 WITH PALLADIUM CHLORIDE AND THIONYL CHLORIDE-DRIED NICKEL CHLORIDE

| Run | Moles of Grignard | Ligand | Initial temperature (°C) | Dimers (%) | | | | Monomer composition (%) | Other products |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 3 | 4 | 5 | Others | | |
| 1 | 1 | — | −70 | 16 | 5 | 11 | 6,7 [a] (traces) | 2 | — |
| 2 | 2 | — | −70 | 18.5 | 4.5 | 14 | 6,7 [a] (traces) | 2 | — |
| 3 | 1 | Ethene | −70 | 35 | — | — | — | 2 | 18 (3–5%) |
| 4 | 1 | COD | −70 | 13 | 4.5 | 17.5 | 6,7 [a] (traces) | 2 | — |
| 5 | 1 | 2 $PPh_3$ [c] | −70 | 66 | traces | — | — | 2 | 20 (traces) |
| 6 | 1 | KOtBu | −70 | 30 | traces | traces | — | 2 | — |
| 7 [b] | 1 | — | −70 | 75 | — | — | — | 2 | — |
| 8 [b] | 1 | — | 100 | 15 | — | traces | 9,10 (traces) | 2 (>99); 15,16 (traces) | 11,12 (traces) |

[a] Inferred from mass and NMR spectroscopy and by hydrogenation to bineophyl 3. [b] Reaction with palladium chloride. [c] $NiCl_2$ was stirred with $PPh_3$ at room temperature for 1.5 h, then at 60°C for 15 min. The solution was then cooled to −70°C and the Grignard reagent added.

TABLE 2

REACTIONS OF COMPOUNDS 1 WITH THERMALLY DRIED NICKEL CHLORIDE

| Run | Moles of Grignard | Ligand | Initial temperature (°C) | Dimers (%) | | | | Monomer composition (%) | Other products (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 3 | 4 | 5 | Others | | |
| 9 | 1 | — | −70 | 4.5 | 2 | 7 | 6,7 [a] (traces) | 2 | — |
| 10 | 2 | — | −70 | 5 | 2.5 | 7.5 | 6,7 [a] (traces) | 2 | — |
| 11 | 1 | — | 20 | 15 | traces | traces | — | 2 | — |
| 12 | 1 | — | 100 | 10 | 3 | 1 | 8 [c] (2) | 2 (>99); 15 (traces) | 11 (1–2); 12 [d] (traces) |
| 13 | 1 | Ethene | −70 | 20–24 | traces | — | — | 2 | 18 (traces) |
| 14 | 1 | Ethyl vinyl ether | −70 | 4.5 | 2 | 7 | — | 2 | — |
| 15 | 1 | COD | −70 | 8.5 | 1.5 | 5 | — | 2 | — |
| 16 | 2 | CO | −70 | 7.5 | 0.5 | 2.5 | — | 2 | 13 (15); 14 (1) |
| 17 | 1 | $PPh_3$ [b] | −70 | 32 | traces | — | — | 2 | — |

[a] Inferred from mass and NMR spectroscopy and by hydrogenation to bineophyl 3. [b] $NiCl_2$ was stirred with $PPh_3$ at room temperature for 1.5 h, then at 60°C for 15 min. The solution was then cooled to −70°C and the Grignard reagent added. [c] Identified in the product mixture by NMR by comparison with the spectrum of an authentic sample. [d] Identified only by mass spectroscopy. Very similar mass spectrum as 11.

TABLE 3

REACTIONS OF COMPOUNDS 1 WITH PRE-PREPARED NICKEL COMPLEXES

| Run | Moles of Grignard | Complex | Initial temperature (°C) | Dimers (%) | | | | Monomer composition (%) | Other products (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 3 | 4 | 5 | Others | | |
| 18 | 1 | (Bipy)$NiCl_2$ | —70 | 40 | 2 | — | — | 2 | — |
| 19 | 1 | (Bipy)$NiCl_2$ + $AlCl_3$ | —70 | 52 | 1 | — | — | 2 | — |
| 20 | 1 | $(PPh_3)_2NiCl_2$ | —70 | 54 | — | — | — | 2 | 20 (0.5—1) |
| 21 | 1 | $(PPh_3)_2NiCl_2$ | 100 | 52 | — | — | 9 (traces) | 2 (86); 15 (8); 16 (6); 17 (traces) | 11,12 (traces); 19 (4); 20 (8) |
| 22 | 1 | $(PPh_3)_2NiCl_2$ + 2 $PPh_3$ | —70 | 51 | — | — | — | 2 | — |
| 23 | 1 | $(PPh_3)_2NiCl_2$ + $AlCl_3$ | —70 | 43 | — | — | — | 2 | — |
| 24 | 1 | (Biphos)$NiCl_2$ | —70 | 53 | — | — | — | 2 | 19 (2.5); 20 (3.5) |
| 25 | 1 | CpNiCl($PPh_3$) | —70 | 33 | traces | — | — | 2 | 20 (traces); 29 (30—40) |
| 26 | 2 | $(PPh_3)_2NiCl_2$ | —70 | 65 | — | — | — | 2 | 19 (2—3); 20 (2) |
| 27 | 2 | (Biphos)$NiCl_2$ | —70 | 36 | traces | — | — | 2 | 19 (6); 20 (4) |
| 28 | — | NeophylNiCl$(PPh_3)_2$ | 100 | 60 | — | — | — | 2 | 19,20 (traces) |
| 29 [a] | 1 | $(PPh_3)_2NiCl_2$ | 100 | 36 | — | — | — | 2 (>98); 15,16 (traces) | 19 (traces); 20 (9) |
| 30 [a] | — | NeophylNiCl$(PPh_3)_2$ | 100 | 52 | — | — | — | 2 | 19,20 (traces) |

[a] 2,6-Di-t-butylphenol added as radical scavenger.

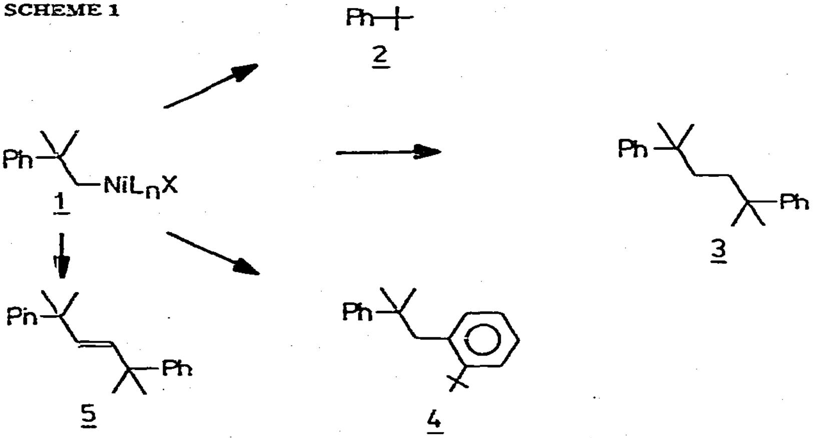
In contrast to arylmetals, alkylmetals frequently give poor yields of coupled products. This is partly due to side reactions such as β-hydrogen elimination, but electronic factors, which reduce the relative efficiency of reductive elimination may also be important. β-Elimination has been studied in considerable detail but the scope of other side reactions, e.g. α-elimination and transmetallation, is not clear. Furthermore, there is no general agreement on the mechanism of reductive elimination (for reviews, see refs. 1j,k) nor on the effect of electronic factors.

In order to study these questions we have investigated the thermal reactions of a number of alkylnickel complexes $Me_2PhCCH_2NiL_nX$ (1), where L is one of several auxiliary ligands (Tables 1—3). The use of the neophyl group for alkyl has two advantages. First, β-hydrogen elimination is not possible and second, radical character can be detected due to the tendency of the neophyl radical to undergo rearrangement [4].

## Neophyl coupling

Neophylnickel chloride and dineophylnickel were prepared from neophyl-Grignard and nickel chloride in THF at —70°C and then decomposed by heating to room temperature. The major products were t-butylbenzene (2) and the dimers 3—5 (Scheme 1). 3 is probably formed via the bineophenyl complex 22, as indicated by the fact that the addition of one or two moles of Grignard reagent gives about the same yield of bineophenyl (see Scheme 2). In addition, small amounts of the dimer 6 and the acetylene 7 were observed (Tables 1,2). When the reaction was carried out at 100°C by adding the Grignard reagent to a hot suspension of nickel chloride in dioxane, the dimer 8 was also detected. The yield of bineophyl (3) was low (<20%). As might be expected, the yield of 3 was strongly dependent on the dryness of the nickel chloride. Refluxing with thionyl chloride [27] was satisfactory, while thermal drying alone resulted in reduction of the yield by about 50% (cf. Tables 1 and 2).

SCHEME 1



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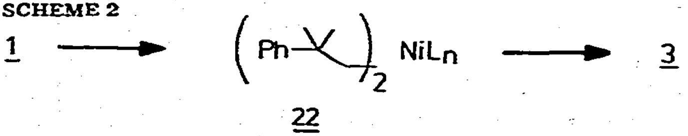

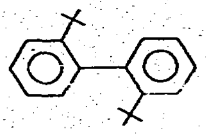

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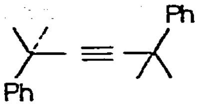

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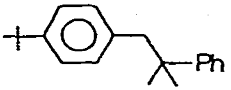

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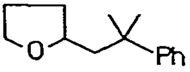

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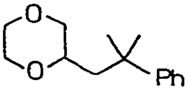

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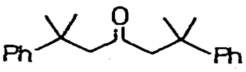

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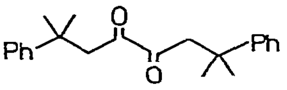

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Addition of auxiliary ligands prior to decomposition in some cases raised the yield of 3. Ethene addition increased the yield to ~35%, while neither 1,5-cyclooctadiene nor ethyl vinyl ether had any appreciable effect (Tables 1,2). The reaction between neophyl-Grignard and compound 28, which may be regarded as an unusual olefin complex, gave a moderate yield (33%) of 3.

Carbon monoxide had only a small effect on the yield of 3, while addition of phosphines resulted in a substantial increase (to 66%). Yields ranging from 50—60% were also obtained by treating neophyl-Grignard with various nickel chloride complexes $NiCl_2L_2$, where L = phosphine or 1/2 bipyridine (Table 3). In no case were the dimers 9 and 10, which are indicative of radical coupling, detected.

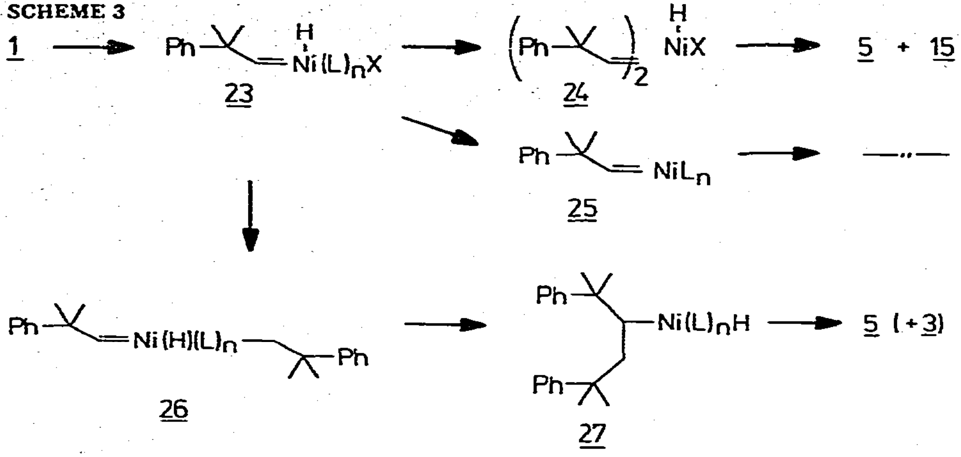
## Side reactions

The major competing reaction is the formation of t-butylbenzene (2). This compound is probably formed by the reaction between 1 and nickel hydrides. These could be formed by α-elimination (1 → 23), but the material balance indicates that they must mainly be formed by reaction with the solvent (THF). Nickel(0) from the reductive elimination can presumably insert into THF to give an alkylnickel hydride, which may react as such or first form nickel dihydride with concurrent dehydrogenation of THF. There are clear precedents for such reactions, since nickel atoms dehydrogenate THF [5] and arylnickel compounds give arenes with incorporation of hydrogen from THF [6].

In the absence of ligands, the formation of the dimeric products 4—8 was observed. Reasonable, but partly speculative pathways may be suggested for the formation of these products.

A probable precursor of 5 is the carbene complex 23, which could be formed by α-elimination from 1. The actual intermediate could be the biscarbene complex 24 (cf. ref. 7) but more attractive candidates are 26 and 27 (Scheme 3).

SCHEME 3

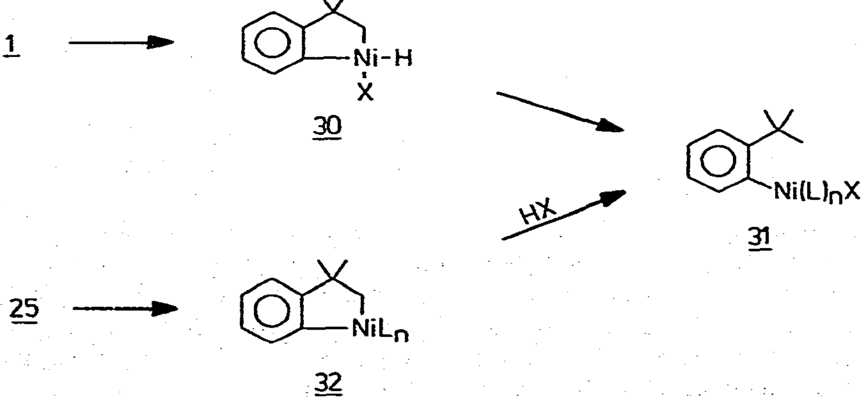


These complexes would yield 5, in a reaction very similar to olefin metatesis [8]. Attempts to capture the anticipated carbene intermediate 23 by reaction with olefins were not successful. Vinyl ether and cyclooctadiene did not seem to interact with the neophylnickel system and ethene inhibited the side reactions, including α-elimination and no metathesis product 21 could be detected. Potassium t-butoxide which was added to trap 23 by deprotonation, had an effect similar to that of ethene (Tables 1, 2, runs 3, 4, 6 and 13—15).

The formation of acetylenes like 7 from alkylmetals does not appear to have been observed before. Since a number of carbyne complexes have recently been prepared by Fischer and his co-workers [9] it is tempting to suggest that 7 is formed from a carbyne complex in a manner similar to the formation of 5.

The products from mixed neophylaryl coupling (4 and 8) and aryl—aryl coupling (6) are probably formed via transmetallation reactions to give t-butyl-

SCHEME 4



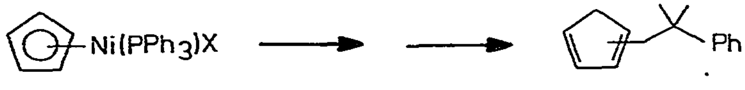
phenylnickel species, e.g. 31. The formation of such species has earlier been implied in reactions between neophylpalladium and olefins [10]. More direct proof is obtained from the detection (by TLC) of the complex 31 (L = $Ph_3P$) in the reaction between neophyl-Grignard and bis(triphenylphosphine)nickel chloride in refluxing dioxane (Table 3, run 21). Further work has shown that such compounds are readily formed from bis(phosphine)neophylnickel species [11]. The actual mechanism for the transmetallation is not clear, but 30 and 32 are reasonable intermediates (Scheme 4).

## Reactions between the neophyl group and added ligands

Decomposition of neophylnickel in the presence of ethene gave small amounts of the insertion product 18. This fact, coupled with the profound influence of ethene on decomposition of neophylnickel strongly indicates complex formation with ethene. Complex formation between nickel(II) and olefins has not been experimentally observed but is predicted by quantum chemical calculations [12].

Ethyl vinyl ether and 1,5-cyclooctadiene gave no insertion products while complex 28 gave a fair yield of neophylcyclopentadiene (29, Scheme 5, 30—40%). Products like 29 have not been detected in earlier studies of alkyl complexes [13] but the corresponding phenyl complex yields phenylcyclopentadiene [14]. The reaction may be of interest for the synthesis of substituted cyclopentadienes.

SCHEME 5



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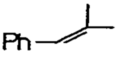

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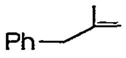

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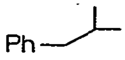

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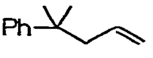

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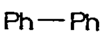

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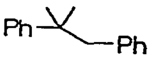

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Carbon monoxide readily participated in insertion reactions, and the ketone 13 and the diketone 14 were formed (Table 2, run 16). Similar reactions are common for alkyl-transition metal compounds [15] although diketones are generally not observed (cf. ref. 16).

In some cases, insertion into both phosphine ligands and the solvent was observed. From triphenylphosphine, biphenyl (19) and neophylbenzene (20) were formed (cf. refs. 17,18). Only trace amounts of 19 and 20 were formed on heating preformed bis(triphenylphosphine)neophenylnickel chloride (Table 3, runs 21,28). Both products thus appear to be associated with reactions of the Grignard reagent rather than of a nickel species. This is of interest since similar products appear to be produced also via insertion of nickel(0) into triphenylphosphine [18]. Neophylbenzene could be formed by nucleophilic attack of the Grignard reagent on coordinated phosphine, while addition of a radical scavenger indicates that biphenyl is formed in a radical reaction (Table 3, runs 21, 29).

Also other potential radical products, e.g. the rearranged dimer 9, the monomers 15—17 and the solvent insertion products appear to stem from reactions of the Grignard reagent rather than from a neophylnickel species (Table 3, runs 21, 28—30).

## Discussion

From both the present and earlier work [19] it is clear that the ligands influence the yield of coupled product both by promoting reductive elimination and by hindering side reactions. $\beta$-Hydrogen elimination has long been recognized as the most competitive side reaction. The present work shows that also $\alpha$-elimination and trans-metallation may interfere, but products from both are effectively blocked by coordinating ligands. The present work also shows that the most important side reaction in the absence of $\beta$-elimination is monomer formation. This reaction, which probably goes via neophylnickel hydride, is hindered by ligands which stabilize the leaving group in the reductive elimination, that is nickel(0). The most reasonable explanation is that the ligands decrease the rate of nickel hydride formation by interfering with the insertion of nickel(0) into the solvent.

The influence of the ligands on the various side reactions thus seems fairly well understood. This is only true to some extent for the reductive elimination itself. Acceptor ligands clearly promote reductive elimination [19f,g,k] but there are conflicting reports on the influence of donor ligands. While there are some reports of acceleration by donor ligands [19a,b], they usually stabilize alkyl- and aryl-nickel species against both reductive elimination and the side reactions [19g,k] *. Such stabilization is evident from the behavior of neophylnickel species 1, which yield coupled products rapidly at ~—40°C in the absence of ligands, but are much more stable in the presence of ethene, and fairly stable at room temperature in the presence of bipyridine or phosphines. In view of these conflicting results, an electronic model for reductive elimination is of interest. Several models have earlier been suggested which emphasize the effect of the ligands on the splitting between the highest occupied and lowest unoccupied levels [cf. 1a,b,j,k,19g]. While such splitting may be important, it is difficult to predict its magnitude, since both occupied and unoccupied levels will be destabilized by donor ligands [cf. e.g. 12]. A more useful model has recently been presented for the reactions of trimethylgold(III) [21]. We offer a somewhat different model here for nickel(II) reactions.

In Fig. 1 the possible arrangements of the highest occupied and lowest unoccupied orbitals in *cis*-dimethylnickel are depicted. The interaction between the metal and the alkyl groups is mainly described by the metal—alkyl bonding orbitals $\psi_{1a_1}$ and $\psi_{1b_1}$ and the corresponding antibonding orbitals $\psi_{2a_1}$ and $\psi_{2b_1}$. The reasonable assumption is made that reductive elimination requires that the highest occupied orbital is bonding between the alkyl groups and antibonding between nickel and the alkyls. This is achieved in the high spin configuration (Fig. 1b). In an alternative and perhaps more correct model it might be assumed

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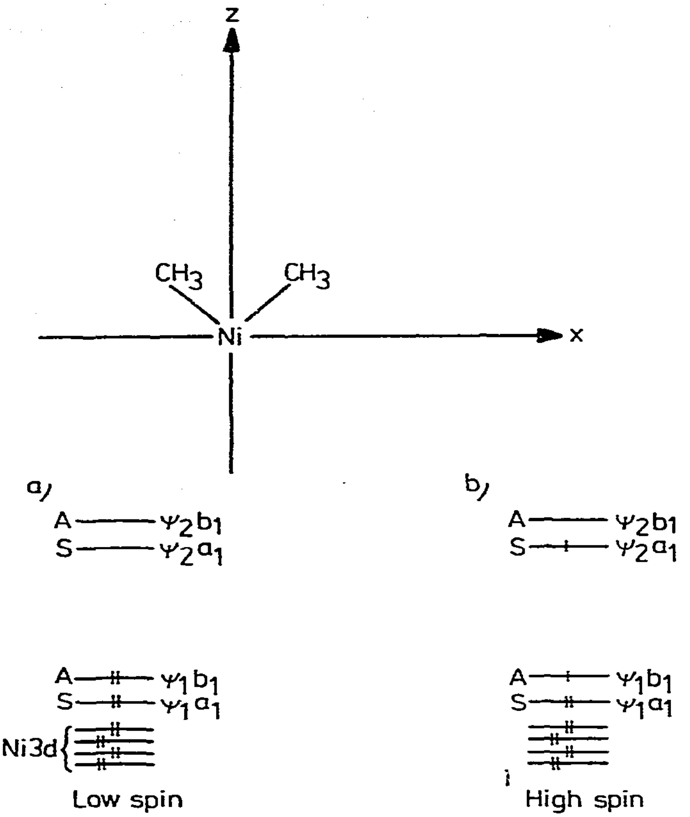
* Cf. ref. 20 for similar concepts for Pt and Au alkyls.



that the sum of the bonding and antibonding interactions is the important factor. Also according to this model, the low spin configuration should be completely stable since there is strong nickel—alkyl bonding but essentially no alkyl—alkyl bonding. By contrast, in the high spin configuration depicted in Fig. 1b, one electron has been promoted from an alkyl—alkyl antibonding and alkyl—nickel bonding orbital ($\psi_{1b_1}$) to an alkyl—alkyl bonding and alkyl—nickel antibonding orbital ($\psi_{2a_1}$). Reductive elimination from this state might therefore be expected to be facilitated.

This is somewhat similar to the early and frequently cited ideas about promoted decomposition of alkylmetals [for reviews, see refs. 1a, 1b, 1j and 1k]. The present model is more complete in two aspects. First, it suggests that concerted elimination is possible only if the highest occupied orbital is symmetric. If for instance in the present case the $\psi_{2b_1}$ orbital should become occupied instead of the $\psi_{2a_1}$ orbital, only stepwise decomposition should take place, presumably via free radicals. Second, electron promotion to $\psi_{2a_1}$ or $\psi_{2b_1}$ does not necessarily lead to bond cleavage, since these orbitals may be essentially pure metal orbitals and thus contribute little to the carbon—carbon interaction between the alkyl groups or the carbon—metal antibonding interaction. The carbon contribution to the orbitals $\psi_{2a_1}$ and $\psi_{2b_1}$ will be determined by the relative energies of the metal and carbon orbitals which interact to form the metal—alkyl bonds. The more similar these orbitals are in energy, the higher the alkyl contribution to $\psi_{2a_1}$ and $\psi_{2b_1}$. Added ligands are expected to raise the energies of the metal orbitals [12]. As a consequence, the alkyl character in the $\psi_{2a_1}$ orbital will decrease relatively to the unsubstituted alkylnickel complex. In this way, donor ligands will stabilize dialkylnickel, as was observed for the neophyl complexes.

The crude theoretical model presented here appears to rationalize fairly well the experimental results. However, a deeper understanding of the mechanism for reductive elimination requires that the energies and electron distributions of the appropriate states are determined quantitatively and more extensive calculations are being carried out.

## Experimental

### *General*

IR Spectra were recorded on Perkin—Elmer models 237 and 231 instruments, NMR spectra on a Jeol MH 100 spectrometer and on a Varian EM 360 spectrometer (TMS intern standard), and mass spectra on an LKB 9000 instrument. Melting points were determined on a micro hot-stage apparatus and are uncorrected. Microanalyses were carried out by Mikroanalyslaboratoriet, Lantbrukshögskolan, Uppsala. Gas chromatography was performed on a Hewlett—Packard model 402 gas chromatograph equipped with a column packed with 3.8% UC-W98 on Chromosorb AW, DMCS, 80—100 mesh. The dimers were analysed at 180—200°C and the monomers at 100°C. All yields are based on added neophyl chloride.

All reactions involving organometallic species were performed under purified nitrogen unless otherwise specified. Ether, dioxane and tetrahydrofuran were freshly distilled from potassium metal and benzophenone, under nitrogen.

The neophyl chloride was prepared as described in Organic Synthesis [22]. The neophyl-Grignard reagent was prepared in THF as described by Whitesides et al. [4b], except that the time of reflux was reduced to 2 h. During the preparation of the Grignard reagent, 1—3% of bineophyl was always formed together with traces of 2-(2-methyl-2-phenyl)propyltetrahydrofuran (11). The yield of the Grignard reagent was 93—97%. $NiCl_2(PPh_3)_2$ [23], $NiCl_2 \cdot$ Biphos [24] and $NiCl_2 \cdot$ Bipy [25] were prepared by literature procedures.

$CpNiCl \cdot PPh_3$ was kindly provided by Dr. Moberg [26]. Dry nickel chloride was prepared from Merck's p.a. quality $NiCl_2 \cdot 6\ H_2O$ by refluxing with thionyl chloride [27]. In spite of excessive degassing in vacuo over solid potassium hydroxide, the material still contained traces of sulfur compounds. Thermally dried $NiCl_2$ was prepared by treating $NiCl_2 \cdot 6\ H_2O$ in vacuo first at 100°C and then at 150°C. A yellow product was obtained which according to its IR spectrum still contained some water. The yields from reactions with the Grignard reagent indicate that the water content is about 0.5 mol water per mol $NiCl_2$ (cf. ref. 28, which suggests a composition $NiCl_2 \cdot 2\ H_2O$).

### *Synthesis of reference compounds*

Bineophyl (3) [29], m.p. 61—62°C, lit. m.p. 60°C, 1,4-diphenyl-2,2,4-trimethylpentane (9) [4b], 1,4-diphenyl-2,2,3,3-tetramethylbutane (10) [4b], 1-phenyl-2-methyl-1-propene (15) [30], and 1-phenyl-2-methyl-2-propene (16) [30] were prepared by literature procedures.

Isobutylbenzene (17) was prepared by the hydrogenation of 1-phenyl-2-methyl-2-propene. B.p. 171—172°C, lit. [30] b.p. 168.5—169.5°C.

*2-Methyl-2-phenylpropanol.* The Grignard reagent from 33.8 g (0.2 mol) of neophyl chloride was prepared in ether (100 ml). Oxygen was bubbled through the mixture with initial cooling in an ice salt bath. The addition of oxygen was continued for 10 min after the volution of heat had ceased. The excess of oxygen was removed with nitrogen, and the mixture was cooled again. Lithium tetrahydridoaluminate (2.5 g, 0.06 mol) was then added to remove the peroxides formed, and the cooling was discontinued. After 15 min at room temperature, excess hydrido aluminate was destroyed by the addition of a 1/1 v/v mixture of finely powdered $Na_2SO_4/10\ H_2O$ and Celite [31]. After filtration, the filter cake was washed with ether, and the combined filtrates dried with sodium sulphate. Removal of the solvent and distillation gave 2-methyl-2-phenylpropanol (18 g, 60%), 99% pure by GC. B.p. 75—77°C/1 mmHg. Lit. b.p. 131°C/30 mmHg [32].

*2-Methyl-2-phenylpropionaldehyde.* 2-Methyl-2-phenylpropanol (7.5 g, 0.05 mol) in dry ether (50 ml) was oxidized at 5°C with Wachtmeister—Stensiö reagent [33], prepared from chromium trioxide (40 g), dry pyridine (65 ml), and glacial acetic acid (300 ml). After addition of the reagent, stirring was continued for 10 min. The mixture was then poured into water (600 ml) and extracted with ether. Standard work-up and distillation gave 2-methyl-2-phenylpropionaldehyde (6.5 g, 89%), b.p. 106—108°C/20 mmHg. Lit. b.p. 98.5°C/17 mmHg [34]. Mass spectrum: 148 ($M^+$); 119 base peak ($C_6H_5C(CH_3)_2^+$).

*2-t-Butylnitrobenzene.* t-Butylbenzene (87.5 g) was nitrated as described earlier [35]. Distillation through a Widmer column gave 2-t-butylnitrobenzene (11 g), b.p. 72—74°C/1 mmHg, containing 5% each of the *m*- and *p*-isomers.

*2-t-Butylaniline.* 2-Nitro-t-butylbenzene (9 g) was hydrogenated in 100 ml methanol with Raney nickel as catalyst. About 95% of the calculated amount of hydrogen was taken up. Standard work-up procedures gave the amine (7 g), which was used in the next step without further purification. Anilide m.p. 158—161°C. Lit. m.p. 161°C [36].

*2-Iodo-t-butylbenzene.* 2-t-Butylamine was diazotised and treated with iodide to give 2-iodo-t-butylbenzene (6.5 g) 53% [37]. During the distillation some decomposition occurred, which made it difficult to obtain a pure product. B.p. 84—88°C/1 mmHg. Lit. b.p. 94—96°C/3 mmHg [37].

*1-(2-t-Butylphenyl)-2-methyl-2-phenylpropanol.* 2-Iodo-t-butylbenzene (3.9 g, 0.015 mol) was allowed to react with 0.4 g Mg in 10 ml THF. The 2-methyl-2-phenylpropionaldehyde (2.22 g, 0.015 mol) in 3 ml THF was added with stirring and cooling. The mixture was stirred at room temperature for 20 min and then refluxed for 30 min. Standard work-up procedures gave a brownish, viscous oil which did not crystallize. It was purified by treatment with activated carbon in light petroleum and filtration through a short column containing neutral aluminium oxide to give 1-(2-t-butylphenyl)-2-methyl-2-phenylpropanol. IR: 3400—3600 $cm^{-1}$, COH, 1720 $cm^{-1}$ (small, minor carbonyl impurity). Mass spectrum: molecular ion not visible; 163 base peak ($2\text{-}C_4H_9C_6H_4\text{-}CHOH^+$; 120 ($C_9H_{12}^+$); 119 ($C_6H_5C(CH_3)_2^+$).

*1-(2-t-Butylphenyl)-2-methyl-2-phenylpropane* (4). A mixture of 1-(2-t-butylphenyl)-2-methyl-2-phenylpropanol (1 g) and 0.5 g $Pd(OH)_2/C$ in 100 ml ethanol was hydrogenated at atmospheric pressure. After 14 h 75 ml

(90%) of hydrogen had been taken up. After filtration and evaporation of the solvent, the product was separated from the unchanged alcohol on a neutral alumina column with light petroleum ether (b.p. 40—60°C) as the eluant. The product 4 0.61 g (65%) was obtained as a colourless oil. NMR (in $CCl_4$): δ 7.3—6.4 ppm (m 10 H, aromatic protons); δ 3.32 ppm (s, 2H) $CH_2$; δ 1.35 ppm (s, 9H) t-butyl; δ 1.27 ppm (s, 6H) *gem*-dimethyl. Mass spectrum: The molecular ion was not observed; 119 base peak ($C_6H_5C(CH_3)_2^+$); 148 (hydrogen transfer from the *gem*-dimethyl group to the benzene ring bearing the t-butyl group).

*4-Bromo-t-butylbenzene.* 11.5 ml bromine was added slowly to a stirred mixture of 28 g t-butylbenzene, 0.6 g iron powder and a small crystal of iodine. The temperature was kept at ≃26°C. After 2.5 h the addition was complete, and the mixture was stirred for an additional 15 min at room temperature then taken up in ether and washed with water, sodium thiosulfate, sodium bicarbonate, and water again, and dried over magnesium sulfate. After evaporation the crude product was distilled to give 35.6 g (80%) *p*-bromo-t-butylbenzene; b.p. 99—101°C/9 mmHg. Lit. b.p. 80—81°C/2 mmHg [38]. The NMR spectrum ($CCl_4$) shows the typical AA′BB′ pattern of 1,4-disubstituted benzenes at δ 7.20—6.92 ppm ($C_4H_9$). The t-butyl group appears at δ 1.22 ppm (s, 9H).

*1-(4-t-Butylphenyl)-2-methyl-2-phenylpropanol.* The Grignard reagent from 4.25 g (0.02 mol) of 4-bromo-t-butylbenzene was prepared in THF (12 ml). To this was added, with stirring and cooling, 2.5 g (0.017 mol) of 2-methyl-2-phenylpropionaldehyde in THF (4 ml). After 15 min at room temperature, the mixture was refluxed for 45 min and then worked up in the usual way to give 1-(4-t-butylphenyl)-2-methyl-2-phenylpropanol, m.p. 108—109°C, (3.6 g, 80%) after recrystallization from light petroleum. NMR (in $CCl_4$): δ 7.3—6.6 ppm (m 9H aromatics); δ 4.33 ppm (s, 1H, benzylic proton); δ 1.33 ppm (1H, OH); δ 1.1 ppm broadened s, 15H methyl protons). Mass spectrum: No molecular ion; (163 base peak $HOCHC_6H_4C(CH_3)_3^+$). Anal.: Found: C, 85.3; H, 9.6; 0, 5.8. $C_{20}H_{26}O$ calcd.: C, 85.2; H, 9.2; 0, 5.6%.

*1-(4-t-Butylphenyl)-2-methyl-2-phenylpropane* (8). 1-(4-t-Butylphenyl)-2-methyl-2-phenylpropanol (0.56 g) was hydrogenated in the presence of 0.15 g $Pd(OH)_2/C$ in 50 ml ethanol. After 40 h there was still ≃20% of the unreacted alcohol. The reaction was interrupted and the product isolated in the way as described for the *ortho*-isomer to give 8 (0.37 g). M.p. 37—38°C. NMR (in $CCl_4$): δ 7.35—6.7 ppm (9H, the AA′BB′ pattern of the *para*-substituted benzene ring is clearly observed; the apparent doublets are centred at δ 7.18 and 6.76 ppm). δ 2.82 ppm (s, 2H, benzylic $CH_2$); δ 1.28 ppm (s, 6H *gem*-dimethyl); δ 1.25 ppm (s, 9H t-butyl). Mass spectrum: No molecular ion detectable, 119 (base peak $C_6H_5C(CH_3)_2^+$); 148 (analogous to the *ortho*-isomer; the intensity of the ion is, however, greater in this case which reflects the greater steric hindrance in the transition state for the hydrogen transfer in the *ortho* case). Anal.: Found: C, 89.9: H, 10.1. $C_{20}H_{26}$ calcd.: C, 90.2; H, 9.8%.

*2,2′-Di-t-butylbiphenyl* (6). A modification of the method described by Lesslie and Mayer was used [37]. 0.5 g 2-iodo-t-butylbenzene and 0.5 g copper bronze were heated in a metal bath at 225°C for 45 min. The product was chromatographed on alumina with ether as the eluant. Recrystallization from ethanol yielded 6 (0.15 g, 59%), m.p. 60—62°C. Lit. m.p. 63°C [37].

*1,2-Diphenyl-2-methylpropane* (20). A twentyfold excess of the neophyl Grignard reagent was added to $NiCl_2(PPh_3)_2$ in THF at —50°C in the presence of bromobenzene. The solution was allowed to reach room temperature. After stirring for 14 h, it was heated at 55°C for 1.5 h. Chromotography on silica gel with 1—5% ether in light petroleum and then on acidic alumina with light petroleum afforded a 50—60% yield of the desired product 20 contaminated with a small amount of neophyl chloride. NMR ($CCl_4$): $\delta$ 7.27—6.57 ppm (m, 10H, aromatic protons) $\delta$ 2.80 ppm (s, 2H, benzylic protons) $\delta$ 1.30 ppm (s, 6H, *gem*-dimethyl group). Mass spectrum: 210, ($M^+$), 119 (base peak; $C_6H_5C(CH_3)_2^+$).

*4-Phenyl-4-methyl-1-pentene* (18). 3-Phenyl-3-methylbutyraldehyde was prepared by the carbonation of the neophyl Grignard reagent, followed by reduction of the acid formed with lithium aluminium hydride, and subsequent oxidation of the alcohol with the Wachtmeister—Stensiö reagent [33]. This aldehyde, 0.03 mol in THF (30 ml) was treated with 0.03 mol of methylenetriphenylphosphorane prepared from methyltriphenylphosphonium bromide and butyllithium in THF (20 ml). The mixture was stirred at room temperature and then at 60°C for 0.5 h. Distillation afforded compound 18 (3.6 g, 75%) b.p. 38—39°C/0.5 mmHg. Lit. b.p. 91°C/11 mmHg [39]. NMR ($CCl_4$): $\delta$ 7.22—6.93 ppm (m, 5H, aromatic protons) $\delta$ 5.95—4.63 ppm (m, 3H, vinyl group) $\delta$ 2.23 ppm (broad d, 2H, allylic proton) $\delta$ 1.28 ppm (s, 6H, *gem*-dimethyl group). Mass spectrum: 160 ($M^+$); 145 ($M$ — methyl); 119 (base peak, $C_6H_5C(CH_3)_2^+$).

### *General procedure for the reaction of the neophyl Grignard reagent with nickel chloride*

#### *I. Low temperature experiments*

Nickel chloride (10 mmol), and the appropriate ligand, or the prepared $NiCl_2 \cdot L_2$ complex was suspended in 15 ml of THF. The suspension was stirred and cooled to —78°C and the neophyl Grignard reagent from 10 mmol of neophyl chloride was slowly added. In the reactions with carbon monoxide and ethylene as ligands, the nitrogen atmosphere was replaced with carbon monoxide and ethylene, respectively. The mixture was allowed to warm to room temperature over a period of about 2 h, and then stirred for an additional 16 h. After hydrolysis with 10 ml of water, extraction with ether and filtration, the ether solution was analysed by GLC.

#### *II. High temperature experiments*

Two methods were used: (a) The neophyl Grignard reagent was added with stirring to a suspension of $NiCl_2$ or $NiCl_2(PPh_3)_2$ in 30 ml of refluxing dioxane. In some experiments 2,6-di-t-butylphenol was added as a radical scavenger. The mixture was then allowed to reflux for 30 min. The work up procedure was the same as in the low temperature experiments.

(b) The neophyl Grignard reagent was added to a suspension of $NiCl_2 \cdot (Ph_3)_2$ in THF at —50°C. After stirring at —50 to —35°C for 1 h, the thick suspension was added to refluxing dioxane. The rest of the procedure was as described above.

*Isolation and identification of 2,5-dimethyl-2,5-diphenyl-3-hexene* (5). The product from the low-temperature reactions of the neophyl Grignard reagent with $NiCl_2$ was heated under vacuum on a water bath to remove most of the t-butylbenzene. The residue was chromatographed on silica gel with light petroleum as eluant. The product 2,5-dimethyl-2,5-diphenyl-3-hexene (5) could be obtained only 90% pure. The rest was bineophyl (3) and 1-(2-t-butylphenyl)-2-methyl-2-phenylpropane (4). NMR ($CCl_4$): $\delta$ 7.25—6.87 ppm (m, 10H, aromatic protons); $\delta$ 5.60 ppm (s, 2H, olefinic protons); $\delta$ 1.40 ppm (s, 6H, *gem*-dimethyl protons). Mass spectrum: 264 ($M^+$); 249 ($M$ — methyl). Hydrogenation with 10% Pd/C in methanol gave a quantitative yield of bineophyl.

*Isolation and identification of 1-(2-t-butylphenyl)-2-methyl-2-phenylpropane* (4). This substance could not be isolated pure in the nickel reactions because of the very low yield and separation difficulties. However, when the dimer mixture from the reaction of $NiCl_2 \cdot$ Bipy with the neophyl Grignard reagent was allowed to stand for several weeks, bineophyl crystallized out. After removal of the crystals, the mother liquor was shown to be a 70/30 mixture of bineophyl and an unknown compound. The presence of a singlet at $\delta$ 3.34 ppm in the NMR spectrum of the mixture, suggested that the compound was either 1-(2-t-butylphenyl)-2-methyl-2-phenylpropane (4) or its corresponding 4-t-butyl isomer 8. Consequently, 4 and 8 were synthesized and the unknown compound and 4 were shown by GLC to be identical. In later experiments with cobalt(II) chloride, a higher yield of the unknown compound permitted its isolation, and its identity was confirmed by comparison with synthetic compound 4 by mass spectrum, NMR and IR. This compound is probably the one described but not identified by Denney and Davis in their experiments with cobalt [40].

*Isolation and identification of 2-(2-methyl-2-phenyl)propyltetrahydrofuran* (11). This compound was isolated from the reaction between $PdCl_2$ and the neophyl Grignard reagent in the presence of triphenylphosphine. Inorganic salts and unreacted $PdCl_2(PPh_3)_2$ were separated from the organic products by filtration through a short alumina column with ether as the eluant. The filtrate was evaporated and the residue was chromatographed on silica gel with 1% ether in light petroleum as the eluant. The product, 11, a viscous oil, was identical as regards GLC retention time and mass spectrum with the corresponding peak in the nickel experiments. Its purity was 95% by GLC. IR: liquid film: 2000—1700 and 700, 770 $cm^{-1}$ monosubstituted benzene; 1060 $cm^{-1}$ ether; 1380 $cm^{-1}$ doublet, *gem*-dimethyl group. NMR: (100 MHZ, $CCl_4$): $\delta$ 7.3—6.9 ppm (m, 5H, aromatic protons); $\delta$ 3.75—3.25 ppm (m, 3H, protons in $\alpha$ position to the oxygen); $\delta$ 1.9—145 ppm (, 6H, ring $CH_2$ and homobenzylic $CH_2$); $\delta$ 1.38 and 1.30 ppm (s, 3H each, two nonequivalent methyl groups). Mass spectrum: Molecular ion not detectable; 120 (base peak, transfer of the tertiary $\alpha$ hydrogen on the THF ring to the phenyl ring with simultaneous breakage of the central benzylic bond); 119 ($C_6H_5C(CH_3)_2^+$); 85 ($C_4H_7OCH_2^+$); 71 ($C_4H_7O^+$).

*Isolation and identification of 2,6-dimethyl-2,6-diphenylheptan-4-one (13) and 2,7-dimethyl-2,7-diphenyl-octane-4,5-dione (14).* The products from the reaction between the neophyl Grignard reagent and $NiCl_2$ in the presence of excess CO were separated by chromatography on silica gel (eluant 5% in light petroleum). The ketones 13 and 14 were obtained as viscous oil; the $\alpha$-diketone 14 was slightly yellow.

*2,6-Dimethyl-2,6-diphenylheptane-4-one (13).* IR. (liquid film): 1710 $cm^{-1}$ carbonyl group; 705 and 770 $cm^{-1}$, 2000—1700 $cm^{-1}$ monosubstituted benzene.

NMR ($CDCl_3$): δ 7.22 ppm (broad s, 10H, aromatic protons); δ 2.35 ppm (s, 4H, methylene protons); δ 1.30 ppm (s, 12H, *gem*-dimethyl groups). The NMR and IR data are in reasonable agreement with those reported by Barclay and Chapman [41]. Mass spectrum: 294 ($M^+$); 176 (McLafferty rearrangement yielding $C_6H_5C(CH_3)_2CH_2C(CH_2)OH^+$); 161 ($C_6H_5C(CH_3)_2CO^+$); 119 ($C_6H_5C(CH_3)_2^+$).

*2,7-Dimethyl-2,7-diphenyloctane-4,5-dione (14).* UV: Weak absorption at 450 nm due to the α-diketone structure [42]. NMR ($CDCl_3$): δ 7.25 ppm (broad s, 10H, aromatic protons); δ 2.83 ppm (s, 4H, methylene protons); δ 1.32 ppm (s, 12H, *gem*-dimethyl groups). Mass spectrum: 322 ($M^+$, very weak); 161 ($C_6H_5C(CH_3)_2CH_2CO^+$); 119 ($C_6H_5C(CH_3)_2^+$). Anal.: Found: C: 81.0; H: 8.2; 0: 9.8. $C_{22}H_{26}O_2$ calcd.: C: 81.95; H: 8.13; 0: 9.92%. This compound is reported in the literature by Urry et al. [43] but no data are presented.

*Isolation and identification of 4-phenyl-4-methyl-1-pentene (18).* The low boiling products from the reaction of the neophyl Grignard reagent and $NiCl_2$ in the presence of $PPh_3$ and ethene were distilled off. The distillate contained mainly t-butylbenzene with minor amounts of neophyl chloride, bineophyl and 18. The mixture was chromatographed on alumina with light petroleum as eluant. t-Butylbenzene and 18, 4/1 could be isolated. The NMR, GLC and mass spectral data of the mixture confirmed that 18 was identical with authentic, independently synthesized 4-phenyl-4-methyl-1-pentene.

*Isolation and identification of neophylcyclopentadiene (29).* The reaction mixture from the reaction of the neophyl Grignard reagent with $CpNiCl \cdot PPh_3$ was filtrated through a short, acidic alumina column. After evaporation of the solvent and the t-butylbenzene in vacuo, a mixture containing mainly bineophyl and neophylcyclopentadiene was obtained. The NMR spectrum of the mixture revealed the typical olefinic cyclopentadienyl protons at δ 6.5—5.6 ppm together with two broad singlets at δ 2.66 ppm (doubly allylic protons) and δ 2.20 ppm (mono allylic protons). The *gem*-dimethyl group appeared at δ 1.30 ppm. The mass spectrum could not be obtained due to the fact that the compound polymerized or dimerized on standing.

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