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# THE THERMAL FORMATION OF BIALKYLS FROM ALKYLMETALS

## III *. THERMOLYSIS OF NEOPHYL COMPLEXES OF THE FIRST ROW TRANSITION METALS

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## Summary

The thermal decomposition of neophyltransition metal complexes has been investigated, in particular, the products of reductive elimination and the symmetry aspects of this reaction. Bineophyl (1) was generally the major product from reductive elimination. A number of other dimeric products were formed, via routes which must involve transmetallation, α-elimination and, in a few cases, radical formation. t-Butylbenzene is the major monomeric product. Products from reactions with added ligands such as carbon monoxide, ethene and triphenylphosphine were also observed.

## Introduction

Reductive elimination, particularly that invoking carbon—hydrogen bond formation, is of synthetic and industrial interest. The synthetic usefulness of reductive elimination involving carbon—carbon bond formation is hampered by the numerous side reactions, e.g. β-elimination and radical cleavage (see ref. 1).

We have been particularly interested in the relative importance of reductive elimination and radical cleavage. Some of the factors are delineated in the previous work [2,3] and in the accompanying paper on symmetry properties [4]. The present paper is an extension to other metals of the previous study of neophylnickel [2]. The decomposition products from all the first row transition metal-neophyl complexes, including nickel, were similar, but the proportions varied markedly with the central metal and the ligands (Table 1).

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* For Part II see ref. 2.

TABLE 1

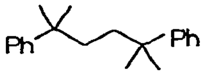
PRODUCTS FROM THE REACTION BETWEEN *n* EQUIVALENTS OF THE NEOPHYL GRIGNARD REAGENT AND ONE EQUIVALENT OF VARIOUS METAL COMPLEXES

| Run | *n* | Complex | Initial temp. (°C) | Dimers (%) [b] | | | | | | | | | Monomers (%) | | | Other products (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | |
| 1 | 1 | $CoBr_2$ | –70 | 39 | 19 | tr | tr | — | — | — | — | 38 | — | — | — | — |
| 2 | 1 | $CoBr_2$ | 100 | 13 | 12 | 1–2 | — | 1 [c] | — | — | — | 66 | — | tr | — | 13, 14 (tr) |
| 3 | 1 | $CoBr_2(PPh_3)_2$ | –70 | 66 | 2 | — | — | — | — | — | — | 30 | — | — | — | — |
| 4 | 1 | $CoBr_2(PPh_3)_2$ | 100 | 37 | 12 | — | — | — | — | — | — | 40 | — | — | tr | 15(2); 16(2,5) |
| 5 | 1 | $CoCl_2$ + CO | –70 | 5 | tr | — | — | — | — | — | — | 15 | — | — | — | 17(51); 18(~10) |
| 6 | 2 | $CoCl_2$ + CO | –70 | 9 | tr | — | — | — | — | — | — | 15 | — | — | — | 17(65); 18(~5) |
| 7 | 1 | $CoCl_2$ + ethene | –70 | 9 | 6 | — | — | — | — | — | — | 60 | — | — | — | 23(1); 24(10) |
| 8 | 1 | $FeCl_3$ | –70 | 76 | — | — | — | — | — | — | — | 15 | — | — | — | 19(~5) |
| 9 | 2 | $FeCl_3$ | –70 | 45 | tr | — | — | — | — | — | — | 50 | — | — | — | — |
| 10 | 1 | $FeCl_3$ + CO | –70 | 55 | — | — | — | — | — | — | — | 30 | — | — | — | 17(6); 18(tr); 19(3) |
| 11 | 2 | $FeCl_3$ + CO | –70 | 42 | — | — | — | — | — | — | — | 25 | — | — | — | 17(25); 18(tr); 19(~3) |
| 12 | 1 | $FeCl_3$ + 2 $PPh_3$ | –70 | 70 | — | — | — | — | — | — | — | 25 | — | — | — | 19(2–3) |
| 13 | 1 | $FeCl_3$ + ethene | –70 | 61 | — | — | — | — | — | — | — | 25 | — | — | — | 19(9) |
| 14 | 1 | $FeCl_2$ | –70 | 11 | 8 | — | — | — | — | — | — | 80 | — | — | — | — |
| 15 | 1 | $FeCl_2$ | 100 | 5 | 13 | tr | tr | — | tr [d] | — | — | 77 | — | — | tr | 13, 14(tr) |
| 16 | 1 | $FeCl_2$ + ethene | –70 | 19 | — | — | — | — | — | — | — | 80 | — | — | — | — |
| 17 | 1 | $FeCl_2$ + 2 $PPh_3$ | –70 | 15 | — | — | — | — | — | — | — | 80 | — | — | — | 16(tr) |
| 18 | 1 | $FeCl_2$ + 2 $PPh_3$ | 100 | 20 | tr | — | — | — | — | — | — | 75 | — | — | — | 13, 14(tr) |
| 19 | 1 | CuI + EVE [a] | –70 | 58 | — | — | — | — | — | — | — | 23 | 1 | 1 | 0,5 | 13(1–2); 21(12) |
| 20 | 1 | $CuBr_2$ + EVE [a] | –70 | 49 | — | — | — | — | — | — | — | 20 | 0,5 | 0,5 | 0,5 | 13(2,5); 20(15–20); 22(5) |
| 21 | 1 | CuI | –70 | 62 | — | — | — | — | — | — | — | 17 | 1,5 | 1 | 0,9 | 13(2–3); 21(~15) |
| 22 | 1 | $CuBr_2$ | –70 | 72 | — | — | — | — | — | — | — | 10 | 0,3 | 0,6 | 0,5 | 13(2); 20(12) |
| 23 | 1 | CuI | 100 | 15 | — | — | — | — | — | 4 | 1 | 53 | 10 | 9 | 2,5 | 13(2–3) 14(~1) |
| 24 | 1 | $TiCl_4$ | –70 | 67 | — | — | — | — | — | — | — | 26 | — | — | — | 19(~3) |
| 25 | 1 | $TiCl_3$ | –70 | tr | — | — | — | — | — | — | — | *e* | — | — | — | — |
| 26 | 1 | $CrCl_3$ | –70 | tr | — | — | — | — | — | — | — | *e* | — | — | — | — |

[a] Ethyl vinyl ether. [b] tr = trace. [c] Identified in the product mixture by NMR by comparison with an authentical sample. [d] Inferred from GC - MS and from the NMR spectrum of the product mixture before and after hydrogenation. [e] Not determined.

## Results and discussion

Among the products resulting from the coupling of two neophyl groups, bineophyl (1) was generally the major product, but in some experiments with



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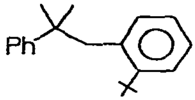

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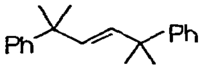

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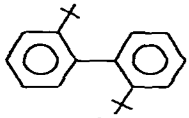

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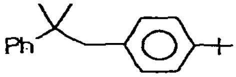

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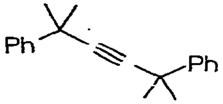

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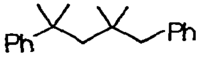

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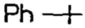

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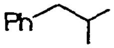

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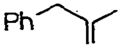

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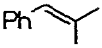

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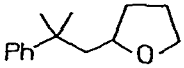

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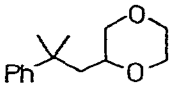

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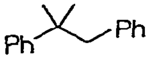
Ph — Ph

15



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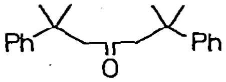

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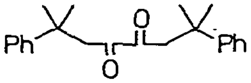

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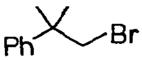

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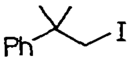

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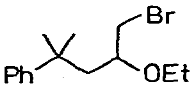

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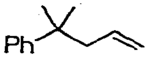

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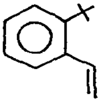

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cobalt and iron complexes (runs 1, 2, 4, 7, 14, 15) comparable amounts of 2 were formed, evidently via partial transmetallation to give 2-t-butylphenylmetal complexes (40). Transmetallation is most probably involved also in the formation of 2,2'-di-t-butylbiphenyl (4) and the compound 5 (runs 2, 15). The "rearranged" dimers 7 and 8, indicative of the formation of free neophyl radicals, were detected only in some copper promoted reactions (runs 19—23).

t-Butylbenzene was the predominant monomeric product, but substantial amounts of the "rearranged" monomers 10—12 were detected, mainly in experiments involving copper as the central metal.

In particular when radical character was indicated by other evidence, the products 13 and 14 from attack on the solvent were formed (runs 19—23).

Finally, a number of products, 15—24, were detected, which originate from reactions involving auxiliary ligands, e.g. triphenylphosphine, carbon monoxide, ethene and halogens.

*Neophyl coupling*

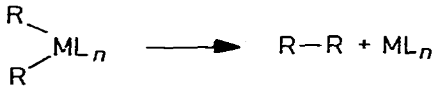
The true structure of the transition state for reductive elimination is, of course, the major problem in attempts to outline a unified mechanism. An attractive intermediate is a mononuclear dialkylmetal 25, since it is easy to visualize direct orbital overlap between the alkyl groups. If, as is generally assumed, reductive elimination takes place with retention at the combining carbon centres, it can be symmetry allowed for a *cis* but not for a *trans* complex [4]. The present discussion deals mainly with complexes of the type 25, but dinuclear and higher clusters will also be discussed briefly in the final part of this paper.

For copper(I), which is a $d^{10}$ system, reductive elimination from an intermediate 25 is symmetry-forbidden [4]. The experimental results for neophylcopper(I) seem to support this.

When the neophyl Grignard reagent and copper(I)iodide were brought into reaction at —70° C and the mixture then allowed to warm to room temperature, a fairly high yield of pure bineophyl was obtained. When the reactants were mixed at 100° C, however, small amounts of the rearranged dimers 7 and 8 were also formed. Since free neophyl radicals rearrange rapidly at 100°C but undergo only limited rearrangement below room temperature [5c], this result strongly indicates some radical component in the decomposition process. The formation of the rearranged monomeric products 10—12 is further indication of radical character, since they are characteristic of free neophyl radicals [5].

The similarity in the product patterns from the reaction of the neophyl Grignard reagent with 1,2-dibromoethane and from the photolysis of bis(neophylcarbonyl)peroxide, which are free radical reactions [6], and that from neophylcopper(I) (Table 1), also suggests radical decomposition. Finally, the formation of neophyltetrahydrofuran in all three reactions is indicative of radical reactions.

The concerted formation of bineophyl from dineophylcopper(II), a $d^9$ system, is also symmetry-forbidden [4]. However, in this case, reductive elimination is symmetry-allowed from an excited state, which probably has low energy. Also for copper(II) the product pattern, which is very similar to that obtained from copper(I), indicates radical character. The amount of bineophyl is higher in both cases than that obtained from neophyl radicals [5,6], indicating partial concerted character in the copper promoted reactions.



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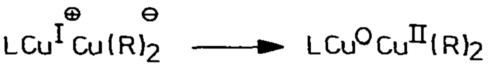
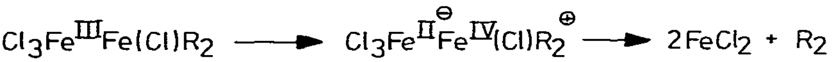
25a R=neophyl



$$\overset{\oplus}{LCu^{I}}\overset{\ominus}{Cu(R)_2} \longrightarrow LCu^{0}Cu^{II}(R)_2$$

26 R=neophyl 27



$$Cl_3Fe^{III}Fe(Cl)R_2 \longrightarrow Cl_3\overset{\ominus}{Fe^{II}}\overset{\oplus}{Fe^{IV}(Cl)R_2} \longrightarrow 2FeCl_2 + R_2$$

28 R=neophyl

$RTi^{IV}X_3$

29 $R = X = (CH_3)_3CCH_2-$
30 $R = X = (CH_3)_3SiCH_2-$
31 $R = X = (CH_3)_3SnCH_2-$
32 $R = Ph(CH_3)_2CCH_2-$ , $X = Cl$

The symmetry-allowedness of the concerted formation of two neophyl radicals from dineophylcopper(II) [4] could perhaps contribute to the ease of radical cleavage. Intramolecular one-electron oxidation of the complexed neophyl carbanions is another possible route to neophyl radicals.

The relevance of the close similarity between the products from neophylcopper(I) and (II) is not clear. A possibility is that the reactive intermediate in both cases is a copper(II) complex. Disproportionation of copper(I) to copper(II) and copper(0) is a well-known phenomenon. In the present case one could even visualize a dinuclear intermediate, that is a copper(I) cuprate, which can yield a mixed copper(0)copper(II) complex 27 after intramolecular electron transfer. The decomposition products from a complex of the type 27 would be expected to be similar to those obtained from the reaction between the neophyl Grignard reagent and copper(II) salts (cf. ref. 20.).

In contrast to the $d^{10}$ and $d^9$ systems, dialkyl complexes of the configurations $d^8$—$d^2$ have reasonable symmetry-allowed pathways to reductive elimination [4]. In accordance, the earlier study of neophylnickel and palladium species, which are $d^8$, indicated exclusively concerted formation of bineophyl [2].

The results of the present study of a cobalt(II) system ($d^7$) are also in accord with the concerted formation of bineophyl (1). As in the nickel experiments, the highest yield of bineophyl (66%) was obtained in the presence of phosphine ligands. Even in decomposition at 100°C none of the rearranged dimers 7 and 8 was observed, although the yield of bineophyl was greatly decreased (Table 1).

The yield of bineophyl was also lower in the absence of phosphine ligands (Table 1). This is probably due to concerted side reactions rather than to radical formation, in accordance with symmetry considerations, which predict that reductive elimination can be symmetry-allowed for all coordination numbers 3—6 [4].

With the exception of 5-coordination this is also true for $d^6$ systems. In the present work neophyliron(II) was investigated as a model system. The formation of bineophyl seems to be concerted as predicted, but the yields were also low after the addition of ligands. Iron(0) inserts very efficiently into carbon—hydrogen bonds, with hydride formation, even in the presence of phosphine ligands [7]. In their absence, insertion into the solvent could be expected. The major product from the iron(II) reactions, t-butylbenzene, may then be expected to be formed from neophyliron and iron hydrides. Similar reactions are most probably important also for the formation of monomer 9 from other neophylmetals.

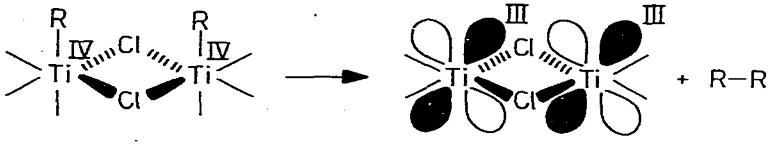
Iron(III), a $d^5$ system, gave a high yield of bineophyl, uncontaminated by isomers. Iron(III) is thus an efficient coupling agent, in contrast to iron(II). A similar, though less marked, difference was noted earlier for some other alkyl groups [8], and is also apparent from the fact that oxidation of a stable dialkyliron(II) species promoted reductive elimination [9].

An unexpected finding for the iron(III) system was that the addition of 1 mol of Grignard reagent per mol of iron(III) chloride gave 76% bineophyl, while the addition of two equivalents led to a decrease to about 45% in the yield, based on added Grignard reagent. This result could be used as an argument for polynuclear intermediates, but a disproportionation reaction, similar to that described for copper(I) is also possible. A reasonable intermediate would be the dinuclear complex 28, in which iron(III) chloride would be the strongest oxidant, perhaps capable of oxidizing a dialkyliron(III) species to iron(IV), which would be expected to undergo facile reductive elimination.

One $d^3$-system, prepared from chromium(III) chloride and neophylmagnesium chloride, was investigated. No bineophyl was formed. Since the reactant complex is probably 6-coordinate, reductive elimination should be permitted if a high spin product is formed and forbidden if a low spin product is formed. A low spin product is thus indicated by the experimental result.

Finally, the neophyl complexes of titanium(III), $d^1$, and titanium(IV), $d^0$, were studied. Reductive elimination should be permitted for the titanium(III) complex provided that low spin $d^3$ products are obtained [4]. The lack of bineophyl formation indicates that this is not the case.

In contrast, a fair yield of bineophyl was formed in the reaction of neophylmagnesium chloride with titanium(IV) chloride (Table 1, run 26). Since none of the rearranged products were formed, a radical reaction is unlikely. The result is surprising since concerted reductive elimination should not be permitted for a $d^0$ dialkylmetal. The exclusive formation of methane from dimethyltitanium(IV) dichloride [12] is thus in accordance with the symmetry rules [4]. The actual mechanism in this case is uncertain but an $\alpha$-elimination, followed by reductive elimination of methane is an attractive route. In principle, reductive elimination of hydrogen and methyl should also be symmetry-forbidden. This reaction, however, may not be a simple reductive elimination since it proceeds much more readily than hydrogen—hydrogen and alkyl—alkyl coupling [13]. Since hydrogen bound to metal frequently has some proton character, the alkyl—hydrogen coupling could perhaps be regarded as an intramolecular protonation of a metal-bound carbanion. With the exception of the compound **31** most titanium(IV) polyalkyls $R_nTiX_{n-4}$, $n \geqslant 2$, yield RH as the major product. Some further examples are the compounds **29** and **30**. The formation of $R_2$ from **31** could perhaps be explained by radical formation. This explanation is also possible for the formation of ethane from methyltitanium(IV) trichloride but less likely for the bineophyl formation from neophyltitanium trichloride. Charge transfer is also conceivable but the most attractive explanation is cluster formation. For symmetry reasons a dinuclear intermediate is insufficient since two electrons in the product **34** must occupy an antisymmetric orbital which is metal—metal antibonding and may have a fairly high energy. However, for a large cluster this antisymmetric orbital may even become bonding. For instance, with a mixed titanium(IV)-titanium(III) cluster **35** reductive elimination yields alkane and a titanium(III) complex in which the



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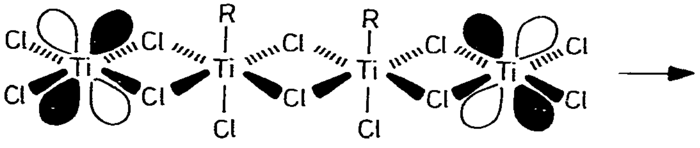

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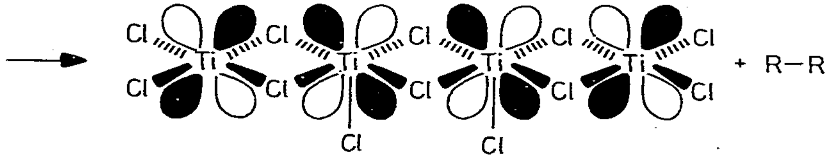

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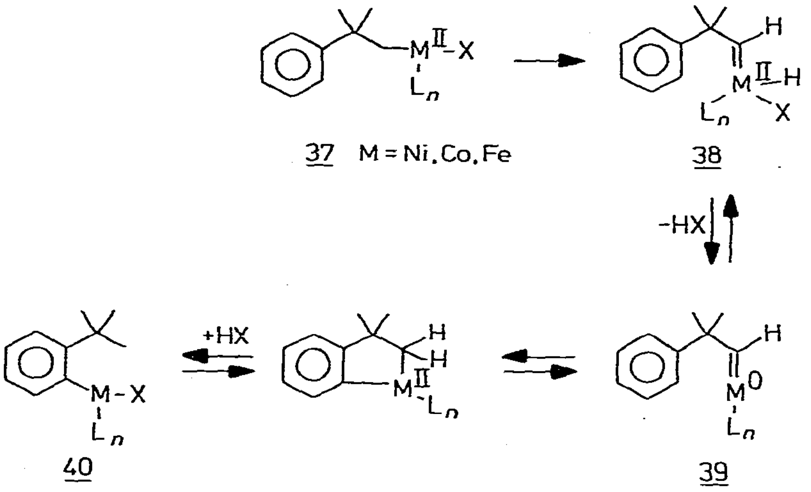
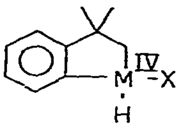
four odd titanium electrons can occupy two metal—metal bonding orbitals. Of these the $b_1$ orbital as depicted in **36** correlates with the $b_1$ combination of the metal—alkyl orbitals as desired. This reaction is consequently symmetry-allowed. The results clearly show that cluster formation might be expected to facilitate reductive elimination and related reactions.

*Other dimers*

In the copper promoted reactions, the dimers **7** and **8** are formed via rearranged neophyl groups. Such rearrangement could in principle go via free radicals, carbonium ions or via some type of metal promoted rearrangement. The radical mode seems most likely since no products indicative of this type of rearrangement are formed from iron, cobalt or titanium, where both carbonium ions and transmetallations are at least as possible as in the copper promoted reactions. The total product distribution in the copper reactions also is qualitatively similar to that obtained in radical reactions [5,6].

The dimer 2 is among the reaction products from the decomposition of neophyliron(II) and cobalt(II). This product probably stems from transmetallation followed by coupling. Again, there are several possible routes to the aryl complex 40, which has only been detected for nickel [2], but, which is probably the intermediate. An attractive route goes via the carbene complex 39 but a (IV)-valent intermediate or transition state 41 is also possible. For cobalt(II),





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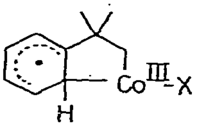

42

a radical attack on the aromatic nucleus is also conceivable. The olefinic dimer 3 and the acetylenic dimer 6 are probably formed via carbene, e.g. 38 or 39, and carbyne complexes as has been suggested in the nickel promoted reaction studied previously [2].

*Monomeric products.*

The formation of monomer, mainly t-butylbenzene (9), is the other major reaction of the neophylmetals investigated. In some cases rearranged monomers (10—12) were detected. They are probably formed by disproportionation of rearranged radicals. However, most of the reactions yielded pure t-butylbenzene. The major route to this compound should be reductive elimination of neophyl and hydrogen, a reaction type that is evidently very facile [13]. There are three reasonable sources of hydride, the solvent, ligands such as triphenylphosphine, and $\alpha$-elimination. Earlier work has shown that $\alpha$-elimination, or the alternative acid-base reaction [10,11], is the most important one for titanium complexes. For iron and cobalt, the main route is probably insertion into the solvent and the ligands. Reactions like *ortho*-metallation of coordinated phosphine to produce a metal hydride have been shown to be very facile with iron(0) [7], the product from a primary reductive elimination. Also cobalt(0) would be expected to insert quite readily. Transfer of hydrogen to a neophylmetal halide by halogen—hydride exchange would yield the required alkylhydride complex.

### *Neophyl halides*

A low yield of neophyl halide was formed from iron(III) and titanium(IV) and a slightly higher yield from copper(I) and copper(II). For the corresponding cobalt and nickel [2] reactions, no such products were detected. Several routes are possible for their formation. Nucleophilic displacement at saturated carbon, which is the main route for palladium [14a] and cobalt [14b], is unlikely for steric reasons. Radical displacement, as suggested by Kochi [15], is probably important for copper, but for iron and titanium there is no indication of radical formation, the most probable reaction is in fact reductive elimination, although there is little precedent for such reactions with halogens. (The formation of iodobenzene from phenylplatinum(IV)iodide [16] may be an exemple.) The lack of halide formation from nickel [2] can perhaps be taken as support for the assumption, since reductive elimination involving halogen—carbon coupling is not facile with nickel [17].

### *Products from reactions with ligands*

In the high temperature (100° C) experiments with the cobalt(II) triphenylphosphine complex, small amounts of neophylbenzene were formed, possibly via the attack or the Grignard reagent on the coordinated phosphine (cf. ref. 2).

Carbon monoxide participated in the reactions of cobalt and iron neophyl complexes and gave rise to moderate to good yields of dineophylketone (17) and small amounts of the diketone 18. Similar results were obtained earlier with nickel [2]. As might have been expected from the efficiency of the hydroformylation reaction, cobalt give the highest yields of the ketones (Table 1).

An electron rich olefin, ethyl vinyl ether, was added in a number of experiments but generally had no effect on the decomposition of the neophylmetals. An exception is the reaction with copper(II) bromide, which gave a low yield of the adduct 22. This compound is most probably formed via bromination of the vinyl ether by the copper(II) bromide, followed by attack of some neophylmetal species. Control experiments with brominated vinyl ether showed that the Grignard reagent alone gave only trace amounts of 22.

Finally, some exploratory experiments involving addition of ethene were performed. No adducts were observed with iron(II) and (III), but neophylcobalt(II) yielded small amounts (1%) of the insertion product 23. In addition fair amounts (10%) of a compound was formed which most probably is 2-t-butylstyrene (24). The insertion of ethene into the neophyl—metal bond is evidently inefficient, perhaps for steric reasons.

## Conclusion

It is difficult to present a unified picture of reductive elimination from alkylmetals. The reason is that there are evidently several competing, metal-dependent processes with approximately the same activation energy. Rather small changes of the reaction conditions will thus have a profound influence on the relative yields of the reaction products. Nonetheless, some generalizations are possible. Symmetry strongly influences the importance of reductive elimination. When the reaction is symmetry-forbidden, as for copper(I) and (II), at least partial homolytic decomposition is indicated by the products. A high formal oxidation state on the metal seems to promote reductive elimination. Here, charge transfer and also recoupling of the metal *d*-electrons [3], may be involved. Electron transfer reactions may be important in the formation of these states with high formal charge on the metal, as also indicated by earlier studies on chemical [9] and electrochemical [17] oxidation of dialkylmetals.

Finally, cluster formation may be important, since the symmetry restrictions imposed upon simple dialkylmetals and even dinuclear clusters may be relieved for higher clusters.

## Experimental

The general experimental procedures and the analytical methods were the same as those reported for neophyl nickel [2] except that the gas chromatography of the monomeric substances was performed on a PYE GCV apparatus with 1% SF96 and OV225 on chromosorb W columns. NMR spectra were recorded on a Varian EM 360 instrument with TMS as the internal standard. The chemical shifts are reported as $\delta$ values (ppm) downfield from TMS. IR spectra were recorded on a Perkin-Elmer 257 instrument, and the mass spectra on an LKB 9000 instrument.

### *Identification of products*

All compounds **1**—**20** and **23** were identified by GC-MS comparison with authentic samples [2,6]. The neophyl iodide **21** and the vinyl ether adduct **22** were identified by comparison with samples prepared by independent syntheses.

### *2-Methyl-2-phenylphenyl iodide (21)*

This compound was prepared in 60% yield from neophylmagnesium chloride and iodide in THF.

B.p. 82°C/0.5 mm. Mass spectrum (*m/e*): molecular ion not visible; 132 (M — HI, base peak); 117 (M — HI — $CH_3$). NMR ($CCl_4$): 7.2 (m, 5H, aromatic protons); 3.35 (s, 2H, methylene protons); 1.45 (s, 6H, *gem*-dimethyl group), the NMR values are in agreement with reported values [18].

### *1-Bromo-2-ethoxy-4-methyl-4-phenylpentane (22)*

This compound was prepared by the oxymercuration of 4-methyl-4-phenyl-1-pentene with $Hg(OAc)_2$ in ethanol, followed by replacement of an acetoxy group on mercury with bromide by the aid of potassium bromide and subsequent bromodemercuration with bromine. The procedure used was essentially that described by Carter and West [19]. The desired product was obtained in about 40% over all yield after column chromatography on $Al_2O_3$ with light petroleum as the eluant.

IR ($cm^{-1}$), neat: 3000—3100, 1600 (aromatic); 2000—1600 and 695, 760 (monosubstituted aromatic); 1090 (ether). NMR ($CCl_4$): 7.3—6.9 (m, 5H, aromatic protons); 3.9—2.8 (5H, complicated region. The ethoxy methylene group can be observed as a quartet centered at 3.22. The $CH_2$—Br and the methine protons occupy the rest of the region. The fact that the $CH_2Br$ protons are unequivalent makes it difficult to assign any shift values); 2.0—1.8 (2H, somewhat distorted AB part of an ABX spectrum, homobenzylic methylene group); 1.36 and 1.28 (two s, 3H each, two nonequivalent methyl groups); 1.04—0.90 (t, 3H, the methyl group of the ethoxy function). Mass spectrum ($m/e$): Molecular ion not visible; 204 ($M^+ - HBr - CH_3$); 151 and 153 ($BrCH_2$-$CHOEt^+$); 119 base peak, ($C_6H_5C(CH_3)_2{}^+$); 85 ($EtOC(CH_2)CH_2{}^+$). It should be noted that the corresponding methoxy compound, which we have also synthesized, shows a well defined molecular ion.

### *Indentification of the neophyl iodide (21), the vinyl ether adduct (22) and the 2-t-butyl styrene (24)*

The neophyl iodide was identified by GC-MS comparison with the synthetic compound.

The vinyl ether adduct was isolated from the product mixture from the $CuBr_2$/neophyl-Grignard reaction by crystallisation of the major part of the bineophyl from ethanol and subsequent chromatography of the evaporated mother liquor on $SiO_2$ with 6% ether in light petroleum as the eluant. The spectroscopic data (IR, NMR, mass spectrum) of the isolated product were identical to the data of the synthetic compound.

The 2-t-butyl styrene was isolated from the $CoCl_2$/ethene/neophyl-Grignard product mixture by preparative GC on a 20% Apiezon L + KOH on Cromosorb W at 190°C.

IR ($cm^{-1}$) in $CCl_4$: 3100—3000 (aromatic and olefinic C—H); 1950, 1920, 1835, and 1815 (C—H, suggested 1,2 disubstituted benzene); 1622 (alkene); 1365 (t-butyl group). Mass spectrum ($m/e$): 160 ($M^+$); 145 ($M^+ - CH_3$, base peak). NMR ($CCl_4$): 7.6—6.8 (m, 5H); 5.5—5.0 (m, 2H); 1.43 (s, 9H, t-butyl group).

Due to the steric bulk and probable anisotropy effect of the t-butyl group it is very likely that the appearance of the vinyl group would be distorted. The =CH—Ph proton probably appears in the aromatic region, which should explain in the integrated relative areas. In order to confirm the identity of the substance, we carried out hydrogenation with Pd/C in methanol at room temperature and 1 atm. of $H_2$ for 3 h to yield 1-t-butyl-2-ethylbenzene. NMR ($CCl_4$): 7.3—6.9 (m, 4H, aromatic protons); 2.84 (q, 2H, benzylic protons); 1.4 (s, 9H, t-butyl group); 1.27 (t, 3H, methyl group, partly obscured by the t-butyl group).

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