

Review

THERMAL DECOMPOSITION OF NICKEL-CARBON AND COPPER-CARBON σ -BONDS

S. PASYNKIEWICZ

Faculty of Chemistry, Technical University, ul.Koszykowa 75, 00-662 Warsaw, Poland

(Received July 7th, 1989)

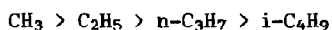
Thermal decomposition reactions of alkyl-transition metal compounds have been intensively studied in recent years because of the importance of these types of compounds in organometallic chemistry and in various organic reactions catalyzed by transition metals. Understanding the behavior of these transition-metal complexes is of fundamental importance in the elucidation of metal-promoted catalytic processes.

The decomposition of alkyl-transition metal compounds has been studied for Ti, V, Cr, Mn, Co, Pt and other metals. However, no general theory for decomposition, or even a clear understanding of specific cases has resulted.

Wilkinson (1), Baird (2), Davidson (3), Whitesides (4) and Schrock (5) among others, widely discussed the thermal decomposition reactions.

The thermolysis of compounds containing a carbon-nickel and carbon-copper σ -bond was not studied in detail until now.

Baird (2) studied nickel compounds of the $R_2Ni \cdot B$ type (where R = Me, Et, n-Bu; B = phosphine or dipyriddy) and determined the gaseous products resulting from the thermal decomposition. Yamamoto (6) studied the stability of the alkyl-nickel bond and presented the following order of stability:

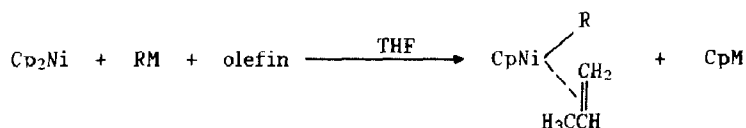


Thomson and Baird (7,8) studied the thermolysis of monoalkylnickel compounds of the $\eta^5-C_5H_5NiR(PPh_3)$ type and concluded that compounds possessing a β -hydrogen decompose via β -hydrogen elimination. All these investigations were carried out within 60-160°C, which must have affected the course of a number of side reactions.

The thermal decomposition reactions of alkylcopper were studied even less. Whitesides (9), Kochi (10) and Yamamoto (11) obtained butyl-, ethyl-, n-propyl- and trimethylsilylmethylene-copper and investigated the gaseous products of their decomposition.

The purpose of our studies was to obtain such nickel and copper complexes which are of low stability at room temperature. Studies at low temperature of the gaseous and solid products of their thermal decomposition avoid side reactions and allow a better explanation of the reaction mechanisms.

Nickel complexes of the $\text{CpNi}(\eta^2\text{-propene})$ type were obtained from the reaction (12,13).

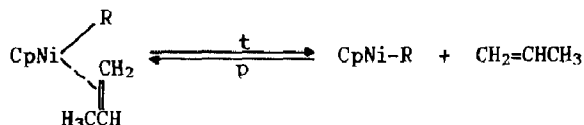


for R = CH_3 ; CD_3 ; $\text{CH}_2\text{Si}(\text{CH}_3)_3$; CH_2CH_3 ; $\text{CH}_2\text{CH}_2\text{CH}_3$

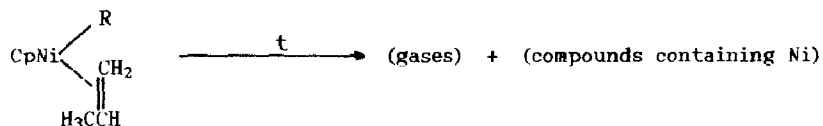
Cp = C_5H_5

M = MgX ; Li

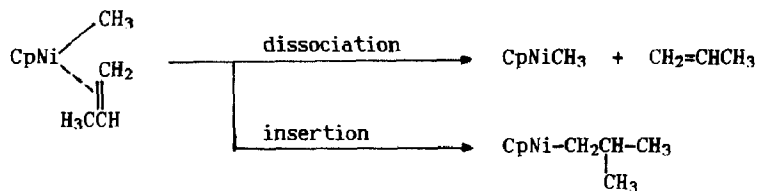
Reactions were carried out under normal pressure at -40 to -20°C , and under increased pressure at 0 to 20°C . The complexes obtained are solid or dense liquids of dark red coloring, stable below -20°C . An equilibrium is established between the complex and its decomposition products (14).



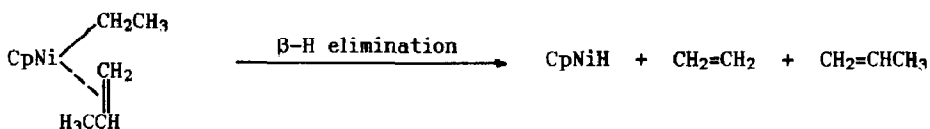
Above room temperature further decomposition reactions proceed



The thermal decomposition mechanism of the studied complexes depends first of all on the nature of the alkyl group bonded to nickel. For alkyl groups not containing β -hydrogen such as CH_3 , CD_3 , $\text{CH}_2\text{Si}(\text{CH}_3)_3$, $\text{CH}_2\text{-C}(\text{CH}_3)_3$ two main reactions proceed - dissociation and insertion.

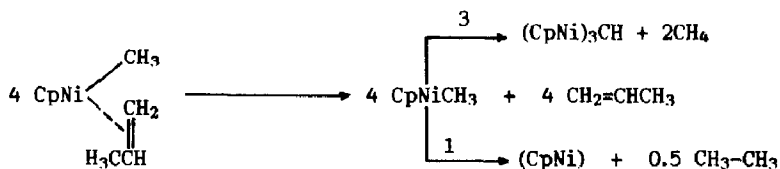


For substituents containing β -hydrogen, such as C_2H_5 and C_3H_7 , β -hydrogen elimination is the main reaction.

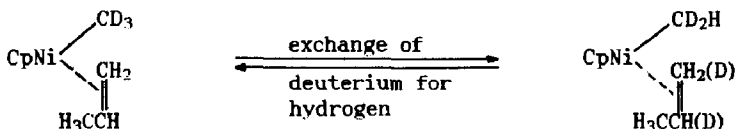


All the gaseous products evolved in the course of the thermal decomposition of the complexes were determined. The composition of these products depends on the temperature and time of thermolysis. On that basis the decomposition course is proposed (Scheme 1).

SCHEME 1

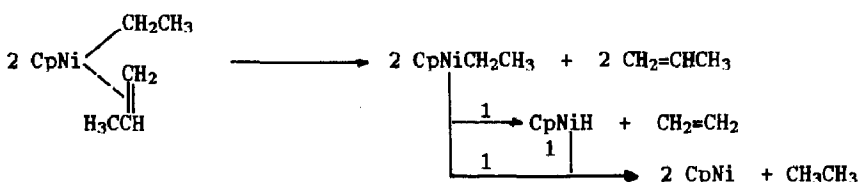


Studies of the $\text{CpNiCD}_3\cdot\text{CH}_2=\text{CHCH}_3$ complex established the decomposition mechanism. Hydrogen exchange between the alkyl and complexed olefin, unknown till now, was observed.



As already mentioned, the mechanism of thermolysis of complexes containing β -hydrogen differs from that of complexes not containing β -hydrogen. The ethyl complex yields 56% of propene, 18% of ethylene, 21% of ethane and about 5% of butanes. The reaction course is shown in Scheme 2.

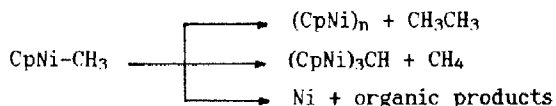
SCHEME 2



The thermolysis of the propyl complex proceeds similarly. Only propane (16%)

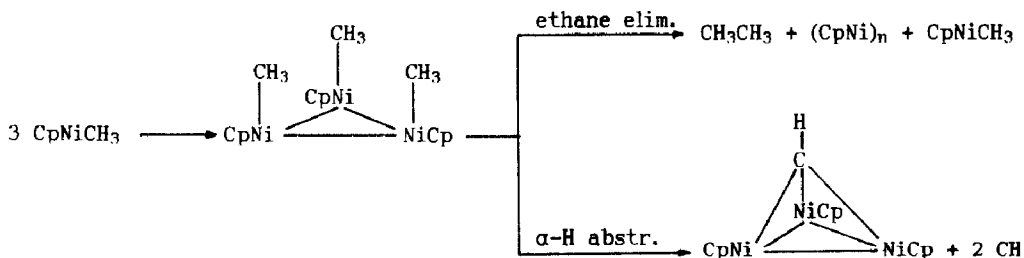
is formed besides propene (83%). The decomposition mechanism is the same. Studying the amount and composition of the gaseous products formed during the thermolysis provides a relatively easy method of determining the course of decomposition. However the solid products formed during the thermolysis were not studied until now.

The decomposition of the complex starts from the loss of the complexed propene molecule. The formed unstable 16 electron methylcyclopentadienylnickel yields a mixture of solid nickel compounds and metallic nickel (15).



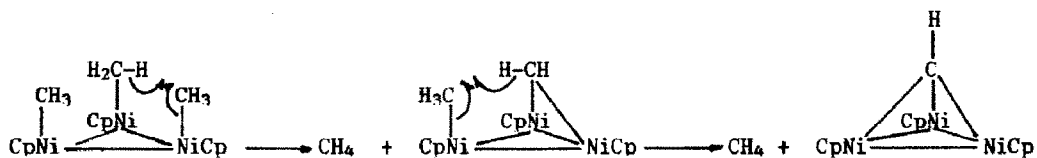
A nickel cluster consisting of three nickel atoms bonded to each other and additionally bonded to one methylidyne carbon atom was isolated from that mixture and identified. This cluster is formed by the aggregation of the unstable species, CpNiCH_3 , in which nickel has 16 electrons. Three molecules of this species bond together forming a trimer, $(\text{CpNiCH}_3)_3$, in which the nickel atom has already 18 electrons. The trimer formed can react in two directions, by ethane elimination and formation of clusters $(\text{CpNi})_n$ (not isolated but determined by MS, where $n=4$ or 6) or by α -hydrogen abstraction from the methyl group with the formation of methane and an unstable trinickel $(\text{CpNi})_3\text{CH}$ cluster (Scheme 3).

SCHEME 3

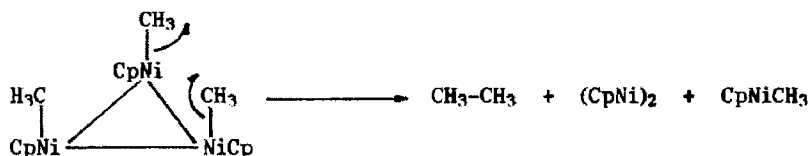


The mechanism of methane formation during the thermolysis of the methyl complex should be considered as α -hydrogen abstraction from the methyl group bonded to nickel. This hydrogen forms methane with the second methyl group. The stability of CpNiCH_3 up to ca. $0\text{-}10^\circ\text{C}$ indicates its aggregation with the formation of a dimer, or more probably, of an 18 electron trimer. Consecutive methane elimination proceeds in this trimer (Scheme 4).

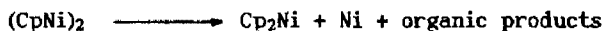
SCHEME 4



Besides α -hydrogen abstraction also reductive elimination proceeds. Ethane and CpNi are formed, the latter producing clusters. The course of this reaction can be explained by heterolytic or homolytic scission of the Ni-C bond. The homolytic cleavage generates short-lived radicals (to be distinguished from "free" radicals), which react with each other yielding ethane.



The formed diamagnetic compounds of the $(\text{CpNi})_2$ type easily decompose yielding a whole range of organic products, metallic nickel and nickelocene.

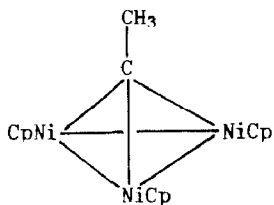


The methylidyne cluster $(\text{CpNi})_3\text{CH}$ has not been isolated until now in the pure state due to its instability. Under the conditions of thermal decomposition of the $\text{CpNiCH}_3(\eta^2\text{-propylene})$ complex it can react further with a CpNiCH_3 species producing higher aggregation products. It can be assumed that the acidic hydrogen in this cluster easily reacts with the methyl group of CpNiCH_3 forming methane and the intermediate tetranickel cluster.

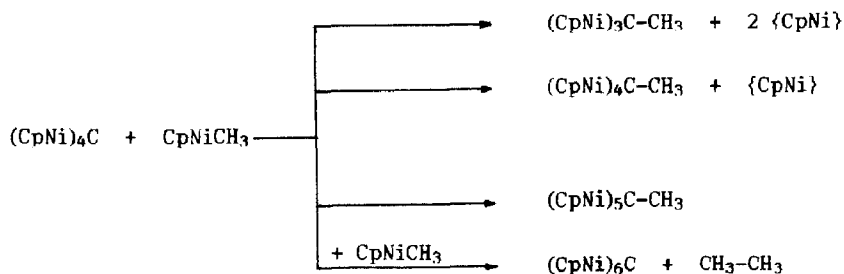


Further reactions of this cluster with CpNiCH_3 lead to the formation of a number of nickel clusters, which is presented in Scheme 5.

The tris(η^5 -cyclopentadienyl)(μ^3 -alkylidyne)trinickel cluster $(\text{CpNi})_3\text{C}-\text{CH}_3$ was isolated chromatographically in the pure state and studied by ^1H and ^{13}C NMR, mass spectroscopy and elemental analysis. Its structure was confirmed by X-ray analysis (15). The trinickel core, in which each nickel atom is bonded to the other nickel atoms, cyclopentadienyl ring and bridging carbon atom, forms a tetrahedral structure.

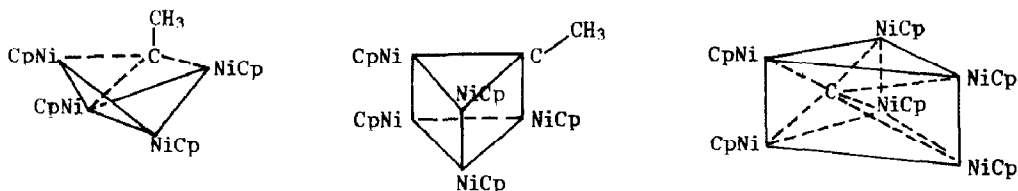


SCHEME 5

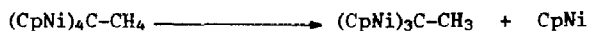


Tetra-, penta- and hexa-nickel clusters were not isolated in the pure state, but their presence in the reaction products was confirmed by MS (Scheme 6).

SCHEME 6



The trinickel cluster is thermodynamically the most stable one among the clusters formed. Therefore, tetra-, and penta-nickel clusters slowly disproportionate to trinickel cluster with the formation of one or two moles of unstable CpNi species.



Tetra-, penta- and hexa-nickel clusters have not been yet isolated in the pure state and therefore their structures have not been determined by X-ray analysis. However, it can be assumed that the tetranickel cluster has a butterfly type

structure, and penta- and hexa-nickel clusters a prism structure (Scheme 6). Moreover, the aggregation of CpNiCH_3 species and the disproportionation of higher clusters to the trinickel one suggest such a structure of the clusters.

In order to confirm the thermal decomposition mechanism of $\text{CpNiCH}_3(\eta^2\text{-propene})$ complex and the mechanism of cluster formation the reaction of nickelocene with methyl lithium was studied. It was found that methane and ethane result from this reaction in the same molar ratio as in the thermal decomposition reaction. Propene is not formed because it is not present in the reaction system. The trinickel cluster was found among the solid reaction products (it was isolated in the pure state), as well as the higher nickel clusters. These experiments proved that CpNiCH_3 is an intermediate product of the reaction of nickelocene with methyl lithium and also of the thermal decomposition of the $\text{CpNiCH}_3(\eta^2\text{-propene})$. As a result of aggregation of this species clusters are formed together with evolution methane and ethane.

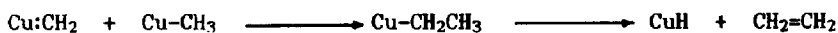
Further studies concerned the thermal decomposition of methylcopper $(\text{CH}_3\text{Cu})_n$ and its complexes with phosphines, $\text{CH}_3\text{Cu}\cdot\text{PCy}_3$ and $\text{CH}_3\text{Cu}\cdot\text{P}(\text{t-Bu})_3$, where Cy=cyclohexyl and Bu=butyl. Methylcopper was chosen for studies, since the thermal decomposition of alkylcopper compounds was not described until now and also because this compound was thermally unstable.

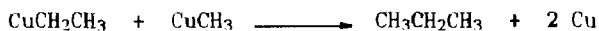
Methylcopper and its complexes were synthesized from copper diacetylacetonate and dimethylaluminium ethoxide. In the pure state methylcopper is stable below 0°C . At ca. 16°C it starts to darken and violently explodes at $35\text{--}40^\circ\text{C}$ (16).

The thermolysis of methylcopper yields ca. 10% of methane, 80% of ethane and 10% of ethylene and propane. Ethane is formed, similarly as in the case of methylnickel, during reductive elimination. In the polymeric aggregate, $(\text{CuCH}_3)_n$, two adjacent methyl groups react yielding ethane and metallic copper.

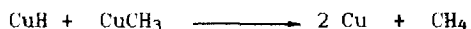


α -Hydrogen abstraction in a synchronous reaction with simultaneous formation of a carbenoid molecule $\text{Cu}:\text{CH}_2$ is the most probable mechanism of methane formation. In a bimolecular reaction, the carbenoid and methylcopper produce ethylcopper, which decomposes further via β -hydrogen elimination of ethylene or reacts with methylcopper forming propane.



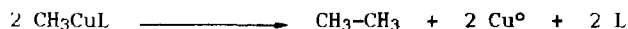


The unstable copper hydride with methylcopper forms methane and metallic copper



The thermolysis of methylcopper complexed with tricyclohexylphosphine, PCy_3 , or tri-*t*-butylphosphine, $\text{P}(t\text{-Bu})_3$, has a different course. In both cases much more methane (~30%) and less ethane (~60%) is formed (16) than for free methylcopper. The amount of the gases evolved indicates that besides α -hydrogen abstraction, hydrogen abstraction from the ligand also proceeds. In order to confirm this proposition, $\text{CD}_3\text{CuPCy}_3$ was synthesised and the gaseous products of its thermal decomposition were studied. Completely deuterated ethane- d_6 , ethylene- d_4 and propane- d_8 as well as CD_3H and CD_4 were identified in the gases. The data obtained are in agreement with the calculations. It results from these that the 6:4 ratio for $\text{CD}_3\text{H}/\text{CD}_4$ corresponds to the ratio of hydrogen abstraction from the ligand to that from the second CD_3 group (17,18).

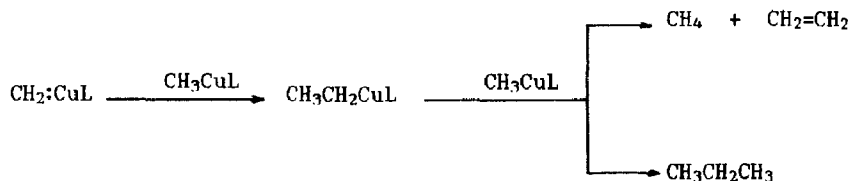
Ethane is formed in the bimolecular reaction of methyl-copper species.



Methane is formed by hydrogen abstraction from both the second methyl group as well as from the ligand.



Ethylene and propane are formed in further reactions of the carbenoid.



From studies on the thermal decomposition of the carbon-metal σ -bond both for alkylnickel and alkylcopper compounds it is found that the mechanism of the C-M bond decomposition with the formation of gases is very similar.

Compounds in which no β -hydrogen is present form corresponding hydrocarbons as

- 12 H. Lehmkuhl, S. Pasynkiewicz, R. Benn, A. Rufinska, *J.Organomet.Chem.*, 240 (1982) C27.
- 13 H. Lehmkuhl, C. Navdowski, F. Danowski, M. Bellenbaum, R. Benn, A. Rufinska, G. Schroth, R. Mynott, S. Pasynkiewicz, *Chem.Ber.*, 117 (1984) 3231.
- 14 S. Pasynkiewicz, H. Lehmkuhl, *J.Organomet.Chem.*, 289 (1985) 189.
- 15 H. Lehmkuhl, C.Kruger, S. Pasynkiewicz, J.Poplawska, *Organometallics*, 7 (1988) 2038.
- 16 S. Pasynkiewicz, J. Poplawska, *J.Organomet.Chem.*, 282 (1985) 427.
- 17 S. Pasynkiewicz, S. Pikul, J. Poplawska, *J.Organomet.Chem.*, 293 (1985) 125.
- 18 S. Pasynkiewicz, J.Poplawska, *J.Organomet.Chem.*, 302 (1986) 269.