Inorganica Chimica Acta, 12 (1975) 105–107

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Thermal Decomposition Reactions of Alkylnickel Compounds

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Received July 4, 1974

Thermal decomposition reactions of the series of compounds π-$C_5H_5NiPPh_3R$ (R = Me, Et, n-Pr, iso-Pr, n-Bu, sec-Bu, $PhCH_2$, Me_3SiCH_2) have been studied in aromatic solvents using n.m.r. spectroscopy. Compounds containing a β-hydrogen atom decompose via a β-elimination reaction, the others apparently via a unimolecular reaction which does not involve free radicals. The order of stabilities is $Me_3SiCH_2 > PhCH_2 > Me > Et \sim n\text{-}Bu > n\text{-}Pr > sec\text{-}Bu \sim iso\text{-}Bu$.

Introduction

Thermal decomposition reactions of transition metal alkyl compounds have been intensively studied in recent years because of the importance of this type of compound in organometallic chemistry.[1] We have previously studied the products of thermal decomposition of the complexes π-$C_5H_5NiPPh_3R$[2] in xylene and in the melt; this series was chosen because it was the only one known for which stable higher alkyls could be prepared and isolated. The relative stabilities of the neat compounds were determined from the temperatures at which they decomposed. The mode of decomposition of alkyl compounds containing a β-hydrogen was in the main *via* elimination of olefin, although the ethyl compound generated a significant amount of ethane in the melt. The methyl compound generated methane and smaller amounts of ethane.

We now present further studies concerning the modes of decomposition of a more extensive series of nickel-alkyl compounds using n.m.r. spectroscopy to determine the species present in solution during thermal decomposition reactions. The results are compared with a variety of other systems described in the literature.

Experimental

The complexes π-$C_5H_5NiPPh_3R$ (R = Me, Et, *n*-Pr, *iso*-Pr, *n*-Bu, *sec*-Bu, CH_2Ph, CH_2SiMe_3) have been previously reported.[2,3]

Thermal Decomposition Studies

The thermal decompositions of the *n*-propyl, *iso*-propyl, *n*-butyl and *sec*-butyl complexes were carried out under nitrogen in sealed, thick-walled n.m.r. tubes on approximately 0.2*M* solutions. The solvent used was 10% benzene in benzene-d_6, the benzene resonance being used for locking purposes. The temperatures of the solutions were initially raised at a rate of five degrees every thirty minutes, the alkyl regions of the spectra being scanned at each temperature when thermal equilibrium had been reached.

Since the expected product of the decomposition of the propyl isomers is propylene,[2] the temperature was raised until a doublet of triplets centred at τ 8.28, indicating the appearance of the olefin, was observed. A freshly prepared sample was then studied from just below the appearance temperature, the temperature being raised at the slower rate of two degrees every thirty minutes. The *iso*-propyl complex was studies similarly, but was seemingly unique in the series in that its decomposition was at least partially autocatalytic, the rate increasing rapidly and erratically after partial decomposition had occurred.

A similar procedure was followed with the *n*- and *sec*-butyl complexes, the expected but-1-ene[2] being detected by a triplet at τ 9.00. In the case of the *sec*-butyl complex, *cis*- and *trans*-but-2-enes were detected by doublets at τ 8.40 and τ 8.43, respectively.

The olefin appearance temperatures are listed in Table I. Observation of the n.m.r. spectra showed that in all cases the cyclopentadienyl resonance at about τ 5 decreased in intensity and was replaced by complex resonances in the olefinic region corresponding to those of dicyclopentadiene. Nickel metal plated out on the walls of the n.m.r. tubes, and the decomposed samples smelled strongly of dicyclopentadiene when opened.

A different method of following the decomposition of the methyl and ethyl complexes was used because of

TABLE I. Olefin Appearance Temperatures for the Complexes π-$C_5H_5NiPPh_3R$.

R	Appearance Temperature
n-Pr	85–87°C
iso-Pr	80–82°C
n-Bu	95–97°C
sec-Bu	81–83°C

TABLE II. The Variation with Temperature of the Relative Intensities of the Ethyl, Methyl and Methylene Regions of the Regions of the N.M.R. Spectra.

Temperature °C	CpNiPPh$_3$CH$_2$CH$_3$	CpNiPPh$_3$CH$_3$	CpNiPPh$_3$CH$_2$Si(CH$_3$)$_3$	CpNiPPh$_3$CH$_2$C$_6$H$_5$
25	1.000	1.000	1.000	1.000
85	.985	–	.995	–
90	.870	.995	–	.920
95	.735	.995	.995	.982
100	.585	.740	.990	.835
105	.480	.600	.755	.750
110	.320	.600	.740	.640
115	–	.590	.690	–
120	–	.530	.675	–
125	–	.515	.570	–
130	–	.445	.465	–

the high vapour pressures of the expected products, methane and ethylene.[2] About 1–2% dioxane was added to the solutions as reference. The temperatures of the samples were raised at a rate of five degrees every thirty minutes and the intensities of the alkyl resonances relative to the dioxane resonance were recorded. A similar procedure was followed for the trimethylsilylmethyl and benzyl complexes, the intensities of the methylene resonances (τ 11.3 and τ 8.65, respectively) being recorded. Hexamethyldisiloxane was used as reference in the latter case because of overlap of the dioxane resonance with those of the decomposition products. The nature of the latter is not known, but the n.m.r. spectrum showed that toluene was not formed.

The results of the decompositions are shown in Table II, the initial intensity at room temperature being designated unity in each case for purposes of comparison.

A similar procedure was used to estimate the order of the decomposition reaction of π-C$_5$H$_5$NiPPh$_3$CH$_2$SiMe$_3$. Solutions containing 1% cyclohexane as internal reference and approximately 0.1*M*, 0.2*M* and 0.3*M* in complex were held for thirty minutes at 110°, 120° and 130° C in sealed tubes. The samples were cooled to room temperature after each thirty minutes period, and the intensities of the methylene resonances were recorded relative to that of the cyclohexane. A smooth decomposition was observed in each case, with 70 ± 10% of the compound in each sample having decomposed after being heated at 130° C. Thus the thermal decomposition reaction is first order in complex.

Because the chemical shifts of the decomposition product, tetramethylsilane, and the Me$_3$Si protons of the complex are very similar, the intensity of the resonance at ~τ 10 did not change significantly. The cyclopentadienyl resonance, on the other hand, both broadened and decreased in intensity.

Thermal decomposition of π-C$_5$H$_5$NiPPh$_3$CH$_2$SiMe$_3$ in toluene-d$_8$ yielded tetramethylsilane which contained (mass spectrum) no deuterium.

Results and Discussion

The olefinic products observed in the variable temperature n.m.r. studies of the *n*-propyl, *iso*-propyl, *n*-butyl and *sec*-butyl complexes were those expected on the basis of our previous study;[2] thus the mode of decomposition is the expected β-elimination, although the apparently autocatalytic behaviour of the *iso*-propyl derivative remains unexplained. Surprisingly, however, no hydride resonance could be observed at higher field, even on adding *t*-butylmagnesium chloride to a solution of π-C$_5$H$_5$NiPPh$_3$Cl in tetrahydrofuran at 0° C*, although the analogous π-C$_5$H$_5$Ni(PCy$_3$)H has been briefly reported.[4] Furthermore, although the single cyclopentadienyl resonances of the alkyl compounds disappeared as the decompositions proceeded, no new cyclopentadienyl resonances appeared. Coupled with the observations of the appearance of cyclopentadiene and metallic nickel, the n.m.r. spectra suggested that although the compound π-C$_5$H$_5$NiPPh$_3$H may have been formed, it is very unstable and readily decomposed to give cyclopentadiene, triphenylphosphine and nickel. The lack of significant broadening of the resonances suggested that paramagnetic nickel species were not formed.

While the ethyl compound decomposed *via* a β-elimination,[2] the methyl compound gave methane and ethane[2] and the trimethylsilylmethyl compound gave tetramethylsilane (the fate of the benzyl compound is not known). Decomposition of the trimethylsilylmethyl complex was first order in complex and, when carried out in toluene-d$_8$, gave no deuterated tetramethylsilane. Thus the latter reaction does not involve free radicals. Because of the bulky cyclopentadienyl and phosphine

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* It has previously been shown[2] that isobutene is spontaneously generated on adding the *t*-butyl Grignard reagent to π-C$_5$H$_5$NiPPh$_3$Cl, presumably *via* the unstable *t*-butylnickel compound.

ligands, as well as the first order reaction kinetics, it seems very unlikely that two molecules can approach sufficiently closely that redistribution or aggregation can occur,[1] and thus that one trimethylsilylmethyl group can somehow abstract a hydrogen atom from another. It seems much more likely that an aromatic cyclopentadienyl or phenyl group is the source of the hydrogen.[5]

On the basis of the olefin appearance temperatures, the relative kinetic thermal stabilities are *n*-Bu>*n*-Pr>*sec*-Bu∼*iso*-Pr, although the differences are not large. Although the ethyl, methyl, trimethylsilylmethyl and benzyl complexes were treated differently, the data in Table II also indicate relative kinetic thermal stabilities, the order being $Me_3SiCH_2 > PhCH_2 > Me > Et$. Combination of the two series suggests that the stabilities decrease in the order $Me_3SiCH_2 > PhCH_2 > Me > Et >$ *n*-Bu∼*n*-Pr>*sec*-Bu∼*iso*-Pr, with the *t*-Bu complex possibly being the least stable.

The order of the olefin appearance temperatures of the propyl and butyl compounds in benzene is different from the order of the decomposition temperatures of these compounds in the melt,[2] suggesting that the factors affecting the activation energies are not identical in the two situations. It is probably significant, however, that the methyl[2], phenyl[6], benzyl[3], *neo*-pentyl[3] and trimethylsilylmethyl[7] all decompose in the range 125°–140°C in the melt, higher than the alkyl derivatives containing a β-hydrogen atom, but much lower than the trifluoromethyl compound[8] (>160°C).

The reported[9] order of stabilities of the dialkylmanganese compounds, $Me \sim PhCH_2 \sim Me_3CCH_2 \gg$ *n*-Pr, *n*-Bu>Et>*t*-Bu>*iso*-Bu, is quite similar to the cyclopentadienylnickel system, *i.e.* alkyl groups containing no β-hydrogens>*n*-alkyl compounds> branched alkyl compounds, although the relative stabilities of the branched alkyls are somewhat different. Extensive studies by Sneeden and Zeiss have shown[10] that, for chromium(III), the order is normal>secondary>tertiary alkyls, while the order Me>Et>*n*-Pr>*iso*-Bu appears to hold generally true for the series $RCrCl_2(THF)_3$, $R_2Fe(bipyridal)_2$ and $R_2Ni(bipyridal)$.[13] The differences in reactivities between the different series may reflect differences in d electron configurations and/or differences in the other ligands on the metal ions.

The complexes $R_2Ni(bipyridal)$ (R = Et, *n*-Pr) decompose to give, apparently, equal amounts of alkane (RH) and olefin (R–H),[13,14] while coordination of an electronegative olefin to give $R_2Ni(olefin)(bipyridal)$ results in generation of the coupling product, R_2, and Ni(olefin)(bipyridal). Addition of triphenylphosphine to $Me_2Ni[tris\text{-}(2\text{-}biphenylphosphito)]_2$ yields ethane and a nickel(0) complex,[15] although the complexes $R_2Ni(PPh_3)_2$(R = *n*-Pr, *n*-Bu) eliminate predominantly the 1-olefins.[16] Clearly the other ligands can have a significant effect.

Acknowledgements

Financial assistance from the National Research Council of Canada, The International Nickel Company of Canada and Queen's University is gratefully acknowledged.

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