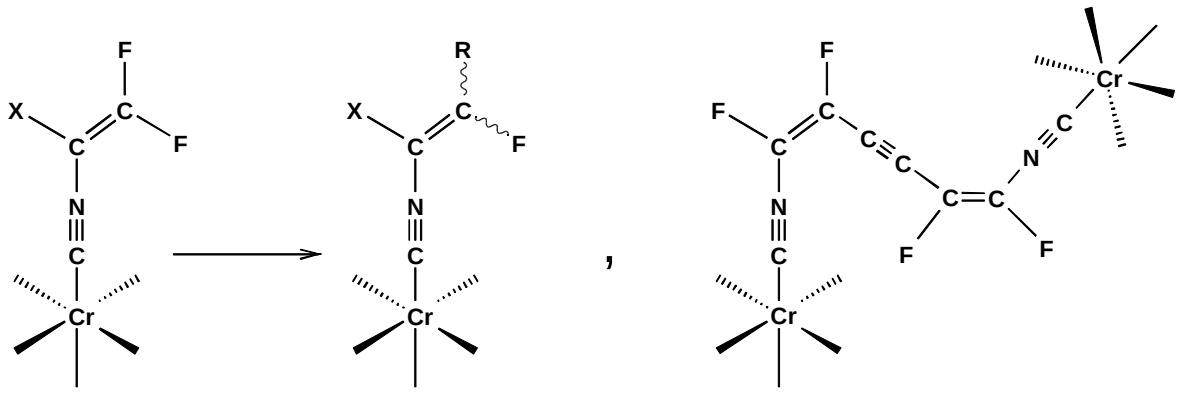
3.1 Summary

Within this thesis the unique synthesis concept for the preparation of isocyanoalkynes through vakuumpyrolyses of suitable metallorganic precursors should be followed. These precursors can be obtained by functionalizing ethenyl isocyanides which are stabilized at a pentacarbonylchromium fragment. A close cooperation with Guarnieri *et al*. should guarantee the characterization of the isocyanoalkynes resulting in the determination of rotational constants which are indispensable for a radioastronomic detection of these molecules which were supposed to exist in interstellar molecule clouds.

Starting with **2a** and the trifluoro analogon **2b** it was possible to synthesize and characterize twelve new substituted ethenyl isocyanide complexes with nine different substituents. They could be obtained by nucleophilic attack at the terminal CF_2-group and substitution of a fluorine atom in **2a** and **2b**, respectively.



2a, b
a : X = Cl , b : X = F

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	3a	**6**	**7a**	**7b**	**8a**	**8b**	**10a**	**10b**	**12**	**13**	**15**
X	Cl	Cl	Cl	F	Cl	F	Cl	F	F	F	F
R	-CN	$-C_2Ph$	$-C_2Si(CH_3)_3$	$-C_2Si(CH_3)_3$	$-C_2H$	$-C_2H$	$-CH_3$	$-CH_3$	$-C_4Si(CH_3)_3$	$-C_4H$	$-OCH_3$

Scheme 31 : Representation of the pentacarbonyl(ethenyl isocyanide)chromium complexes synthesized in this work.

8a and **8b** are potential precursor for isocyanobutadiyne. They were obtained by the reaction of ethynyl(trimethyl)silylmagnesium bromide with **2a** and **2b**, respectively, followed by a desilylation of the isolated and fully characterized isocyanide complexes **7a** and **7b**. Suitable single crystals for a X-ray structure analyses could be obtained of both complexes. Pentadiynenitrile the isomer of the target molecule was the only detected product of the pyrolysis experiments.

The synthesis of a precursor for the next higher homologues isocyanohexatriyne was possible by monolithiation of 1,4-bis(trimethylsilyl)butadiyne, with methyl lithium, reaction with **2b** followed by desilylation of the isolated and fully characterized complex **12**. The unstable **13** was obtained only in small amounts and could be characterized solely by nmr spectroscopy.

A precursor for isocyanopropynenitrile **5** which hitherto had only been obtained in an argon matrix and characterized by infrared-spectroscopy could be synthesized in high yields allowing detailed pyrolysis experiments. The ”free” ethenyl isocyanide as well as the target molecule isocyanopropynenitrile **5** could be isolated by fractional condensation of the pyrolysis products. The unstable 3-chloro-2-fluoro-3-isocyano-2-propenenirtile **4** could be characterized by mass- and one- and two-dimensional nmr spectroscopy. The unambiguous experimental characterization of the binary carbon-nitrogen compound **5** was possible by mass spectroscopy, high resolution infrared-spectroscopy in the region of 2400 - 2000 cm^{-1} and above all, by millimeter-wave-spectroscopy which is particularly informative for linear molecules. The synthesis and pyrolysis of the isomers with a ^{13}C- or ^{15}N marked nitril function allowed the determination of the rotational constants of ten different isotopomers of **5**. By using these spectroscopic constants it was possible to determine the ground state structure. The C-N-single bond distance to the isocyanide group is 130.6(1) pm which is the shortest ever found experimentally.

The extensive numerous rotational spectroscopic data could allow to detect cyanoisocyanoacetylene **5** in interstellar medium by radioastronomy in the near future. Such a detection would expand the knowledge of interstellar chemistry.