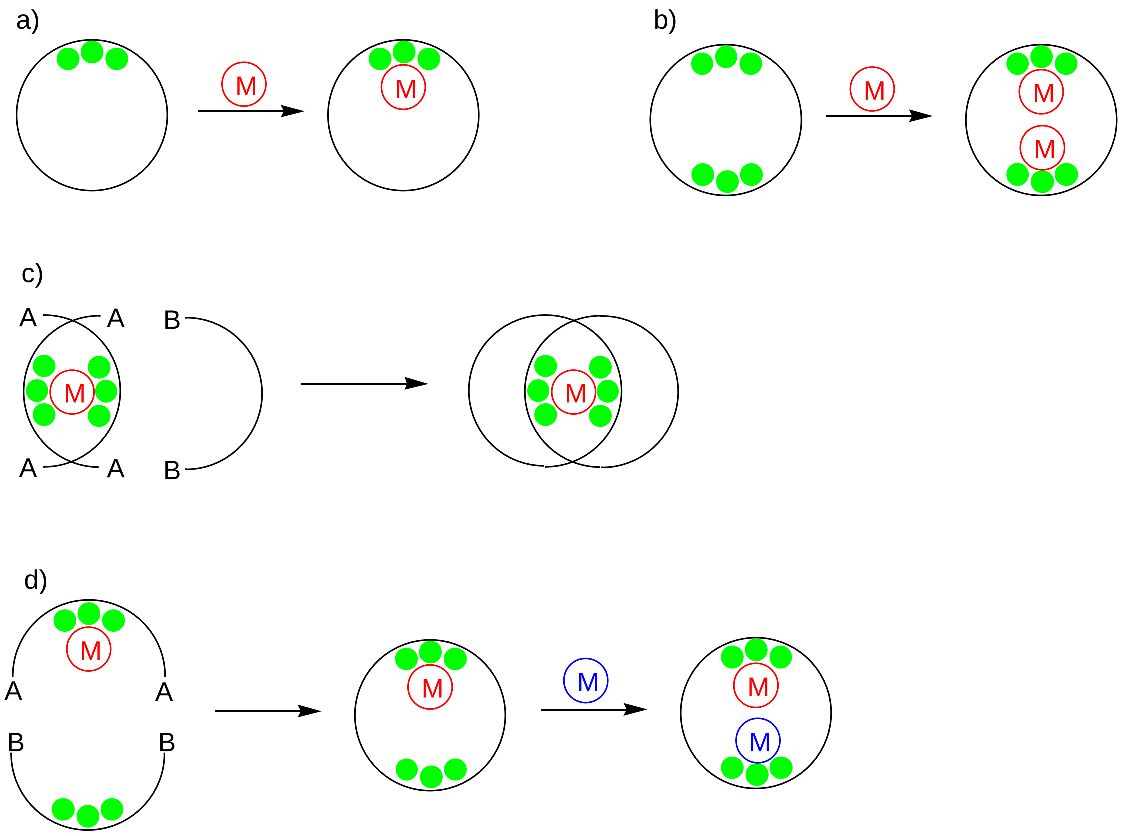
4.7 Outlook: Metal Complexes

A set of different terpyridine macrocycles is accessible now, and further modifications in their side chain pattern or size are possible with the building block approach described. The next step is to study the metal complexation of these systems. The results gained from these investigations can help to synthesize improved macrocycles by tailoring their building blocks. Also, a characterization of the macrocycles which have not yet been fully characterized will probably be possible as metal complexes.[171] The cyclization of complexed ring precursors may lead to better solubility, thus, in the case of the poorly soluble macrocycles, significantly improving their accessibility. Many examples for Sonogashira couplings in the presence of Ru^{2+}-terpyridine complexes have been described in literature.[172]



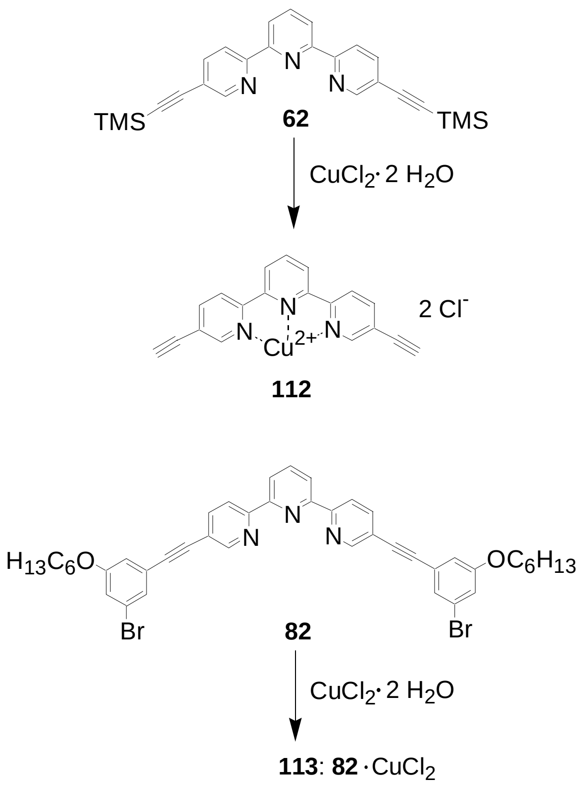
Scheme 47. Outlook: complexation of the macrocycles can lead in various directions.

For the cycles which have the same size but a different number of terpyridine units, a stepwise approach to one- or twofold complexed macrocycles is possible (Scheme 47,a,b). This opens the path towards metal wires, an important long-term goal of this work. Furthermore, the synthesized structures also allow interesting investigations in other directions. For example, from two equal half rings complexed to one metal center, a twofold cyclization would selectively lead to catenanes (Scheme 47,c). By this, not only the question about the structure of the tetrameric cyclic oligomers (see Chapter 4.6.7) could be solved by comparison. Catenanes of shape-persistent macrocycles of this size have not been described yet and can be expected to show interesting properties, e.g., for photophysical applications. Another objective would be to modify the synthesis of the macrocycle with two terpyridine units in such a way that one complexed and one metal free half ring precursor are cyclized. Thus, a onefold complexed macrocycle would result, which can be complexed in a second step with a second metal ion to yield a shape-persistent macrocycle with two different metal ions held at a defined distance (Scheme 47,d). This new compound can be expected to show interesting properties, e.g., when arranged in a 2-D ordered monolayer on a surface.

In the course of this work, however, only a few orientating experiments were undertaken which prove the principal accessibility of these paths but also show that much experimental work will still be necessary to reach this goal.

Octahedral hetaromatic complexes of Ru^{2+} are easily accessible and show interesting photo- and redoxchemical properties; thus, a large number of terpyridine complexes of Ruthenium have been published.[118,120] For our purposes, Ru^{2+} also seems convenient for several reasons: (i) The complexes are generally thermodynamically and kinetically stable, and ligand exchange reactions are not observed (ii) In these octahedral complexes, the 6 d electrons are located in the three degenerated t_{2g} orbitals and the resulting diamagnetic low-spin complexes can easily be characterized with NMR methods (iii) The metal can be stepwise complexed with two different terpyridine ligands.

A disadvantage is the demand in space for the large ligands in octahedral complexes. Therefore, one should also try to make complexes with different geometries accessible. $Cu(II)tpyX_2$ complexes, which can basically adopt a square pyramidal or a trigonal bipyramidal geometry,[173] are easy to prepare and do not oxidize under ambient conditions. Their disadvantage is their paramagnetic character, which does not allow NMR investigations. The two terpyridine derivatives **62** and **63** were reacted with $CuCl_2 \cdot 2H_2O$ in boiling methanol under nitrogen for 5 minutes (Scheme 48).[174] The green precipitate formed was collected and washed with ether. While the FAB spectra (Fig. 45) showed the expected $[M\text{-}Cl]^+$ peaks - in the case of **62**, deprotection to **63** has taken place -, no correct elementary analyses were gained. In crystallization experiments, only brushes of thin needles were obtained. It is, therefore, not clear whether the terpyridine units act as ligand, or (esp. in the case of **63**), interactions with the acetylene units occur. Metal complexes located at the acetylene units (of shape-persistent macrocycles) have been described.[54]



Scheme 48. Complexation of terpyridine precursors with Cu^{2+}*.*

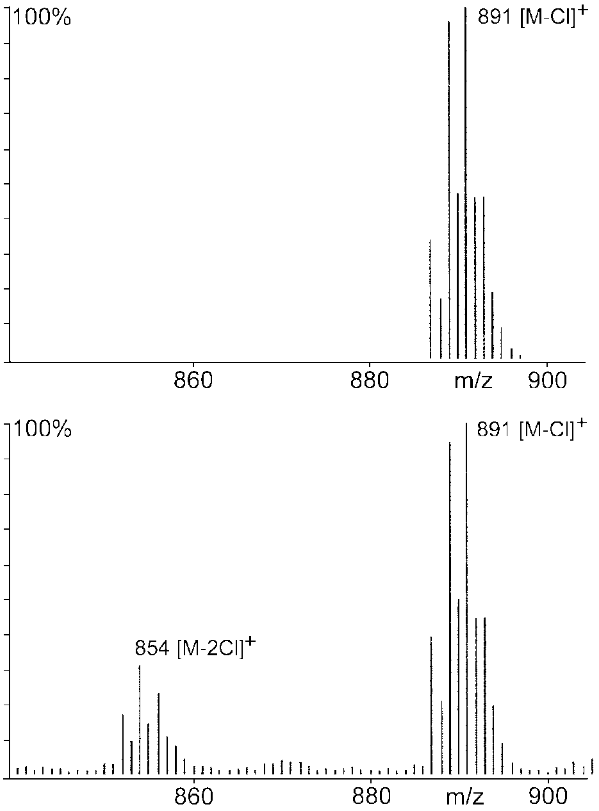
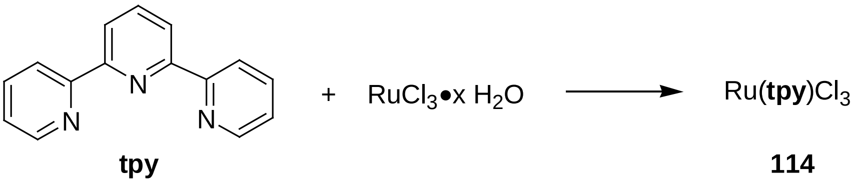


Figure 45. FAB mass spectrum of ***113****. Top: Spectrum calculated for* $[M\text{-}Cl]^+$*; bottom: experimental data.*

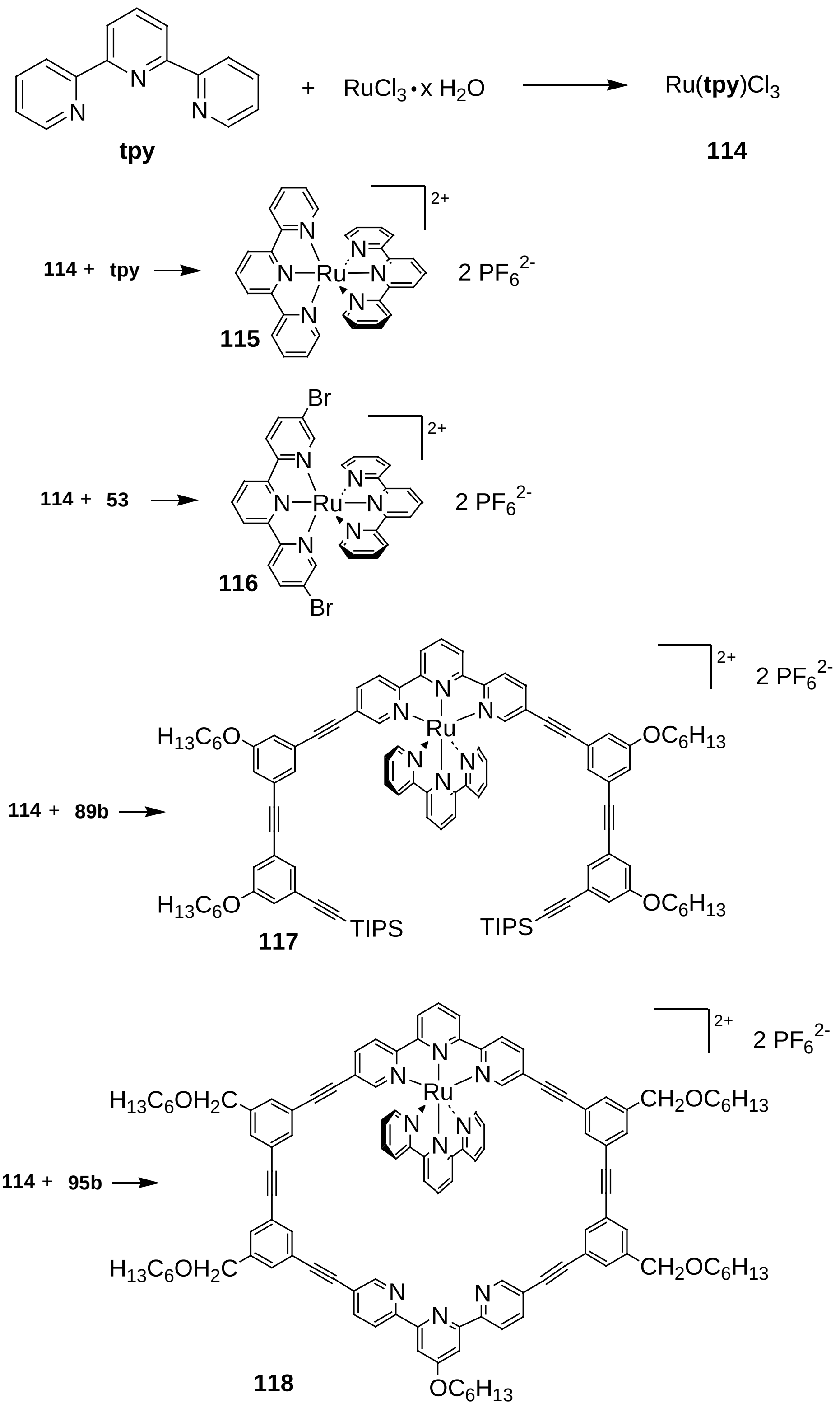
For the Ruthenium complexes, Ru^{3+} precursor complex **114** was synthesized according to a literature protocol.[175] This complex is paramagnetic and its purity can therefore not be controlled by NMR; the elementary analysis showed a deviation of ca. 3 %. To gain experience with the complexes, **114** was reacted with unsubstituted terpyridine in boiling methanol under reducing conditions (N-ethylmorpholine) for 2 hrs.[176] The reaction mixture was then deeply red. The raw product was chromatographed over silica gel using a mixture of MeOH (7 parts), $NH_4Cl_{aqu.}$ (2 parts) and $MeNO_2$ (1 part).[177] Slight modifications of this mixture resulted in the precipitation of NH_4Cl. The resulting RuL_2^{2+} complex **115** was precipitated as PF_6^--salt. Accordingly, the simple $RuLL'^{2+}$ complex **116** was synthesized from **53** and **114**. With these experiences, it was expected that the large half ring precursor **89b** would react with **114** in a similar way. However, no product could be isolated. Probably, the solubility of **89b** in methanol was too low for reaction; its substitution by ethanol[178] or even DMF[179] brought no improvement, as was easily seen by the color of the reaction mixture. Finally, **89b** and **114** could be brought to reaction in a mixture of ethylene glycol and dioxane.[180] The raw product was purified by column chromatography. With the eluent mixture described above, the side products were removed, and the product **117** elued with $CH_3CN/KNO_{3(aq.)}$ 7:1.[178] The yield, however, was only 22 %. For the reaction of **114** and either **63** or **80a** with their free acetylenes, following the above procedure, no product could be isolated; the reason could be that further reactions take place, which are promoted by a possible ruthenium acetylide.[181]



*Scheme 49. Preparation of Ru(III)-precursor complex **114**.*

Finally, complexation of macrocycle **95b** was attempted under the same conditions as those for **89b**. This was expected to be more difficult than the coupling of a linear precursor, as the geometry of the terpyridine unit is “fixed” by the cyclic scaffold and thus may not be easily accomplished with the steric demand of a terdentate ligand for Ru(II). Constable compared the X-ray data of a terpyridine and its Ni(II) complex. The dihedral angle between the terminal and the central pyridine ring increased from 5.7 to 7.1°, while the C-C-N angles reduced from 116 to 114° by complexation.[182] This, however, is not too much of a difference, and values for different terpyridines from literature show some variety. For a related terpyridine and its Ru(II) complex, C-C-N angles of 7.4 and 10.9°, resp., were found.[176] Other authors found much smaller C-C-N angles of 2.0 - 7.6° for a variety of Ru(II) complexed terpyridines.[178] For the uncomplexed macrocycles **95** investigated here by X-ray diffraction, dihedral angles between 112 and 117°, and C-C-N angles between 1.5 and 13° were found. All in all, these data imply that both the inherent flexibility of our macrocycles and the tolerance of Ru(II) towards geometric variations of its ligands will be large enough to allow complexation. From the reaction of **95b** and **114**, only 13 % of a red-brown material was obtained. The signals in the ^{1}H-NMR spectrum were broadened. The MALDI-TOF spectrum, however, shows a set of signals attributable to characteristic fragmentation ions of the macrocycle (Fig. 46). The signals attributed to Cu adducts have isotope patterns which are qualitatively in accordance with the calculated ones. These signals were also found in the FAB(+) spectrum of **118**, which suggests that the copper ions come from the sample itself rather than from the spectrometric preparation. The reason for this is not clear. In the

FAB(+)/MALDI-TOF MS of uncomplexed macrocycle **95b**, signals assignable to Cu adducts were not observed.



*Scheme 50. Preparation of Ru(II)LL'-complexes **114 - 118**.*

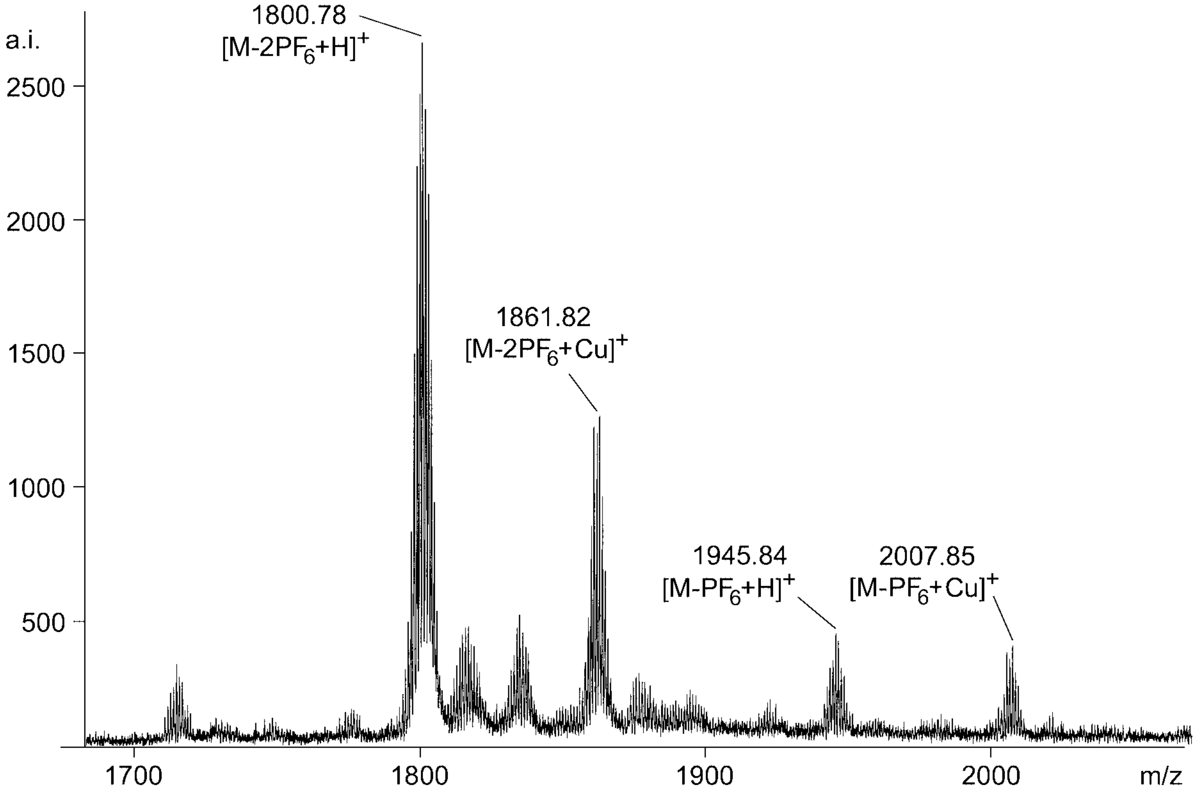


*Figure 46. MALDI-TOF spectrum (excerpt, reflector mode) of the Ru(II) complex **118** of macrocycle **95b**.*