2,2':6',2''-Terpyridines and their Metal Complexes

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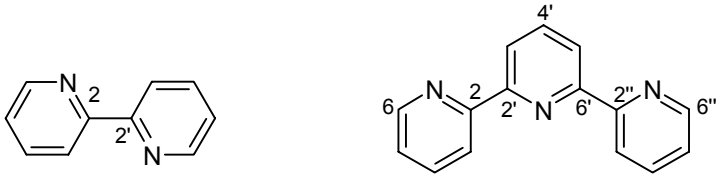
All the ligands and metal complexes described in the text are currently available at HetCat.

1. Introduction

Supramolecular chemistry has received enormous importance in the last decades. Starting with development of chemistry of crown ethers and cryptnads, the investigation led to self-organised molecules, e. g. membranes and micells, and organic semiconductor/conductor. In the recent time, progress from molecular materials to supramolecular structures has been achieved. The coordination chemistry plays a fundamental role in supramolecular chemistry. Elements of groups 15 and 16, especially, nitrogen, phosphorus, oxygen and sulphur are mostly used atoms for formation of covalent bonds. In particular, oxygen, nitrogen and phosphorus atoms were extensively used, especially in reaction with transition metals, which have been investigated due to their catalytic activities. A special part of nitrogen ligands is the chemistry of oligopyridines (Figure 1).



2,2'-Bipyridine 2,2':6',2''-Terpyridine

Figure 1

Oligopyridines have attracted special interest in coordination chemistry. Although 2,2'-bipyridine (bpy) has been announced to be "the most used ligand in coordination chemistry" [1], 2,2':6',2''-terpyridine (tpy) also has a rich chemistry. Almost 70 years ago, Burstall and Morgan reported the first synthesis of 2,2':6',2''-terpyridine [2-3]. The coordination chemistry of the substituted terdentate ligand has attracted many chemists. 2,2':6',2''-Terpyridine has been reacted with very many metals to prepare complexes. The kinetics and mechanism of formation of metal complexes and their stability have also been studied [4-7].

2,2':6',2"-Terpyridine has found wide application in the field of supramolecular chemistry which has led to the formation of racks, ladders and grids [8], helicates [9-11], catenanes [12-15], knots [12] [16-17] and dendrimers [18-27]; and as a result of their chemical and photochemical properties, these metal containing compounds have been extensively studied. In particular, the photochemical properties of $[Ru(bpy)_3]^{2+}$ containing species have been extensively investigated [28] and have initiated interest in the related complexes of the higher oligopyridines, especially terpyridines [29-31]. The photochemistry of tpy metal complexes is very well investigated [32-36].

As catalysts, tpy complexes of transition metals have found special interest, and the higher oxidation state of transition metals, e.g. Ru(IV) or Ru(VI), have been applied to the oxidation of alcohols [37-40], as bleaching agents [41-43], in the carbonylation of aromatic compounds [44-6], hydroformylation [47-49] and as oxygen-binding molecules [50-51]. An interesting aspect of the catalytic activation is the separation of Am(III)/Eu(III) in solution [52-53]. Chiral derivatives of 2,2':6',2"-terpyridine ligands have been prepared [54-56], and applied to enantioselective reactions [57-60] or to the formation of helicates with transition metals [10] [61-66].

Functionalised tpy ligands have been anchored to TiO_2-surfaces [67-77], gold surfaces [78] or to silica-titania surfaces [79] to build monolayers or semiconductors [78] and their energy transfer has been investigated. In this manner metal clusters of tpy ligands have also been prepared [80-84]. 2,2':6',2"-Terpyridine was polymerised [21] [85-87] and used for detection of transition metals [88]. Helical polymers have been reported [89]. Platinum complexes of tpy derivatives have been applied in biological systems [91-101].

2,2':6',2"-Terpyridines may be linked together by spacers. Metal-bonded tpy ligands with spacers at C(4') provide a means of directionality, and thus a means of linear communication, it means, the electronic communication can occur along the coordination axis (Figure 2). In addition, the insertion of a single substituent in the 4'-position of the tpy ligand causes no enantiomeric derivatives (contrast this

with bpy derivatives). Therefore, the functionalisation of tpy at this position is of particular importance.

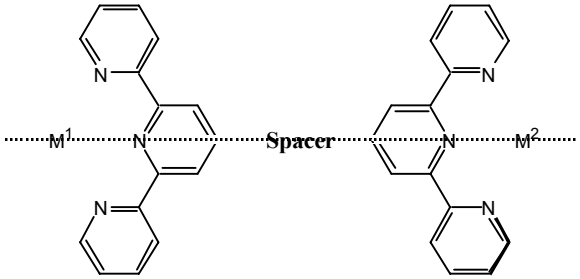


Figure 2

2. The configuration of 2,2':6',2''-terpyridine

In the solid state the three pyridine rings exhibit *transoid* configurations about the interannular carbon-carbon bonds (Figure 3a). This configuration minimises electrostatic interactions between the nitrogen lone pairs and also the Van der Waals interactions between H^3 atoms. When a tpy ligand is bonded to a metal, it isomerises to a *cis*-configuration (Figure 3b), but preferably to *cis*-*cis*-configuration (Figure 3c).

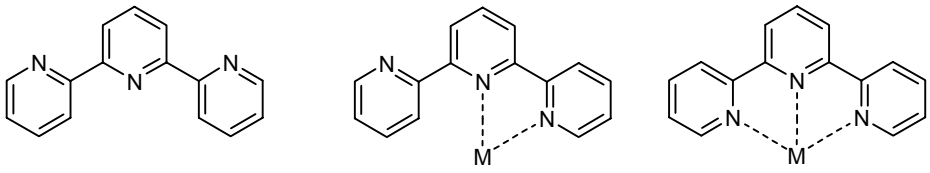


Figure 3

In terpyridine derivatives, the three pyridine rings are usually close to being coplanar. The interplanar angles of the two terminal rings with the central ring are similar and range between 5.7° (4'-phenyl-2,2':6',2"-terpyridine) [102], 7.4° (4'-dimethylamino-2,2':6',2"-terpyridine) [103], 11.4° (4'-ethoxy-5,5"-dimethyl-2,2':6',2"-terpyridine) [104] and 10.9° (6,6"-dibromo-4'-phenyl-2,2':6',2"-terpyridine) [105].

In 4'-amino-2,2':6',2"-terpyridine, however, the interplanar angles of the two terminal rings with the central ring are 11.2° and 20.7°, respectively [106]. This deviation from the expected angles is due to the hydrogen bond formation (Figure 4). Such effects have also been observed in similar compounds [107].

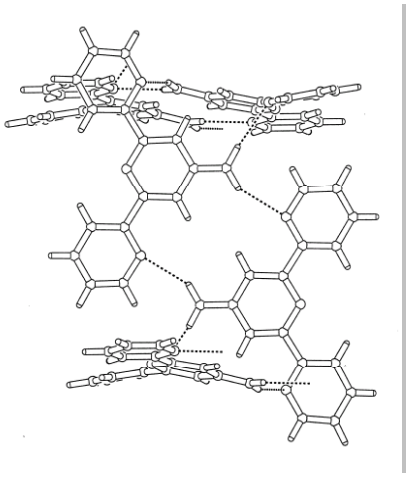
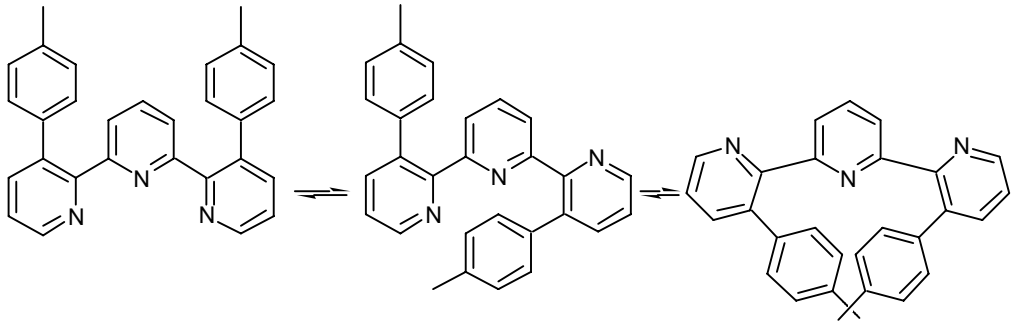


Figure 4

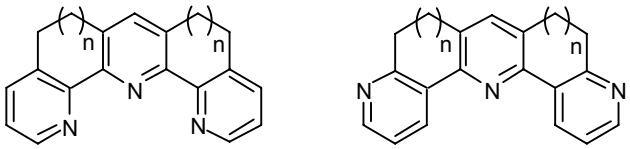
While almost all tpy ligands are unsubstituted at C(3) or C(3"), two examples are known possessing substituents at these positions [108-110]. Due to steric hindrance the two terminal pyridine rings avoid the *trans*-configuration and this tpy ligand is assumed to adopt three different isomers involving π-π-stacking interactions (Figure 5).



5a **5b** **5c**

Figure 5

The situation changes, however, when the tpy ligand is a part of an annulated ring system. There exist two types of ligands: a) the U-shaped (Figure 6a) and b) the S-shaped one (Figure 6b). In the U-shaped derivatives the *cis*-configuration is fixed [111-113].



6a **6b**

Figure 6

3. Methods for the synthesis of tpy ligands

The two general methodologies used in the synthesis of 2,2':6',2"-terpyridines involve either the synthesis of the central ring (Figure 7a) or the coupling of the three pyridine rings (Figure 7b).

7a **7b**

Figure 7

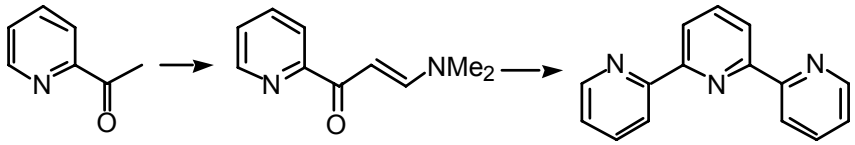
From the synthetic point of view there are only a few methods leading to this system which were known or have been developed during our work. While the Ullman coupling [2-3] of bromopyridines is of historical interest, the main methodologies can be divided into the following categories: i) condensation methodology; ii) pyrolysis; iii) Tohda methodology; iv) metal mediated coupling reaction; v) cycloaddition (Sauer methodology).

3.1. Condensation methodology

Hantzsch [114] and Tschitschibabin [115] have initiated the first two methods for pyridine synthesis.

3.1.1. 2,2':6',2''-Terpyridine 3

Many attempts have been made to optimise the preparation of 2,2':6',2"-terpyridine [2-3] [3] [116-118]. Maybe the most efficient methodology for the synthesis of 2,2':6',2"-terpyridine **3** was reported by Jameson and Guise [119]. 2-Acetylpyridine **1** was reacted with N,N-dimethylformamide dimethyl acetal to give the enaminone **2**. This enaminone **2** is condensed with the potassium salt of 2-acetylpyridine with loss of dimethyl amine, the resulting 1,5-dione is not isolated prior to ring closure by ammonium acetate (Scheme 1).



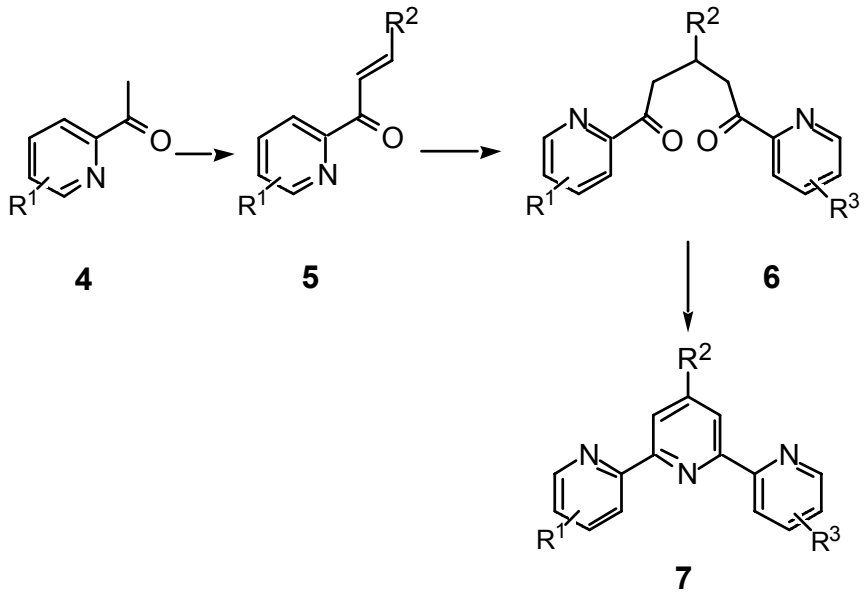
1 **2** **3**

Scheme 1

3.1.2. Kröhnke methodology

Starting with the Hantzsch methodology to improve the yields and product specificity led to the development of various multi-step synthetic strategies. F. Kröhnke has developed the methodology of condensation procedures leading to oligopyridines [120]. The basis of this reaction is the aldol condensation of 2-acetylpyridine (or a substituted derivatives) with an aldehyde in basic aqueous or alcoholic media to give an α,β-unsaturated ketone or enone **5**. Michael addition of a suitable enolate then affords a 1,5-diketone **6**. Ring closure with ammonium acetate results in the formation of a

dihydropyridine which undergoes oxidation to the desired terpyridine **7**. Symmetrical and unsymmetrical 2,2':6',2"-terpyridines were prepared in moderate to good yields by this route, a major advantage. A disadvantage is, however, that the substituents R^2 must be aromatic (Scheme 2). In addition, some functional groups are not tolerated under the reaction conditions. Using this methodology, a series of compounds possessing aromatic substituents at C(4') of tpy ligand were prepared. An excellent review has already been published describing tpy ligands attached to aromatics using this methodology [121]. Recently, this methodology was examined in solvent free one-pot reactions for the synthesis of oligopyridines [122-123].

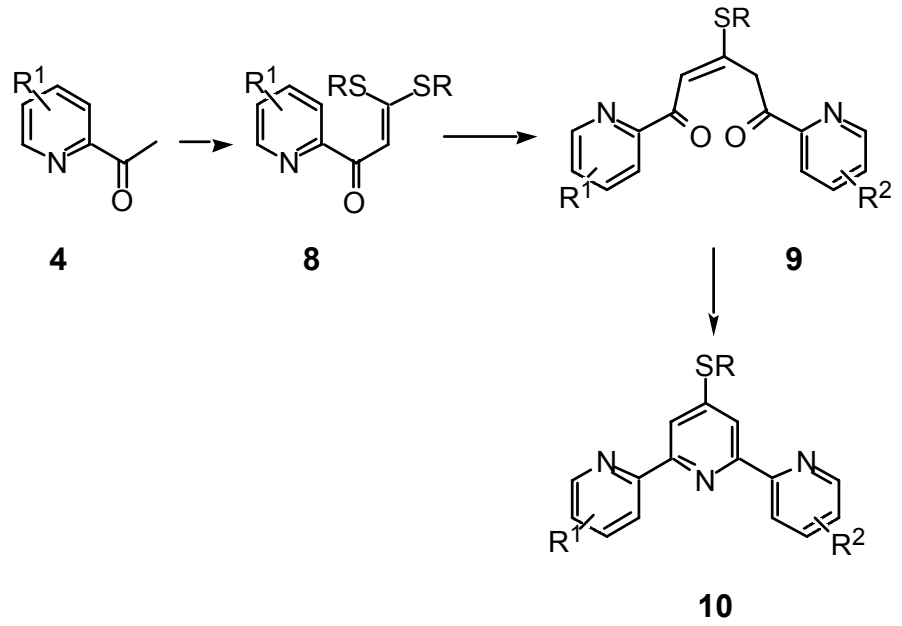


Scheme 2

3.1.3. Potts methodology

Potts and coworkers have also developed a methodology for the synthesis of substituted pyridines from the corresponding 1,5-dione and hydroxylamine. Though in many aspects similar to the Kröhnke methodology, this procedure has found wide applications in the synthesis of oligopyridines, especially when C(4') is substituted by a thiol group [124-125] (Scheme 3). The reaction of the potassium enolate

of 2-acetylpyridine (or a substituted derivatives) with carbon disulfide followed by methyl iodide gives an α-oxoketene dithioacetal **8**. Reaction with a further equivalent of the potassium enolate of 2-acetylpyridine (or a substituted derivatives) affords an enedione intermediate **9**, which gives **10** after *in situ* ring closure with ammonium acetate in glacial acetic acid at reflux. The advantage of this method is that symmetric and unsymmetrical tpy ligands can be prepared in good yields. An excellent review has already been published [118].



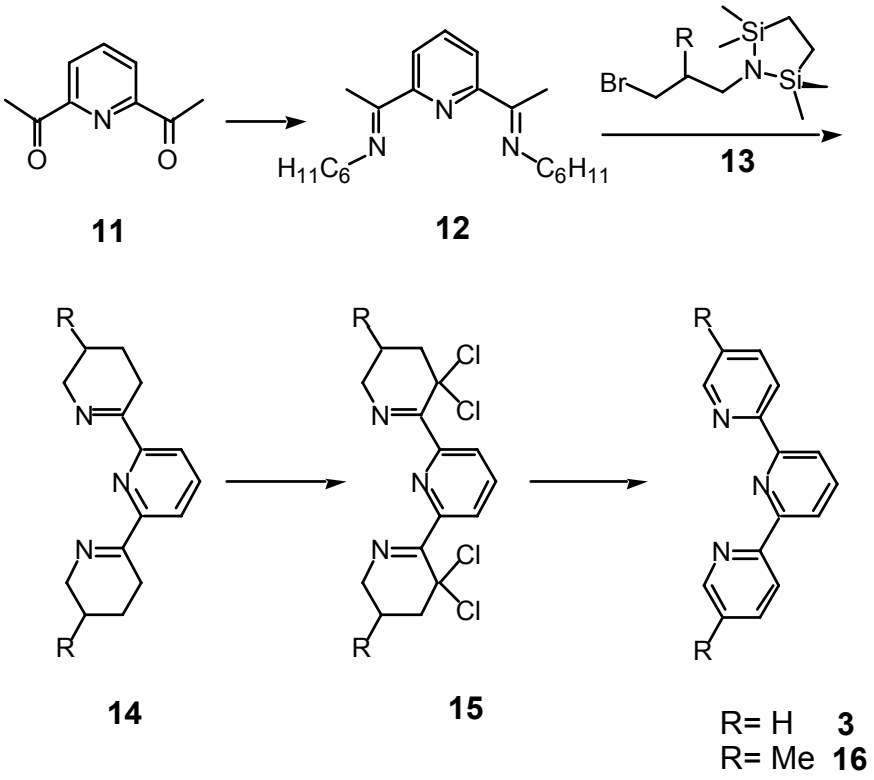
4 **8** **9** **10**

Scheme 3

3.1.4. New approach

A new approach was made to synthesise symmetrical 2,2':6',2"-terpyridines, though this methodology is limited to two examples **3** and **16** only (Scheme 4) [126]. 2,6-Diacetylpyridine **11** was quantitatively converted to 2,6-bis(n-cyclohexylacetamidoyl)pyridine **12** by reaction of cyclohexylamine in refluxing benzene. The tetrahydropyridines **14** were obtained by cyclisation of the bis-imine **12** with the ethylenetetramethyldisilyl-protected 3-bromopropylamines **13** in excellent yield via α-alkylation, N-

deprotection and transamination. The tetrachlorination of **14** was accomplished by reaction with N-chlorosuccinimide (NCS) in carbon tetrachloride at room temperature. The tetrachloro adducts **15** were not isolated, but immediately converted by the action of sodium methoxide in methanol at room temperature directly to the desired tpy ligands **3** and **16**. Despite of the high yield of each step, this method is long (8 steps) and very costly.

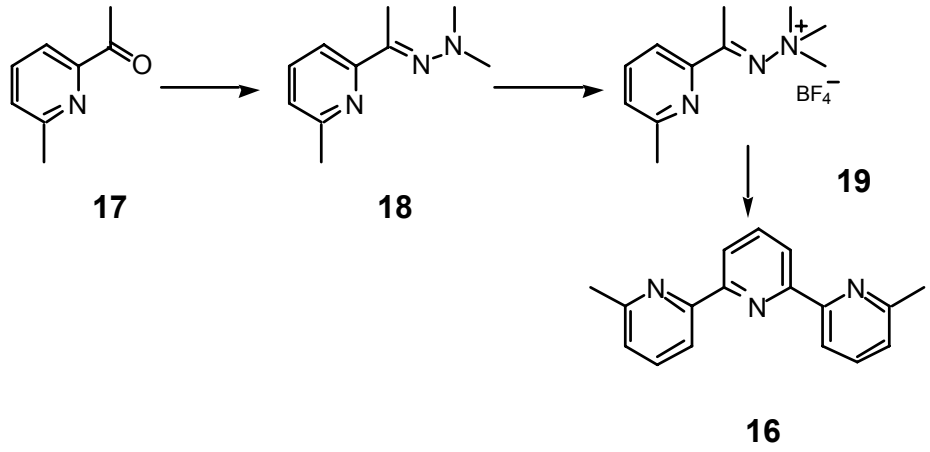


Scheme 4

3.2. Pyrolysis of hydrazonium salt

6-Methyl-2-acetylpyridine **17** was reacted directly with anhydrous N,N-dimethylhydrazine to give the corresponding N,N-dimethyhydrazone **18** in 55% yield. The quaternization of **18** with alcoholic methyl iodide afforded the corresponding N,N,N-trimethylhydrazonium iodide which was then converted to the N,N,N-trimethylhydrazonium tetrafluoroborate **19** upon reaction with sodium

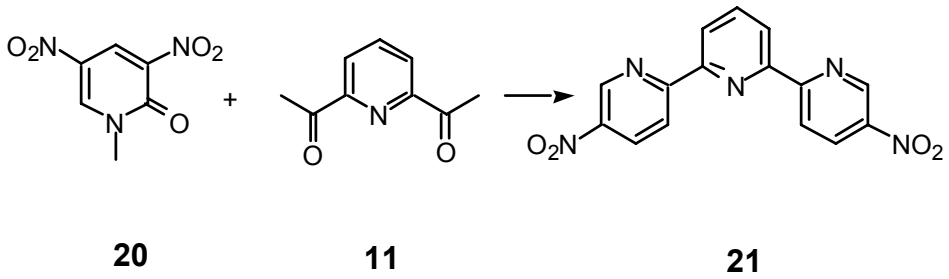
fluoroborate. The pyrolysis of **19** at 200°C gave 6,6"-dimethyl-2,2':6',2"-terpyridine **16** in 47% yield (Scheme 5) [127]. Though this method was extensively investigated for the synthesis of pyridine derivatives, in the series of tpy ligands, compound **16** only was prepared by this method.



Scheme 5

3.3. Tohda methodology

The reaction of the electron-deficient 1-methyl-3,5-dinitro-2-pyridone **20** with ketones or aldehydes in the presence of ammonia gave alkyl- and/or aryl-substituted 3-nitropyridines. Upon reaction of **20** with 2,6-diactylpyridine **11**, 5,5"-Dinitro-2,2':6',2"-terpyridine **21** was obtained in 74% yield (Scheme 6) [128].



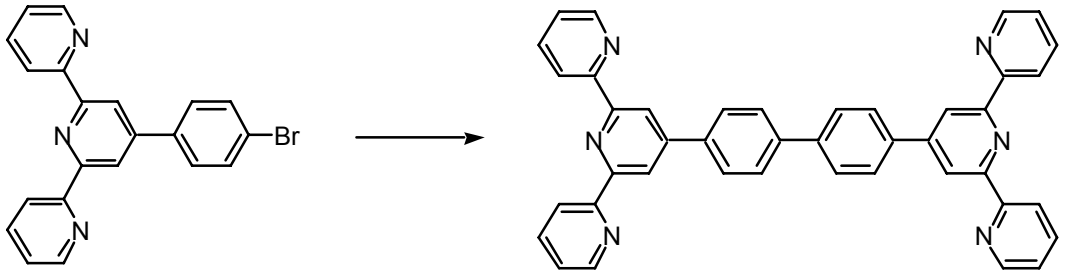
Scheme 6

3.4. Metal-mediated Methodologies

Metal-mediated coupling reactions have found wide application in organic chemistry. A relevant book has been published [129]. Examples applied in the synthesis of oligopyridines are mentioned below.

3.4.1. Nickel-mediated reactions

This type of reaction is widely used in the homocoupling of aromatic compounds while in the heterocyclic series it is not widely used [130]. Nickel(0) which is produced *in situ* by the reaction of $Ni(PPh_3)_2Cl_2$ [131] or even better $Ni(PPh_3)_2Br_2$ [132] with metallic zinc is able to couple two aromatic halogenides, preferably bromides, though some chlorides [133] are also reported. In the series of the synthesis of tpy ligands, those ligands possessing halogenated aromatic substituents at C(4') or 4'-bromo-tpy were coupled. Among several examples known, only an example is given to demonstrate this methodology. It should also be mentioned, that symmetrical ligands only can be prepared (Scheme 7).



22 **23**

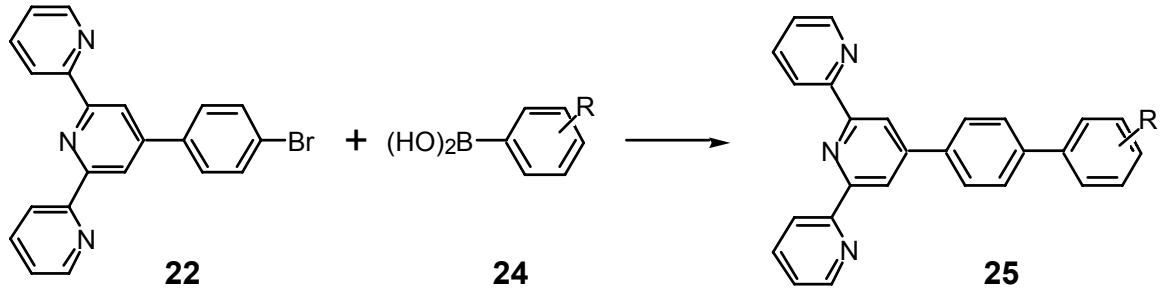
Scheme 7

3.4.2. Palladium-mediated reactions

The palladium catalysed formation of carbon-carbon bonds has been extensively studied. Palladium(II) or palladium(0) can be prepared *in situ* and are the catalysts used. The reactions may be pursued either in organic or in aqueous media. An excellent review has been published [134].

3.4.2.1. Suzuki-reaction

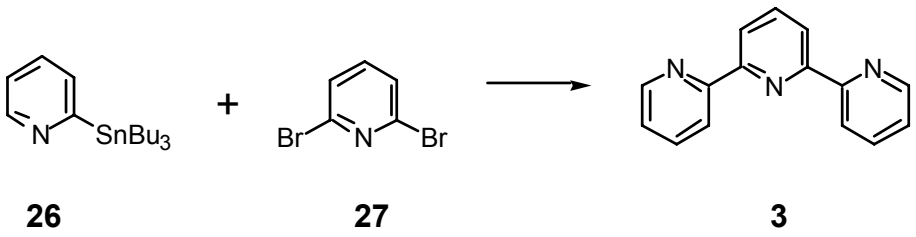
The Suzuki coupling reaction is an important coupling reaction which is catalysed by palladium(II) compound and takes place between an aromatic boric acid **24** and an aromatic halogenide, preferably, a bromide **23** [135] (Scheme 8). These reactions are very useful and the yield is normally high. This reaction is used in coupling of aromatic compounds, though some alkyl bromides were also used. It was applied to prepare symmetrical and unsymmetrical tpy ligands.



Scheme 8

3.4.2.2. Stille coupling reaction

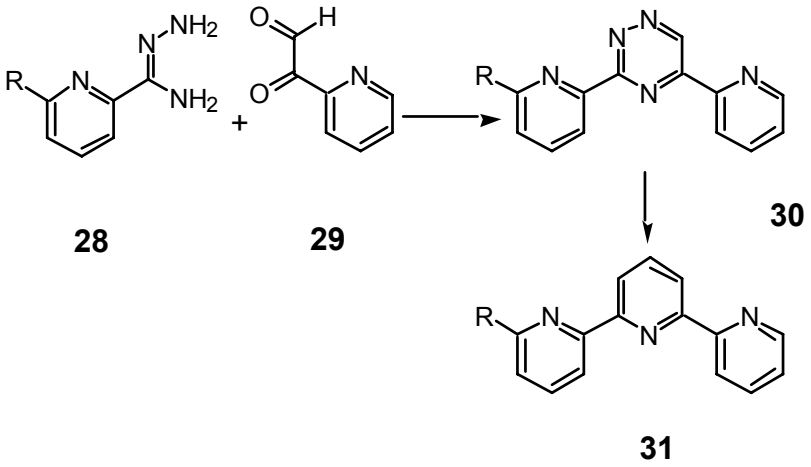
The Stille coupling reaction, which consists of the reaction of stannyl compound **26** and bromo compound **27** in the presence of a catalytic amount of palladium(0) and palladium(II), respectively, has found wide application in the synthesis of aromatic and heterocyclic compounds (Scheme 9). An excellent review article has already been published [136]. The advantage of this method is that many functionalities such as nitro, carboxylate, carbonyl, cyano groups or pyridine-N-oxides are not affected by the reaction conditions.



Scheme 9

3.5. Sauer methodology

This is a regiospecific cyclocondensation of carboxamidrazones **28** with α-pyridylglyoxal **29** in aqueous ethanol at room temperature leading to 3,5-di-(pyridin-2-yl)-[1,2,4]-triazines **30** in reasonable yields. These triazines undergo inverse-type Diels-Alder reactions with either norborna-2,5-diene or with ethynyltributyltin to form oligopyridines **31** by heating in 1,2-dichlorobenzene in good yields (Scheme 10) [137].



Scheme 10

4. Our contribution.

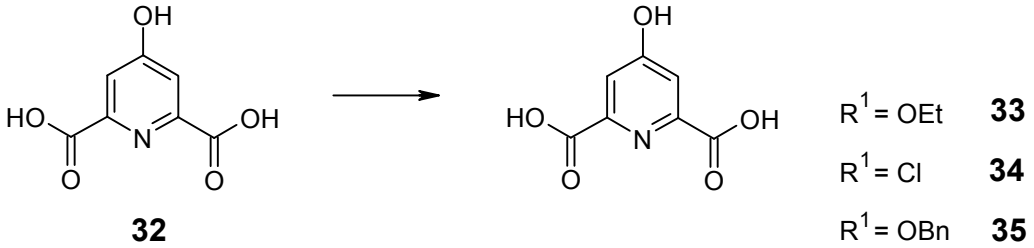
The goal of this work was to prepare novel tailored oligopyridine ligands and their application in the synthesis of multinuclear metal complexes. The metal complexes are of interest due to their ability to transfer energy. The new ligands were reacted with iron(II) and ruthenium(II) ions to obtain the desired complexes. As shown in Figure 2, linking of substituents to C(4') of 2,2':6',2''-terpyridine is of enormous importance. Therefore, we used methods to insert the desired functional groups to carbon atoms of starting materials which destined to become, *e.g.*, C(4') of 2,2':6',2''-terpyridine. This strategy allows the attachment of a series of functional groups to the desired positions.

Our work involves the following two parts: i) synthesis of novel functionalised oligopyridines, especially, 2,2':6',2''-terpyridines and 2,2'-bipyridines; ii) preparation of metal complexes and their photochemical investigations.

4.1. Synthesis of ligands

4.1.1. Preparation of 4-chloro-, 4-ethoxy- and 4-benzyloxy-2,6-diacetylpyridines 33-35

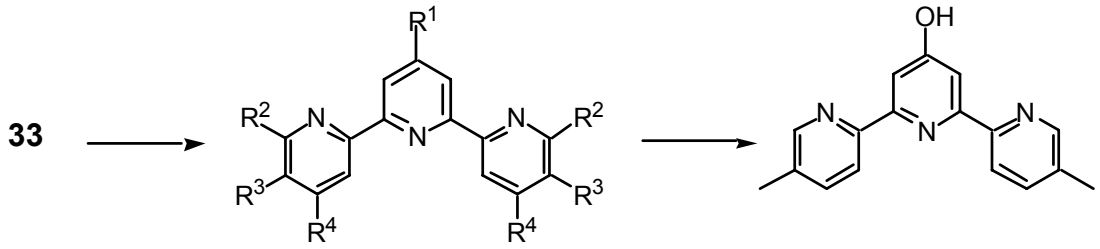
Chelidamic acid **32** is an attractive precursor due to the presence of the functional group at C(4) destined to become C(4') of 2,2':6',2''-terpyridine. For this purpose compound **32**, which is commercially available or can be easily prepared in multi-hundreds gram scale, was converted to 4-functionalised-2,6-diacetylpyridines **33-35** [104] [138-139] (Scheme 11).



Scheme 11

2,6-Diacetylpyridines are generally ideal starting materials for the formation of macrocycles and for the synthesis of pyridines, respectively.

4.1.2. Synthesis of substituted 4'-ethoxy- and 4'-hydroxy-2,2':6',2''-terpyridines bearing functional groups (substituents) at the terminal pyridine rings 36-39



R^1= OEt, R^2=Me, R^4=p-tolyl, R^3=H **36**
R^1= OEt, R^2=Me, R^3=R^4=H **37**
R^1= OEt, R^3=Me, R^2=R^4=H **38**

39

Scheme 12

The Kröhnke methodology for pyridine synthesis was applied to 4-ethoxy-2,6-diacetylpyridine **33** and reacted to the functionalised 2,2':6',2''-terpyridines **36-39**. All these 2,2':6',2''-terpyridines bear a protected hydroxy group at C(4') in addition to substituents at C(4), C(5) and C(6) of the terminal pyridines (Scheme 12) [104] [138]. The protecting group of **33** was cleaved to yield the 4'-hydroxy-5,5''-dimethyl-2,2':6',2''-terpyridine **39**. In this manner, we have established a methodology for preparing terpyridines **36-39** which have the potential for undergoing regioselective reactions both at C(4)/C(4''), C(5)/C(5''), C(6)/C(6'') and, more importantly, at C(4') which possesses an ethoxy or a hydroxyl group. The structure of 4'-ethoxy-5,5''-dimethyl-2,2':6',2''-terpyridine **38** in the solid state is presented in Figure 8.

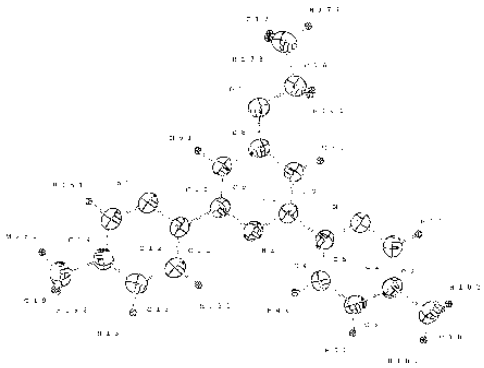
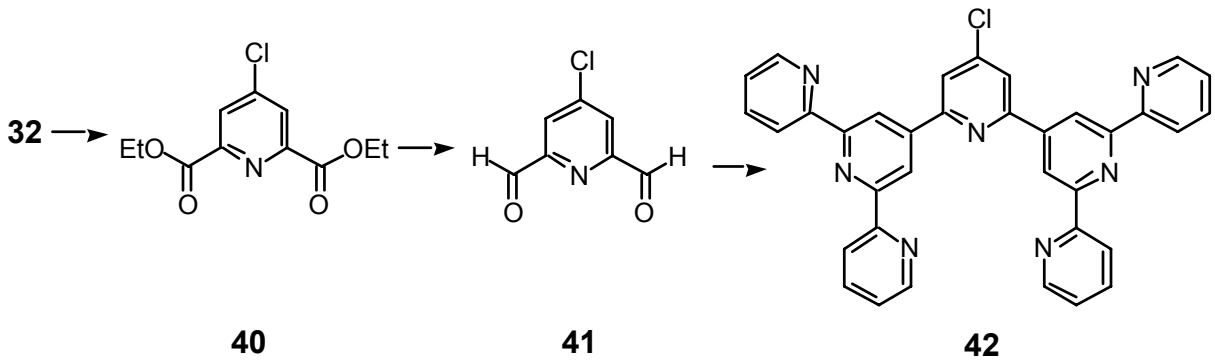


Figure 8

4.1.3. Synthesis of 2,6-[bis-(2,2':6',2''-terpyridin-4'-yl)]-4-chloropyridine 42

Once again, chelidamic acid **32** was converted to diethyl 4-chloropyridine-2,6-dicarboxylate **39** which was then reduced in two steps to the dialdehyde **41**. Aldehyde **41** was used in the Kröhnke methodology of pyridine synthesis to prepare ligand **42** in good yield (Scheme 13) [140] [183].



Scheme 13

In the ^{1}H NMR spectrum of **42** two singlets were observed at δ 9.23 and δ 8.16 assigned to C(3') of tpy and the hydrogen atoms adjacent to chlorine atoms, respectively. The hydrogen atoms at C(6) and C(3) were observed as doublets at δ 8.71 and at δ 8.79, respectively, while hydrogen atoms at C(4) and C(5) were observed as doublet of doublet of doublets at δ 7.81 and at δ 7.40, respectively (Figure 9).

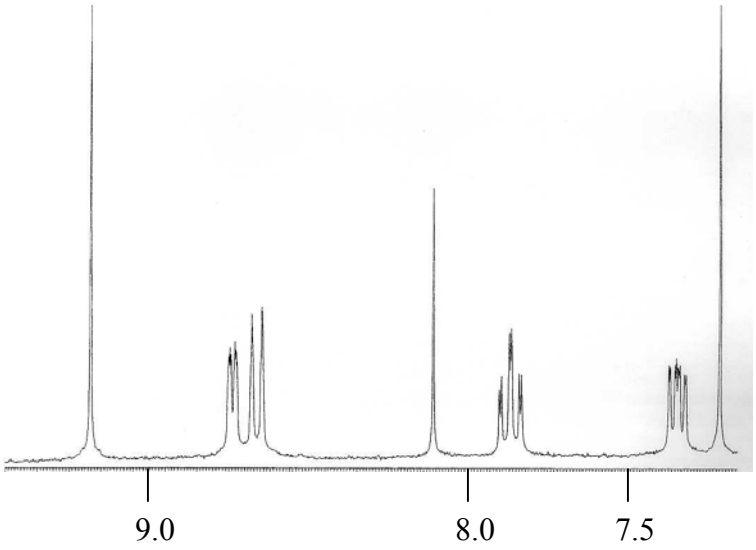


Figure 9

The analytical and spectroscopic results are good evidence for **42**, and this conclusion is confirmed by the results of the X-ray diffraction (Figure 10) [140].

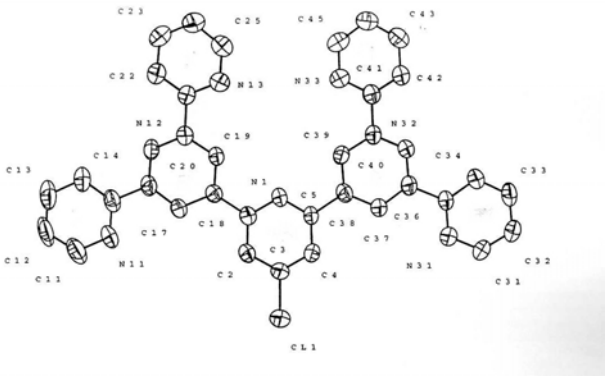


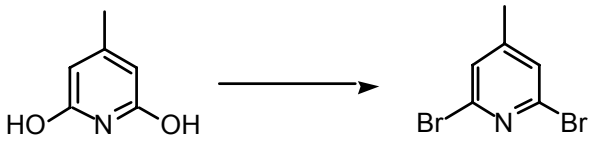
Figure 10

4.1.4. Preparation of trimethyl derivatives of 2,2':6',2''-terpyridine 48-51

4'-Methyl-2,2':6',2"-terpyridine is extremely good precursor for further functionalisation. The long chain substituted tpy ligands were synthesised by nucleophilic reaction of alkyls with lithium salts of 4'-methyl-tpy [141]. However, the oxidation to an aldehyde or carboxylic acid failed. Its reaction with NBS gave indefinite products, but not the desired 4'-bromomethyl-tpy ligand. Ethyl 4'-tpy-carboxylate was reduced to 4'-hydroxymethyl-tpy followed by the conversion to 4'-bromomethyl-tpy upon reaction with tetrabromomethane [142]. This bromo compound is of high reactivity and was reacted with amines to give tpy-methyl-crown ethers [142]. 4'-Methyl-tpy was reacted with LDA followed by reaction with phosphorus electrophiles to obtain diphenylphosphine methyl-tpy and its oxidised derivative [143] [144]. Following the same procedure, 4'-methyl-tpy was reacted with carbon electrophiles to give tpy derivatives linked to carborane [145] and fullerene [145-146], respectively. While the ethylene group was easily attached to C(4') of tpy by Potts methodology [147], the acetylene group was linked to C(4') by the palladium catalysed reaction with 4'-bromo-tpy [148].

While tpy ligands possessing alkyl substituents at C(4,4',4") were easily prepared by the Kröhnke methodology [149-150], 4'-methyl-tpy was first reported by Potts [151] by the substitution reaction of 4'-methylthio-tpy. Meanwhile some other methods have also been developed for its synthesis [145-146] [152]. The Stille coupling reaction allows the preparation of substituted and unsymmetrical tpy ligands [152].

The Stille coupling reaction consists of the reaction of stannyl compounds with bromo or triflate compounds in the presence of a catalytic amount of palladium(0). Using this methodology, the following functionalised oligopyridines **48-51** have been prepared. The key compound of the Stille coupling reaction was 4-methyl-2,6-dibromopyridine **44** (Scheme 14) [152].

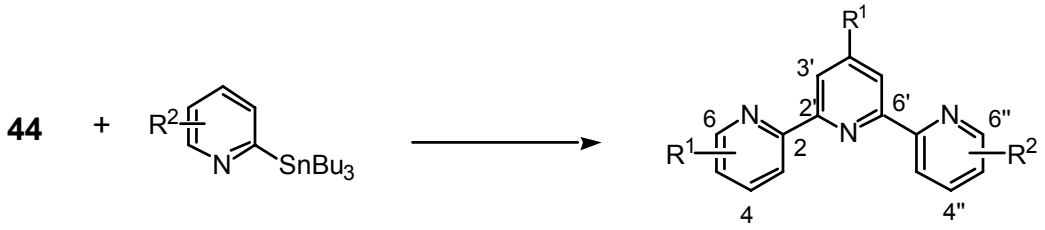


43 **44**

Scheme 14

The commercially available 4-methyl-2,6-dihydroxypyridine **43** was reacted with PBr_3 to give **44** [153].

2-Bromopyridine, 4-methyl-2-bromopyridine, 5-methyl-2-bromopyridine and 6-methyl-2-bromopyridine were converted to derivatives of tributyl(pyridin-2-yl)stannanes **45-47** upon reaction with n-butyl lithium and n-tributyl tin chloride in tetrahydrofuran. The stannyl compounds were reacted with **44** in the presence of $Pd(PPh_3)_4$ to give 4'-methyl-2,2':6',2''-terpyridine **48**, trimethyl-2,2':6',2''-terpyridines **49-51** in 50-65% yields, respectively (Scheme 15).



R^2=H	**26**	R^1= Me, R^2=H	**48**
R^2=4-Me	**45**	R^1= Me, R^2=4,4''-Me_2	**49**
R^2=5-Me	**46**	R^1= Me, R^2=5,5''-Me_2	**50**
R^2=6-Me	**47**	R^1= Me, R^2=6,6''-Me_2	**51**

Scheme 15

4.1.4.1. Work-up of the Stille coupling reaction

A major consideration in working up of reaction mixtures from the Stille cross coupling is the removal of tin byproducts. While trimethyltin chloride is water soluble and rather volatile, tributyltin chloride

has a low volatility and is soluble in most organic solvents. Separation on silica gel is difficult due to the tendency of tributyltin chloride to elute under non-polar conditions, and to streak on the column.

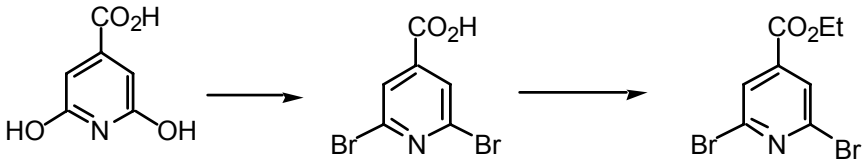
We have first reported the easy work-up of the Stille coupling reaction, applied in the synthesis of oligopyrdines [106] [152] [154-156]. Once one is working with basic compounds, e.g. oligopyridines, however, the work up is made very easy. While bases are soluble in concentrated hydrochloric acid, the tin byproducts can be removed by extraction with dichloromethane. Neutralisation of the acidic aqueous phase with an inorganic base, usually sodium carbonate or sodium hydroxide, gives the free ligands. The organic compound, which contains no trace of tin by-products, can be extracted with dichloromethane and, if necessary, easily purified by chromatography. If some sensitive groups, such as carboxylates, are present, the neutralisation should be carried out with sodium carbonate rather than with sodium hydroxide.

4.1.5. Carboxylate derivatives of oligopyridines

Carboxylic, phosphonic and sulfonic acids derivatives of tpy ligands have received special attention due to their ability to anchor to surfaces and be used for energy transfer [67-78].

While 3',5'-$(CO_2H)_2$-tpy and 3',4'-$(CO_2H)_2$-tpy ligands are directly available by the Hantzsch methodology [120], other carboxylic derivatives have been synthesised by more complicated reactions. The easiest way appears to be the oxidation of methyl groups. The methyl derivatives of tpy ligands are readily accessible by the Kröhnke methodology or other methods [152]. By the oxidation of 4,4',4''-trimethyl-2,2':6',2''-terpyridine, which is accessible by the Kröhnke methodology, with chromium trioxide in sulphuric acid, 2,2':6',2''-terpyridine-4,4',4''-tricarboxylic acid was obtained [70]. Selective oxidation of the methyl groups is not possible and any other functional groups sensitive to oxidation or hydrolysis should be avoided. In addition, yields are low and the oxidation and work-up of such reactions are not so easy. The synthesis of butyl 2,2':6',2''-terpyridine-4'-carboxylate and some other

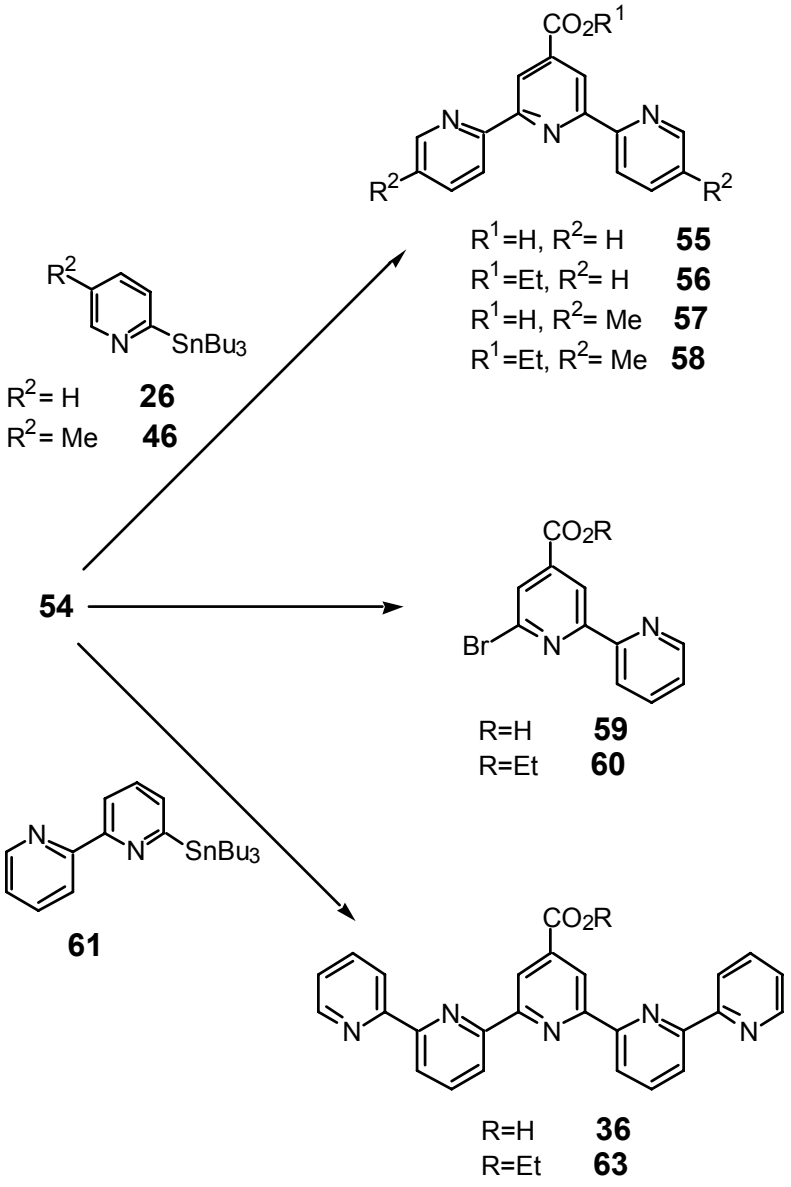
pyridine derivatives have also been reported [157-158]. Some of the starting materials are not so easily accessible. Furthermore, this method does not allow any other functional groups, especially at the tpy ligand. We have also been involved in the preparation of carboxylic derivatives of tpy ligands. The Stille coupling reaction was shown to be an efficient and easy method. The key compound of the Stille coupling reaction was ethyl 2,6-dibromo-4-pyridinecarboxylate **54** (Scheme 16) [156].



52 **53** **54**

Scheme 16

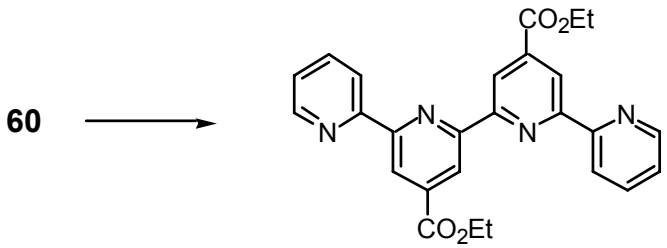
Commercially available citrazinic acid **52** was converted to 2,6-dibromopyridine-4-carboxylic acid **53** upon reaction with $POBr_3$ [159]. Subsequent esterification with sulphuric acid and ethanol produced ethyl 2,6-dibromo-4-pyridinecarboxylate as a yellow microcrystalline compound **54** in excellent yield. Compound **54** was reacted with **26** to give 2,2':6',2"-terpyridine-4'-carboxylic acid **55** and ethyl 2,2':6',2"-terpyridine-4'-carboxylate **56** in good yields (Scheme 17). When **54** was reacted under the same conditions with **46**, 5,5"-dimethyl-2,2':6',2"-terpyridine-4'-carboxylic acid **57** and ethyl 5,5"-dimethyl-2,2':6',2"-terpyridine-4'-carboxylate **58** were obtained as colourless microcrystalline solids. Following our procedure, ethyl 6,6"-dimethyl-2,2':6',2"-terpyridine-4'-carboxylate was also reported [160].



Scheme 17

However, if **54** was reacted with only one equivalent of **26** in the presence of the catalyst under the same conditions, 6-bromo-2,2'-bipyridine-4'-carboxylic acid **59** and ethyl 6-bromo-2,2'-bipyridine-4'-carboxylate **60** were obtained as colourless microcrystalline solids. These reactions was extended to

synthesise higher oligopyridines, symmetrical or unsymmetrical ones, e.g. 2,2':6',2":6",2"':6"',2""-quinquepyridine-4"-carboxylic acid derivatives **62** and **63**, respectively.



64

Scheme 18

Ethyl 6-bromo-2,2'-bipyridine-4'-carboxylate **60** was coupled with a Ni(0)-catalyst to obtain diethyl 2,2':6',2":6",2"'-quaterpyridine-4',4"-dicarboxylate (Scheme 18). This quaterpyridine was anchored to a TiO_2-surface and its photochemical and photophysical properties were investigated [161].

In the ^{1}H NMR spectrum of **64** two singlets were observed at δ 9.16 and at δ 9.07 assigned to C(3') and C(5'), respectively. The hydrogen atoms at C(6) and C(3) were observed as multiplets at δ 8.76 and at δ 8.70 respectively, while hydrogen atoms at C(4) and C(5) were observed as doublet of doublet of doublets at δ 7.92 and δ 7.39 respectively (Figure 11).

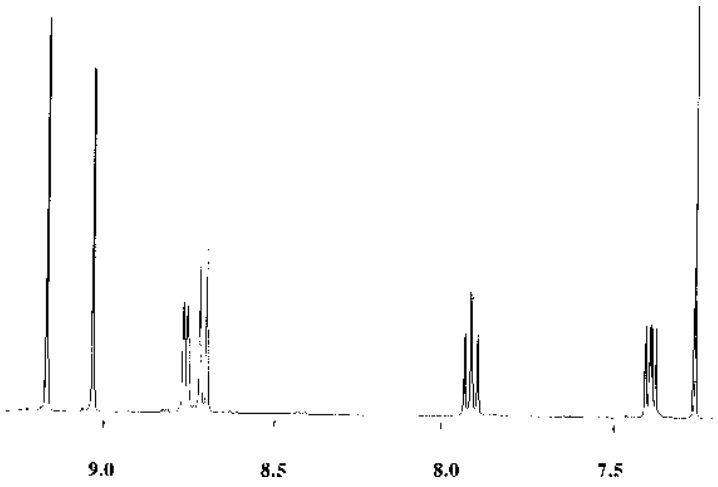
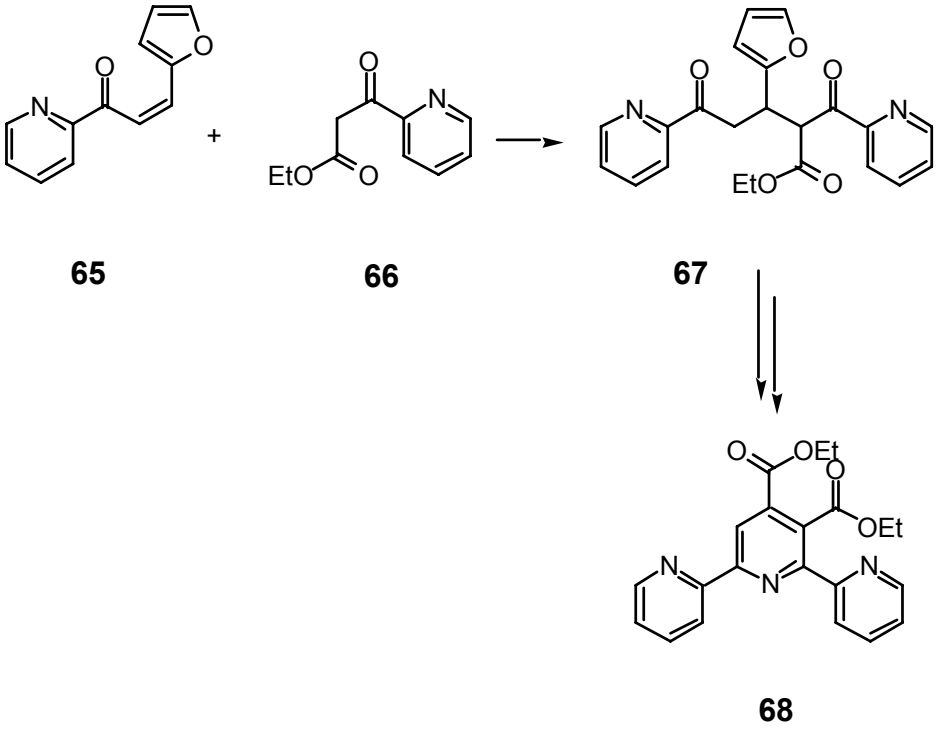


Figure 11

Recently, the preparation of vicinal unsymmetrical 3',4'-dicarboxylic ligands were also reported (Scheme 19). The 1,4-Michael addition of ethyl 3-oxo-3-pyridylpropane carboxylate **66** afforded the necessary 1,5-diketone **67** for use in the Kröhnke methodology, which was then cyclised to give the 4'-(2-furyl)-tpy derivative. The furyl group was oxidised to give tpy-3',4'-dicarboxylic acid. The ester **68** was obtained by esterification [162-163].



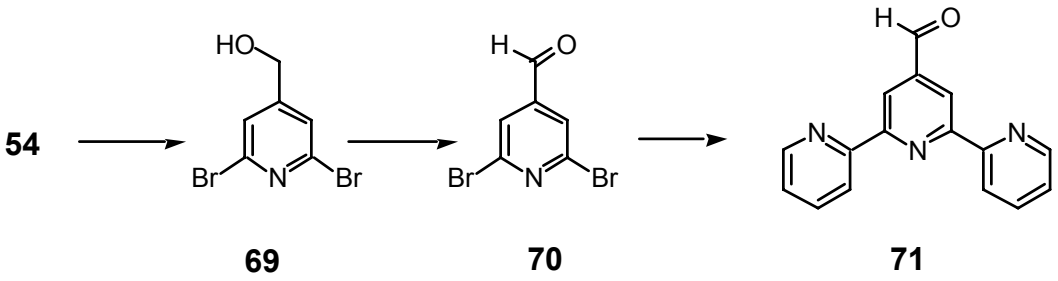
65 **66** **67** **68**

Scheme 19

4.1.6. Carbonyl derivatives of tpy ligands

Aldehydes are versatile functional groups in organic synthesis. 4'-Formyl-tpy was reacted with an amine to obtain imine [164] or with ferrocene derivative in an aldol condensation to hydroxy compound or to the ethylene bridged one, respectively [165]. The two radical anions were prepared in a multiple condensation of 4'-formyl-tpy with N,N'-dihydroxy-2,3-diamino-2,3-dimethylbutane followed by dehydration of N-hydroxyimidazoline by selenium dioxide [166].

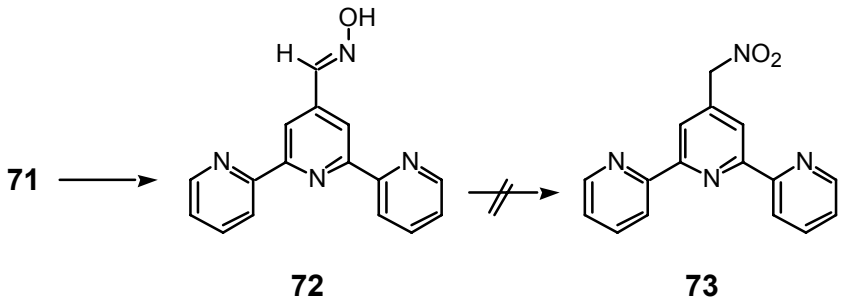
Compared to other methods, we have shown that the Stille coupling reaction is an attractive method for the preparation of 4'-functionalised tpy ligands. Ethyl 2,6-dibromo-4-pyridinecarboxylate **54** was reduced to 4-hydroxymethyl-2,6-dibromopyridine **69** followed by the Swern oxidation to the aldehyde **70**. It was reacted with stannyl compound **26** in the presence of $Pd(PPh_3)_4$ to give 4'-carbaldhyde-2,2':6',2''-terpyridine **71** in reasonable yield (Scheme 20) [152].



Scheme 20

4.1.7. Synthesis of 4'-carbaldhyde oxime-2,2':6',2''-terpyridine 72

While 4'-carbaldhyde-2,2':6',2''-terpyridine **71** was reacted to a series of products, it was also converted to 4'-carbaldhyde oxime-2,2':6',2''-terpyridine **72** upon reaction with hydroxyl ammonium chloride in good yield (Scheme 17). An oxidation of **72** to 4'-nitomethyl-2,2':6',2''-terpyridine **73** by ozone, however, failed [172].



Scheme 21

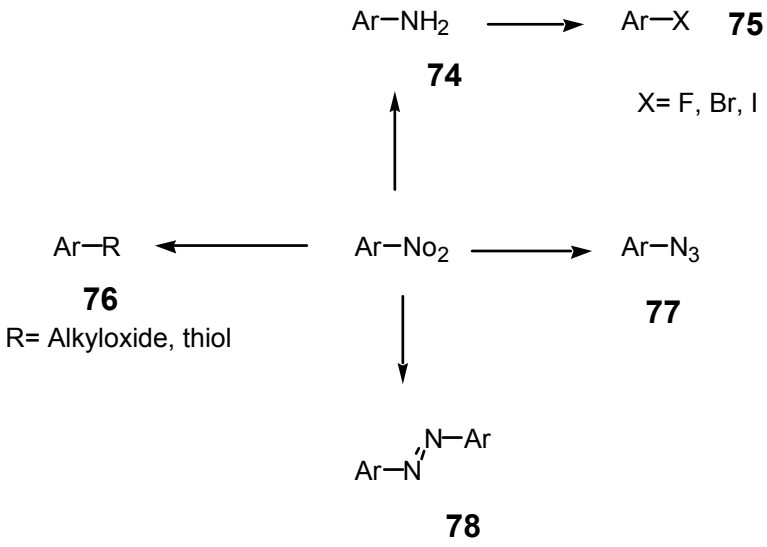
4.1.8. Synthesis of 4'-nitro-2,2':6',2''-terpyridines 82-84 and 4-nitro-2,2'-bipyridines 80-81

As mentioned before, there is much interest raised in linking the functional group directly to C(4') of tpy ligands. One of such interesting functional groups is the nitro group. Up until now, this is the strongest electron-withdrawing group directly attached to C(4'). Table 1 lists the Hammet parameters of the substituents and the ^{1}H NMR spectroscopic shifts of hydrogen atoms at C(3',5').

R	σ_p	δ	R	σ_p	δ
NMe_2	-0.63	7.79	Cl	0.24	8.48
NH_2	-0.57	7.75	Br	0.26	8.64
OH	-0.38	7.08	I	0.28	8.86
OEt	-0.28	8.00	CO_2Et	0.44	8.97
Me	-0.14	8.29	CHO	0.47	8.88
H	0	8.46	SO_2Me	0.73	8.97
F	0.15	8.20	NO_2	0.81	9.16

Table 1. Shifts of hydrogen atoms at C(3') of tpy ligands in $CDCl_3$-solution

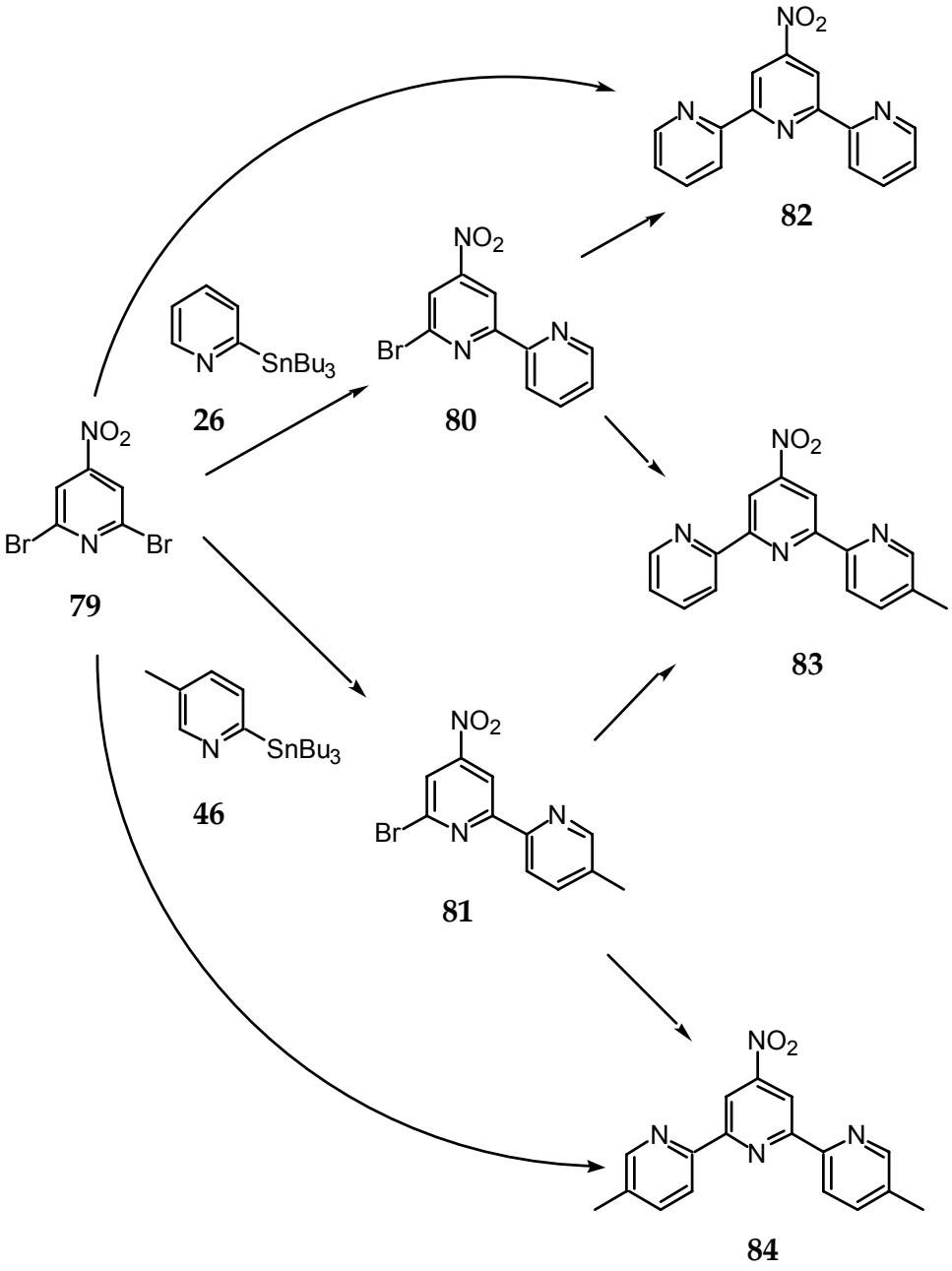
Aromatic nitro compounds are very interesting target molecules due to their versatile abilities for reduction, cyclisation and substitution reactions; and they play a key role in organic synthesis. They can be reduced to amine, azo and other nitrogen derivatives. The amino compounds may be converted to the halogenated ones (F, Br, I). The substitution reactions of aromatic nitro compounds with nucleophiles also have widespread applications in chemistry. By nucleophilic substitution with alkoxides or thiolates compounds (alkoxide, thiolate) may be obtained (Scheme 22).



Scheme 22

The ligand 4,4',4"-trinitro-tpy ligand was prepared by the exhaustive nitration of tpy-1,1',1"-trioxide followed by deoxygenation [116]. The selective synthesis of symmetrical, unsymmetrical 4'-nitro-2,2':6',2"-terpyridines, however, were performed by the Stille coupling reactions. The key compound of the synthesis of the Stille coupling reaction is 2,6-dibromo-4-nitropyridine **79**. Compound **79** was reacted with 1 equivalent of tributyl(pyridin-2-yl)stannane **26** in the presence of 0.01 equivalent of $Pd(PPh_3)_4$ in toluene to give 6-bromo-4-nitro-2,2'-bipyridine in 60% yield. When **79** was reacted under the same conditions with 1 mole equivalent of tributyl(5-methylpyridin-2-yl)stannane **46**, 6-bromo-5-methyl-4-nitro-2,2'-bipyridine **81** was obtained in 69% yield. However, if **79** was reacted with two equivalents of **26** in the presence of the catalyst under the same conditions, ligand **82** was directly obtained in 68% yield. Alternatively **79** was reacted with two equivalents of **46** under the same conditions to give **84** in 64% yield. The unsymmetrical tpy-ligand **83** was obtained upon reaction of bipyridines **81** or **82** with tributyl(5-methylpyridin-2-yl)stannane **46** or tributyl(pyridin-2-yl)stannane **26**, again in toluene, in the presence of 0.01 equivalent of $Pd(PPh_3)_4$ in good yield, respectively

[106][154] (Scheme 23). Using this methodology the novel tpy ligands possessing nitro substituents directly attached to C(4') were prepared and these are precursors to a new class of oligopyridines.



Scheme 23

4.1.9. Reduction of 4'-nitro-2,2':6',2''-terpyridines

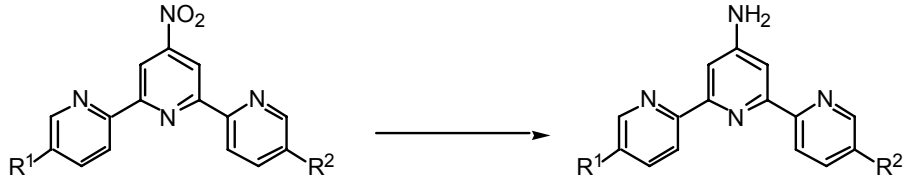
4.1.9.1. Synthesis of 4'-amino-2,2':6',2''-terpyridines

4'-Dimethylamino-tpy was obtained from the reaction of 4'-chloro-2,2':6',2"-terpyridine with dimethylamine and iron(II) salt to form a complex, followed by oxidation with hydrogen peroxide [103]. Derivatives of aza crown ethers were prepared upon reaction of 4'-bromo-tpy with aza crown ethers, containing one or two nitrogen atoms [167]. 4'-Bromomethyl-tpy was reacted with aza crown ether or cyclam to give the heterocyclic compounds [142].

Amine substituted tpy ligands were mostly prepared by three different ways: i) by reduction of the nitro group: ii) by conversion of 4'-chloro-2,2':6',2"-terpyridine; iii) by substitution reactions. The latter two methods are limited to unsubstituted tpy ligands only.

4.1.9.1.1. Reduction of 4'-nitro-2,2':6',2''-terpyridines 82-84 to 4'-amino-2,2':6',2''-terpyridines 85-87

The reduction of the nitro group is the most convenient way to prepare amines. 4,4',4"-Triamino-2,2':6',2"-terpyridine was easily obtained from reduction of 4,4',4"-trinitro-tpy [116]. 4'-Amino-2,2':6',2"-terpyridines ligands **85-87** were also readily prepared by reduction of the corresponding 4'-nitro-tpy ligands **82-84** [106]. This method allows the preparation of substituted and/or unsymmetrical ligands (Scheme 24).



R^1= H, R^2= H	**82**	R^1= H, R^2= H	**85**
R^1= H, R^2= Me	**83**	R^1= H, R^2= Me	**86**
R^1= Me, R^2= Me	**84**	R^1= Me, R^2= Me	**87**

Scheme 24

The three nitroterpyridines **82-84** are readily reduced with hydrazine hydrate in the presence of palladium on charcoal in ethanol [106]. In the IR spectra of **85-87**, no bands assigned to nitro groups were observed, but bands attributed to amino groups were observed at about 3400 cm^{-1}. All the data are in accord with the proposed structures. The X-ray crystal structure of the compound 4'-amino-2,2':6',2''-terpyridine **85** confirms the proposed structure, and is presented in Figure 12.

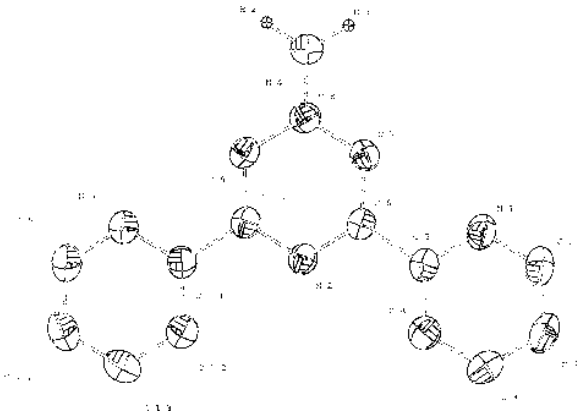
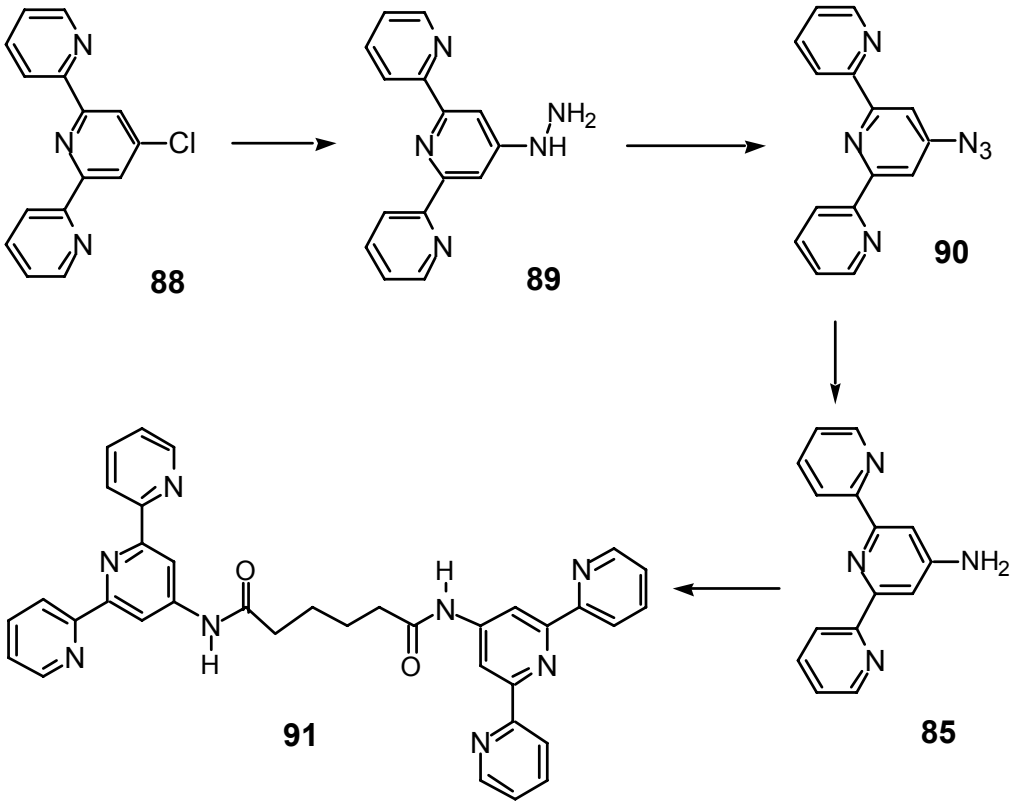


Figure 12

The exception was, as it was reported in other tpy derivatives, that the three pyridine rings in the amino derivatives of tpy would be close to being coplanar. However, the X-ray structure data showed a greater deviation from planarity than expected, with interplanar angles of 11.23° and 20.68°, respectively. This extent of twisting can be attributed to hydrogen bonding as already illustrated in Figure 4, which illustrates that a hydrogen bonded network extends through the lattice involving amino hydrogen atoms and nitrogen atoms of the terminal pyridine rings. The distances N(1)-H(1) of 2.271 Å and N(3)-H(2) of 2.333 Å are in accord with the known values. As a result, the interplanar angles within each terpyridine ligand are 11.23° and 20.68°. The distance N(4)-C(8) of 1.364(3) Å strongly suggests sp^2 character for the nitrogen atom and a high degree of π-conjugation between the amino group and the aromatic ring.

4.1.9.1.2. Conversion of 4'-chloro-2,2':6',2''-terpyridine 88 to 4'-amino-2,2':6',2''-terpyridine 85

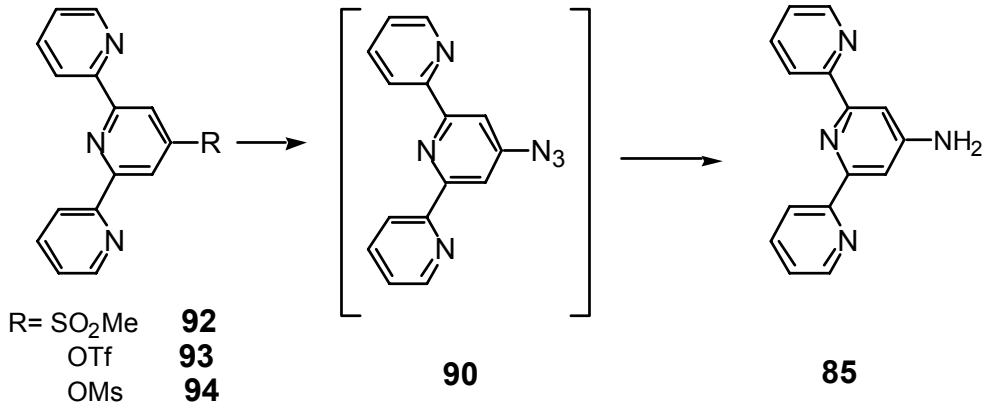
4'-Chloro-2,2':6',2"-terpyridine **88** was reacted with hydrazine to 4'-hydrazino-tpy **89** which was then converted to 4'-azido-tpy **90** upon reaction with nitrite ion in acidic medium, followed by reduction to obtain 4'-amino-tpy **85** (Scheme 25). By the reaction of 4'-amino-tpy **85** with adipic acid, compound **91** was obtained [168].



Scheme 25

4.1.9.1.3. Substitution reaction for the synthesis of 4'-amino-2,2':6',2''-terpyridine 85

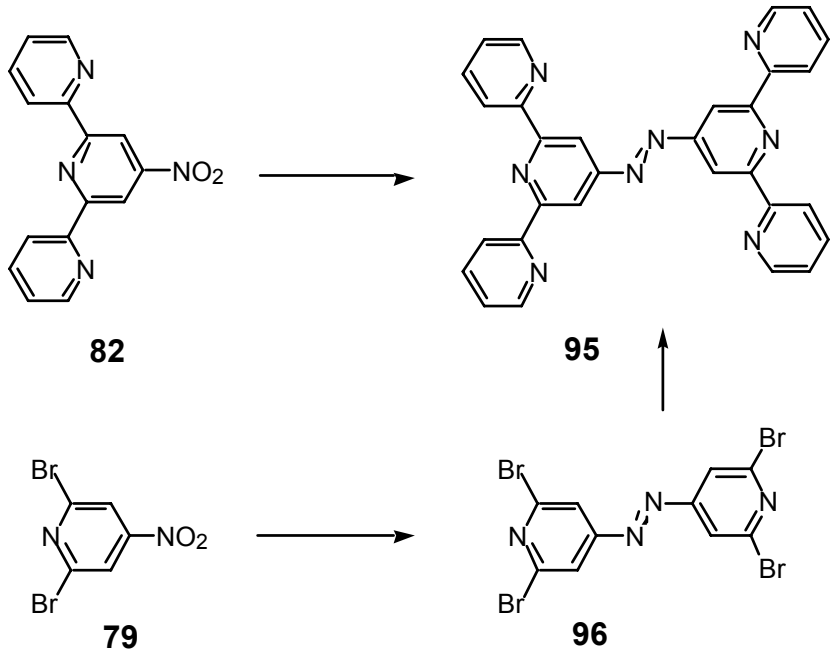
The substitution reaction of 4'-methylsulfono-2,2':6',2"-terpyridine (tpy-SO_2Me) **92**, 4'-triflate-2,2':6',2"-terpyridine (tpy-OTf) **93** or 4'-mesylate-2,2':6',2"-terpyridine (tpy-OMs) **94** with sodium azide in DMF at 150°C gave or 4'-azido-2,2':6',2"-terpyridine **90** which undergoes further reaction to give 4'- amino-2,2':6',2"-terpyridine **85** in good yields [172] (Scheme 26).



Scheme 26

4.1.9.2. Reduction of 4'-nitro-2,2':6',2''-terpyridine 82 to 4,4'-azo-bis(2,2':6',2''-terpyridine) 95

While 4'-nitro-2,2':6',2"-terpyridine compounds were easily reduced to 4'-amino-2,2':6',2"-terpyridines **85-87** (Scheme 24), 4'-nitro-2,2':6',2"-terpyridine **82** was reduced to the azo compound **95** in moderate yields by using a relatively weak reducing agents such as $NaBH_4$ or $SnCl_2.2H_2O$, respectively (Scheme 27) [169].



Scheme 27

Alternatively, 4-nitro-2,6-dibromopyridine **79** was reduced to the azo compound **96** which was then converted into **95** by 4-fold Stille coupling. The structure of **96** was determined by an X-ray crystal structure analysis and was found to exhibit the *trans*-form (Figure 13). Compound **96** is a planar molecule, the angle between the two pyridine rings is almost 0°. Due to its *cis/trans*-isomerism the azo compound is of special interest. The photochemical isomerisation of this ligand was investigated and the lifetime of the *trans* isomer is 40 min.

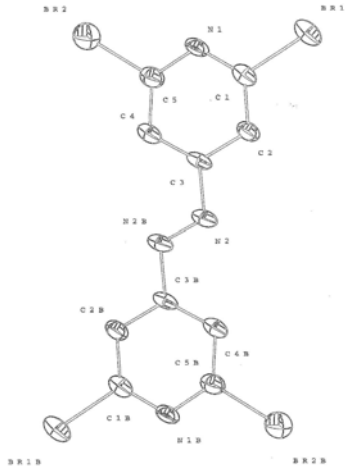
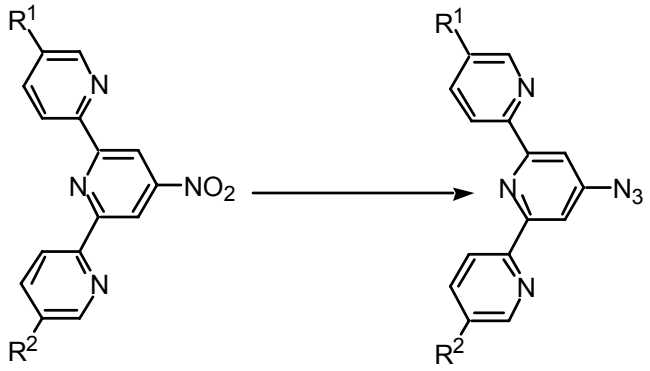


Figure 13

4.1.10. Substitution reaction of 4'-nitro-2,2':6',2''-terpyridines 82-84

4.1.10.1. Synthesis of 4'-azido-2,2':6',2''-terpyridines 90, 97-98

As already discussed in section 4.1.9.1.1, 4'-nitro-2,2':6',2"-terpyridines **82-84** were readily reduced to 4'-amino-2,2':6',2"-terpyridines **85-87**. The substitution reactions of aromatic nitro compounds with nucleophiles are also of wide-spread application in chemistry. Though aromatic nitro groups have been displaced by azide at 0°C [170], the reaction of 4'-nitro-2,2':6',2"-terpyridines **82-84** with sodium azide in excess in dimethylformamide took place above 100°C and the three 4'-azido-2,2':6',2"-terpyridines **90, 97-98** were obtained in 70-75% yield [155] (Scheme 28).



R^1=R^2= H **82**
R^1=R^2= Me **83**
R^1=H, R^2=Me **84**

R^1=R^2= H **90**
R^1=H, R^2=Me **97**
R^1=R^2= Me **98**

Scheme 28

The reactions were also easy to follow due to the blue colour of the iron(II) complexes with 4'-nitro-2,2':6',2"-terpyridines **82-84** compared with the purple iron(II) complexes of 4'-azido-2,2':6',2"-terpyridines **90, 97-98**.

The IR spectra of 4'-azido-2,2':6',2"-terpyridines **90, 97-98** exhibited bands at about 2110 cm^{-1} assigned to the azide groups. In the ^1H NMR spectra of the three terpyridines **90, 97-98** we observed a singlet due to hydrogen atoms $H^{3'}$ at δ 8.16, δ 8.11 and δ 8.08, respectively, which is fully consistent with the inductive effect of the methyl groups. In the unsymmetrical terpyridine **97**, while each hydrogen was observed as a separate signal, the hydrogen $H^{5'}$ was also observed at δ 8.12 additional to the hydrogen $H^{3'}$ at δ 8.11, in other words, the hydrogen atoms $H^{3'}$ and $H^{5'}$ are not identical.

The X-ray crystal structure of the compound 4'-azido-2,2':6',2"-terpyridine **90** confirms the proposed structure, and is presented in Figure 14. In 4'-azido-2,2':6',2"-terpyridine **90**, however, the interplanar angles of the two terminal rings with the central ring are 2.35° and 8.42°, respectively. The three nitrogens of the azide group are not exactly linear and form an angle of 173°. The distances N(4)-C(8) of 1.426(2) Å, N(4)-N(5) of 1.239(2) Å and N(5)-N(6) of 1.124(2) Å strongly suggesting that electron density is at the terminal azide nitrogen.

In conclusion, we established a methodology for the synthesis of symmetrical and unsymmetrical 4'-azido-2,2':6',2''-terpyridines which are able to undergo further reactions.

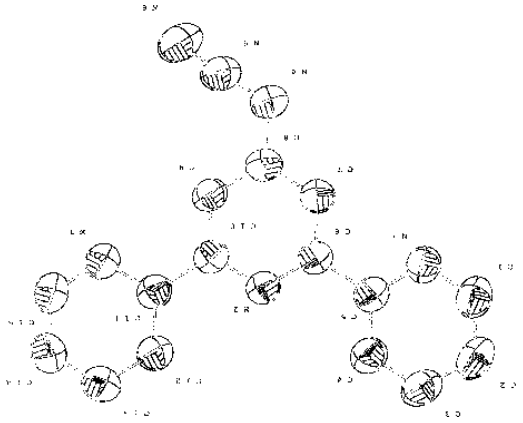
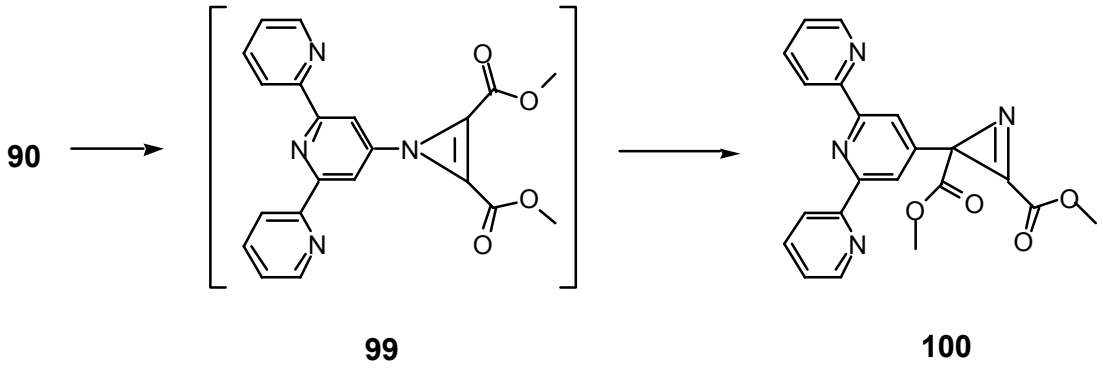


Figure 14

4.1.10.1.1. Thermal reaction of 4'-azido-2,2':6',2''-terpyridine 90

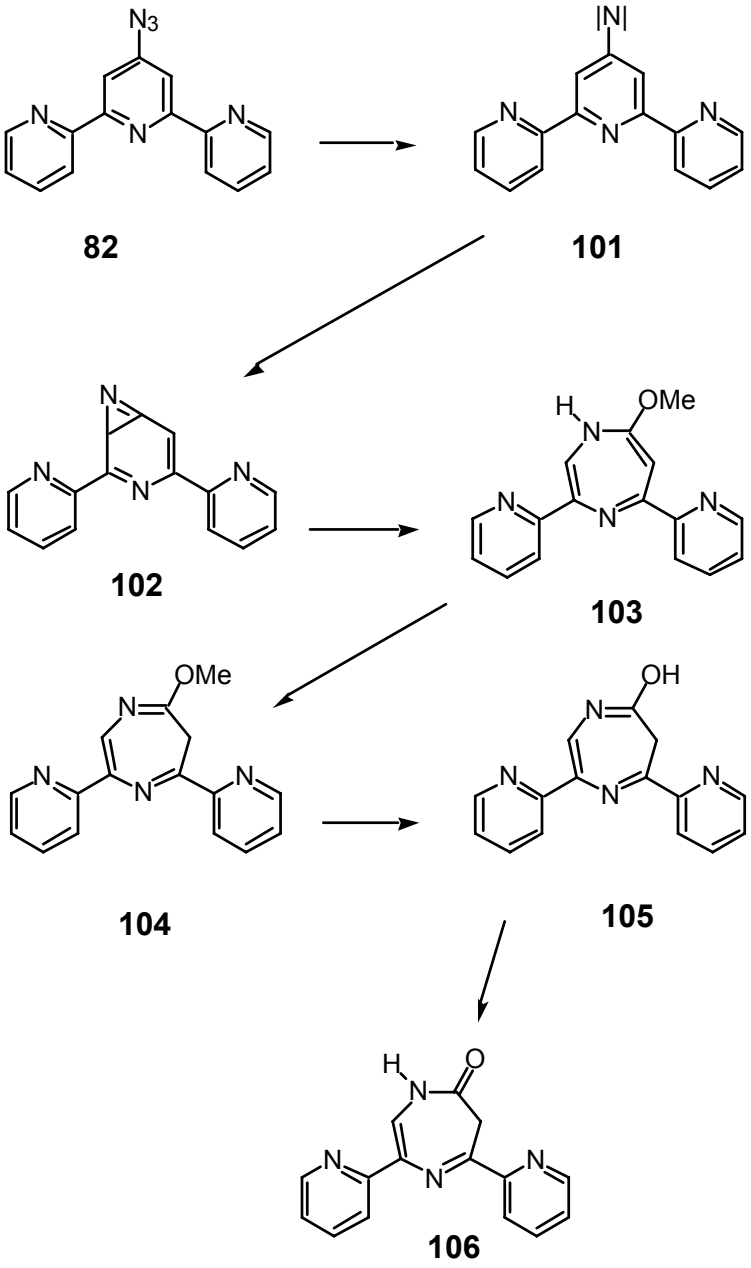
The thermal reaction of azide with suitable multiple bonds gives 2*H*-azirines which are directly attached to oligopyridines. As an example, 4'-azido-2,2':6',2''-terpyridine **90** was reacted with dimethyl acetylendicarboxylate (DMA) in chlorobenzene to yield **100** in which the 2*H*-azirine ring is directly attached to the tpy ligand (Scheme 29) [171]. The antiaromatic 1*H*-azirines such as **99** are known to be very short-lived or postulated intermediates which immediately rearrange to give more stable 2*H*-azirines.



Scheme 29

4.1.10.1.2. Photochemical reactions of azido-oligopyridines

The photochemical reactions of azido-oligopyridines under basic conditions were investigated. The singlet terpyridine nitrene **101**, generated from azido compound **90** reacts intramolecularly with the pyridine ring to give compound **102** (Scheme 30) [171].

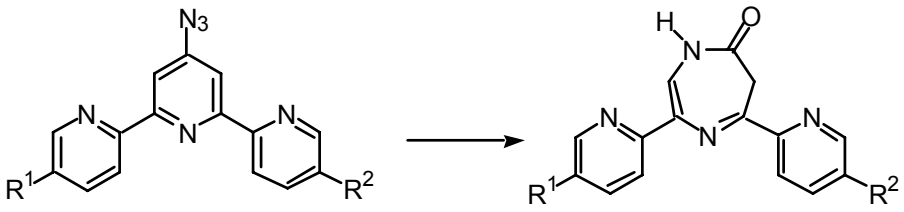


Scheme 30

By the nucleophilic addition of sodium methoxide to **102** followed by electrocyclic ring opening of diazanorcaradiene, the unstable *anti-aromatic* NH-diazepine compound **103** was formed which isomerised to the more stable CH-form **104** by a hydrogen shift. Under the work-up conditions compound **104** is not stable and loses methanol to give compound **105**, which then tautomerises to **106**.

4.1.10.1.2.1. Photochemical reactions of symmetrical 4'-azido-2,2':6',2''-terpyridines 90 and 98

The photochemical reaction of azides under basic conditions produced nitrenes, which rearrange to form diazepinones. The two symmetrical tpy ligands **90** and **98** have been irradiated in a mixture of methanol-dioxane (1/1) containing sodium methoxide for 3 hours. A red brownish solution resulted in yellow crystalline compounds **106-107** after work-up in good yields (Scheme 31).



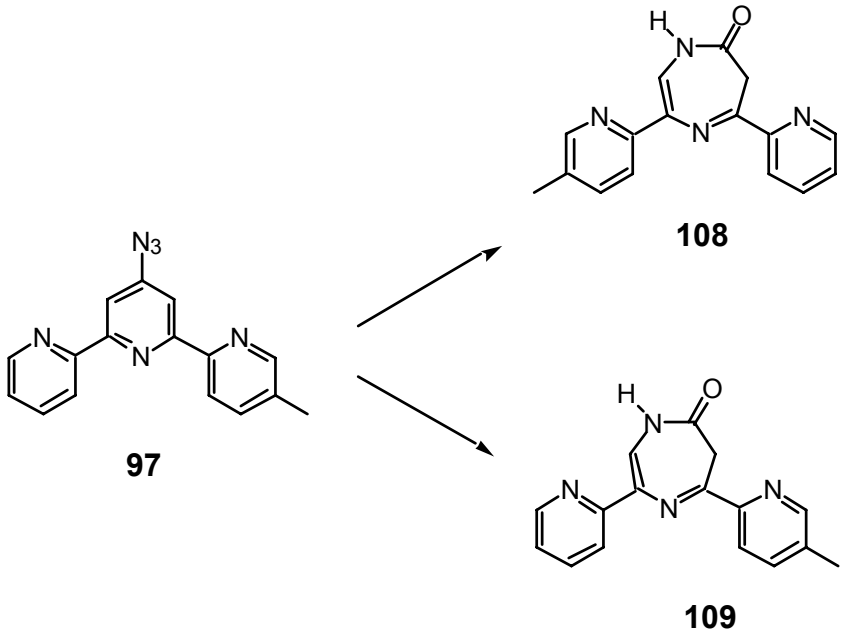
$R^1=R^2=$ H **90**
$R^1=R^2=$ Me **98**

$R^1=R^2=$ H **106**
$R^1=R^2=$ Me **107**

Scheme 31

4.1.10.1.2.2. Photochemical reactions of unsymmetrical 4'-azido-2,2':6',2''-terpyridines 97

The unsymmetrical tpy ligand **97** has also been irradiated under the same reaction conditions. A red brownish solution resulted in two compounds **108** and **109** in 1:1 ratio (determined by ^{1}H NMR) (Scheme 32). In the ^{13}C NMR spectrum, all 32 signals assigned to the both isomers were observed. The isomers were separated by reversed-phase HPLC.

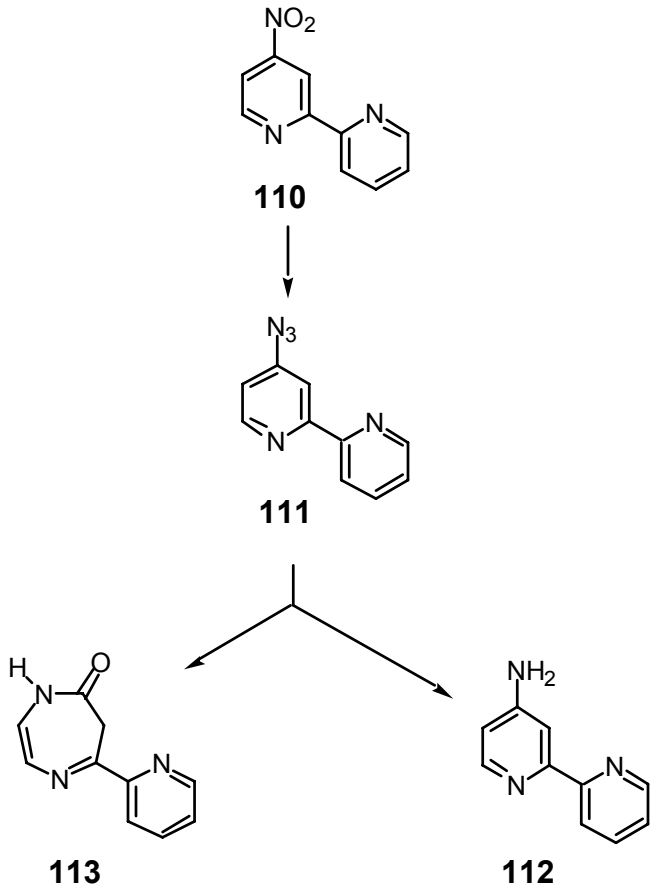


Scheme 32

While both isomers possess similar or the same IR, UV spectroscopic and mass spectrometric properties and elemental analysis, it was possible to distinguish them by ^{1}H and ^{13}C NMR spectroscopy; in the ^{1}H NMR spectrum the two methyl groups were observed at δ 2.31 and at δ 2.35. The assignment of the products **108** and **109** was confirmed by COESY and heteronuclear multiple bond correlations (HMBC) and heteronuclear multiple quantum correlations (HMQC) between the hydrogen and the carbon atoms. As already shown in oligopyridines, both compounds exhibit an *s-trans* conformation even in solution so that no NOE of the methylene group was observed. Almost all of the hydrogen atoms of both isomers are identical in ^{1}H NMR spectra, and the only way to distinguish them is to find out if there is any interaction between H^{3} and carbons C(2') of **108** or C(2'') of **109**. Indeed, a long range coupling between the H^{3} and C(2') rather than to C(2'') exists. By applying methods, the two isomers **108** and **109** were correctly assigned.

4.1.10.1.2.3. Photochemical reactions of 4-azido-2,2'-bipyridine 111

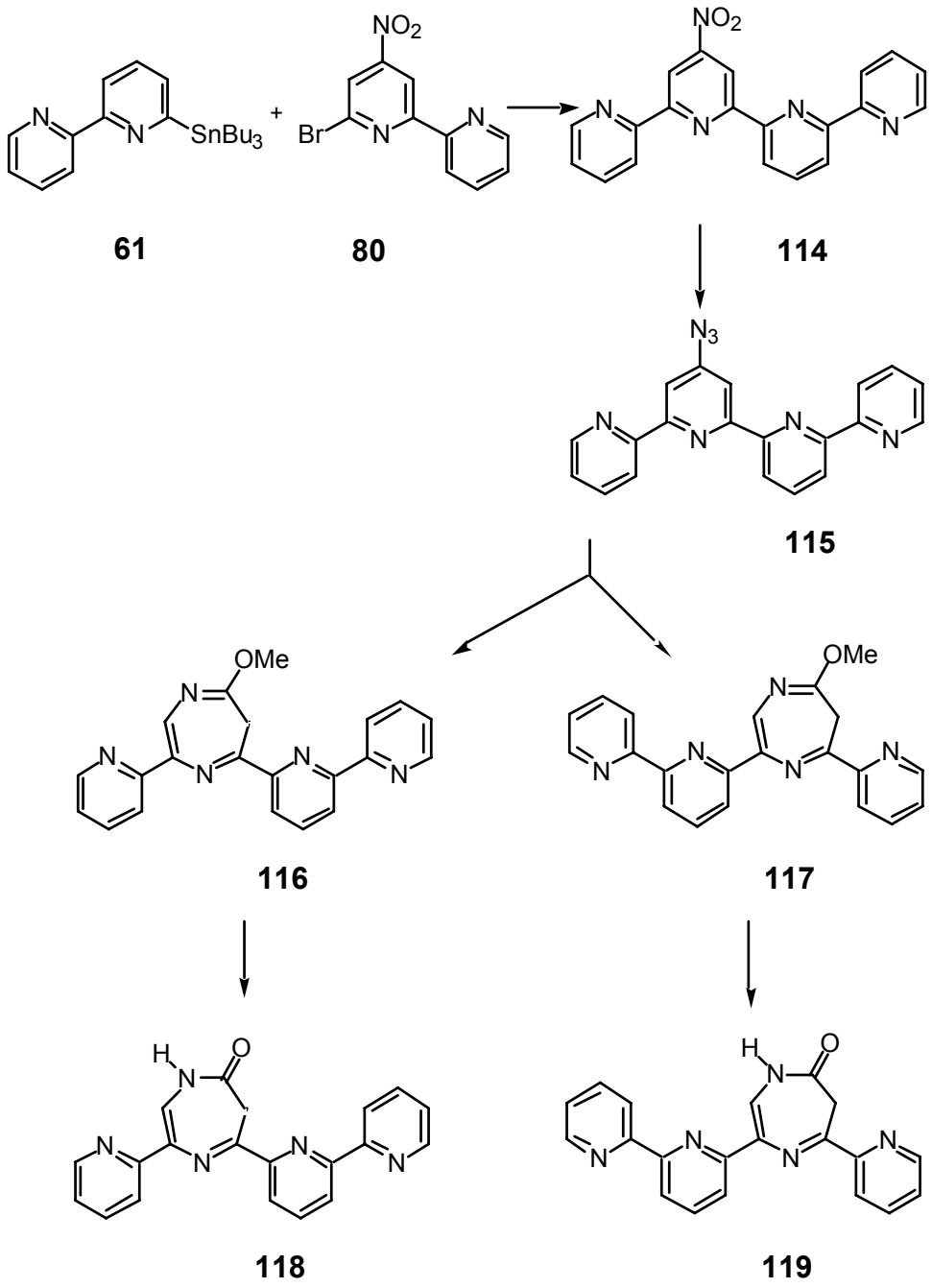
Following the same strategy, 4-azido-2,2'-bipyridine **111** was prepared upon reaction of 4-nitro-2,2'-bipyridine with sodium azide in DMF. The irradiation of the unsymmetrical 4-azido-2,2'-bipyridine **111** in methanol-dioxane under basic conditions resulted in two main products in 64% yield (Scheme 33). The two main products were separated by chromatography on silica gel. Interestingly, a part of 4-azido-2,2'-bipyridine **111** was reduced to 4-amino-2,2'-bipyridine **112** [173] under the reaction conditions in 30% yield. The other main product was isolated as a yellow microcrystalline solid in 34% yield. The IR spectrum of the latter compound exhibited a strong band at 1657 cm^{-1} assigned to the carboxylic group. In the Maldi-TOF mass spectrum, a parent ion peak was observed at m/z 187. The assignment of the compound, however, was based on ^{1}H NMR spectroscopic data. In compound **113** one would expect a doublet of doublets for H^3 along with a doublet for H^2. Indeed, the latter compound was assigned as **23** exhibiting doublet of doublets of H^3 at δ 6.02 along with the doublet of H^2 at δ 6.89.



Scheme 33

4.1.10.1.2.4. Photochemical reactions of 4'-azido-2,2':6',2'':6'',2'''-quaterpyridine 115

We have extended our investigations to higher oligopyridines. Upon displacement of the nitro group of 4'-nitro-2,2':6',2":6",2"'-quaterpyridine **114** by sodium azide in DMF, 4'-azido-2,2':6',2":6",2"'-quaterpyridine **115** was obtained as a pink microcrystalline solid in 70% yield (Scheme 34). The IR spectrum of **115** exhibited band at 2110 cm^{-1} assigned to the azide group.



Scheme 34

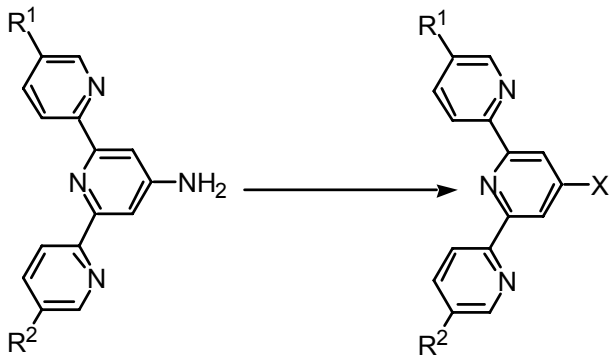
The irradiation of the unsymmetrical 4'-azido-2,2':6',2":6",2"'-quaterpyridine **115** in methanol-dioxane under basic conditions resulted, once again, in two isomers **116-117** in a ratio of 1:1 in 70% yield. The two isomers have easily been separated by chromatography on silica gel. Although the methoxy-

diazepines are extremely susceptible to decomposition on silica gel or aluminium oxide, compounds **116-117** were isolated. Interestingly, in the IR spectra of separated **116-117** no bands at 1700 cm^{-1} due to the carboxylic group were observed. However, in the Maldi-TOF mass spectra parent ion peaks at m/z 355 were observed. The first eluted compound, assigned as **116**, and the second one, assigned as **117**, exhibit similarities to compounds **108** and **109** in the ^{1}H NMR spectra. Hydrogen $H^{5''}$ of **116** was observed as *ddd* at δ 7.17 while the hydrogen $H^{5'''}$ in **117** was shifted to low field and was observed at δ 7.32. The methoxy and methylene groups, both, were observed at δ 3.78 (**116**) and at δ 3.81 (**117**), respectively. Upon reaction of **116-117** with dilute aqueous hydrochloric acid, compounds **118-119** were obtained. In the IR spectra of **118-119** bands at 1700 cm^{-1} due to the carboxylic group were observed.

4.1.10.2. Synthesis of halogen derivatives of 2,2':6',2''-terpyridine

Halogen derivatives of tpy ligands are very reactive, and therefore of high interest. They react readily with heterocyles [168] and were also used in a series of palladium catalysed coupling reactions.

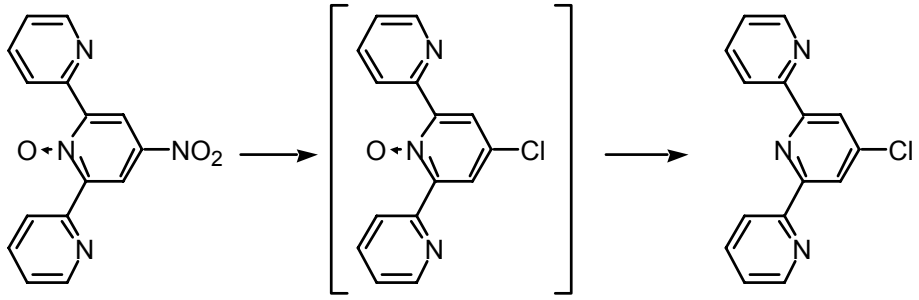
One of the established ways, however, to introduce a halogen is the reaction of diazonium salts with halogenides. Symmetrical, unsymmetrical, substituted and unsubstituted 4'-amino-tpy ligands **85-87** were reacted with sodium nitrite in acidic medium followed by reaction with tetrabromo fluoride, hydrobromo acid and potassium iodide to give 4'-fluoro-2,2':6',2''-terpyridine **120**, 4'-bromo-2,2':6',2''-terpyridine **121**, 5-methyl-4'-bromo-2,2':6',2''-terpyridine **122**, 5,5''-dimethyl-4'-bromo-2,2':6',2''-terpyridine **123** and 4'-iodo-2,2':6',2''-terpyridine **124**, respectively [172] (Scheme 35). 4'-Iodo-tpy ligand was also prepared by another method [168].



R^1= H, R^2= H	**85**	R^1=R^2= H	X= F	**120**
R^1= H, R^2= Me	**86**	R^1=R^2= H	X= Br	**121**
R^1= Me, R^2= Me	**87**	R^1=H, R^2=Me	X= Br	**122**
		R^1=R^2= Me	X= Br	**123**
		R^1=R^2= H	X= I	**124**

Scheme 35

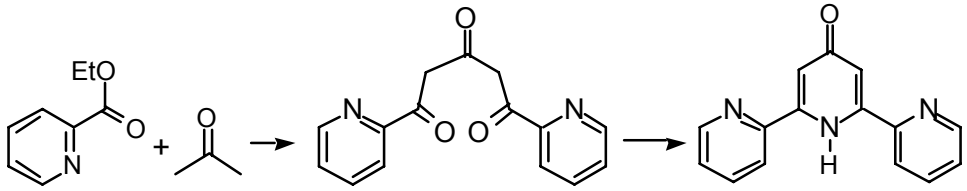
Tpy ligands were exhaustively oxidised to 1,1',1''-tpy-trioxide followed by nitration (see section 4.1.11). These compounds are precursors to halogen derivatives of tpy ligands. 1,1',1''-Tpy-trioxide was converted to 4,4',4''-trichloro and 4,4',4''-tribromo tpy ligands, respectively [124]. By the reaction of tpy-1'-oxide (see section 4.1.11) with acetyl chloride followed by deoxygenation, 4'-chloro-tpy ligands were prepared (Scheme 36). This method allows the preparation of symmetrical and unsymmetrical halogen- terpyridine ligands.



Scheme 36

4.2.10.2.1. Synthesis of 4',4'-bis(2,2':6',2''-terpyridyl)amine

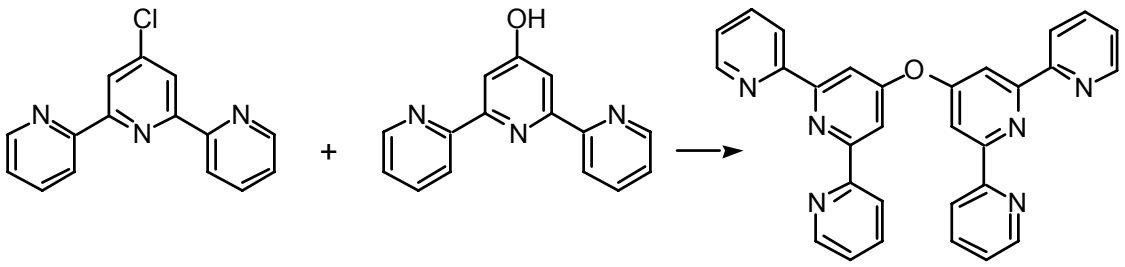
Using the Kröhnke methodology of 1,5-diketones and extending to 1,3,5-trione **129**, the most used ligand in this series was prepared. 4'-Hydroxy-2,2':6',2''-terpyridine **130**, or more correctly, 2,2':6',2''-terpyridine-4'(1'H)-one which is prepared in two steps by the Claisen condensation of acetone **128** with ethyl picolinate **127** [175] (Scheme 37). The structure of **130** in the solid state was reported [176].



Scheme 37

The hydroxy group was readily converted to the protected compounds (OTs, OTf, OMs) [124], or to 4'-chloro-2,2':6',2''-terpyridine **88**. 4'-Chloro-2,2':6',2''-terpyridine **88** and 4'-hydroxy-2,2':6',2''-

terpyridine **130** are the most investigated tpy ligands. These two tpy ligands were reacted together to obtain the ether-bridged-2,2':6',2"-terpyridine **131** (Scheme 38) [19].



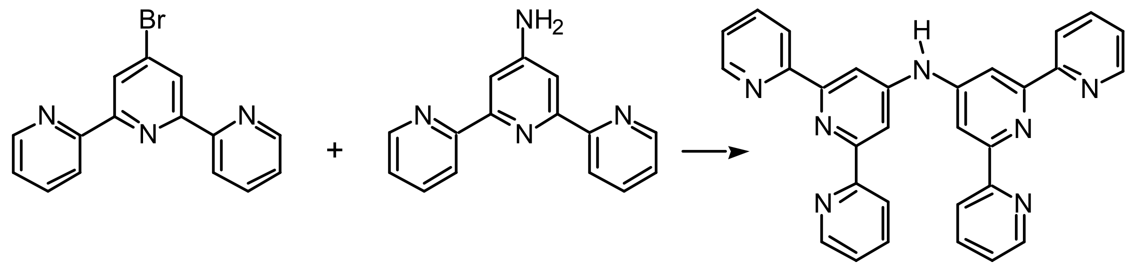
88 **130** **131**

Scheme 38

We were interested in amine-bridged tpy ligands due to their application in the formation of metal complexes. When we applied the same methodology of preparation of ether-bridged tpy ligand **131** to prepare our desired ligand **132** in acetonitrile or DMSO in the presence of a base, even in the form of a complex, the reaction failed. Tpy ligands are generally weak nucleophiles and by the deprotonation of ligand **121** by butyl lithium at low temperature upon reaction with **85**, no trace of **132** was identified. However, when **85** and **121** were reacted in the melt at 240°C, compound **132** only was formed beside the rest of some unreacted starting materials **85** and **121**, respectively. That is a clean reaction and the yield is quantitative in respect to the reacted compounds. The turnover of the reaction is 80%, which does not depend on the reaction time and the ratio of the starting materials. By the reaction of **85** and **121** in the ratio of 1:1 compound **132** was isolated. Even when more equivalents of **121** were reacted with **85**, the same product **132** only was isolated in the same yield (Scheme 39).

Compound **132** is also accessible in the melt when 4'-chloro- 2,2':6',2"-terpyridine **131** was reacted

with **85**. The same product and yield was obtained. No difference in the reaction time or products was observed.



121 **85** **132**

Scheme 39

Due to the symmetry of the molecule, one expects, and observes, only five signals in the ^{1}H NMR spectrum of bis-(2,2':6',2"-terpyridine)-amine **132** (Figure 15).

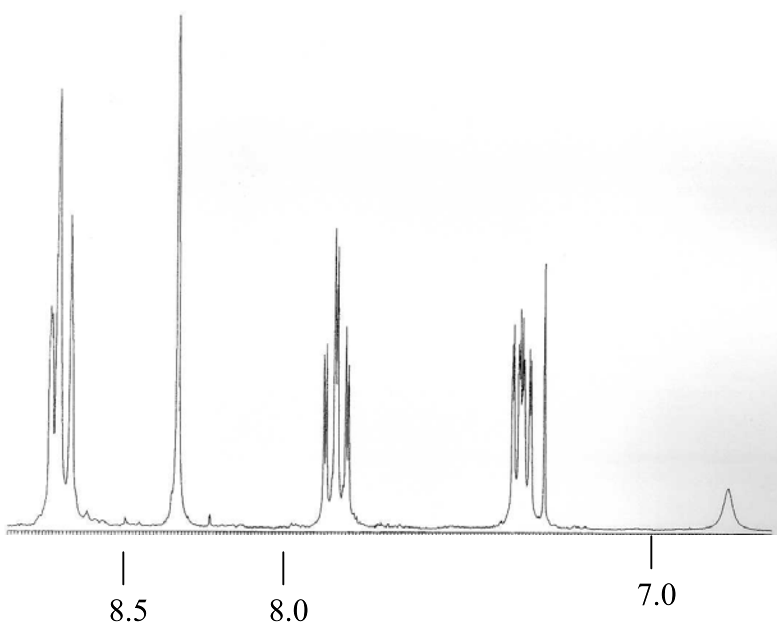


Figure 15

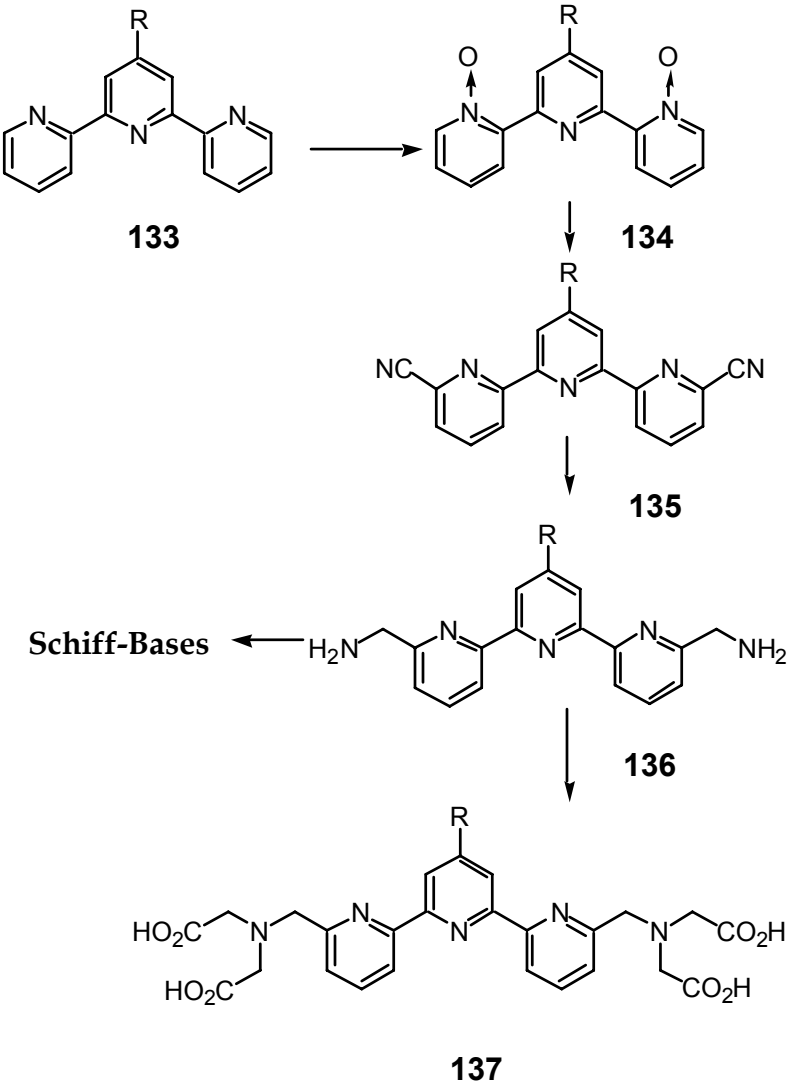
In the ^{1}H NMR spectrum of **132** the hydrogen atoms at C(6) and C(3) were observed as a doublets at δ 8.68 and at δ 8.65, respectively. The hydrogen atoms at C(3') were observed as a singlet at δ 8.33 which is shifted, in comparison with 4'-amino-2,2':6',2"-terpyridine **85**, to low field (Δδ = 0.59). This is in accord with the electron-withdrawing effect of tpy ligand. Hydrogen atoms at C(4) and C(5) were observed as doublets of doublet of doublet at δ 7.87 and at δ 7.34, respectively. The amine hydrogen was observed as a broad signal at δ 6.86 (Figure 16). In the MALDI-TOF mass spectrum of **132**, parent ion peaks were observed at m/z 492. All the analytical and spectroscopic data are in accord with the proposed formulation and structure.

4.1.11. Synthesis of 2,2'-bipyridine-1-oxides 139-140 and 2,2':6',2''-terpyridine-1'-Oxides 125, 141-142

Although electrophilic reactions on pyridine rings do not normally occur, oxidation of the ring nitrogen to form pyridine-N-oxide facilitates electrophilic attack at C(4) of the pyridine ring. The exhaustive oxidation of 2,2':6',2"-terpyridine by hydrogen peroxide in glacial acetic acid yielded 2,2':6',2"-terpyridine-1,1',1"-trioxide [116]. The selective oxidation of 2,2':6',2"-terpyridine by one mole *m*-chloroperbenzoic acid (*m*-CPBA) in chloroform gave 2,2':6',2"-terpyridine-1-oxide, while the use of at least two equimolar of *m*-CPBA affords the formation of 2,2':6',2"-terpyridine-1,1"-dioxide [176].

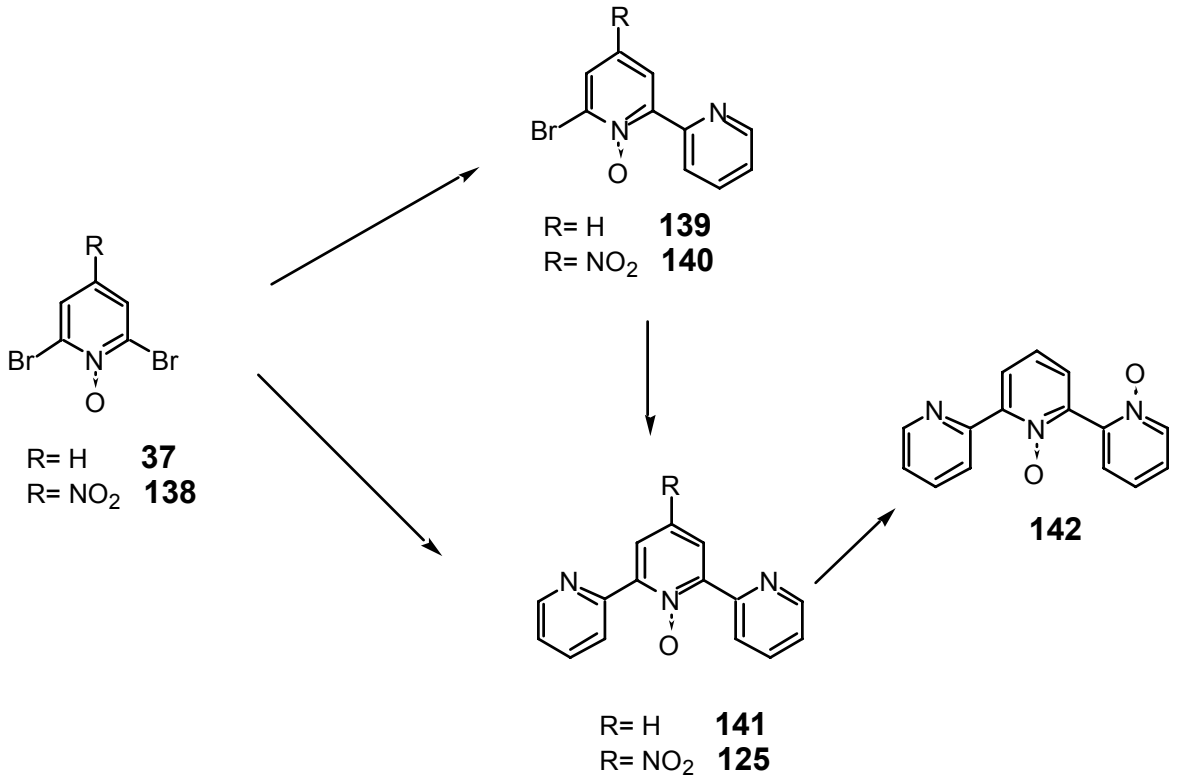
By utilising standard methods, 2,2':6',2"-terpyridine-1,1"-oxides were then reacted with nitric acid in sulphuric acid to give 4-nitro-2,2':6',2"-terpyridine-N-oxides. In addition, 4-nitro-2,2':6',2"-terpyridine-N-oxides are versatile starting materials for electrophilic substitution reactions. An example is the reaction of 2,2':6',2"-terpyridine-1,1"-dioxide **133** with Me_3SiCN followed by benzoyl chloride to give 2,2':6',2"-terpyridine-6,6"-dicarbonitrile **134** (Scheme 40) [177]. Compound **134** was then reduced and converted to **136**. These compounds are tetradentate ligands, in addition to the tpy moieties. In

addition, 2,2':6',2"-terpyridine-1,1',1"-trioxide was reported to react with NaOD in D_2O to give the perdeuterio 2,2':6',2"-terpyridine-1,1',1"-trioxide in 67% yield [178].



Scheme 40

Just recently we have established a methodology for preparing 2,2':6',2"-terpyridine-1'-oxides **125, 141-142** (the central pyridine ring is selectively oxidised) and 2,2'-bipyridine-1-oxides **139-140** (the more hindered pyridine ring is oxidised), respectively (Scheme 41) [179].



Scheme 41

2,6-Dibromopyridine-*N*-oxide **137** was reacted with 1 equiv. tributyl(pyridin-2-yl)stannane **44** in the presence of $Pd(PPh_3)_4$ to give 6-bromo-2,2'-bipyridine-1-oxide **139** in good yield as a colourless microcrystalline solid. The reaction of **139** with another mole equivalent of **44** yielded **141** in good yield as a colourless microcrystalline solid. However, if **137** was reacted with 2 equiv. **44** under the same conditions, 2,2':6',2"-terpyridine-1'-oxide **141** was directly obtained in good yield. This is the first example of a 2,2':6',2"-terpyridine containing N-oxide specifically at the central pyridine ring.

Once again, 4-nitro-2,6-dibromopyridine-N-oxide **138** was reacted with **44** under the same reaction conditions to give 6-bromo-4-nitro-2,2'-bipyridine-1-oxide **140** as yellow needles. Its solid state structure was determined (Figure 16).

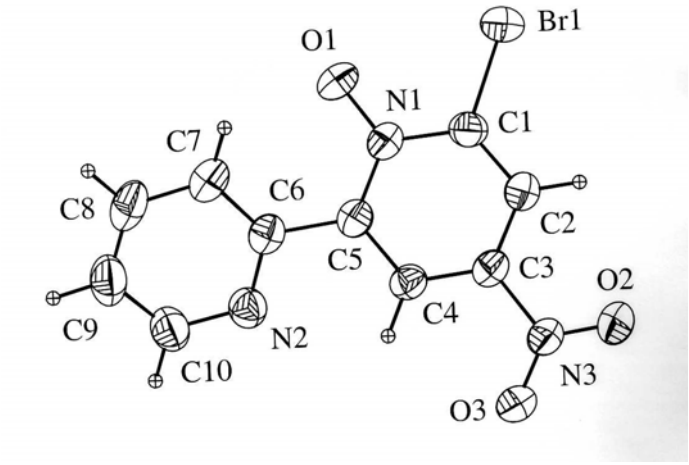


Figure 16

Compound **140** is not planar and the interplanar angle of the two pyridine rings is 32° (Figure 16). The reaction of **140** with **44** yielded **125** in 75% yield as a yellow microcrystalline solid. However, if **138** was reacted with 2 equiv. **44** under the same conditions, 4'-nitro-2,2':6',2"-terpyridine-1'-oxide **125** was obtained in 73% yield.

By using standard methods, 2,2':6',2"-terpyridine-1'-oxide **141** was oxidised with 1 equiv. *m*-CPBA in dichloromethane to give 2,2':6',2"-terpyridine-1,1'-dioxide **142** in 35% yield as colourless orthorhombic plates. The solid state structure of **142** was determined (Figure 17).

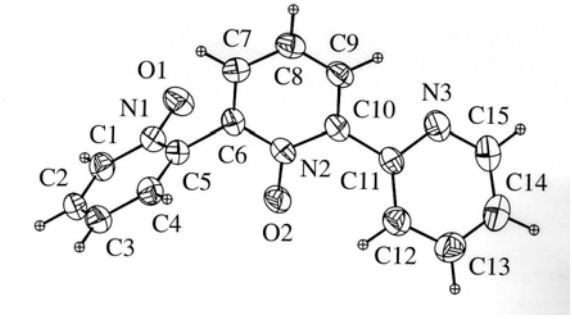
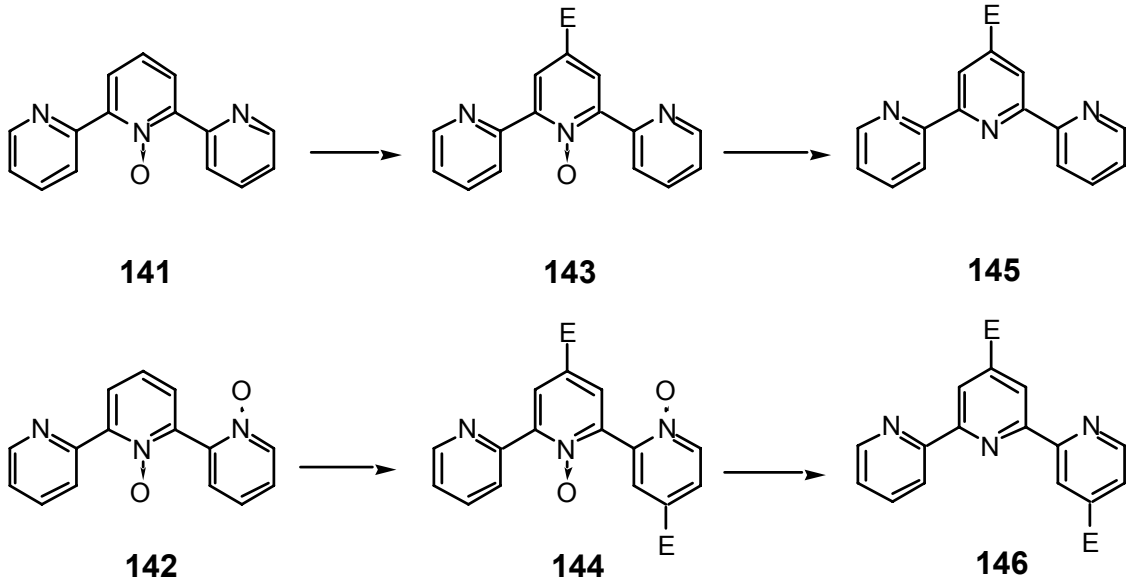


Figure 17

While 2,2':6',2"-terpyridine is almost a planar molecule, 2,2':6',2"-terpyridine-1,1'-dioxide is not planar. The two pyridine-N-oxide rings are almost orthogonal and show an interplanar angle of 87.66° while the interplanar angle between the central pyridine-N-oxide ring and the terminal pyridine ring is 38.47°. The interplanar angle between the two terminal pyridine rings is 70.99°.

By electrophilic reactions of the activated 2,2':6',2"-terpyridine-1,1'-dioxides **141** and **141**, the symmetrical and unsymmetrical tpy ligands may be obtained, respectively (Scheme 42) [172]. In addition, the novel tpy-oxides are potential ligands in reaction with metals. By deoxygenation of **143**-**144** the parent tpy ligands may be obtained.



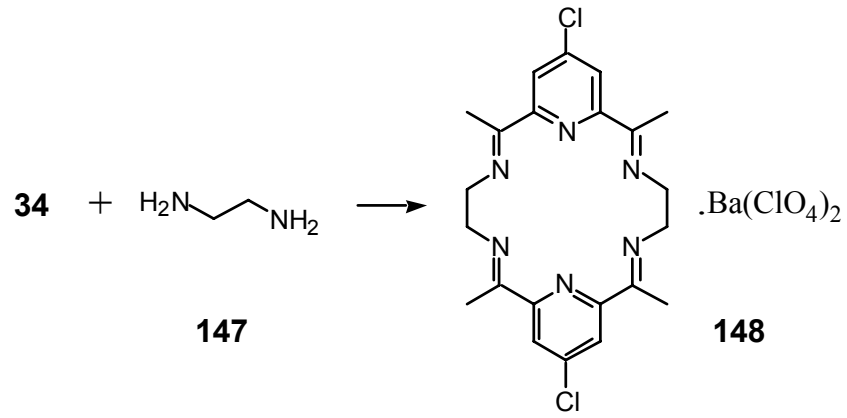
Scheme 42

4.2. Metal complexes

4.2.1. Synthesis of a triangular barium macrocyclic complex encapsulating perchlorate ions 148

Tetraimine Schiff-base macrocyclic compounds, derived by template reactions, from heterocyclic dicarbonyls "head" and diamines "lateral" have proved to be versatile ligands for both mononuclear and binuclear metal complexes [180]. One of the interesting reactions is the use of alkaline-earth metal ions Ca^{2+}, Sr^{2+} and Ba^{2+} as templates in the stepwise synthesis of macrocyclic Schiff-base ligands derived from the [2+2] condensation of 2,6-diacetylpyridine with diamines, such as 1,2-diaminoethane [181-182].

Reaction of 4-chloro-2,6-diacetylpyridine **34** with 1,2-diaminoethane **147** in the presence of Ba^{2+} in 2:2:1 molar proportions in refluxing methanol afforded complexes of the 18-membered [2+2] macrocycle **148** (Scheme 43) [139].



Scheme 43

In the solid state each barium atom is positioned on a centre of C_2 symmetry being bonded to six nitrogen atoms of the macrocycle **148** defining the equatorial hexagonal plane and four oxygen atoms of two encapsulated perchlorate groups (Figure 18). Additionally each barium atom is bonded to an oxygen atom of water positioned outside the triangle. The barium atom has a coordination number of

eleven. An uncoordinated perchlorate is also present in the solid state. The geometry of this triangular macrocycle is unique. These three macrocycles, kept together with two encapsulated perchlorate groups, form a triangular array (intersection angle of Ba-Ba-Ba is 60°).

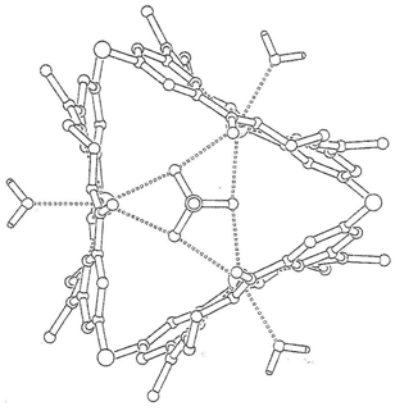
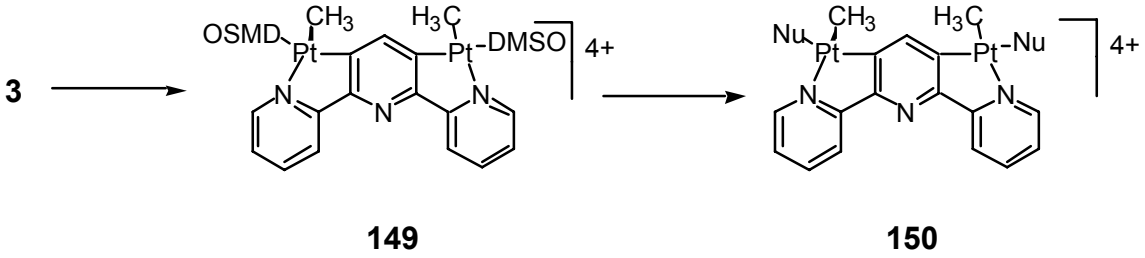


Figure 18

4.2.2. Metal complexes of Oligopyridines

Tpy is normally a terdentate ligand in reaction with metals to give octahedral complexes. In other words, all three nitrogen atoms bind to metal. In a few cases, one nitrogen atom remains unreacted [184-185]. An unusual tpy complex has been reported, in which nitrogen atoms of the terminal pyridine rings and C(3) of the central pyridine ring are bonded to two platinum metals [186] (Scheme 44). 2,2':6',2"-Terpyridine **3** was reacted with *cis*-[$Pt(CH_3)_2(DMSO)_2$] giving complex **149**, The DMSO ligand was exchanged by nucleophiles to give complexes of type **150**.



Scheme 44

Almost all transition metal ions were reacted with tpy ligands to form square planar (Pt(II) [187] and Ni(II)) [6] [188], octahedral (most metals), 5-coordinated (Co(II)) [189] and 7-coordinated (Mo) [190-191] complexes. We were interested in those metal ions, which could be used for electron and energy transfer (Fe, Co, Ru, Os).

Starting from different tpy and bpy ligands which had been previously synthesised in our laboratory, several metal complexes with iron(II) and ruthenium(II) have been prepared, characterised and their photochemical and electrochemical behaviours have been studied. Among others the first synthesis of a heteroleptic iron(II) complex (2 different tpy ligand) has to be emphasised. Iron(II) and ruthenium(II) complexes of 4'-nitro- and 4'-amino-2,2':6',2"-terpyridines have also been prepared. It should be mentioned that the nitro group is the strongest electron withdrawing group which has ever been attached to C(4') of 2,2':6',2"-terpyridine. The stronger the electron withdrawing group, the stronger is the luminescence [192]. While the iron(II) complex of 4'-azido-2,2':6',2"-terpyridine has been easily prepared, the azido group was reduced to an amine in the ruthenium(II) complex under the standard reaction conditions. We were interested in ruthenium(II) complexes of 4'-azido-2,2':6',2"-terpyridines due to their potential for thermal and photochemical reactions. It may be anchored to a surface for energy transfer. Ruthenium complexes of 4,4'-azo-bis(2,2':6',2"-terpyridine) **95** are also of interest since they can function as a switch in energy and electron transfer. A series of metal complexes of oligopyridines possessing carboxylate groups were prepared and anchored to the TiO_2-surfaces; and the energy transfer was investigated.

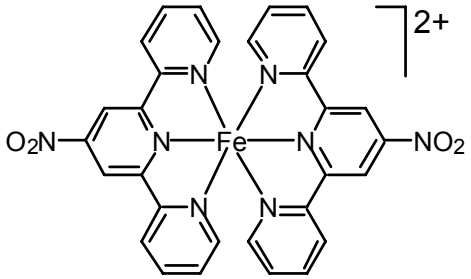
4.2.2.1. Iron(II) complexes

Iron(II) reacts readily with tpy ligands to give purple or blue complexes, depending on the electron-withdrawing or –donating substituent at C(4'). These complexes are stable in the solid state, but isomerise in solution. Fe(III) complexes, in contrast to Fe(II) complexes, are labile. This property is utilised in the purification of tpy ligands or to synthesise new ones [103]. Tpy ligand is normally reacted with Fe(II) salts to give complexes. The isolated and purified Fe(II) complexes are then, under basic conditions, oxidised with hydrogen peroxide in aqueous acetonitrile. By filtration the tpy ligands can be isolated and purified. Only the 6,6''-disubstituted tpy ligands react with iron(II) at elevated temperatures. 6,6''-Diphenyl-tpy ligands were prepared and their spin-spin-crossover was investigated [193].

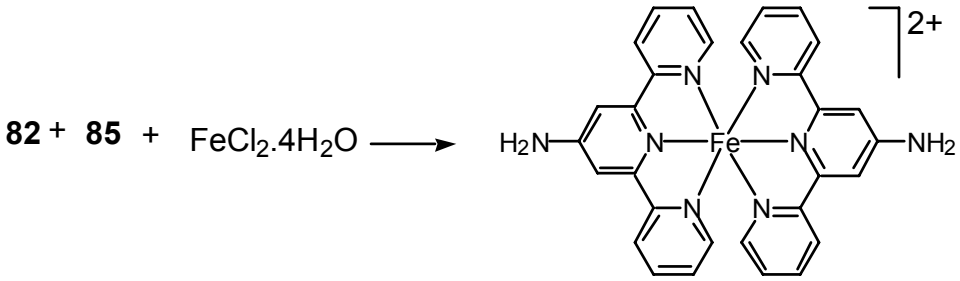
4.2.2.1.1. First example of a heteroleptic iron(II) complex 153 of 4'-amino-2,2':6',2''-terpyridine 85 and 4'-nitro-2,2':6',2''-terpyridine 82

While iron(II) complexes are formed in one step, normally the homoleptic complexes are isolated. However, we have first examined the formation of the homoleptic and heteroleptic Fe(II) complexes upon reaction of 4'-nitro-2,2':6',2''-terpyridine **82** and 4'-amino-2,2':6',2''-terpyridine **85** with Fe(II) salts [106]. All three possible complexes were formed (Scheme 45).

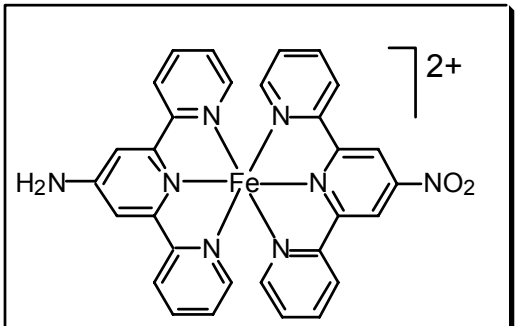
Due to the extreme difference in the polarities of the amine and the nitro groups, all three complexes were easily separated on silica gel. The heteroleptic complex **153** was isolated in 29% yield.



151



152



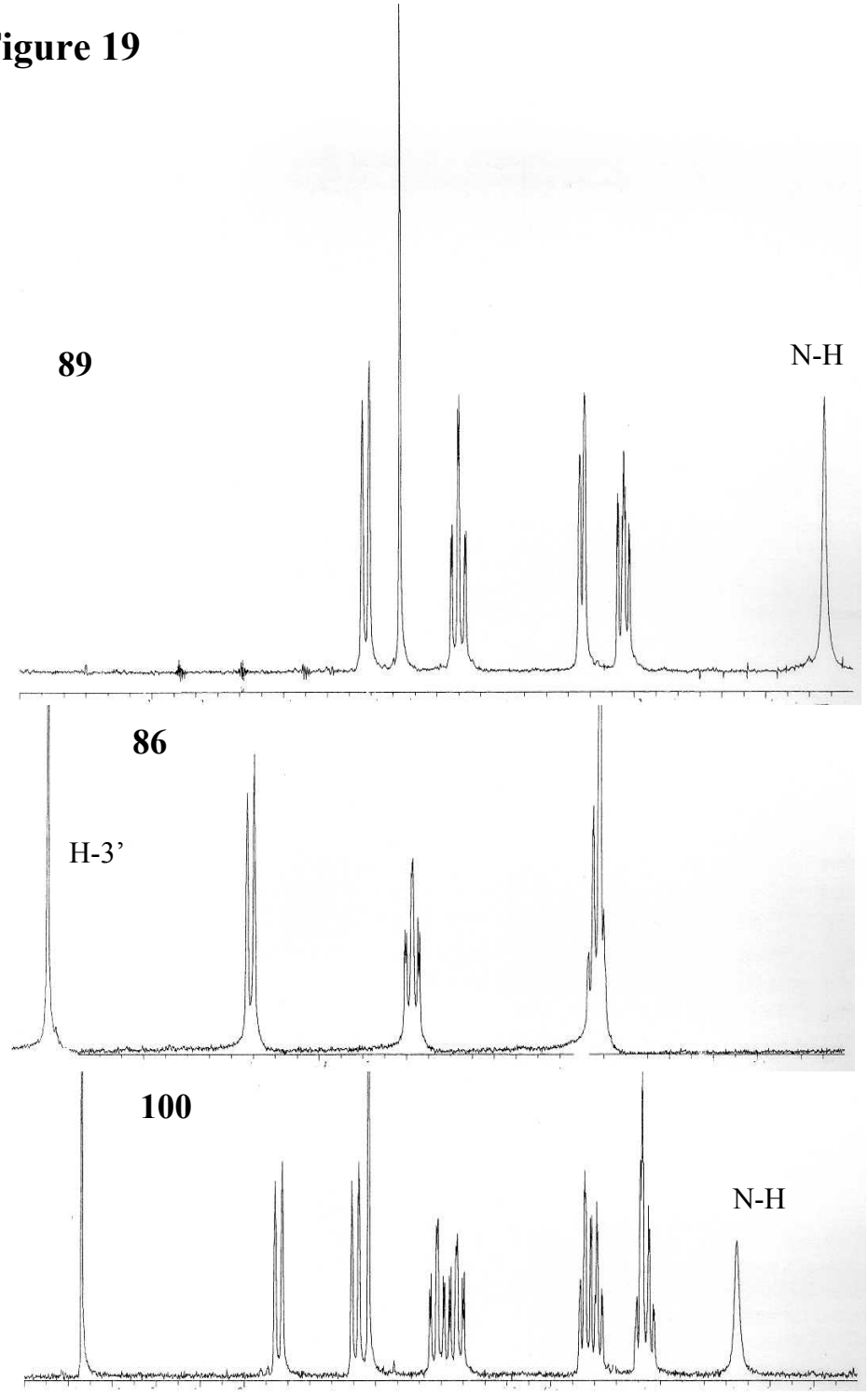
153

Scheme 45

The ^{1}H NMR spectrum of the heteroleptic iron(II) complex of **153** shows significant shifts of some signals when compared to the homoleptic complexes **151** and **152** (Figure 19). The hydrogen $H^{3'}$ of the aminoterpyridine moiety **152** was shifted to low field and observed at δ =8.23 ($\Delta\delta$ = 0.22) while

hydrogen $H^{3'}$ of the nitroterpyridine moiety **151** was shifted to high field and observed at $\delta = 9.54$ ($\Delta\delta = 0.10$). More dramatically, the amino hydrogen atoms were shifted to low field at $\delta = 6.55$ ($\Delta\delta = 0.42$). All other signals belonging to the aminoterpyridine moiety were shifted to low field while the hydrogen atoms of the nitroterpyridine moiety were shifted to high field.

Figure 19



The electronic spectra of all three Fe(II) complexes are shown in Figure 19. The MLCT absorption of **153** was shifted about 17 nm to lower energy and was observed at 623 nm. The MLCT absorption of **151** was observed at 605 nm (Figure 20).

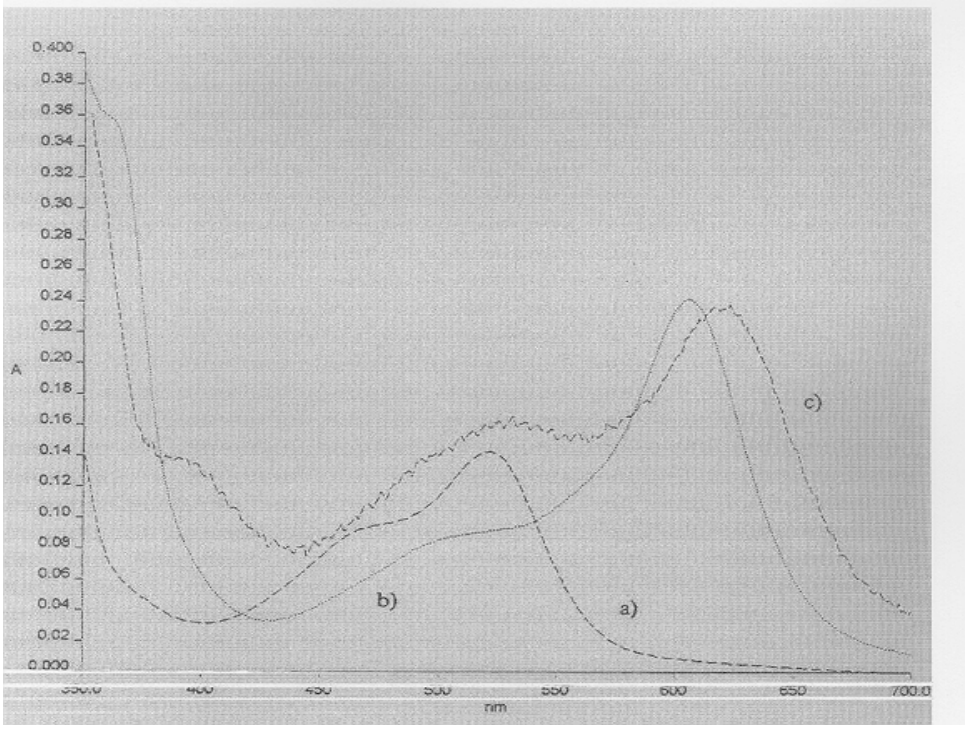
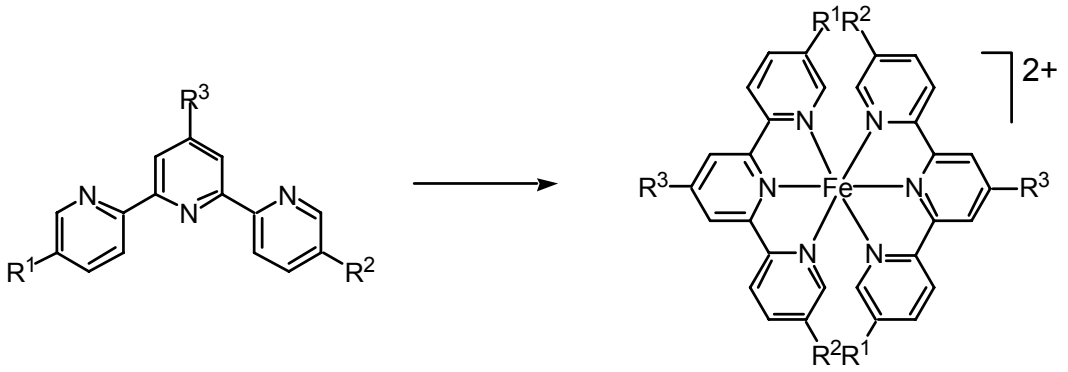


Figure 20

4.2.2.1.2. Iron(II) complex of 4'-nitro-2,2':6',2''-terpyridine 82-84 and 4'-amino-2,2':6',2''-terpyridines 85-87

The homoleptic complexes of 4'-amino-2,2':6',2"-terpyridines **152**, **156-157** and 4'-nitro-2,2':6',2"-terpyridines **151, 154-155** were readily synthesised and their properties were investigated (Scheme 46).

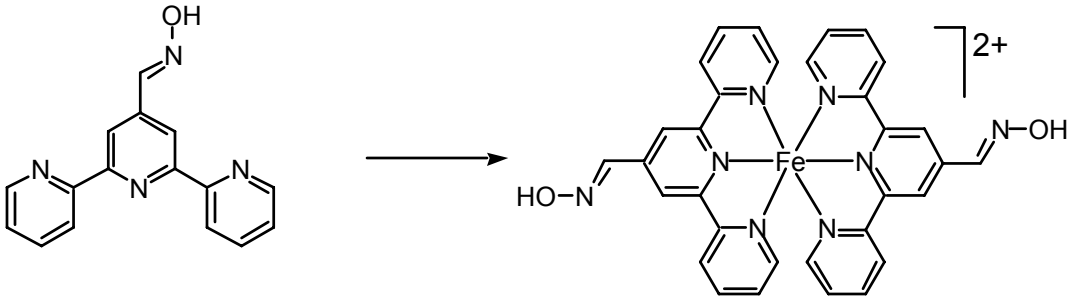


R^1= H, R^2= H, R^3= NO_2 **151**
R^1= Me, R^2= Me, R^3= NO_2 **154**
R^1= H, R^2= Me, R^3= NO_2 **155**
R^1= H, R^2= H, R^3= NH_2 **152**
R^1= Me, R^2= Me, R^3= NH_2 **156**
R^1= H, R^2= Me, R^3= NH_2 **157**

Scheme 46

4.2.2.1.3. Iron(II) complex of 4'-carbaldoxime-2,2':6',2''-terpyridine

The homoleptic Fe(II) complexes of 4'-carbaldehyde oxime-2,2':6',2''-terpyridines **72** was readily synthesised upon reaction of **72** with $FeCl_2.4H_2O$ in ethanol. This complex was precipitated as the hexafluorophosphate salt, and its properties were investigated (Scheme 47).



72 **158**

Scheme 47

The solid state structure of this complex was determined (Figure 21).

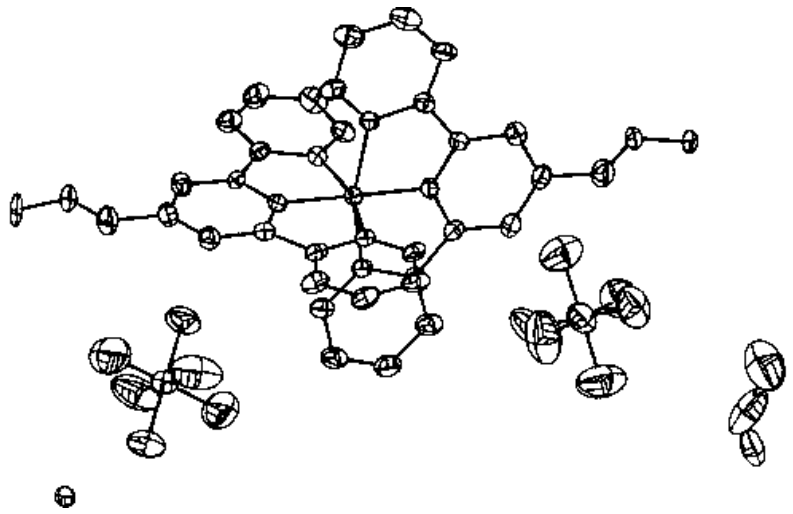
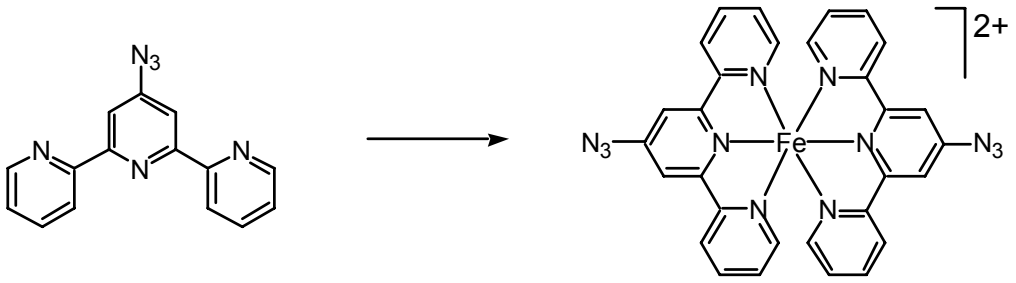


Figure 21

Figure 21 4.2.2.1.4. Iron(II) complex of 4'-azido-2,2':6',2''-terpyridines

4'-Azido-2,2':6',2"-terpyridines react readily with iron(II) salts at room temperature to yield purple metal complexes (Scheme 48). 4'-Azidoterpyridine (N_3-tpy) **90** was reacted with excess $FeCl_2.4H_2O$ in ethanol at room temperature to give the purple complex **149**. The electronic spectrum of the complexes in acetonitrile solution exhibits a characteristic MLCT transition at 564 nm. In the IR spectrum of **149** a strong signal due to the azide group was observed at 2121 cm^{-1}. In the ^1H NMR spectrum the shifting of the signal due to $H^{3'}$ is of interest. This was observed as a singlet at δ 8.57, comparable with that in the iron(II) complex of 4'-amino-2,2':6',2"-terpyridine. Once again, in Maldi-TOF mass spectrum of this complex parent ion peak was not observed but a strong peak at m/z 576 and a less intense one at m/z 548 corresponding to the nitrene ($M-N_2$) and bisnitrene ($M-2N_2$), respectively, were present. The elemental analysis of the iron(II) complex **149** is consistent with the proposed structure.

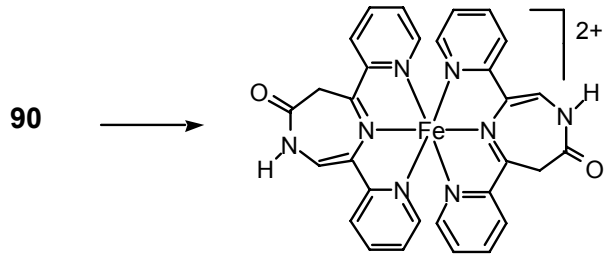


90 **159**

Scheme 48

4.2.2.1.5. Iron(II) complex of diazepinones

The homoleptic Fe(II) complexes of the novel ligand **106** was readily synthesised upon reaction of **106** with $FeCl_2.4H_2O$ in ethanol. The complex was precipitated as the hexafluorophosphate salt, and its properties were investigated (Scheme 49). Interestingly, this complex is green in acetonitrile solution.



160

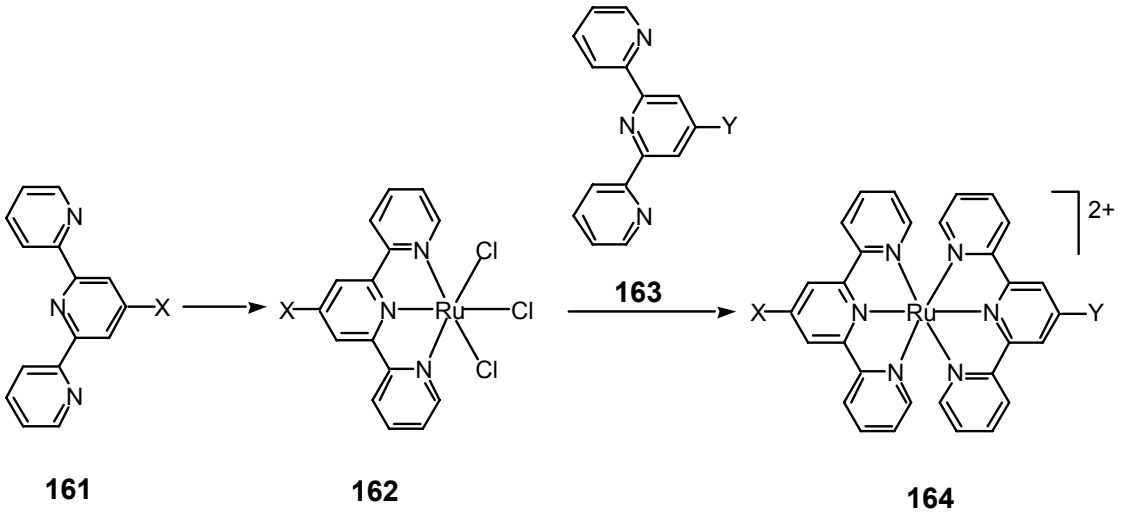
Scheme 49

4.2.2.2. Co(II) complexes of 2,2':6',2''-terpyridines

The paramagnetic Co(II) complexes are also easily formed at room temperature, Co(II) complexes, however, can be easily oxidised by bromine to the diamagnetic Co(III) complexes. The hydrogen atoms in H NMR are then shifted to low field, some even to δ 60-70. Therefore, Co(III) complexes function as "shift reagents" to assign hydrogen atoms of tpy ligands.

4.2.2.3. Ru(II) complexes of 2,2':6',2''-terpyridines

The kinetically inert ruthenium(II) complexes are perhaps the best investigated ones. On contrary to iron, Ru(II) complexes may be formed in two steps, an advantage. The homoleptic complex is formed by the reaction of $RuCl_3$ with tpy ligand in alcohol just by heating. This reaction was pursued in two steps to increase the yield and to prepare the heteroleptic complexes (Scheme 50).



161 **162** **164**

Scheme 50

First $RuCl_3$ was reacted with one mole tpy **161** to form the insoluble dark coloured complex **162**, which is normally isolated [194]. The solid state structures of such compounds were determined by X-ray analyses [195]. In the next step **162** reacts with another tpy ligand **163** in alcohol in the presence of a reducing agent, N-ethyl morpholine [106]. X and Y may or may not be identical.

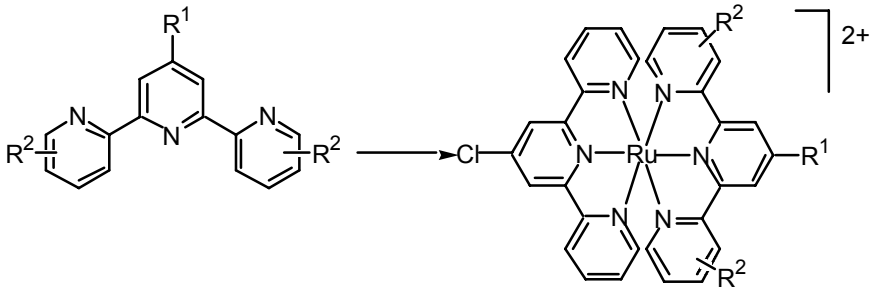
The formation of homoleptic and heteroleptic Ru(II) complexes was also reported in a microwave oven in a high boiling solvent, usually, ethylene glycol [196] and nowadays this belongs to routine methods, due to the short reaction times and high yields. These methods lead, however, to some undesired side-products, especially, when some groups are present, which are sensitive to reduction or

temperature. It was reported, e.g. that the azido group was reduced to an amine [155] or nitro to hydroxylamine [106] under the reaction conditions. To prevent these undesired side-reactions, Ru(III) salts were reduced to Ru(II) salts just in the first step. For this purpose, $RuCl_2PR_3$ [197], $RuCl_2(DMSO)_4$ [198], $RuCl_2(CO)_4$ [199] or Ru_2(*p*-cymene)Cl_2 [200] were prepared. These Ru(II) salts were reacted with tpy ligands to give the homo- and heteroleptic complexes. Using this modified method, Ru(II) complexes of 4'-azido and 4'-nitro complexes were prepared.

Ruthenium(II) normally gives octahedral complexes in reaction with ligands, e.g. pyridine or bpy derivatives were also prepared [200-203] and their solid state structures reported [203]. Also Ru(IV) and Ru(VI) complexes have been prepared which were used in oxidation reactions [204-205].

4.2.2.3.1. Ruthenium(II) complexes of substituted 4'-ethoxy- and 4'-hydroxy-2,2':6',2''-terpyridines 36-39

Substituents such as methyl in pyridine ligands are very reactive and they can be functionalised in further reactions to aldehydes, carboxylates and bromomethyl compounds among others (Scheme 51).



R^1= OEt, R^2= 6,6''-Me_2	**35**	R^1= OEt, R^2= 6,6''-Me_2	**165**
R^2= 4,4''-(p-tolyl)$_2$		R^2= 4,4''-(p-tolyl)$_2$	
R^1= OEt, R^2= 6,6''-Me_2	**36**	R^1= OEt, R^2= 6,6''-Me_2	**166**
R^1= OEt, R^2= 5,5''-Me_2	**37**	R^1= OEt, R^2= 5,5''-Me_2	**167**
R^1= OH, R^2= 5,5''-Me_2	**38**	R^1= OH, R^2= 5,5''-Me_2	**168**

Scheme 51

However, our work was concerned with complexes, which are of interest in energy and electron transfer. We have prepared ruthenium(II) complexes and compared them to the unsubstituted ones. In one case the structure of **167** was determined in solid state (Figure 22) [104]. This is in accord with the proposed and known structures.

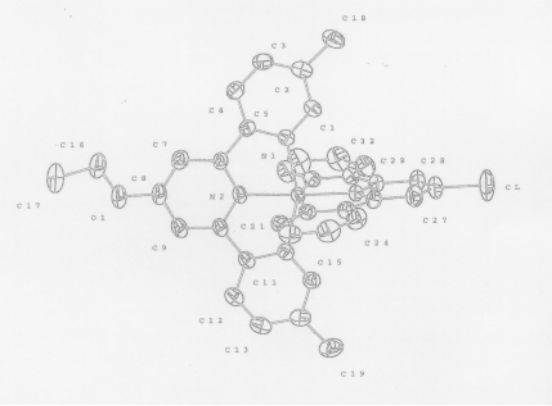
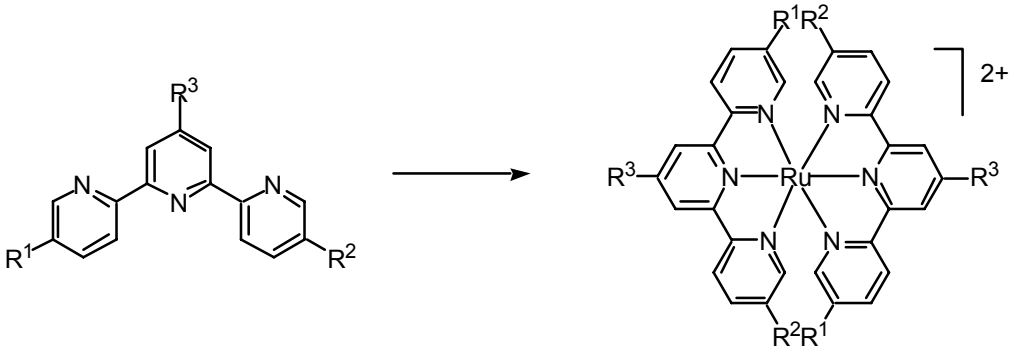


Figure 22

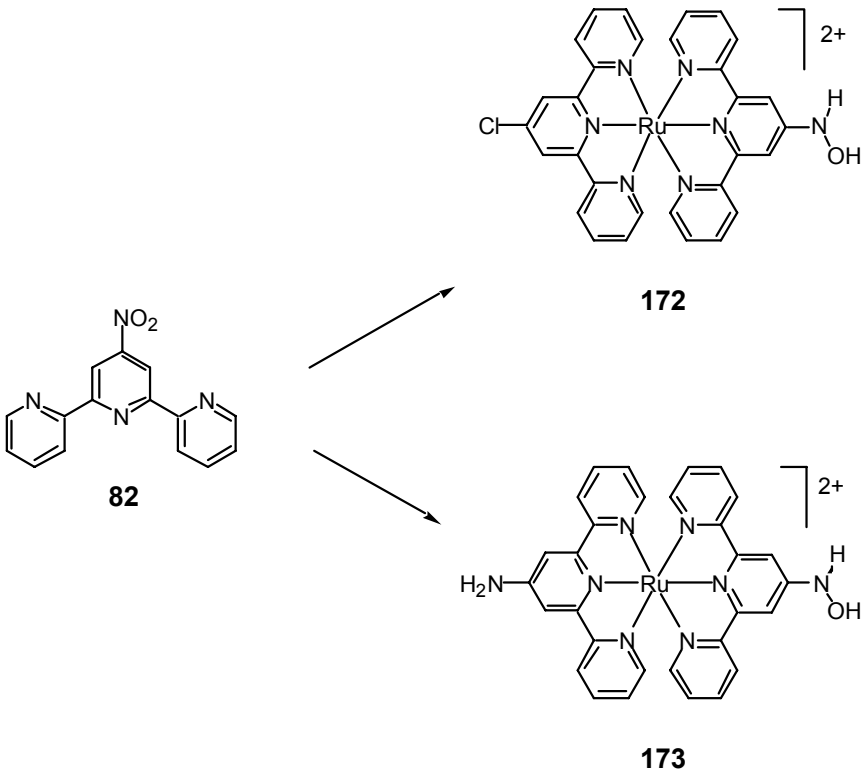
4.2.2.3.2. Ruthenium(II) complexes of 4'-nitro-2,2':6',2''-terpyridines 82-84

All three 4'-nitro-2,2':6',2"-terpyridines **82-84** have been reacted with ruthenium(II) to give the homoleptic complexes **169-171** (Scheme 52).



R^1 = H, R^2 = H, R^3 = NO_2 **169**
R^1 = Me, R^2 = Me, R^3 = NO_2 **170**
R^1 = H, R^2 = Me, R^3 = NO_2 **171**

Scheme 52

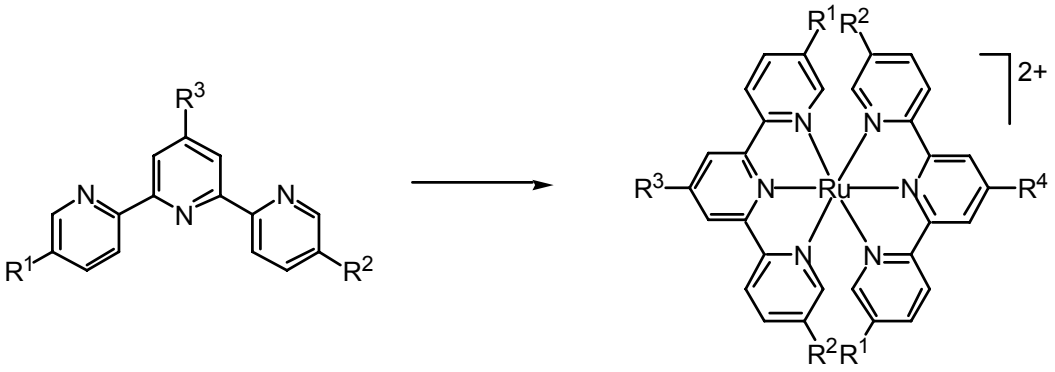


Scheme 53

The nitro group, however, was reduced to hydroxyl amine under the reaction conditions to give ruthenium(II) complexes **172**-**173** (Scheme 53).

4.2.2.3.3. Ruthenium(II) complexes of 4'-amino-2,2':6',2''-terpyridines and of a push-pull system

The 4'-amino-2,2':6',2''-terpyridines **85-87** have been reacted with ruthenium(II) to give the homoleptic complexes **174-176** (Scheme 54) [106] [154]. A donor-acceptor (push-pull) complex **177** was also prepared. All these complexes were investigated in respect of their photochemical and electrochemical properties.

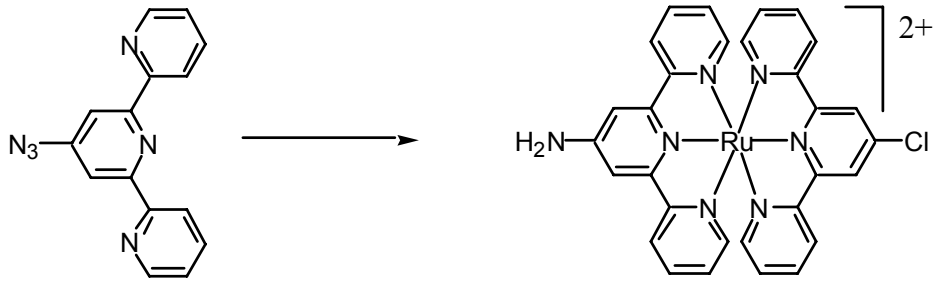


R^1= H, R^2= H, R^3=R^4= NH_2 **174**
R^1= Me, R^2= Me, ^{3}=R^4= NH_2 **175**
R^1= H, R^2= Me, ^{3}=R^4= NH_2 **176**
R^1= H, R^2= H, R^3= NO_2 ,R^4= NH_2 **177**

Scheme 54

4.2.2.3.4. Ruthenium(II) complexes of 4'-azido-2,2':6',2''-terpyridines

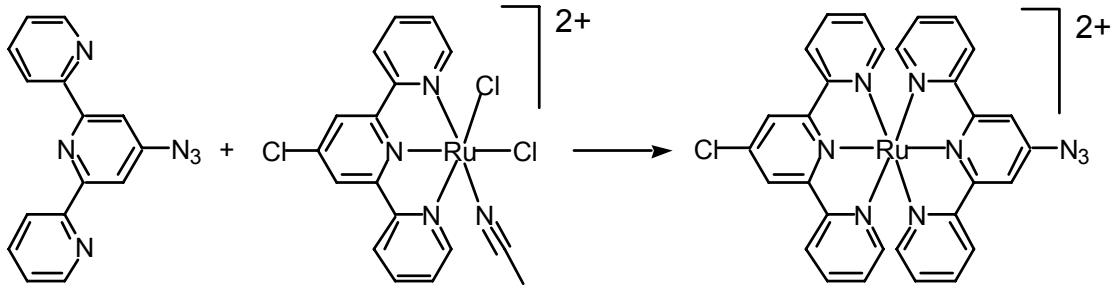
Using standard methods, Ru(II) complexes were prepared. [(4'-Chloro-2,2':6',2"-terpyridine)$RuCl_3$] was reacted with 1 mole equivalent **90** at reflux in ethanol in the presence of N-ethylmorpholine, to obtain the ruthenium(II) complex containing azide groups. Under these reaction conditions the azide group, however, was reduced to an amine and we obtained the dark red amino complex **178** (Scheme 55) [155]. This complex was independently prepared upon reaction of [(4'-chloro-2,2':6',2"-terpyridine)$RuCl_3$] with 4'-amino-2,2':6',2"-terpyridine **85**, which showed exactly the same properties.



90 **178**

Scheme 55

Just currently we have managed to prepare the desired ruthenium(II) complex **180**. Ru_2(*p*-cymene)Cl_2 was reacted with tpy ligand **126**, and the dark red complex **179** was obtained [172]. When **90** was reacted with ruthenium(II) salt **179** in methanol, complex **180** was isolated (Scheme 56). In the IR spectra of **180** the ν(N_3) absorption was observed at 2110 cm^{-1}.



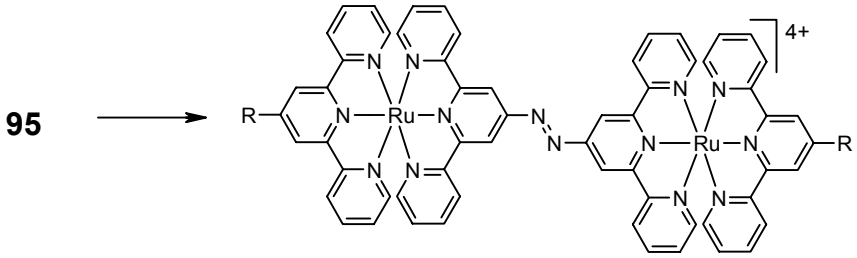
90 **179** **180**

Scheme 56

An interest in 4'-azido-2,2':6',2''-terpyridine has arisen due to its possible application in medicine. Lowe *et al.* have prepared a series of Pt(II) complexes with linear linkers of varying length. They have been designed to bis-intercalate into two DNA duplexes in close proximity, the azido groups allowing the sites of intercalation to be photoaffinity labeled.

4.2.2.3.5. Ruthenium(II) complexes of 4,4'-azo-bis(2,2':6',2''-terpyridine)

The two ruthenium complexes of this ligand have been prepared by standard methods, to exemplify the reactivity and properties. Compound **95** was reacted with 4'-hydroxy-2,2':6',2''-terpyridine-ruthenium trichloride [Ru(HO-tpy)Cl_3] and 4'-chloro-2,2':6',2''-terpyridine-ruthenium trichloride [Ru(Cl-tpy)Cl_3] in methanol to obtain the two complexes **181** and **182**, respectively (Scheme 57) [169].



Scheme 57

We assume that both complexes **181** and **182** exist in the *trans* form due to the steric hinderance. While ruthenium complexes of tpy ligands are usually red to orange, and the metal-to-ligand charge transfer (MLCT) band is observed in the range of 460-550 nm, in the electronic spectra of the complexes **181** and **182**, the MLCT absorption was shifted to lower energy and was observed at 633 nm and 578 nm, respectively. The π-π absorption of the azo group was observed in both complexes at 470 nm (Figure 23). These are the first examples of blue ruthenium(II) complexes containing tpy ligands.

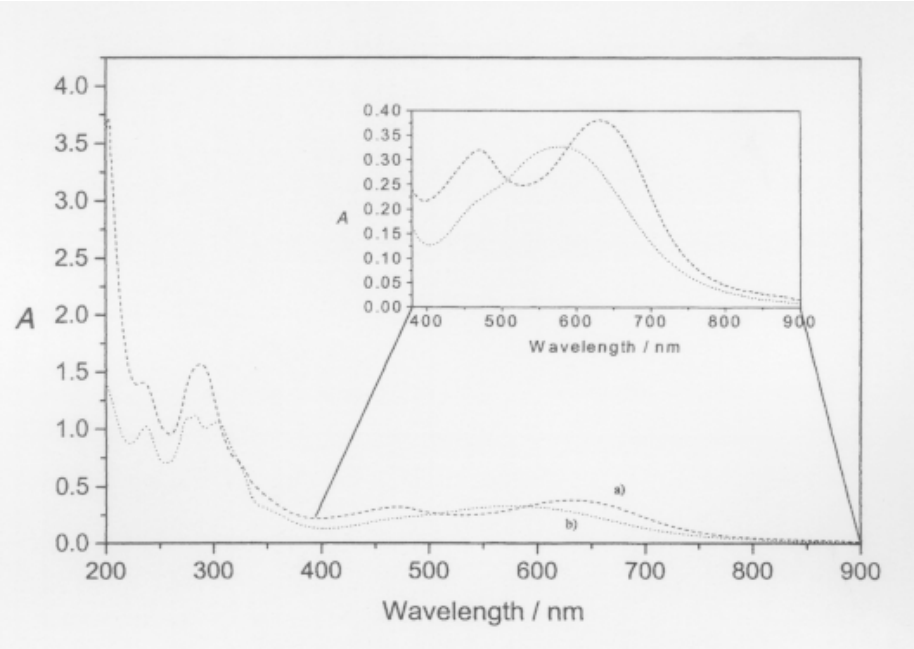
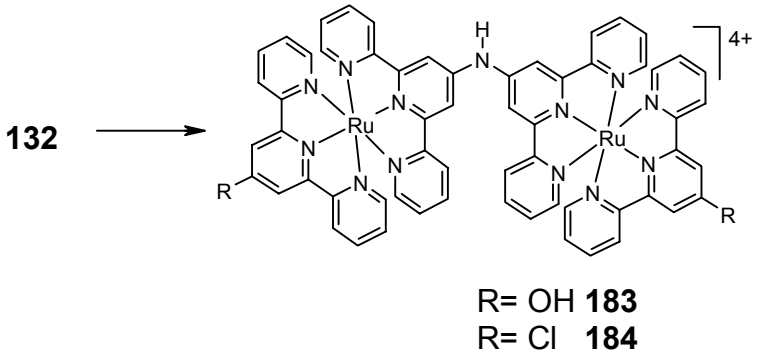


Figure 23

In this series novel photoisomerisation of rhodium(II) binuclear complexes of an azobenzene-bridged bis(terpyridine) ligand was studied and showed strong effect of counterion, solvent and the induction of redox potential shift [206].

4.2.2.3.6. Ruthenium(II) complexes of 4',4'-bis(2,2':6',2''-terpyridyl)amine

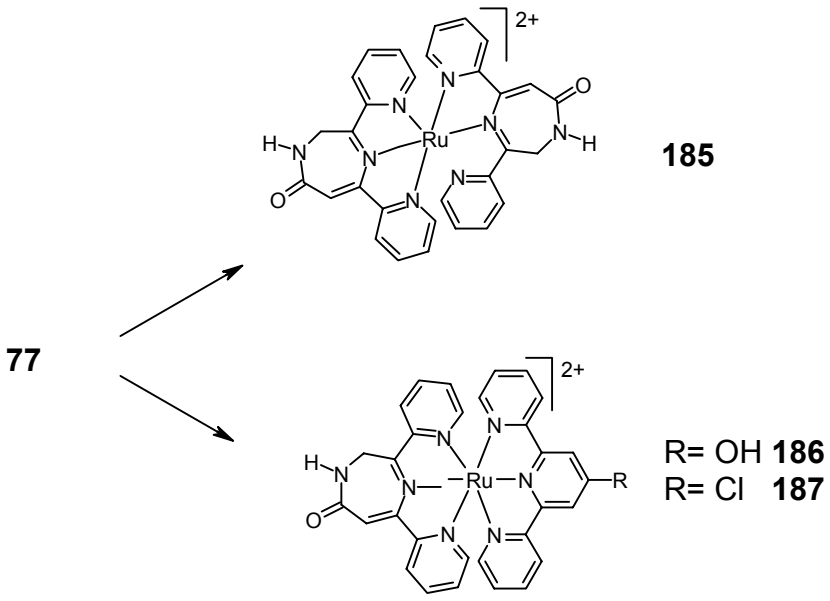
Two ruthenium complexes of ligand **132** have been prepared by standard methods upon reaction with 4'-hydroxy-2,2':6',2"-terpyridine-ruthenium trichloride [Ru(HO-tpy)Cl_3] and 4'-chloro-2,2':6',2"-terpyridine-ruthenium trichloride [Ru(Cl-tpy)Cl_3] in methanol to obtain the two complexes **183** and **184**, respectively (Scheme 58) [207]. Their photochemical and electrochemical properties are comparable with the ruthenium(II) complexes of ether-bridged ligand **131**. Compared with the ether-bridged tpy ligands, it may be used as a core for metallodendrimers.



Scheme 58

4.2.2.3.7. Ruthenium(II) complexes of Diazepinone

Using standard methods, homo- and heteroleptic Ru(II) complexes of the novel ligand **77** were prepared (Scheme 59).



Scheme 59

4.2.2.4. Osmium(II) complexes of oligopyridines

Osmium complexes have received special attention, (especially in combination with Ru(II)) in photochemical investigations [31]. These complexes are usually prepared in two steps, similar to Ru(II) complexes, however, with lower yields. A series of Ru(II)/Os(II) complexes of tpy/bpy ligands were prepared and investigated. For more detailed information, refer to the excellent review articles [29-30]. A mixed complex of Ru(II)/Os(II) was prepared and its structure in the solid state determined [208-209].

4.2.2.5. Platinum(II) complexes of oligopyridines

Pt(II) complexes are best prepared by the method developed by Lowe [210]. The kinetic stability of such complexes was also investigated [211]. The application of cisplatin in medicine led to the preparation of a series of Pt(II) complexes of tpy ligands. Their interactions with biological system have been investigated.

4.2.2.6. Topological Isomers

Inspired by nature and driven by applications in materials sciences, supramolecular chemistry has received special interest in recent years [212-214]. Starting from the early works of purely organic compounds, formed by strong bonds, recent research has been directed at thermodynamically controlled self-assembly using weak interactions, hadrogen bonds or Van der Waals interactions. Transition metal complexes are kinetically labile but thermodynamically stable coordinated bonds; and serve as “natural pool” into large, highly charged, complex structures.

Three principal strategies have been utilised to achieve these approaches:

a) A transition metal salt is mixed with a linker ligand and allowed to crystallise [215] [216]. By this method, large, complex crystalline arrays can be formed. The structure of complexes depends on

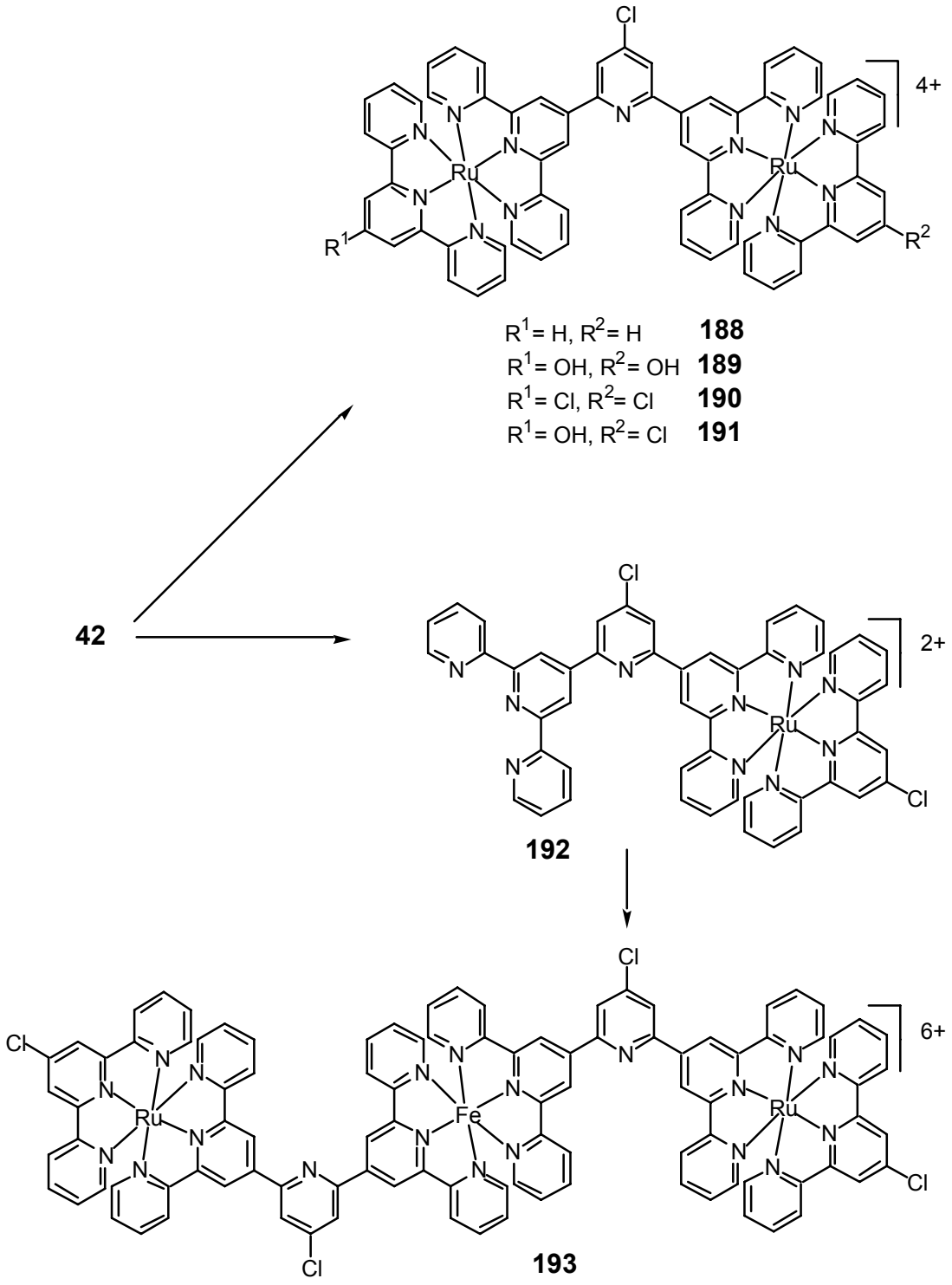
the valence geometry of the metal, the shape of the linking ligand, the counterion and solubility. This kind of crystal engineering may lead to oligomeric or polymeric structures. The disadvantage of this method is the difficulty in prediction of the final structures.

b) This method involves the synthesis of polybidentate, or in some cases, polyterdentate ligands which may bind several metals in sequence. Such ligands have been proved to form helicates and grids [217-218]. In the same manner, bidentate ligands supported by spacers give macrocyclic polyhedra [219-223]. The shape and size of the macrocycles is controlled by the denticity of the ligands, the spacer components and the coordination properties of metals.

c) This method consists of the number of geometry of the metal coordination sites combined with a special linker ligand geometry and denticity to obtain supramolecular structures of a specific size and topology. This method developed by Fujita [224-225] and Stang [226-227] was successfully proved to predict the structures of the formed supramolecules. The yield is normally quantitative and reactions are thermodynamically controlled.

4.2.2.6.1. Metal(II) complexes of 2,6-[bis-(2,2':6',2''-terpyridin-4'-yl)-4-chloropyridine

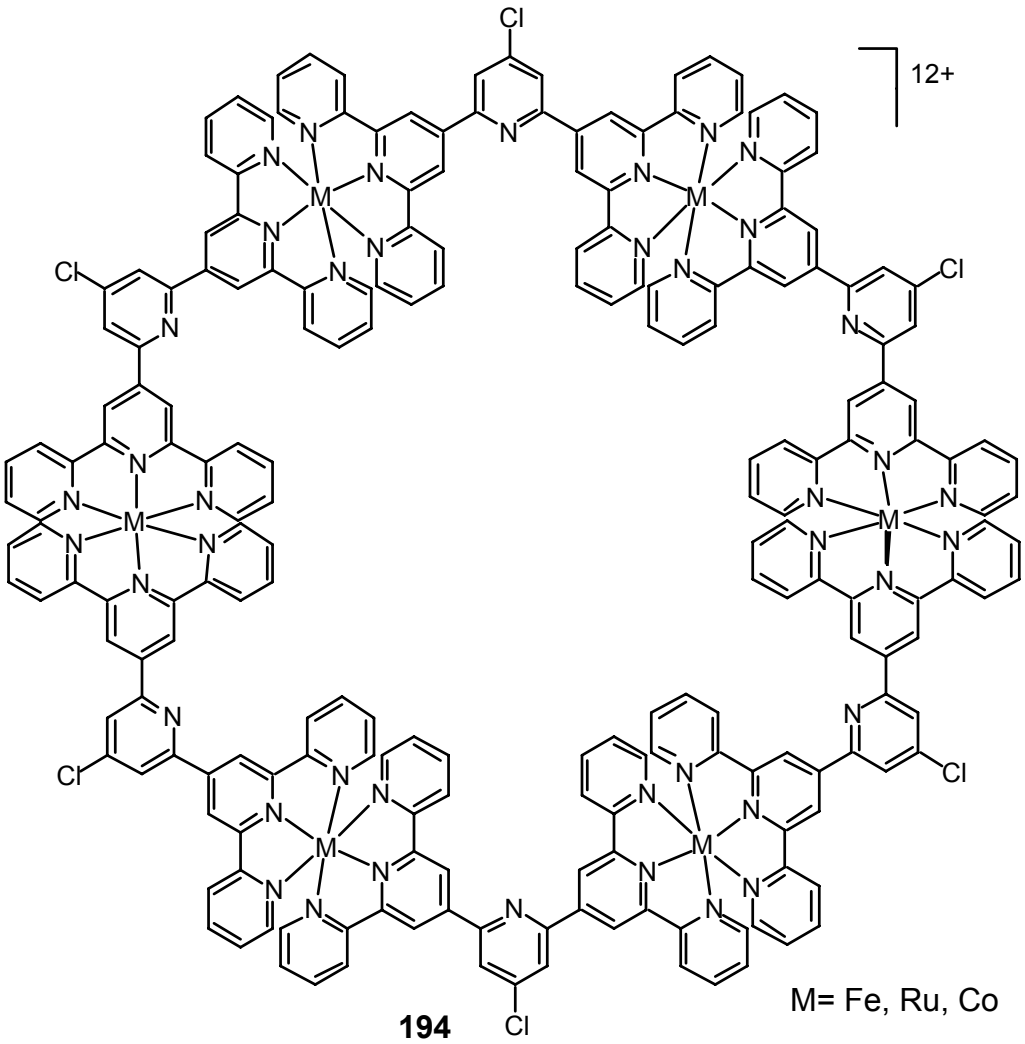
We have been interested in metal complexes, especially in the cyclic ones. For this purpose, tpy ligand **42** with predetermined angles was synthesised. We have prepared the homoleptic dinuclear ruthenium(II) complexes **188**-**190** and the heteroleptic one **191** in good yields (Scheme 60). Compound **42** was reacted to ruthenium(II) complex **192** which was then reacted in further reaction to the trinuclear complex **193** [140].


Cl
4+
Ru
Ru
N
R1
R2
R1= H, R2= H 188
R1= OH, R2= OH 189
R1= Cl, R2= Cl 190
R1= OH, R2= Cl 191
42
2+
192
6+
Fe
193

Scheme 60

In the electronic spectrum of the trinuclear complex **193** in acetonitrile, in addition to the signals in UV region, the metal-to-ligand charge transfer (MLCT) bonds of both metals were observed at 490 nm and at 578 nm due to ruthenium and iron, respectively.

Due to the angle of 60° between both terpyridine units, ligand **42** was originally prepared for the synthesis of a cyclic metal complex **194** (Scheme 61).



194

Scheme 61

Our evidence of the formation of such cyclic metal complexes in solution is their solubility, mass spectrum, and NMR spectroscopic properties. The compounds of type 194 are soluble in acetone and acetonitrile. The higher the charge is, e.g. in polymers, the less soluble they are. The proposed structure could not be confirmed in the solid state because suitable crystal could not be grown. A similar cyclic complex, also not determined in solid state, however, was recently reported [228].

4.2.2.7. Material Sciences

Photooxidation is an interesting part of oligopyridine chemistry. Metal complexes of oligopyrdines have found wide applications in electron and energy transfer. While the heteronuclear complexes, normally Ru(II) and Os(II), has been intensively investigated, some of them, specially, the Ru(II) complexes have been applied to transfer energy. Tpy ligands were attached as photosentisiser [229] to TiO_2-surface [230]; and nanocrystalline materials [70] were prepared. Ag(I) complexes [231] as well as trinuclear [232] or hexanuclear [233] complexes were also investigated.

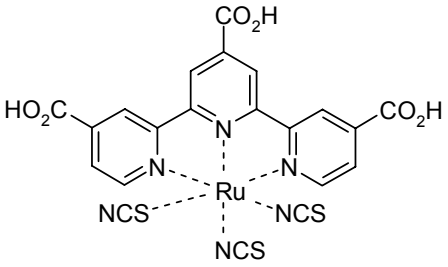
For this reason, metal complexes of those tpy ligands with functional groups to anchor to surfaces were synthesised. Only a few functional groups may play this role. There exist three types of anchoring: i) oxygen containing fuctional groups (carboxylic, phosphonic and catechol groups) linked to TiO_2-surface; ii) oxygen functionalised groups attached to a silica-titania-surface; iii) thiol groups which are usually linked to gold surface. While the gold- and silica-surface chemistry do not play so an important role, maybe due to the difficulty of ligand synthesis, energy transfer of Ru(II) complex on TiO_2-surface is widely investigated. In almost all cases, at least one functional group is attached to C(4') of tpy ligands.

Ruthenium polypyridine complexes are well established as photosensitisers for use in photovoltaic cells based on nanocrystalline TiO_2 films [234-247]. The widely used and most efficient heterogeneous charge transfer sensitiser in the nanocrystalline TiO_2 solar cell is the *cis*-dithiocyanato-bis(2,2'-

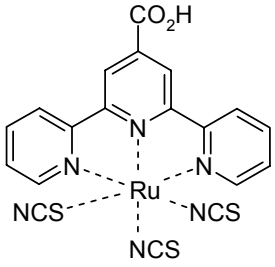
bipyridyl-4,4'-dicarboxylate) ruthenium(II) complex. Using this dye as a charge transfer sensitiser, incident photon-to-current conversion efficiencies (IPCE) of 80 to 85% have been obtained [242]. The electron injection rates of this complex have been measured in different laboratories and were found to occur in the femtosecond time scale [243]. However, the main drawback of this sensitiser is the lack of absorption in the red region of the visible spectrum, a factor which needs to be addressed. The optimal sensitiser for the dye sensitised solar cell should be panchromatic, i.e. absorb visible light of all colours. Ideally, all photons below a threshold wavelength of about 920 nm should be harvested and converted to electric current [244].

Geometrical isomerisation (*cis*-to-*trans*) is another interesting and exciting approach for tuning the spectral properties of metal complexes. The absorption spectral data have been reported for several *trans*-ruthenium-polypyridine complexes whose lowest energy MLCT transitions are significantly red shifted compared to their analogous *cis*- complexes [245]. Nevertheless, a drawback of the use of the *trans* complexes is their thermal and photoinduced isomerisation back to the *cis* configuration [246].

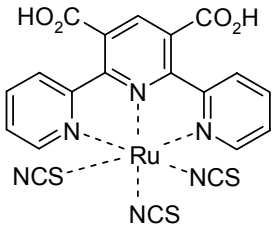
The most used functional group is a carboxylic group, due to its easy accessibility. This group can be either prepared by oxidation of methyl groups or by coupling reactions. The most efficient compound was found to be the Ru(II) complex of tpy-4,4',4"-$(CO_2)_3$ which showed a current of ca. 20 mA cm^{-2}. However, there was a disadvantage of synthesis difficulties. Some carboxylic derivatives of other oligopyridine ligands were also prepared and their photochemical and physical properties were investigated. We have also been involved in this field and prepared Ru(II) complexes of a series of oligopyridines and measured their activities (Table 2).



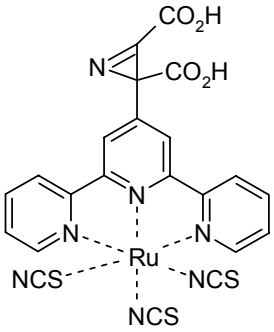
195 $\lambda = 620$ nm
Current = 20.5



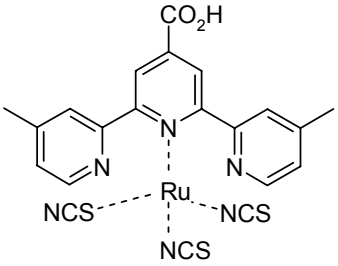
196 $\lambda = 590$ nm
Current = 12



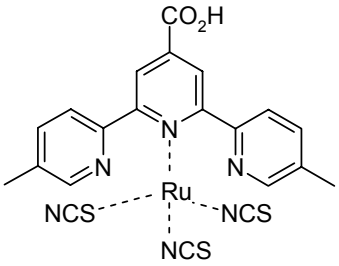
197 $\lambda = 570$ nm
Current = 11



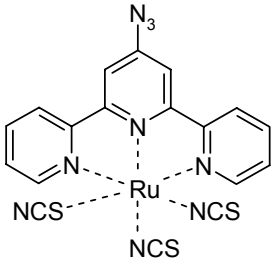
198 $\lambda = 508$ nm
Current = 8



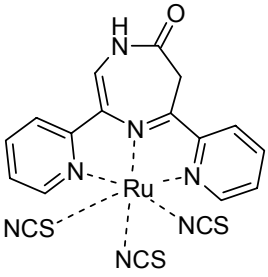
199 $\lambda = 585$ nm
Current = 12



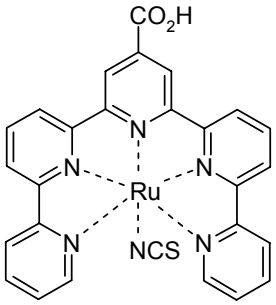
200 $\lambda = 580$ nm
Current = 12



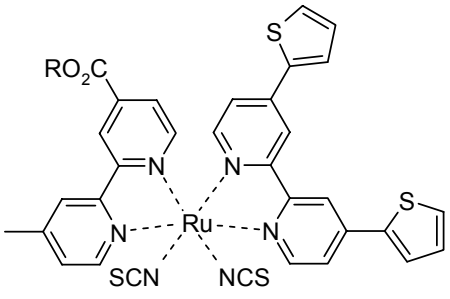
201 not anchoring



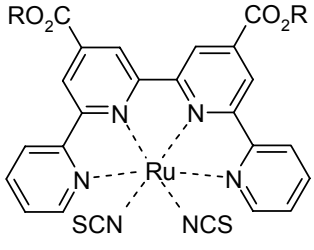
202 $\lambda = 630$ nm
not anchoring



203 under investigation



204 under investigation

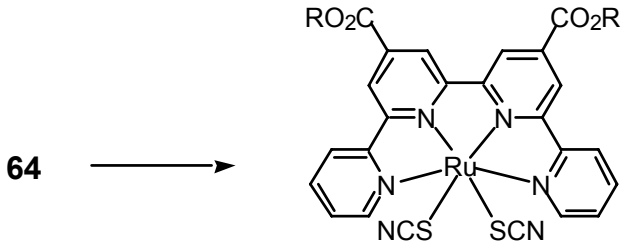


205 $\lambda = 610$ nm
Current = 18

Table 2

Ruthenium complexes of tpy-4'-carboxylic acid **196** and tpy-3',5'-$(CO_2H)_2$ **197** have shown a current of ca. 12 $mAcm^{-2}$, while the 2*H*-azirine-tpy **198** showed even less current (8 mA cm^{-2}). Insertion of two methyl groups at C(4) **199** or at C(5) **200** does not specially affect the efficiency of the dyes. Dyes based on azido-tpy **201** and diazepinone **202** were not efficiently grafted to TiO_2 surfaces. It should be mentioned, however, that the MLCT absorption is at 630 nm. This ligand is an attractive candidate due to its light absorption, if it might be grafted to the surface via an appreciate functional group. The properties of dyes based on quinquepyridine **203** and bpy-4,4-dithiophene **204** are still under investigation.

Driven by these results, bpy-derivative **60** was coupled in a Ni(0)-mediated reaction to give diethyl 2,2':6',2":6",2"'-quaterpyridine-4',4"-dicarboxylate **64** in a moderate yield. The desired Ru(II) complexes have been prepared in next step (Scheme 62).



R= Et **205**
R= H **206**

Scheme 62

Dye solutions of complex **205** was prepared in ethanol (2×10^{-4} M). TiO_2 electrodes, which were treated with titanium tetrachloride solution [247] were heated up to 500°C at a rate of 35°C/min under oxygen and left at this temperature for 10 minutes and then allowed to cool to ≈ 100°C. The complex **206** was hydrolysed to **205**. In contrast to the ester solutions, when the TiO_2 electrodes were dipped into the solution of hydrolysed complex **205** the electrodes were intensely coloured.

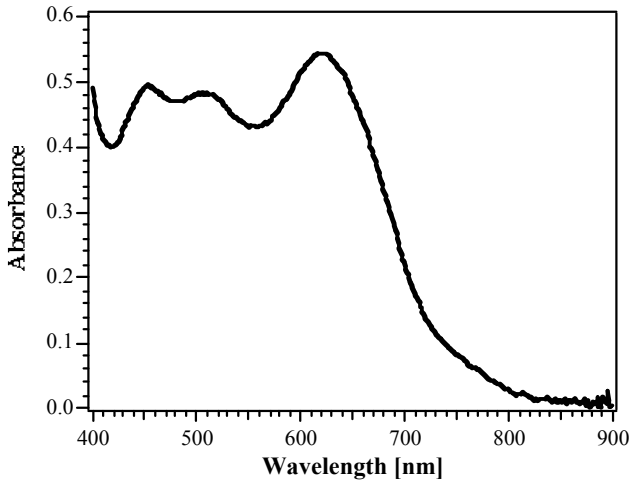


Figure 24

Figure 24 shows absorption spectra of hydrolysed complex **205** anchored onto 6μm thick TiO_2 nanocrystalline electrode. The absorption spectra of the hydrolysed complex **205** on TiO_2 nanocrystalline electrode is very similar to the solution spectra except for a 10 nm red shift, which is due to anchoring onto TiO_2 surface [248].

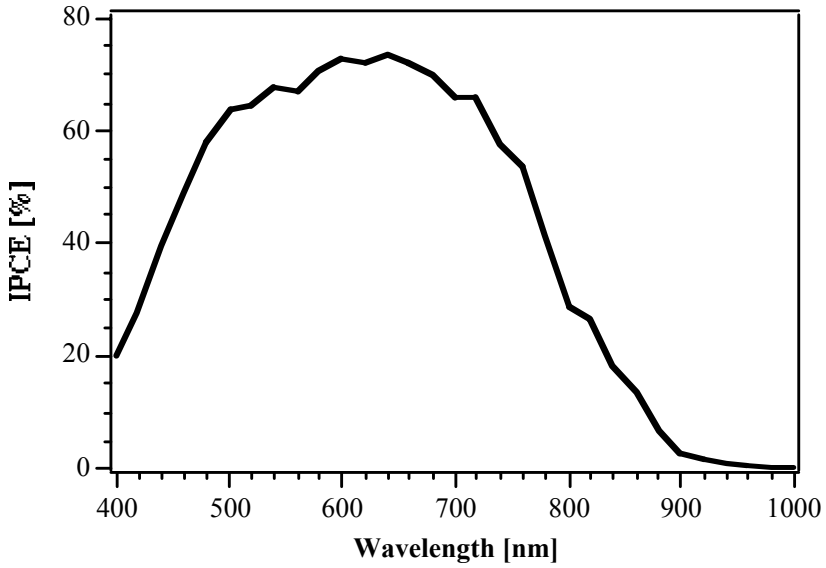


Figure 25

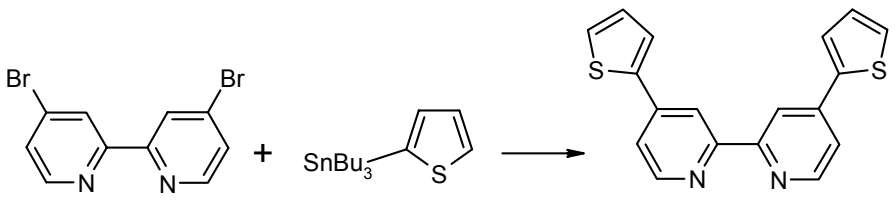
Figure 25 shows the photocurrent action spectrum of such a cell containing hydrolysed complex 205, adsorbed onto TiO_2 electrodes where the incident photon to current conversion efficiency is plotted as a function of wavelength. A broad feature appears covering the entire visible spectrum and extending into the near IR region up to 940 nm. The incident photon-to-current conversion efficiency (IPCE) value in the plateau region being about 75%. The overlap integral of this curve with the standard global AM 1.5 solar emission spectrum yields a short circuit photocurrent density (isc) of 18 ± 0.5 $mAcm^{-2}$. A current of 18 $mAcm^{-2}$ for a 12 μm thick TiO_2 electrodes under AM 1.5 solar emission spectrum is really impressive.

The noteworthy feature is success in developing anchoring panchromatic sensitisers based on ruthenium, which display absorption bands in the entire visible and near IR region. The enhanced spectral response of these complexes compared to the widely used N3 dye is expected to improve significantly the overall efficiency of a dye-sensitised solar cell.

Another functional group at C(4') which was attached to TiO_2-surface is the phosphono group (PO_3H_2). This type of compound shows less current and lost some interest. Recently, sulphone groups have been linked to tpy ligand. This type of complex shows, in comparison to carboxylic groups, less efficiency.

5. Conclusion

We have investigated the preparation of oligopyridines, especially terpyridines, involving a series of novel functional groups at C(4'). More importantly, the ligands possess substituents at the terminal pyridine ring, too. These substituents may be used in further reactions to give new functionalities. Following the Kröhnke methodology or the Stille coupling reaction, symmetrical, unsymmetrical oligopyridines were prepared, respectively. The functional groups linked to C(4') of tpy ligands are methyl, carbonyl, carboxylate, halogenide, amines, oxime, hydroxylamine, azide, azo, nitro and oxypyridines. The nitro group was readily reduced to an azo group. Ruthenium(II) complexes of azo compounds may function as switches in electron and energy transfer. By substitution reactions of the nitro oligopyridines, azido derivatives were synthesised, which photochemically afforded the 7-membered rings (diazepinones), a novelty in coordination chemistry. We have also prepared the amino-bridged tpy ligands, the isoelectronic analogue of the ether-bridged one. This ligand may find application in the synthesis of metallodendrimers. Using the Stille coupling reaction, novel bpy-oxides (oxidised at the more hindered pyridine ring) or tpy-oxides (the central pyridine ring is oxidised). They are new ligands in coordination chemistry, and, in addition, facilitate electrophilic reactions on pyridine rings, so that a series of unsymmetrical tpy or bpy ligands may be synthesised, respectively. In the series of bpy ligands, we utilised the Stille coupling reaction to prepare the 4,4'-bisthiophene-2,2'-bipyridine **209** (Scheme 63).



207 **208** **209**

Scheme 63

In the series of metal complexes, a triangular ring system **148** was prepared and its structure is unique, which confirms the proposed structures. Another ring metal complex, based on oligopyridine **42** upon reaction with octahedral metals such as iron(II) or ruthenium(II) was also prepared.

Besides all metal complexes prepared in this group, we have first reported the synthesis of a heteroleptic Fe(II) complex **152**. A series of Ru(II) complexes were examined which were attached to a TiO_2-surface. While some of them showed normal photocurrent, the activity of complex **205** is remarkable. It showed a photocurrent of 18 mA cm^{-2}, and is the second best in this series, so far.

Meanwhile a few oligopyridines are commercially available, among them are compounds **55**, **56**, **57**, **58**, **62** and **63** of carboxylic derivatives of oligopyridines synthesised in our laboratory [249]. Among this list are 6,6''-dimethyl-2,2':6',2''-terpyridine and 6,6''-dibromomethyl-2,2':6',2''-terpyridine, which were synthesised using our method.

6. Acknowledgement. I would like to thank Prof. Edwin C. Constable and Prof. Catherine Housecroft for their generous support. I should also like to thank the University of Basel.

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