vanish at all) [173]. Besides this, the chemical-shift range is remarkably wide, even ranging over *ca*. 200 ppm in ^{1}H-NMR. Two factors contribute to the hyperfine shift (*i.e.*, the difference between the chemical shift of a proton in a diamagnetic environment *vs*. a paramagnetic one) – the so-called contact and pseudo-contact shifts. In the case of transition-metal complexes, the former is known to vanish quickly with increasing number of bonds since spin-density is mainly located on the metals' d-orbitals [174]. Whereas the latter effect is based on magnetic anisotropy with a distance and angular dependence. Finally, paramagnetism often entails short relaxation times (T_1); this, in turn, brings along high spectral acquisition rates. These aspects in concert make ^{1}H-NMR spectroscopy on paramagnetic complexes rather unalluring. However, the Co^{II} ion represents one notable exception since the spectra of its complexes, such as $[Co(tpy)_2]^{2+}$, appear well-resolved. This behavior is attributed to a hyperfine interaction between the ion's unpaired electrons and the ligand's protons; this coupling results in a considerable downfield shift of the signals – the so-called Knight's shift [175] – without affecting the signals' shapes [176]. According to the ligand-field theory, metals with d^6-electron configuration, such as the Co^{II} ions, might form high-spin as well as low-spin complexes (HS and LS, respectively). Constable *et al*. reported that one can distinguish between these two scenarios on the basis of the ^{1}H-NMR spectra (Figure 1.23): LS complexes, such as $[Co(tpy)_2]^{2+}$, exhibit their lowest resonance at *ca*. 100 ppm; whereas weak-field ligands give complexes with high-spin configuration and lower symmetry. For such complexes, the most downfield signal can be observed at *ca*. 255 ppm (*e.g.*, in $[Co(Br\text{-}tpy)_2]^{2+}$; Br-tpy: 4′-Br-tpy) [177, 178].

Beyond conventional ^{1}H-NMR spectroscopy, further versatile information can also be gained from NMR studies making use of various NMR-active nuclei that can be coordinated to the tpy ligand (*e.g.*, ^{7}Li, ^{31}P, ^{119}Sn, ^{195}Pt, ^{207}Pb, *etc*.). As listed in Figure 1.5, $Ru^{II/III}$ complexes of tpy ligands have been studied most intensively. Has $^{99/101}$Ru-NMR also been in this context? Despite its lower natural abundance and sensitivity, the ^{99}Ru nucleus is the more NMR-relevant one, due to the lower quadrupole moment (^{99}Ru, $I = 3/2$; ^{101}Ru: I = 5/2) [179, 180]. Elsevier *et al*. reported that the ^{99}Ru chemical shifts and signal line widths of complexes and organometallic

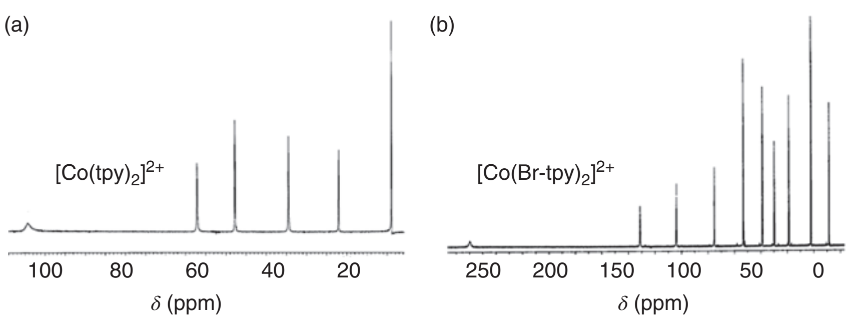

Figure 1.23 ^{1}H NMR spectra of $[Co(tpy)_2]^{2+}$ (a) and $[Co(Br\text{-}tpy)_2]^{2+}$ (b), which show the characteristic signal shifts for low-spin and high-spin complexes, respectively (spectra measured in CD_3CN at 250 MHz) [177] / with permission of Royal Society of Chemistry.

Table 1.2 ^{15}N-NMR chemical and coordination shifts of tpy and its homoleptic *bis*-complexes with various M^{II} ions (all values listed in ppm).

	$\delta_{N,N''}$	$\delta_{N'}$	$\Delta\delta_{N,N''}$ c)	$\Delta\delta_{N'}$ c)
tpy a)	−73.0	−82.8		
$[Fe(tpy)_2]^{2+}$ b)	−134.6	−95.2	−61.6	−12.4
$[Ru(tpy)_2]^{2+}$ b)	−140.1	−101.8	−67.1	−19.0
$[Os(tpy)_2]^{2+}$ b)	−163.8	−117.3	−90.8	−34.5

a) Measured in d_6-DMSO.
b) Measured in D_2O.
c) $\Delta\delta$ represents the coordination shift, *i.e.*, the resonance difference between the respective complex and tpy.
[181] / with permission of John Wiley & Sons.

compounds strongly depended on the compounds' electronic and steric properties. Even though ^{99}Ru-NMR is suited for the analysis of Ru^{II} complexes, tpy complexes have not yet been studied with this technique. Attempts have also been made to study the interaction of tpy ligands with metal centers in solution by comparing the ^{15}N-NMR chemical shifts before and after coordination (the ^{15}N nucleus with a spin of ½ provides a chemical-shift range from 0 to 900 ppm) [181–183]. In one study, Pazderski *et al.* performed ^{15}N-NMR for the tpy *bis*-complexes of the divalent group-8 ions (Table 1.2) [181]. Complex formation resulted in a considerable shielding of the ligand's *N*-atoms. This effect was most pronounced for the *N*-atoms of the outer pyridine rings, whose ^{15}N resonances were shifted by 60–90 ppm; whereas the central pyridine moiety was less affected ($\Delta\delta$ of 10–35 ppm). In either case, the shielding effect increased in the order $Os^{II} > Ru^{II} > Fe^{II}$. However, this method is, due to the isotope's poor natural abundance (0.37% for ^{15}N), by far less sensitive when compared to other NMR experiments and, thus, hardly applicable as a routine experiment.

Finally, Mößbauer spectroscopy can be used to study the chemical environment of complexes. However, this spectroscopic technique, which is based on the so-called Mößbauer effect (*i.e.*, the resonant and recoil-free emission/absorption of γ-radiation), is only applicable to a number of nuclei (the so-called Mößbauer-active elements). In particular, the ^{57}Fe, ^{129}I, ^{119}Sn, and ^{121}Sb nuclei are most frequently studied. Regarding the latter two nuclei, Mößbauer spectroscopy was frequently applied in the 1960s to study the coordination geometry of Sn^{II} and Sn^{IV} complexes with tpy ligands [29]. The high sensitivity of the method enabled those authors to distinguish, *e.g.*, between five- and six-coordinate species [184]. In a similar fashion, ^{121}Sb Mößbauer spectroscopy was applied to tpy complexes with Sb^{III} ions [185]. Regarding the ^{57}Fe nucleus, Menzel *et al.* utilized Mößbauer spectroscopy to confirm the absence of Fe^{III} ions in Fe^{II}–tpy coordination polymers [186]. Moreover, this method was applied to determine the spin-states in homoleptic Fe^{II} and Fe^{III} complexes [187, 188]; Sarkar *et al.* noted that the spin-state of Fe^{II} *bis*-complexes plays a crucial role regarding their electrocatalytic performance in CO_2 reduction

[189]. Wieghard *et al.* used Mößbauer spectroscopy in combination with density functional theory (DFT) calculations to analyze the electronic structures of complexes within the electron-transfer series $[Fe(tpy)_2]^n$ (n = 3+, 2+, 1+, 0, 1–) [190]. This study corroborated the assumption that stepwise one-electron reductions down to the $[Fe(tpy)_2]^-$ species were all ligand-centered and did not affect the metal center in terms of charge and spin-state. This short excursion into the field of Mößbauer spectroscopy reveals that versatile information on tpy complexes can be gained from this method (*e.g.*, regarding spin-state or electronic structure); however, this technique is intrinsically limited to only a handful of nuclei.

1.5 Synthesis of Terpyridine Ligands – A Short Overview

As mentioned beforehand (Section 1.2), the parent tpy ligand was initially obtained from the oxidative dehydrogenation of pyridine in a disappointing yield of only *ca.* 4% [28]. Since then, numerous synthetic strategies have been followed to prepare tpy or its substituted derivatives. This topic was already covered in our previous books [144, 172] and has been summarized in various review articles [114, 191–193]. Therefore, we will discuss the synthesis aspects only briefly at this stage.

1.5.1 Synthesis of the Parent 2,2′:6′,2″-Terpyridine

The very low yield (*i.e.*, 55 g of tpy from a 15 kg batch of pyridine), which was encountered by Morgan and Burstall, called for significant improvement. However, Sasse's protocols to use Raney nickel, as the dehydrogenation catalyst, afforded a good selectivity for bpy, as the main product (tpy was only obtained in marginal amounts) [194, 195]. The same holds true for Burstall's attempts to cross-couple 2-bromopyridine and 6-bromo-bpy in an Ullmann-type fashion (here, bpy and qtpy were the main products) [54]. All these nondirected coupling reactions were inefficient with respect to tpy syntheses (yield <10%) and required enormous effort for product separation and purification [192]. This also holds true for the reaction of pyridine *N*-oxide with 3-methylpyrimidin-4(3*H*)-one in the presence of platinated Pd/C catalyst – this reaction also gave a complex product mixture, in which tpy was represented in *ca.* 13% yield.

Special credit goes to Kauffmann *et al.*, who presented the first applicable tpy synthesis [196]. The reaction between bpy and pyrid-2-yl lithium, as the nucleophile, at −40 °C gave tpy, as the exclusive product (40% yield). However, when the reaction was re-examined by Newkome *et al.* some years later, the chiral dimer **11**, which presumably resulted from an anionic [6 + 4]-cycloaddition, was observed as the by-product (Figure 1.24a). As one notable improvement to Kauffmann's protocol, Wakabayashi, Oae *et al.* introduced a sulfinyl-substituent in the 6-position of bpy, which could readily be replaced in an *ipso*-substitution (Figure 1.24a) [198].

With the emergence of the directed transition-metal catalyzed cross-coupling reactions, a substantial breakthrough in tpy synthesis was achieved [114]. To the best of our knowledge, the first such tpy synthesis *via* a Stille-type cross-coupling

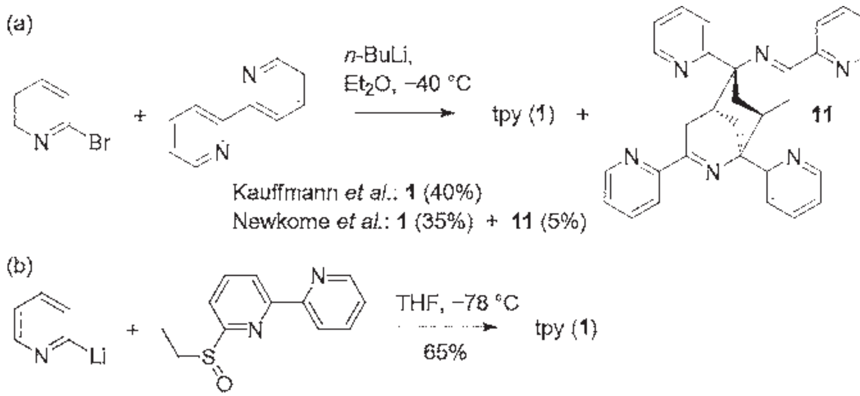

Figure 1.24 (a) Schematic representation of Kauffmann's tpy synthesis [196], which was revisited by Newkome *et al.* [197]. (b) Schematic representation of the tpy synthesis according to Wakabayashi, Oae *et al.* Adapted from [198].

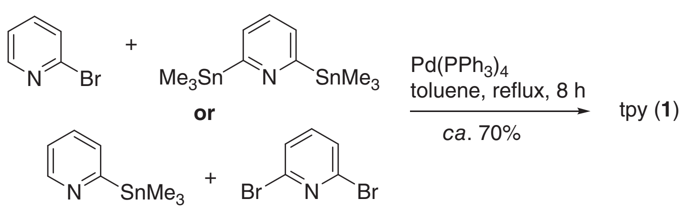

Figure 1.25 Schematic representation of Yamamoto's tpy synthesis. Adapted from [199].

was reported in 1996 by Yamamoto *et al.* (Figure 1.25) [199]. In order to overcome the intrinsic disadvantage of the Stille reaction, *i.e.*, the use of harmful organotin reagents, other Pd^0-catalyzed cross-coupling methods were also subsequently tested: Negishi [200], Suzuki-Miyaura [201], Hiyama [202], *etc.*

Besides the synthesis of tpy *via* coupling procedures, directed as well as nondirected ones, ring-assembly methods have also gained significant attention. As detailed in Section 1.5.3, pyridines can be prepared by condensation reactions, which use carbonyl derivatives as the starting materials. However, neither the original Chichibabin reaction nor the more general approaches according to Frank and Seven [203] or Kröhnke [204] are applicable for the synthesis of the parent molecule. Nonetheless, various ring-assembly methods have been published, in which at least one of the three pyridine rings is formed during the synthesis [114]. Firstly, Potts *et al.* disclosed that "ketene dithioacetals" represented versatile synthons for the synthesis of pyridine derivatives [205–207]. The optimized three-step synthesis afforded **1** in an overall yield of *ca.* 60% (Figure 1.26a). However, the last step, *i.e.*, the crucial borohydride reduction, is hardly applicable to a large-scale synthesis. A similar protocol was developed by Jameson and Guise, in which an enaminone served as the starting material (Figure 1.26b) [208]. The procedure is advantageous to Pott's one for several reasons: applicable on a multi-gram scale, avoidance of smelly sulfur compounds and absence of the uncomfortable reductive

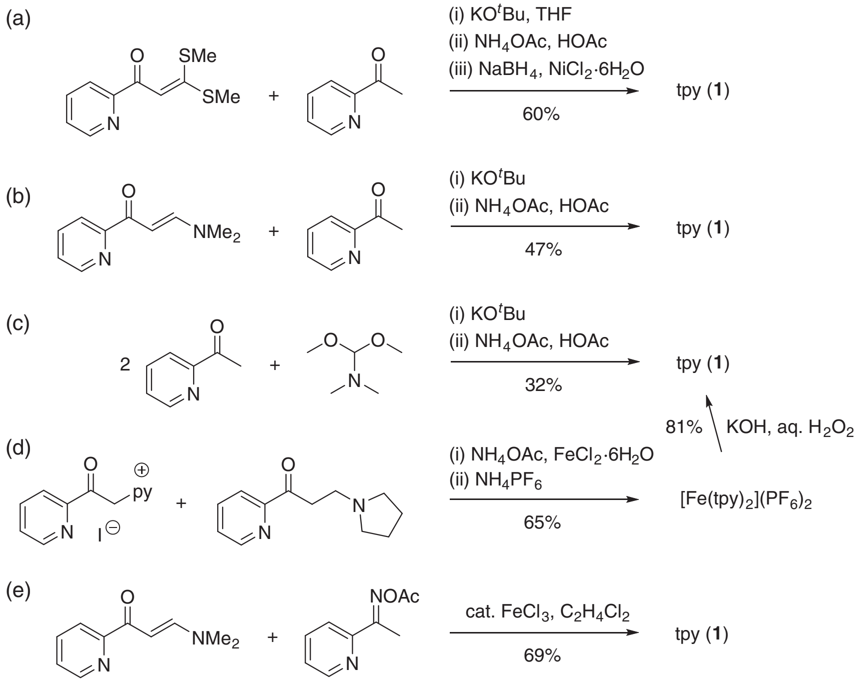

Figure 1.26 Schematic representation of various tpy syntheses, in which the central pyridine ring is assembled by condensation reactions. Adapted from [207–210].

elimination step. However, the reversibility of the initial Michael-addition step might give rise to the scrambling of substituents and, thus, by-products might be formed (*e.g.*, 2,2′:6′,4″-terpyridine) [211]. In 2006, Hanan *et al.* re-evaluated the aforementioned methods and established an easy-to-handle protocol to prepare **1** in a one-pot reaction under mild and benign conditions (Figure 1.26c) [209]. Constable *et al.* utilized a template synthesis to overcome one intrinsic limitation of the conventional Kröhnke-type synthesis, *i.e.*, the poor-yield synthesis of parent tpy (see Section 1.5.3). These authors used Fe^{II} ions to trap the *in situ* formed tpy ligand as its $[Fe(tpy)_2]^{2+}$ *bis*-complex; subsequently, tpy was liberated from the complex by oxidative hydrolysis (Figure 1.26d) [210]. This short overview on tpy synthesis does not claim to be exhaustive and research on pyridine synthesis is still ongoing. In this context, oxime acetates have emerged as versatile synthons for the transition-metal catalyzed formation of pyridine rings [212]. For example, Vidavalur *et al.* recently reported the Fe^{III}-catalyzed [3+4]-annulation between an oxime acetate and an enaminone, both prepared from 2-acetylpyridine; this highly modular protocol gave tpy in 69% yield (Figure 1.26e) [213]. Whereas the dehydrogenative coupling of pyridines in the presence of sodium dispersions, as the catalyst, afforded the bpy derivatives with high chemoselectivity (*i.e.*, the corresponding tpy derivatives were obtained in <10% yield) [214].

A fundamentally different strategy for the synthesis of **1** was reported by Pabst and Sauer (Figure 1.27) [215]. First, a 3,5-disubstituted 1,2,4-triazine derivative

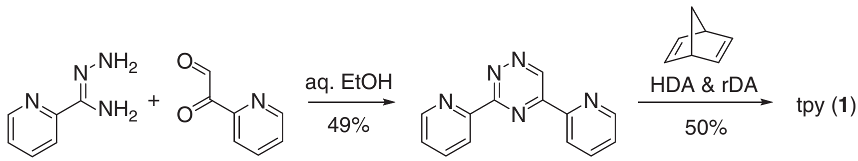

Figure 1.27 Schematic representation of the Papst-Sauer synthesis *via* a 1,2,4-triazine intermediate. Adapted from [215].

was obtained from the regioselective condensation of picolinamidrazone with 2-pyridylglyoxal. This intermediate, as a highly electron-deficient diene, reacted in a sequence of a hetero-Diels–Alder (HDA) and retro-Diels–Alder (rDA) reaction to afford **1** in 50% yield (norbornadiene was used as a masked acetylene equivalent).

Finally, tpy synthesis has also been targeted *via* the ring-assembly of both outer rings. In one example, Adrian *et al*. converted 2,6-diacetylpyridine by a sophisticated four-step strategy into tpy [216]. Although the overall yield of *ca*. 70% was relatively high, Adrian's protocol misses the straightforwardness, cost-efficiency, and experimental ease of the aforementioned approaches. Alternative strategies, also starting from 2,6-diacetylpyridine, relied on Chichibabin- or Kröhnke-type ring-closure (see Section 1.5.2). However, these strategies were only useful for the synthesis of tpy derivatives with substituents on the outer rings, but failed for the synthesis of parent **1** [217].

These various methods for the synthesis of unsubstituted tpy have also been applied to prepare a plethora of ring-substituted derivatives; however, a detailed listing of all the chemical structures, the wide range of reported reaction conditions, and discussion of practical aspects and yields goes far beyond the scope of this book. Basically, all the protocols rely on the fundamental concept mentioned in this section beforehand.

1.5.2 Synthesis and Modification of 4′-Chloro-2,2′:6′,2″-Terpyridine

Besides the parent tpy ligand, its 4′-chloro derivative (**12**, Cl-tpy) has also received widespread attention – this commercially available ligand is mentioned in >450 journal articles and >110 patents (SciFinder^{n} research on 1st April 2025). The ligand's prominent role results from the possibility to replace the chloro-substituent *via* an aromatic substitution reaction (S_NAr). For this purpose, a wide range of nucleophiles has already been used (*e.g*., alcohols, amines, thiols, phosphines, carbanions, *etc*.) [218]. The synthesis of **12**, which was reported by Constable and Ward, involves the initial formation of a 1,3,5-triketone derivative, which is cyclized to a dihydropyridin-4(1*H*)-one species using NH_4OAc, as the source for NH_3; subsequent chlorination with PCl_5 in $POCl_3$ afforded **12** in 62% yield (Figure 1.28) [219]. This protocol from the early 1990s still represents the method of choice for the preparation of this particular compound.

As shown in numerous publications, the nucleophilic displacement of the chloro-substituents enables one to prepare 4′-substituted tpy derivatives. This strategy has *inter alia* been employed in the field of macromolecular chemistry:

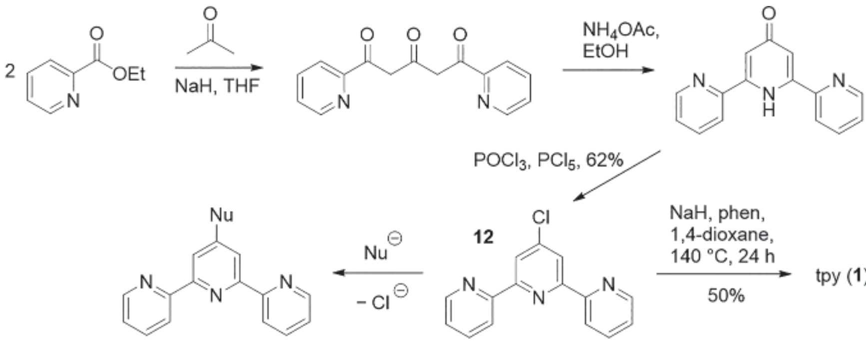

Figure 1.28 Schematic representation of Constable's synthesis of Cl-tpy (**12**). Adapted from [219] and its derivatization *via* nucleophilic or radical nucleophilic aromatic substitution.

The chain-end functionalization of preformed polymers paved the way toward metallo-supramolecular block copolymer architectures [220]. Moreover, polymers with tpy moieties within the side chains have been prepared from tpy-containing monomers; these, in turn, were synthesized from **12** according to Figure 1.28 [144, 172]. Such polymers are applied, for example, in the context of self-healing and shape-memory polymers, which are discussed in Chapter 9 [15, 143].

Recently, Studer *et al.* reported that aryl bromides and chlorides can be hydrodehalogenated by NaH in 1,4-dioxane using phen as the initiator for this radical nucleophilic aromatic substitution ($S_{RN}1$) [221]. In this context, also the reduction of **12** to afford tpy (**1**) in *ca.* 50% yield was shown (Figure 1.28). This $S_{NR}1$ methodology represents a notable extension of the preparative toolbox to synthesize tpy derivatives with unsubstituted central rings.

1.5.3 Synthesis of 4′-Aryl-2,2′:6′,2″-Terpyridines

The thermal cyclo-condensation of aldehydes and ammonia in the presence of an appropriate catalyst (*e.g.*, alumina) affords pyridine derivatives. Although this observation was already made by Lyubavin in 1873 [222, 223], this pyridine synthesis is today named after Chichibabin, who was the first to thoroughly analyze its outcome [224, 225]. Almost 20 years later, Chichibabin republished his results also in German [226]; this disclosure is commonly cited instead of the original paper from 1905, which is only available in Russian [227]. The primary protocol was revised in 1949 by Frank and Seven, who reacted an enolizable ketone with a non-enolizable aldehyde in the presence of a source for ammonia (*e.g.*, NH_4OAc). The reactions are typically performed in a protic environment (*e.g.*, acetic acid, ethanol, or acetamide). As outlined in Figure 1.29, a 1,5-diketone intermediate ("chalcone") is formed *via* a sequence of Claisen-Schmidt condensation and Michael addition. The subsequent cyclization with an NH_3 equivalent affords a 2,4,6-trisubsituted 1,4-dihydropyridine (DHP) derivative. This, in turn, is oxidized to the corresponding pyridine compound by air or by adding an external oxidant (the stability of the DHP strongly depends on the electronic nature of its substituents). As recently summarized by Shabalin,

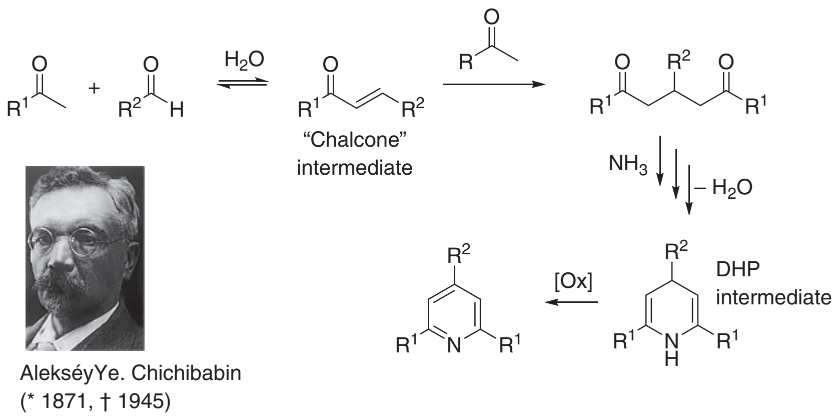

Figure 1.29 Schematic representation of the mechanism of Chichibabin's pyridine synthesis (R^1, R^2 = alkyl or aryl). [228] with permission of Royal Society of Chemistry. A photograph of A. Ye. Chichibabin is also shown [227] / with permission of John Wiley & Sons.

numerous variants to the original protocol are available; these include solvent-free or microwave-assisted reactions, the use of homogeneous or heterogeneous catalysts, *etc.* [228]. Furthermore, benzyl amines or oxime acetates have been utilized as alternative starting materials to the conventional carbonyl derivatives.

In order to circumvent one major limitation of the Chichibabin-type pyridine synthesis, which is the ability of the chalcone intermediate to act also as an internal oxidant (thereby significantly reducing the yield), Kröhnke suggested the use of a CH-acidic pyridinium salt in combination with a chalcone derivative (Figure 1.30) [204]. The Michael reaction of these two components affords an unsaturated 1,3-diketone, which, upon cyclization with NH_3, directly yields the corresponding pyridine (instead of the DHP). Thus, the crucial oxidation step becomes obsolete. Moreover, the use of preformed chalcones enabled this author to also synthesize unsymmetrical pyridine derivatives (*i.e.*, different substituents in 2,6-positions). The acylmethylpyridinium salts, such as 2-pyridacylpyridinium iodide, were obtained *via* an Ortoleva–King reaction of the respective ketone and iodine in pyridine [230–232]. In one application of this method, Kröhnke prepared 4′-aryl-substituted 2,2′:6′,2″-terpyridines, which are often referred to as the Kröhnke-type tpys; thus ascribing credit to his notable contributions to the field of pyridine synthesis [204].

Today, Kröhnke-type terpyridines are conveniently prepared by the condensation between 2-acetylpyridine and an aromatic aldehyde to directly (or sequentially *via* the chalcone intermediate) afford the respective 4-aryl-1,5-di(pyridine-2-yl)pentane-1,5-dione [233]. In this context, Raston *et al.* developed a solvent-free method, in which the 1,5-diketone was prepared by grinding in a mortar [234, 235]. Whereas various one-pot protocols were reported, in which ethanol or poly(ethylene glycol) (PEG) in combination with aqueous ammonia was used as the reaction medium [209, 236, 237]. Moreover, Tu *et al.* performed such a synthesis under microwave irradiation [238]. To rectify a common misunderstanding: Although Kröhnke-type

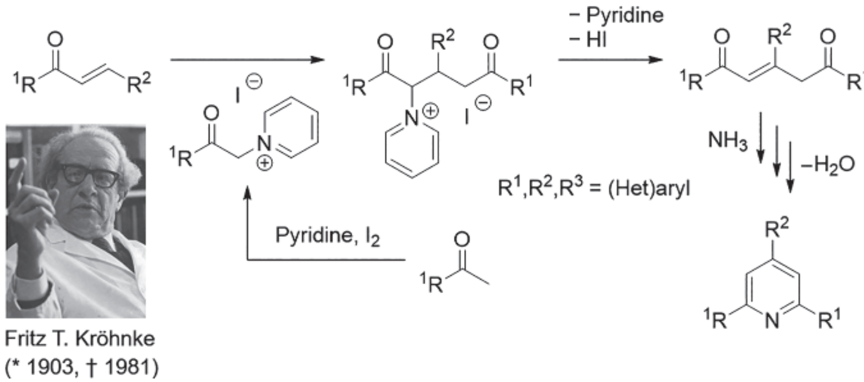

Figure 1.30 Schematic representation of the mechanism of Kröhnke's pyridine synthesis including the formation of the pyridinium-salt reactant (R^1, R^2 = alkyl or aryl) [204]. A photograph of F. T. Kröhnke is also shown [229] / with permission of John Wiley & Sons.

tpys are obtained *via* the aforementioned methods, these reactions are strictly speaking rather Chichibabin-type ones, but not Kröhnke-type (the latter requires the pyridinium-salt reagent).

However, one has to be aware that the tpy synthesis still has some shortcomings, which are due to the formation of by-products [233]. Already in the 1890s, von Kostanecki and Rossbach proposed the formation of a condensation product with a ketone-to-aldehyde stoichiometry of 3:2 (Figure 1.31a) [239]; surprisingly, the proof of structure for this triketone was provided only recently [240]. Such ketones often undergo an intramolecular aldol addition to afford penta-substituted cyclohexanol derivatives, as a diastereoisomeric mixture (Figure 1.31b); in some cases, these have been isolated even as the major products [233]. In addition to this, cyclohexane-1,3-diols might arise from the condensation of aromatic ketones and aldehydes in a 3:1 ratio and subsequent aldol-type ring closure (Figure 1.31c) [241]. Moreover, 6′-aryl-2,2′:4′,2″-terpyridines are formed if the chalcone intermediate

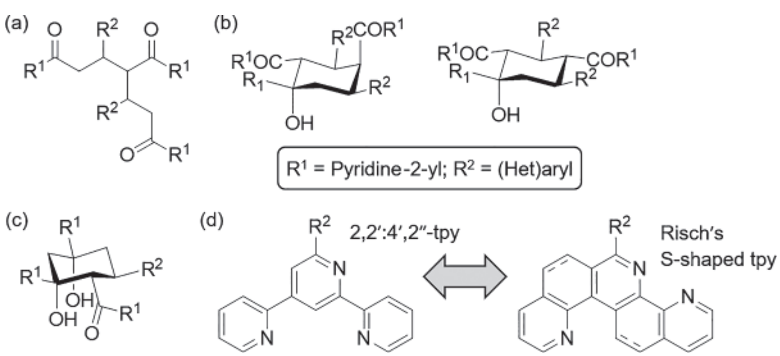

Figure 1.31 If tpy synthesis goes wrong … Schematic representation of typical by-products of Chichibabin-type tpy synthesis: (a) Kostanecki's ketone, (b) cyclohexanols, (c) cyclohexandiols, and (d) 2,2′:4′,2″-terpyridines. Adapted from [233].

reacts with 2-acetylpyridine in an aldol-type fashion (instead of the usual Michael addition), followed by cyclization with an NH_3-equivalent (Figure 1.31d) [242]. The latter correspond to the so-called S-shaped tpys, which were introduced by Risch *et al.* [243–245].

1.6 Beyond the Classical Terpyridine Motif

As mentioned beforehand, the ligand's architecture has a profound impact on the complex formation as well as on its properties. In this respect, preorganization represents one important aspect. The DPA ligand, for example, represents tpy's dibenzannelated analogue (Figure 1.15, Table 1.1). Due to its rigid structure, this ligand formed complexes with higher K_a values (at least in those cases, where the size of the metal ion fitted into the ligand's rigid cleft) [130]. DPA is conveniently prepared *via* Friedländer condensation and subsequent dehydrogenation of intermediate **12** (Figure 1.32a) [246]. Thummel *et al.* also prepared ligand **13** as the tetrahydro derivative of DPA *via* an enamine route [247]. The same strategy was chosen for the synthesis of the substituted derivatives **14**, which are not accessible *via* conventional Chichibabin-type or Kröhnke-type reactions [248]. An alternative, highly modular procedure for the synthesis of **14** was developed by Risch *et al.* (Figure 1.32b); these authors used *in situ*-generated imines and preformed ternary iminium salts as the reactants in their one-pot, two-step protocol [244]. In none of these studies, K_a values for the complexation of metal ions were determined in order to elaborate the effect of rigidity.

The synthesis of tpy complexes typically proceeds in a straightforward fashion and affords the assemblies with mostly octahedral or square-planar geometry (Section 1.3). However, the ligand structure prevents the complexes from taking up the ideal geometry and, thus, considerable distortion occurs. This issue, which has been intensively discussed at the example to the Ru^{II} complexes, is highly detrimental regarding optoelectronic applications of such complexes [249]. Unlike $[Ru(bpy)_3]^{2+}$, whose *tris*-bidentate coordination environment allows for a non-distorted octahedral geometry, $[Ru(tpy)_2]^{2+}$ is practically non-emissive at room temperature (*i.e.*, 1150 *vs.* 0.25 ns). As depicted in Figure 1.33, emission quenching

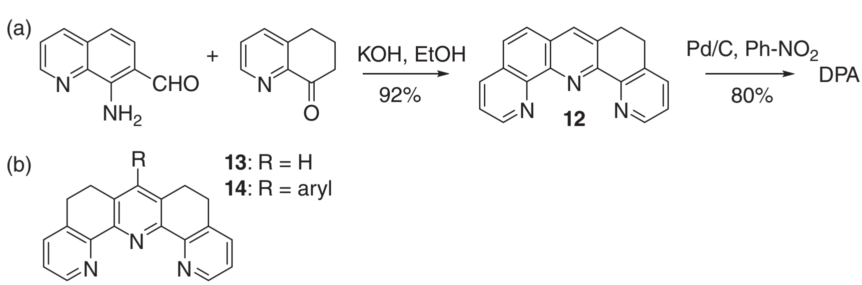

Figure 1.32 (a) Schematic representation of Thummel's DPA synthesis. Adapted from [246]. (b) Schematic representation of the semirigid ligands **13** and **14** [247, 248].

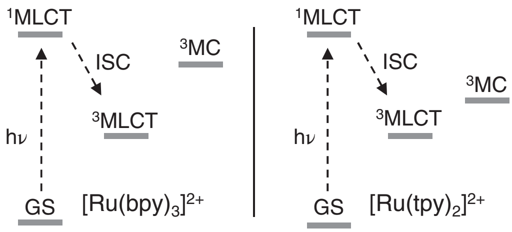

Figure 1.33 Comparison of the Jablonski diagrams of photophysically attractive $[Ru(bpy)_3]^{2+}$ (left) *vs.* the easily accessible $[Ru(tpy)_2]^{2+}$; only a simplified version of the diagram is shown for clarity [249] / with permission of Royal Society of Chemistry.

is due to the ligand's weak ligand-field strength, which decreases the energy of the metal-centered triplet state (^{3}MC). As a result, the energy gap between the metal-to-ligand charge-transfer triplet state (^{3}MLCT) and ^{3}MC becomes smaller, and the latter can be thermally populated; this, in turn, facilitates the non-radiative decay back to the ground state (GS).

To counteract this, some fundamentally different approaches have been followed: Introduction of electron-withdrawing or -donating substituents, increasing the ligand's planarity, increasing the ligand-field strength and decreasing the ligand's steric strain. The latter strategy affords complexes with almost ideal octahedral (or square-planar) geometry and, thus, significantly improved photophysical properties. Three representative examples for tridentate ligands, as "tpy mimics," which fulfil this requirement, are shown in Figure 1.34a. From these, the dqp ligand has attracted the most notable attention so far: Its modular synthesis also allows one to introduce substituents on the central ring [255] and, thus, the dqp moiety has already been incorporated into various architectures, including

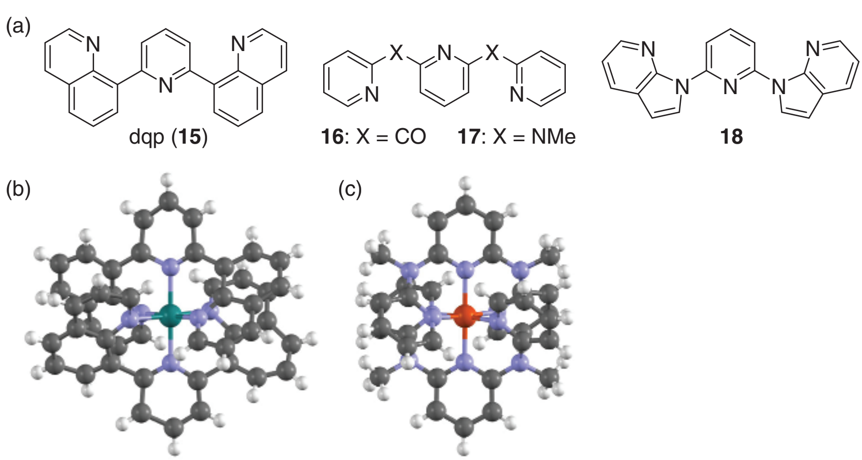

Figure 1.34 (a) Schematic representation of tridentate ligands **15–18** [250–253]. (b) Solid-state structure of *mer*-$[Ru(dqp)_2]^{2+}$. Adapted from [250]. (c) Solid-state structure of *mer*-$[Cr(\mathbf{17})_2]^{3+}$. Adapted from [254]. In panels (b) and (c), counterions and solvent molecules were omitted for clarity.

metallo-supramolecular block copolymers [256] and coordination polymers [257]. The $[Ru(dqp)_2]^{2+}$ complex exhibits a remarkably long excited-state lifetime of *ca*. 3 μs and good photo-stability [258]. However, when dealing with such more flexible ligands, one has to take the formation of coordination isomers into account; unlike for tpy, *bis*-tridentate coordination might lead to the *mer*-, *cis-fac* as well as *trans-fac* species (Figure 1.7). In general, the meridional one represents the thermodynamically favored isomer. Representatively, the solid-state structures of *mer*-$[Ru(dqp)_2]^{2+}$ and *mer*-$[Cr(\mathbf{17})_2]^{3+}$ are shown in Figure 1.34b,c [250, 254].

1.7 Conclusion

2,2′:6′,2″-Terpyridine was incidentally discovered in the 1930s, and its ability to form complexes with transition-metal ions was discovered right away [28]. Thus, the pioneering work by Morgan and Burstall paved the way to the wide field of tpy chemistry, which started to flourish in the 1980s when the photophysical and electrochemical properties of tpy complexes were discovered (Figure 1.1). Today, a wide range of strategies for the synthesis of tpy ligands is known, and tpy ligands have been combined with almost all elements in the periodic table (Figure 1.5). The coordination behavior of tpy ligands is widely understood: Complexes with octahedral or square-planar geometry represent the most prevalent ones (but many other coordination architectures are known). The stability of such complexes depends on the ligand's structure as well as on the coordinated metal ion (*i.e.*, its ionic radius, oxidation state, *etc.*). Regarding the characterization of tpy complexes, XRD analysis is favored, but only applicable if suited single crystals can be obtained. Besides, NMR spectroscopy and MS are commonly used.

As discussed in the subsequent chapters, tpy complexes have been used to assemble a plethora of novel and interesting compounds – ranging from discrete mononuclear complexes to dyads, triads, and oligonuclear species, 2D/3D nanoarchitectures, coordination networks, and eventually polymers. The range of potential applications is as wide and *inter alia* includes pharmaceuticals, photovoltaics, optoelectronics, materials science, *etc*.

However, if ligand preorganization is required or if one aims for complexes with non-distorted coordination geometries, one has to step away from the classical tpy framework and utilize other types of tridentate ligands. In particular, the dqp ligand has emerged as one alternative to the tpy system since it offers the ability to assemble complexes with superior photophysical properties. The parent $[Ru(dqp)_2]^{2+}$ complex, for example, possesses a remarkably long excited-state lifetime of several μs [258]. Complexes of this ligand have already been incorporated into sophisticated architectures, such as redox- and photoactive polymers [256, 259]. On the other hand, the synthetic effort to prepare functionalized dqp (or other ligands) is higher when compared to a related tpy synthesis. Thus, ligands from the tpy family still represent the more favorable ligands when aiming for the self-assembly of metallo-supramolecular materials – as long as photophysical aspects play only a minor role.

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