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Review

Coordination chemistry of 1,3,5-triazapentadienes

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ABSTRACT

The methods of synthesis of 1,3,5-triazapentadienes (also known as imidoylamidines), as well as the preparation of their complexes, are reviewed. The former methods include mainly the Pinner, Ley and Muller syntheses, the amination of N-imidoylimidoates or of nitriles bearing strong electron-withdrawing groups, the desulfurizing amination of N-tiobenzoylbenzamidines and the reaction of perfluoro-5-aza-4-nonene with primary amines. The synthetic procedures for the complexes involve not only the coordination of a pre-formed 1,3,5-triazapentadiene but also the generation *in situ* of such a species, namely by condensation of amidines, by direct one-pot template synthesis from nitriles, by nucleophilic addition of amidines or related reagents to coordinated nitriles, by nucleophilic additions to dicyanamidate or hydrolytic conversion of triazines.

1. Introduction

Many complexes of *O,O*-chelating β-diketones (Scheme 1) have been synthesized and find wide application in different areas of chemistry [1]. In the last years, complexes with N-containing isoelectronic analogs of diketones, *e.g.* with β-diimines, have also attracted increased attention [2], though still remaining much less explored in comparison with the former. Less studied is the coordination chemistry of 1,3,5-triazapentadienes (*tap*)[1]

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[1] 2-py, 2-pyridyl; 3-py, 3-pyridyl; 4-py, 4-pyridyl; AcO, acetate; *c*-Hex, cyclohexyl; cod, cyclooctadiene; *c*-Pent, cyclopentyl; dca, dicyanamide; dcadpz,

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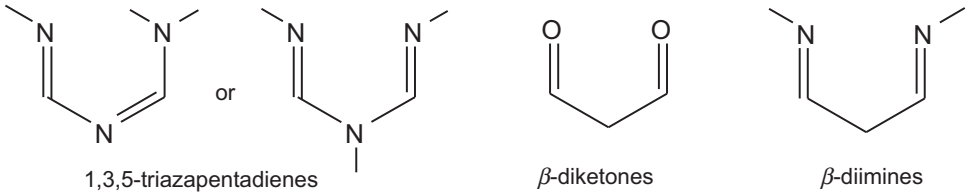
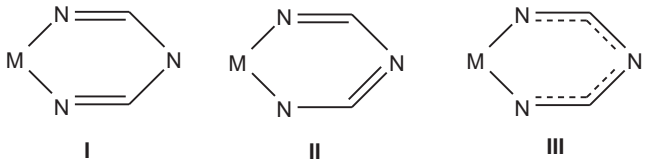
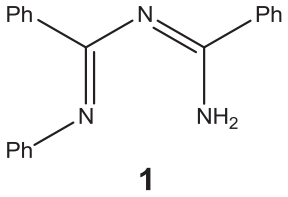


Scheme 1. Main structural motifs of 1,3,5-triazapentadienes (*tap*) and some isoelectronic analogs.



Scheme 2.



Scheme 3.

(Scheme 1), the least explored members of this family of isoelectronic species.

Notwithstanding their discovery more than a century ago, the data on pure organic and coordination chemistry of *tap* compounds (with the exception of a few particular cases, namely biguanidine $NH_2C(=NH)NHC(=NH)NH_2$ [3] and biuret $NH_2C(=O)NHC(=O)NH_2$ [4]) remain very scant. For example, a Cambridge Structural Database [5] search on the structures containing fragments **I** and **II**, which can be generalized as **III** (Scheme 2), provided in 2009 less than 300 hits for all types of compounds (aliphatic, aromatic, heterocycle- and heteroatom-containing), which can be considered as a modest result, taking in mind the high potential of triazapentadienes in coordination chemistry: unlike β-diketones or β-diimines, *tap* bears one additional N donor site, and DFT calculations [6] indicate that they possess an even greater ability for sequestering various metal centers than, *e.g.* β-diimines. In spite of their potential for organic (*e.g.* as building blocks for 1,2-dihydro-1,3,5-triazines and oligonitriles) [7], medicinal [8] and coordination chemistry [6,9], a systematic review devoted to the chemistry of this type of ligands (excluding biguanidine and biuret which have already been reviewed [3,4] and will not be considered herein), their syntheses and interaction with different metal ions had not yet appeared. This review is an attempt to partially fill this gap since we believe such an information should be of wide interest.

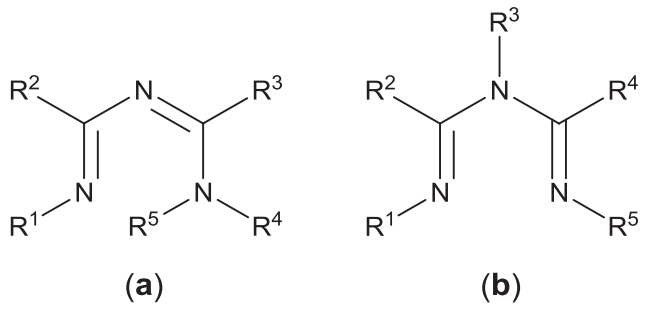
2. Syntheses of 1,3,5-triazapentadienes

2.1. Terminology and structural features

Although synthetic methods for *tap* have been known for a long time, references on these compounds in pure organic chemistry are very scarce. For example, in the classical book of Patai's series devoted to the chemistry of amidines and imidates [10], the 1,3,5-triazapentadienes are mentioned only twice, as intermediates in the formation of triazines [11] and starting materials for the synthesis of aminotriazines [12].

Moreover, a clear terminology has been lacking. For example, the first example of such compounds, **1** (Scheme 3), synthesized in 1907 [13] was regarded as a derivative of the hypothetical "biformamidide" HN=CH–NH–CH=NH and was named "2:4:5-triphenylbiamidide". The name given to this compound in the Beilstein Handbook [14] is "N-phenyl-N′-(alpha-iminobenzyl)-benzamidin", whereas "(1E,NZ)-N-(amino(phenyl)methylene)-N′-phenylbenzimidamide" is that provided by ChemDraw [15]. Cooper et al. [16] in 1951 used the generic term "diamidide" for this class of compounds but individual examples were named as derivatives of a 1,3-diene, HN=CH–N=CH–NH_2; *e.g.* **1** in this system becomes 1,2,4-triphenyl-1,3,5-triazapenta-1,3-diene. Later on, in the 1980s and 1990s, the term "imidoylamidines" for such compounds appears more frequently [17,18], but other less common names, *e.g.* azapentane-2,4-diiminate [19], were also used. In the beginning of the XXI century both terms "triazapentadiene" and "imidoylamidines" are equally applied, but to the end of the decade the former is becoming more common, and will be used along this work (with the corresponding abbreviation *tap*).

1,3,5-Triazapentadienes (Scheme 4) are polyfunctional, nitrogen-containing analogs of pentadienes bearing formally fused amidine, imide and amine functions which form an unsaturated N–C–N–C–N chain. On the other hand, they may also be considered as formal products of a nitrile dimerization, induced by an amine nucleophile. One can view two main isomeric forms of such compounds, namely 1,3,5-triaza-1,3-pentadienes (Scheme 4**a**) and 1,3,5-triaza-1,4-pentadienes (Scheme 4**b**), depending on the position of the double bond. On account of the number of protons at the nitrogen atoms, one can differentiate primary (three protons at the nitrogen atoms), secondary (two protons at the nitrogen atoms), tertiary (one NH group) and quaternary triazapentadienes. In spite of this structural isomerism of the organic molecules, in



Scheme 4.

di(pyrazolecarbimido)aminate; DFT, density functional theory; dipp, 2,6-diisopropylphenyl; en, ethylene; Et, ethyl; H_4edta, ethylenediaminetetraacetic acid; Hpz, pyrazole; Iii, iminoisoindolinone; *i*-Pr, *iso*-propyl; Me, methyl; mes, mesityl (2,4,6-trimethylphenyl); *n*-Bu, *n*-butyl; Nii, N-imidoylimidoate; *n*-Pr, *n*-propyl; OTf, triflate ($SO_3CF_3^-$); Pc, phthalocyanine; pdm, 2,6-pyridinedimethanol; Ph, phenyl; Py, pyridyl; pz, pyrazyl; *tap*, 1,3,5-triazapentadiene or 1,3,5-triazapentadienate type species (i.e. either the neutral or the deprotonated anionic form, respectively); *t*-Bu, tert-butyl; *t*BuDPA, bis(2-pyridylmethyl)tert-butylamine; tea, triethanolamine; THF, tetrahydrofuran; tmeda, N,N,N′,N′-tetramethylethylenediamine; tpa, tris(2-pyridylmethyl)amine; tren, tris(2-aminoethyl)amine.

many coordination compounds with *tap* chelating a metal center these ligands are deprotonated (*e.g.*, in structure (**a**), $R^5 = 0$; or in structure (**b**), $R^3 = 0$), thus facilitating the delocalization of the double bond system over the entire molecule and equalizing both isomers [20]. On the other hand, if the *tap* remains neutral upon coordination, the CN bonds are usually distinguishable and one can differentiate both isomers by crystallographic and NMR data [6].

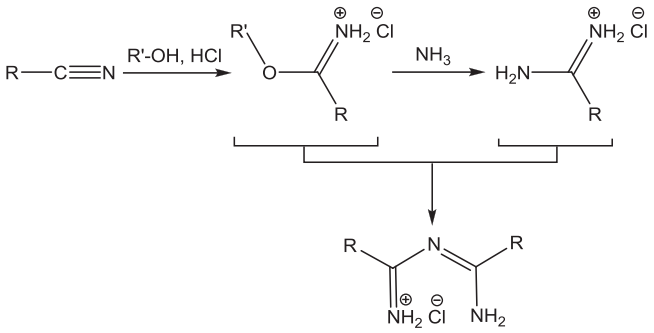
Until now, apart from diguanidine and biuret (see above) derivatives, few organic compounds possessing the open-chain N–C–N–C–N system have been described and applied as ligands, most of them being summarized in Table 1. Apart from those mentioned in this table, one may refer to related oligonitriles (polyazapolyenes) [21–26], including pyridine-based [23] and 1-oxa-polyazapolyenes [24–26], which were valuable ligands for, *e.g.* palladium(II), copper(II), cobalt(II), zinc(II) and nickel(II) [22–25].

Table 1
Examples of known 1,3,5-triazapentadienes (*tap*).

Structure according to Scheme 4	R^1	R^2	R^3	R^4	R^5	Ref.
a	Ph	Ph	Ph	H	H	[6,7,9,13,16]
a	Tolyl-4	Tolyl-4	Ph	H	H	[7]
a	Tolyl-4	C_6H_4(Cl-4)	Ph	H	H	[7]
a	Ph	*t*-Bu	Ph	H	H	[7]
a	*c*-Hex	*t*-Bu	Ph	H	H	[7]
a	*c*-Pent	*t*-Bu	Ph	H	H	[7]
a	*i*-Pr	*t*-Bu	Ph	H	H	[7]
a	*c*-Pent	*t*-Bu	Ph	Ph	H	[7]
a[a]	*c*-Hex	*t*-Bu	Ph	=2-adamantylidene[b]	7	
a[a]	*c*-Hex	*t*-Bu	Ph	=9-fluorylidene[b]	7	
a[a]	*c*-Hex	*t*-Bu	Ph	$=CPh_2$[b]	7	
a	C=O(Tolyl-4)	Ph	Ph	Ph	H	[7]
a	C=O(Tolyl-4)	Ph	*t*-Bu	*c*-Pent	H	[7]
a	*t*-Bu	Ph	*t*-Bu	*c*-Pent	H	[7]
a	*c*-Pent	*t*-Bu	Ph	Ph	C=O(Tolyl-4)	[7]
a[c]	Ph	Ph	Ph	=C(*t*-Bu)(NH–*c*-Pent)[b]	7	
a[c]	*c*-Hex	*t*-Bu	Ph	=C(*t*-Bu)(NH–*c*-Hex)[b]	7	
a[c]	*i*-Pr	*t*-Bu	Ph	=C(*t*-Bu)(NH–*i*-Pr)[b]	7	
a[d]	C(Ph)=N–C(Ph)=O	Ph	*t*-Bu	*c*-Pent	H	[7]
a[d]	C(Ph)=N–C(Ph)=O	Ph	*t*-Bu	*i*-Pr	H	[7]
a[e]	C(Ph)=N–C(Ph)=N–C(Ph)=O	Ph	*t*-Bu	*i*-Pr	H	[7]
a	Ph	$C_6H_4(NO_2$-4)	Ph	H	H	[9]
a	*c*-Hex	*t*-Bu	Ph	Ph	H	[9]
a	*i*-Pr	*t*-Bu	Ph	Ph	H	[9]
a	Ph	*t*-Bu	Ph	$(CH_2)_4$[f]	$(CH_2)_4$[f]	[9]
a	Ph	Ph	Ph	Ph	*t*-Bu	[9]
a	Ph	Ph	$C_6H_4(NO_2$-3)	H	H	[16]
a	Ph	Ph	Ph	Ph	Me	[16]
a	Ph	Ph	Ph	Ph	Ph	[16]
b	Me	Ph	Ph	Ph	Ph	[16]
b	Ph	Ph	Ph	Ph	Ph	[16]
b	Ph	Ph	Ph	Ph	H	[16]
a	Ph	Ph	Ph	Ph	H	[9,16]
a	Ph	Ph	Ph	C_6H_4(Cl-4)	H	[16]
a[g]	Ph	Ph	Ph	Ph	CPh=NPh	[16]
a	H	Ph	Ph	H	H	[36]
a	H	C_6H_4(OMe-4)	C_6H_4(OMe-4)	H	H	[36]
a	H	C_6H_4(Cl-4)	C_6H_4(Cl-4)	H	H	[36]
a	H	C_6H_4(OMe-4)	Ph	H	H	[36]
a[c]	$CPh(=N^-)$	Ph	Ph	Piperidyl	–	[21]
b	H	Et	H	Et	H	[33]
b	H	$CH_2C_6H_4$(OMe-4)	H	$CH_2C_6H_4$(OMe-4)	H	[33]
a	H	pz	pz	H	H	[37]
a	H	CF_3	CF_3	H	H	[38]
a	H	C_2F_5	C_2F_5	H	H	[38]
a	H	C_3F_7	C_3F_7	H	H	[38]
a	H	CF_3	C_3F_7	H	H	[38]
a	H	C_2F_5	C_3F_7	H	H	[38]
a	Ph	C_3F_7	C_3F_7	Ph	H	[27,28]
a	C_6H_3(*i*-Pr-2,6)	C_3F_7	C_3F_7	C_6H_3(*i*-Pr-2,6)	H	[29,30,40,41]
a	C_6F_5	C_3F_7	C_3F_7	C_6F_5	H	[31]
a	C_6H_3(F-2)(CF_3-6)	C_3F_7	C_3F_7	C_6H_3(F-2)(CF_3-6)	H	[31]
a	C_6H_3(Cl-2,6)	C_3F_7	C_3F_7	C_6H_3(Cl-2,6)	H	[39]
a	C_6H_2(Me-2,4,6)	C_3F_7	C_3F_7	C_6H_2(Me-2,4,6)	H	[30,41]
b	H	$C(OH)(CO_2Et)_2$	CH_2Ph	$C(OH)(CO_2Et)_2$	H	[42]
b	C_6H_3(*i*-Pr-2,6)	Me	C_6H_3(*i*-Pr-2,6)	Me	C_6H_3(*i*-Pr-2,6)	[43]

[a] Can also be considered as a 1,3,5-triazahexa-1,3,5-triene.
[b] Corresponding to $R^4 + R^5$.
[c] Can also be considered as a 1,3,5,7-tetraazahepta-1,3,5-triene.
[d] Can also be considered as a 3,5,7,9-tetraazanona-1,3,5,7-tetraene.
[e] Can also be considered as a 3,5,7,9,11-pentaazaundeca-1,3,5,7,9-pentaene.
[f] Cyclic form.
[g] Can also be considered as a 1,3,5,7-tetraazahepta-1,3,6-triene.

The reported methods for the preparation of free *tap* were described mostly for *N*-substituted triazapentadienes containing bulky groups at the terminal nitrogen atoms and/or strong electron-acceptor functionalities at the C atoms [6–9,13,21–31]. Generally, free triazapentadienes and analogues are unstable and undergo hydrolysis [16,32,33] or cyclization [7,11], *e.g.* "dibenzimidine", first associated with the structure HN=CPh–NH–CPh=NH [34], was later shown to be a triazine [35]. Hence, they usually must be stabilized by, *e.g.* protonation with strong acids [9,16,33,36], although sometimes are considerably stable in the neutral form [27–31,37–41].



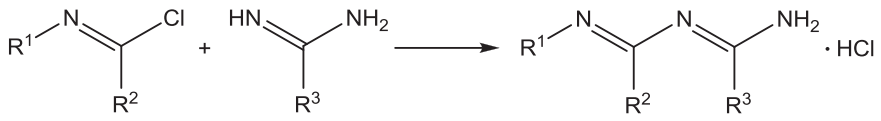
Scheme 5.

2.2. Pinner synthesis

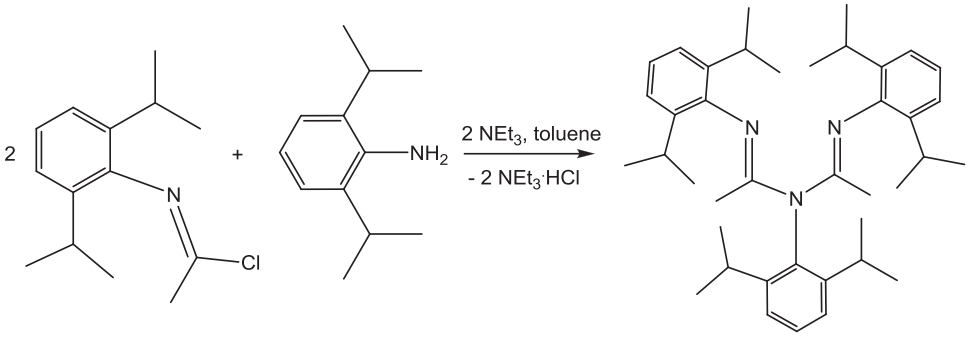
This method, introduced in the 19th century, includes a reaction between the first [*i.e.*, the imino ester RC(=NH)OR′] and the second [*i.e.*, the amidine R″C(=NH)NH_2] products of the Pinner synthesis (Scheme 5). Although in some patents there is a description of the *tap* preparation by this method [44], references from academic sources [36] indicate that yields are rather low, with a number of by-products being formed. In view of these difficulties, the method is not generally used in laboratory practice.

2.3. Ley and Muller's synthesis

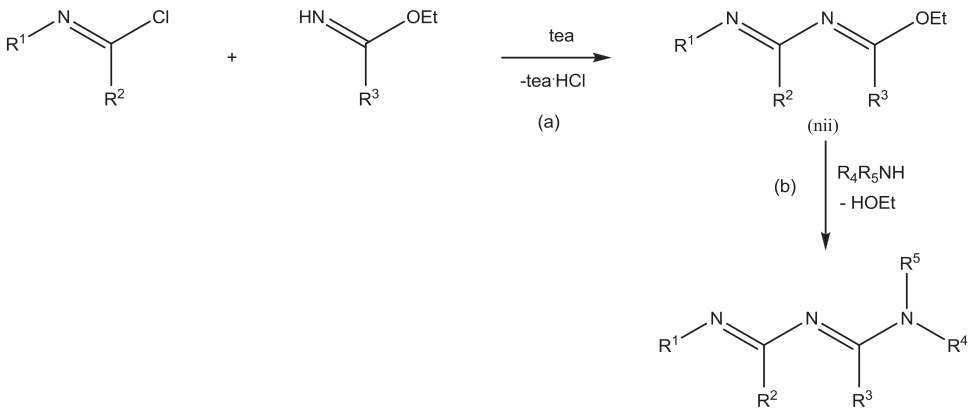
According to the method proposed by Ley and Muller [13], an amidine is treated with a N-imidoyl chloride (Scheme 6). The use of an equimolar excess of amidine, as was proposed initially, leads to separation difficulties during the isolation of the product [6,16], while equimolar amounts of the starting materials react with formation of a mixture of amidine hydrochloride and triazapentadienilium chloride. The former can be removed by washing with hot water, the preparation procedure thus being significantly simplified [6]. Modifications of the method involving an amine instead of an amidine [43] (Scheme 7) or thionyl chloride/phosphorus pentachloride [16] were introduced expanding the number of available *tap* products. This method of synthesis of *tap* seems to be the most versatile one, leads to relatively good yields and was applied to most of the compounds represented in Table 1.



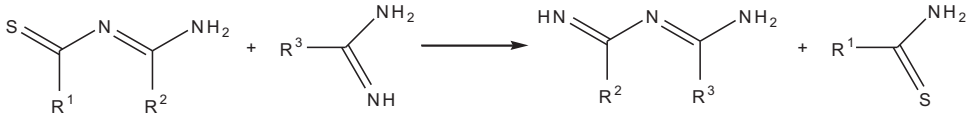
Scheme 6.



Scheme 7.



Scheme 8.



Scheme 9.

2.4. Amination of N-imidoylimidoates

The Ley and Muller procedure can be adopted to the synthesis of N-imidoylimidoates (Nii), as was demonstrated recently [9]. In such a way, Nii can be obtained by reaction of imidoates or imidoate hydrochlorides with N-imidoyl chlorides under basic conditions, *e.g.*, in the presence of triethanolamine (tea) (Scheme 8a). Further reaction of Nii with a primary or a secondary amine gives a tertiary or a quaternary *tap*, respectively (Scheme 8b).

2.5. Desulfurizing amination or amidination of N-tiobenzoylbenzamidines

Notwithstanding their rather general character, the previous methods (Sections 2.3 and 2.4) are not applicable to the synthesis of *tap* in which the nitrogen atoms carry no aryl or alkyl substituents, owing to the instability of the corresponding imidoyl chlorides containing an unsubstituted imido-group [36]. As an alternative route, a desulfurizing amination or amidination of N-tiobenzoylbenzamidines (Scheme 9) was proposed [36]. The starting N-thioamidines can be prepared, *e.g.* by condensation of thiobenzamide with phenyl cyanide in saturated ethereal hydrogen chloride, or starting from N-substituted amidines by the method of Titherley and Hughes [45], and then converted to corresponding *tap* by the desulfurizing reaction with an amine or amidine.

2.6. Amination of nitriles bearing strong electron-withdrawing groups

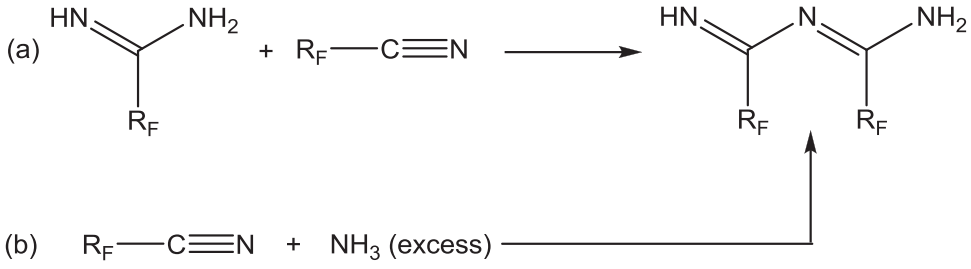
Similarly to amidines, which can be formed by nucleophilic attack of ammonia or amines to nitriles bearing electron-withdrawing groups [10], *tap* can be obtained by condensation of perfluorocarbon activated amidines with similarly activated nitriles (Scheme 10a) or by the reaction of a perfluoroalkylnitrile with an excess of anhydrous ammonia (Scheme 10b). Reaction (a) presents a method for preparing *tap* with dissimilar R_F groups [38]. Also it was found [38] that perfluoroalkyl containing amidines undergo a condensating dimerisation under thermal deammonation to give the corresponding stable *tap*.

Some of the first Cu(II), Zn(II), Ni(II), and Hg(II) complexes containing a genuine chelating *tap* were obtained using ligands prepared by this method [38]. Thus, a high coordination potential of such a type of ligands was demonstrated. The formation of similar *tap* having trichloromethyl groups was also observed [46]. Such *tap* species are rather unstable and readily cyclize converting to the corresponding triazines [46].

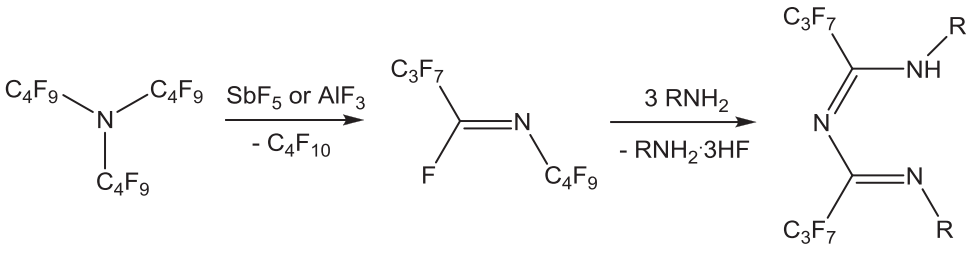
2.7. Reaction of perfluoro-5-aza-4-nonene with primary amines

Another versatile method for the synthesis of *tap* containing perfluoro moieties is the reaction of perfluoro-5-aza-4-nonene, C_3F_7–CF=NC_4F_9 with primary amines RNH_2 (Scheme 11) [27]. The imine C_3F_7–CF=NC_4F_9 can be prepared by acid-catalyzed α-elimination reaction from the perfluoro-amine $(C_4F_9)_3N$ in the presence of SbF_5 or AlF_3, with heating (loss of C_4F_{10} occurs) [27]. In principle, other starting imines can be synthesized by this method from linear, cyclic and heteroatom-substituted perfluoroalkylamines and then used for the synthesis of *tap* [47–49], but until now only the above imine appears to have been used.

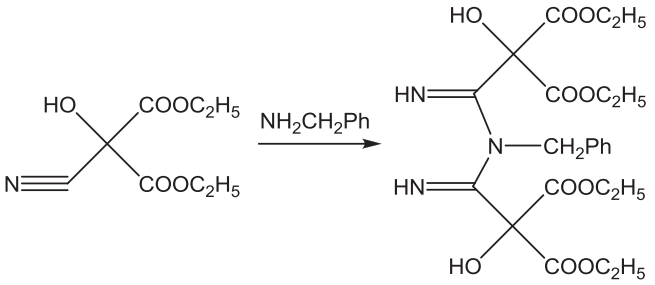
Hence, treatment of a solution of the amine RNH_2 with C_3F_7–CF=NC_4F_9, in, *e.g.* ether, results in a series of addition and HF elimination steps, and the *tap* C_3F_7–C(=NR)–N=C(NHR)–C_3F_7 together with the insoluble RNH_2·3HF are produced. This quite general synthesis of triazapentadienes has been followed for a wide variety of primary amines of diverse functionality [27–32,39–41]. The procedure is rather versatile for *tap* with perfluoro containing moieties and deserves further exploration on account of the high thermal stability, oxidative resistance and fluorocarbon or carbon dioxide solubility of their metal complexes [50,51].



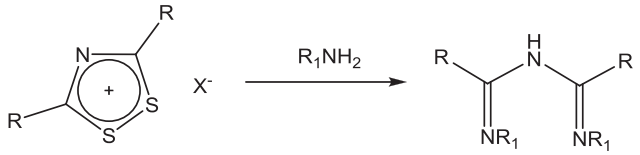
Scheme 10.



Scheme 11.



Scheme 12.



Scheme 13.

2.8. Other methods

A curious addition of benzylamine to ethyl cyanotartronate to afford the unstable *tap* **2** was described by Curtiss and Nickell almost one century ago (Scheme 12) [42]. The molecule of **2** offers many coordination possibilities including chelating ones and potentially can be stabilized upon coordination, but no further attempts to synthesize similar compounds or their metal complexes have been reported.

Another way (Scheme 13) to produce *tap* R–C(=NR$_1$)–N=C(NHR$_1$)–R (R = (un)substituted aryl or heteroaryl; R$_1$ = H, alkyl, cycloalkyl, and aryl) and corresponding salts is described in a patent [52] and consist of reacting a 1,2,4-dithiazolium salt (X^- = Cl^-, Br^-, I^-, and $[FeCl_4]^-$) with an amine R_1NH_2, in the presence of an oxidant (*e.g.* H_2O_2) or a base (*e.g.* NEt_3). This method is attractive, but no further development was found in the literature, thus preventing a clear evaluation of its relevance.

(5-Imino-4,5-dihydro-3H-pyrrol-2-yl)amines (Scheme 14) may be considered as sterically constrained cyclic 1,3,5-triazapenta-1,3-dienes. They are easily prepared from 2,2,3,3-tetramethylsuccinonitrile and lithium amides with subsequent aqueous workup to give the cyclic pyrrole-like compounds [53]. The steric hindrance in such compounds can have an important role in coordination chemistry which has not yet been investigated.

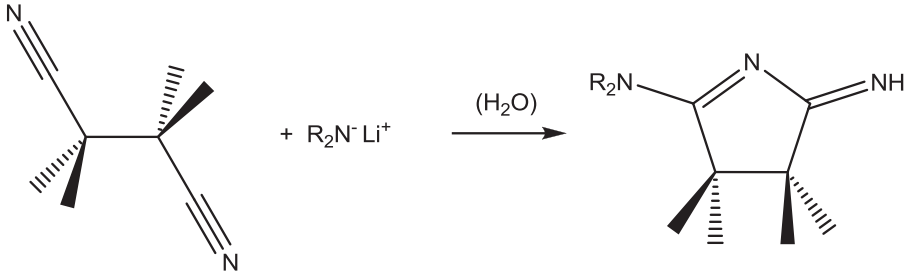
3. Syntheses of complexes

There are several possible ways to prepare *tap* complexes: reaction of a pre-prepared *tap* with a metal source, template condensation of nitriles (or analogs) and/or amidines (or analogs) at a metal center, metal-mediated hydrolytic decomposition of triazines, etc. In this section, the various synthetic methods are discussed; leading to *tap* complexes that usually can be described by the general formulae depicted in Scheme 15 and are collected in Table 2.

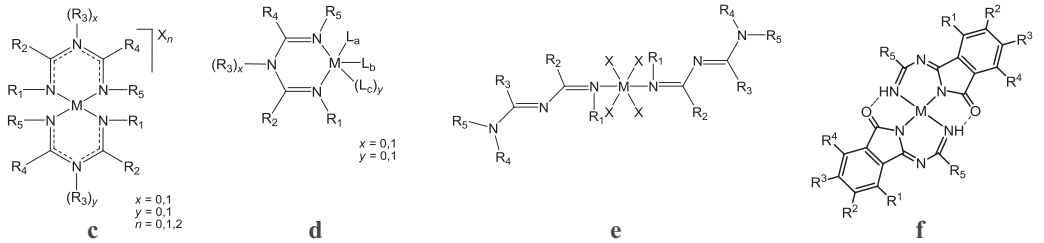
3.1. Reaction of a pre-formed 1,3,5-triazapentadiene with a metal ion source

One of the first publications describing the synthesis of complexes containing a genuine *tap* was by Brown et al. in 1963 (Scheme 15) [38]. In this case, a perfluoroalkyl containing *tap* was first pre-synthesized separately and then mixed with a metal acetate. The course of the reaction was followed by monitoring the pH, since proton loss occurs from tpa which thus binds the metal in the anionic basic form. Complexes of Cu(II), Zn(II), Ni(II) and Hg(II) were synthesized accordingly, as the R groups being restricted to perfluoro methyls, ethyls and propyls. The complexes were characterized by elemental analysis, infrared and UV spectroscopies (Scheme 16).

Similar perfluoro containing (but N-substituted) ligands, C_3F_7–C(=NR)–N=C(NHR)–C_3F_7, were synthesized from the reaction of primary amines RNH_2 with the fluorinated imine C_3F_7–CF=N–C_4F_9 (see above). They exhibit an extensive coordination chemistry [27–32,39–41,77,78]. The *tap* thus synthesized usually acts as a bidentate anionic ligand (deprotonated form) toward, *e.g.* the molecular fragments M = Pd(C_3H_5),



Scheme 14.



Scheme 15.

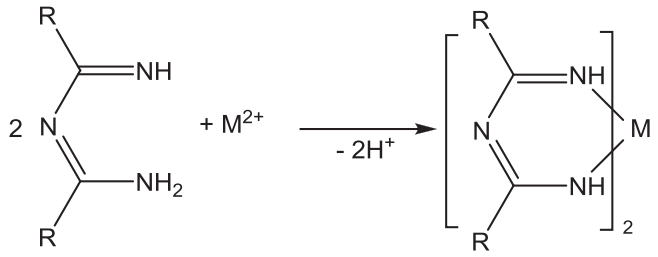
Table 2
Some *tap* complexes (for the types **c**–**f**, see Scheme 15).

M	R_1	R_2	R_3	R_4	R_5	X or L	Ref.
Type **c**							
Ni	H	H	{Cu(tren)}, $\{Ni(NCS)_n\}$	H	H	ClO_4^- ($n=1$)	[54] [a]
	H	Me	H ($x=0$, $y=1$)	Me	H	Cl^- ($n=1$)	[17,33,55]
	H	Et	H ($x=0$, $y=1$)	Et	H	Cl^- ($n=1$)	[33]
	H	*n*-Pr	H ($x=0$, $y=1$)	*n*-Pr	H	Cl^- ($n=1$)	[33]
	H	*i*-Pr	H ($x=0$, $y=1$)	*i*-Pr	H	Cl^- ($n=1$)	[33]
	H	*n*-Bu	H ($x=0$, $y=1$)	*n*-Bu	H	Cl^- ($n=1$)	[33]
	H	CH_2Cl	H ($x=0$, $y=1$)	CH_2Cl	H	Cl^- ($n=1$)	[33]
	H	$CH_2C_6H_4$(OMe-4)	H ($x=0$, $y=1$)	$CH_2C_6H_4$(OMe-4)	H	C_6H_4 (OMe-4)$CH_2CO_2^-$ ($n=1$), Cl^- ($n=1$)	[33]
	H	$C_6H_4(NO_2$-3)	$x=0$, $y=0$	$C_6H_4(NO_2$-3)	H	$n=0$	[56]
	H	$C_6H_4(NO_2$-4)	$x=0$, $y=0$	$C_6H_4(NO_2$-4)	H	$n=0$	[56,57]
	H	C_6H_4(CN-3)	$x=0$, $y=0$	C_6H_4(CN-3)	H	$n=0$	[56,58]
	H	C_6H_4(CN-4)	$x=0$, $y=0$	C_6H_4(CN-4)	H	$n=0$	[56,58]
	H	$C_6H_4(CF_3$-4)	$x=0$, $y=0$	$C_6H_4(CF_3$-4)	H	$n=0$	[56]
	H	C_6H_4(Cl-4)	H ($x=0$, $y=1$)	C_6H_4(Cl-4)	H	Cl^- ($n=1$)	[58]
	H	3-py	H ($x=0$, $y=1$)	3-py	H	Cl^- ($n=1$)	[59,60]
	H	4-py	H ($x=0$, $y=1$)	4-py	H	Cl^- ($n=1$)	[58,60,61]
	H	4-Py(Cl-3)	H ($x=0$, $y=1$)	4-Py(Cl-3)	H	Cl^- ($n=1$)	[58]
	H	pz	$x=0$, $\{Ni(MeOH)(H_2O)_2\}$ ($y=1$)	pz	H	NO_3^- ($n=1$)	[37] [a]
Pd	H	2-Py	H ($x=0,1$; $y=0,1$)	2-Py	H	Cl^- ($n=0,2$)	[62,63]
	H	3-Py	H ($x=0,1$; $y=0,1$)	3-Py	H	Cl^- ($n=0,2$)	[62,63]
	H	4-Py	H ($x=0,1$; $y=0,1$)	4-Py	H	Cl^- ($n=0,2$)	[62,63]
	H	4-Py(Cl-2)	H ($x=0,1$; $y=0,1$)	4-Py(Cl-2)	H	Cl^- ($n=0,2$)	[62]
	H	3-Py(Me-5)	H ($x=0,1$; $y=0,1$)	3-Py(Me-5)	H	Cl^- ($n=0,2$)	[62]
	H	Ph	$x=0$, $y=0$	3-Py	H	$n=0$	[63]
	H	Ph	$x=0$, $y=0$	4-Py	H	$n=0$	[63]
	H	Ph	$x=0$, $y=0$	Ph	Ph	$n=0$	[9]
	H	Ph	$x=0$, $y=0$	$C_6H_4(NO_2$-4)	Ph	$n=0$	[9]
Cu	H	H	H ($x=1$, $y=1$)	H	H	ClO_4^- ($n=2$)	[64]
	H	OMe	$x=0$, $y=0$	OMe	H	$n=0$	[65–70]
	H	pz	$x=0$, $y=0$; Cu(Hpz), Co(pdm), Ni(pdm) ($x=1$, $y=1$)	pz	H	ClO_4^-, NO_3^- ($n=1$)	[37] [a], [69,70]
	H	2-Py	$x=0$, $y=0$; Cu(AcO) ($x=1$, $y=1$)	2-Py	H	$n=0$; ClO_4^- ($n=2$)	[71] [a]
	H	4-Py	$x=0$, $y=0$	4-Py	H	$n=0$	[61]
	Ph	Ph	H ($x=1$, $y=1$)	Ph	H	OTf^- ($n=2$)	[6]
	Ph	Ph	$x=0$, $y=0$	Ph	Ph	$n=0$	[9]
	H	Ph	$x=0$, $y=0$	Ph	Ph	$n=0$	[9]
Co	H	OMe	$x=0$, $y=0$	OMe	H	$n=0$	[72] [b]
	Ph	C_3F_7	$x=0$, $y=0$	C_3F_7	Ph	$n=0$	[27]
Pt	H	Ph	$x=0$, $y=0$	Ph	H	$n=0$	[20]
	H	CH_2Ph	$x=0$, $y=0$	Ph	Ph	$n=0$	[73]
	H	C_6H_4(Cl-4)	$x=0$, $y=0$	Ph	Ph	$n=0$	[73]
	H	Ph	$x=0$, $y=0$	Ph	Ph	Cl^- ($n=1$)	[73,74]
	H	Et	$x=0$, $y=0$	Ph	Ph	$n=0$	[74]
	H	CH_2Ph	$x=0$, $y=0$	Ph	Ph	$n=0$	[74]
	H	NEt_2	$x=0$, $y=0$	Ph	Ph	Cl^- ($n=1$)	[74]
	H	Ph	Me ($x=1$, $y=1$)	Ph	Ph	OTf^- ($n=2$)	[73]
	H	Et	$x=0$, $y=0$	NHPh	Ph	$n=0$	[75]
	H	CH_2Ph	$x=0$, $y=0$	NHPh	Ph	$n=0$	[75]
	H	Ph	$x=0$, $y=0$	NHPh	Ph	$n=0$	[75]
Type **d**							
Cu	H	OMe	$x=0$	OMe	H	$L_a=L_b=HN=C(pz)NC{\equiv}N$, $y=0$	[69] [c]
	H	2-pyrimidyl	CuCl[a]	2-Pyrimidyl	H	$L_a=L_b=Cl$, $y=0$	[76]
	H	Ph	H	Ph	Ph	$L_a=L_b=Cl$, $y=0$	[6]
	C_6H_3(Cl-2,6)	C_3F_7	$x=0$	C_3F_7	C_6H_3(Cl-2,6)	$L_a=L_b=$ en, $y=0$	[32]
	C_6H_3(*i*-Pr-2,6)	C_3F_7	$x=0$	C_3F_7	C_6H_3(*i*-Pr-2,6)	$L_a=$ MeCN, $L_b=L_c=0$; $L_a=$ CO, $L_b=L_c=0$; $L_a=$ *t*-BuNC, $L_b=L_c=0$; $L_a=$ EtC≡CEt, $L_b=L_c=0$	[40,77]
	C_6F_5	C_3F_7	$x=0$	C_3F_7	C_6F_5	$L_a=$ MeCN, $L_b=L_c=0$; $L_a=$ CO, $L_b=$ MeCN, $y=0$; $L_a=L_b=$ en, $y=0$	[31]
	C_6H_3(F-2,CF_3-6)	C_3F_7	$x=0$	C_3F_7	C_6H_3(F-2,CF_3-6)	$L_a=$ CO, $L_b=L_c=0$	[31]
B	H	Ph	$x=0$	$C_6H_4(NO_2$-4)	Ph	$L_a=L_b=F$, $y=0$	[9]
	Ph	Ph	$x=0$	Ph	Ph	$L_a=L_b=F$, $y=0$	[9]
Ni	H	Ph	H	Ph	Ph	$L_a=L_b=NO_3$, $y=0$	[6]
Co	Ph	Ph	H	Ph	Ph	$L_a=L_b=Cl$, $y=0$	[9]

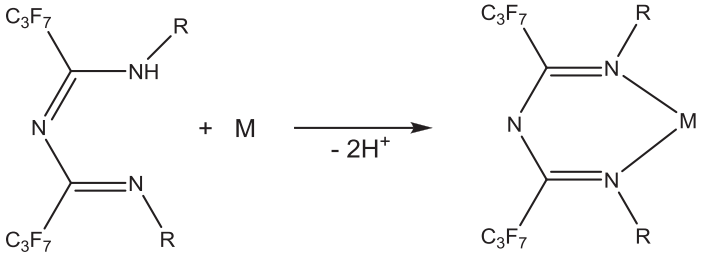
Table 2 (*Continued*)

M	R_1	R_2	R_3	R_4	R_5	X or L	Ref.
Pt	H	Me	H	Me	H	$L_a = L_b = Cl$, $y = 0$	[75]
	H	Et	H	Et	H	$L_a = L_b = Cl$, $y = 0$	[75]
	H	CH_2Ph	H	CH_2Ph	H	$L_a = L_b = Cl$, $y = 0$	[75]
	H	Ph	H	Ph	H	$L_a = L_b = Cl$, $y = 0$	[75]
	H	Et	Ph	Et	H	$L_a = L_b = Cl$, $y = 0$	[75]
	H	CH_2Ph	Ph	CH_2Ph	H	$L_a = L_b = Cl$, $y = 0$	[75]
	H	Et	H	Et	H	$L_a = L_b$ = tmeda, $L_c = OTf^-$, $y = 2$	[75]
Zn	Ph	Ph	H	Ph	Ph	$L_a = L_b = Cl$, $y = 0$	[9]
Ag	Ph	C_3F_7	$x = 0$	C_3F_7	Ph	$L_a = L_b = L_b = 0$	[77]
	C_6H_3(*i*-Pr-2,6)	C_3F_7	$x = 0$	C_3F_7	C_6H_3(*i*-Pr-2,6)	L_a = MeCN, $L_b = L_c = 0$;[d] L_a = *t*-BuNC, $L_b = L_c = 0$;[d] $L_a = PPh_3$, $L_b = L_c = 0$; L_a = EtC≡CEt, $L_b = L_c = 0$	[29,78]
Au	C_6H_3(Cl-2,6)	C_3F_7	$x = 0$	C_3F_7	C_6H_3(Cl-2,6)	$L_a = L_b$ = en, $y = 0$	[39]
	C_6H_3(*i*-Pr-2,6)	C_3F_7	$x = 0$	C_3F_7	C_6H_3(*i*-Pr-2,6)	L_a = EtC≡CEt, $L_b = L_c = 0$	[78]
Ga	H	CF_3	$x = 0$	CF_3	H	$L_a = L_b$ = Me, $y = 0$	[18]
Al	H	Ph	$x = 0$	Ph	H	$L_a = L_b$ = Me, $y = 0$	[18]
Ir	H	CF_3	$x = 0$	CF_3	H	$L_a = L_b = PPh_3$, L_c = CO	[79]
Ru	H	CF_3	$x = 0$	CF_3	H	$L_a = PPh_3$, $L_b = \mu$-C_5H_5, $y = 0$; $L_a = P(OMe)_3$, $L_b = \mu$-C_5H_5, $y = 0$;	[80]
K	Ph	C_3F_7	$x = 0$	C_3F_7	Ph	$L_a = L_b = L_b = 0$	[77]
Li	Ph	C_3F_7	$x = 0$	C_3F_7	Ph	$L_a = L_b = L_b = 0$	[77]
	C_6H_2(Me-2,4,6)	C_3F_7	$x = 0$	C_3F_7	C_6H_2(Me-2,4,6)	$L_a = L_b$ = THF, $y = 0$	[30]
	C_6H_3(*i*-Pr-2,6)	C_3F_7	$x = 0$	C_3F_7	C_6H_3(*i*-Pr-2,6)	L_a = THF, $L_b = L_c = 0$	[30]
Tl	C_6H_2(Me-2,4,6)	C_3F_7	$x = 0$	C_3F_7	C_6H_2(Me-2,4,6)	$L_a = L_b = L_b = 0$	[41] [d]
	C_6H_3(*i*-Pr-2,6)	C_3F_7	$x = 0$	C_3F_7	C_6H_3(*i*-Pr-2,6)	$L_a = L_b = L_b = 0$	[41] [d]
Hg	Ph	C_3F_7	$x = 0$	C_3F_7	Ph	$L_a = CH_3$, $L_b = L_b = 0$	[28] [d]
Type **e**							
Pt	H	Me	Ph	Ph	H	Cl	[74]
	H	Et	Ph	Ph	H	Cl	[74]
	H	Ph	Ph	Ph	H	Cl	[74]
	H	NEt_2	Ph	Ph	H	Cl	[74]
Type **f**							
Ni	H	H	H	H	Me	$x = 0$	[81,82]
	H	H	H	H	Et	$x = 0$	[81,82]
	H	H	H	H	*n*-Pr	$x = 0$	[81,82]
	H	H	H	H	*i*-Pr	$x = 0$	[81,82]
	H	H	H	H	$(CH_2)_3Cl$	$x = 0$	[81]
	H	H	H	H	*n*-Bu	$x = 0$	[82]
	H	H	H	H	CH_2Cl	$x = 0$	[82]
	H	H	H	H	CCl_3	$x = 0$	[82]
	H	H	H	H	CH_2Ph	$x = 0$	[82]
	H	H	H	H	$CH_2C_6H_4$(OMe-4)	$x = 0$	[82]
	H	H	Me	H	Me	$x = 0$	[82]
	H	H	Me	H	Et	$x = 0$	[82]
	H	H	Me	H	*n*-Pr	$x = 0$	[82]
	H	H	Me	H	*i*-Pr	$x = 0$	[82]
	H	H	Me	H	CCl_3	$x = 0$	[82]
	H	H	Me	H	CH_2Ph	$x = 0$	[82]
	F	F	F	F	Et	$x = 0$	[82]
Cu	H	H	H	H	Me	$x = 0$	[83]
	H	H	H	H	Et	$x = 0$	[83]
	H	H	H	H	*n*-Pr	$x = 0$	[83]
	H	H	H	H	*i*-Pr	$x = 0$	[83]
	H	H	H	H	C_6H_{11}	$x = 0$	[83]
	H	H	H	H	CH_2Ph	$x = 0$	[83]
	H	H	Me	H	Me	$x = 0$	[83]
	H	H	Me	H	Et	$x = 0$	[83]
	H	H	Me	H	*i*-Pr	$x = 0$	[83]
	H	Cl	Cl	H	Et	$x = 0$	[83]
	F	F	F	F	Et	$x = 0$	[83]

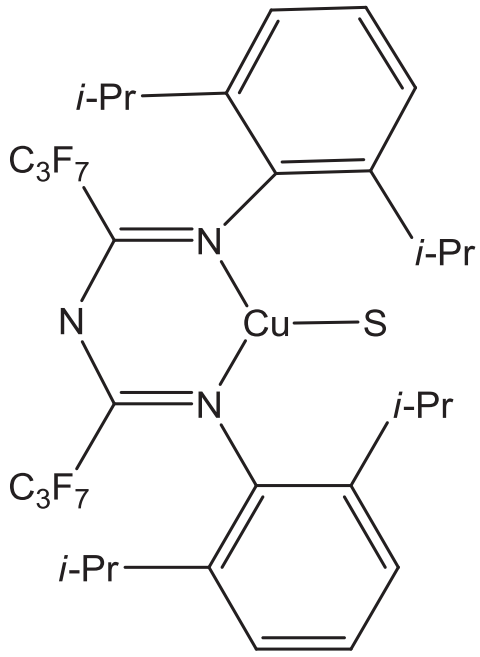
[a] More complicated complexes (coordination polymers) were formed, but only their main structural unit is indicated.
[b] Three *tap* ligands are coordinated to the Co(II) ion.
[c] Heteroligand complex.
[d] The triazapentadienyl ligand coordinates via the central nitrogen atom.



Scheme 16.



Scheme 17.

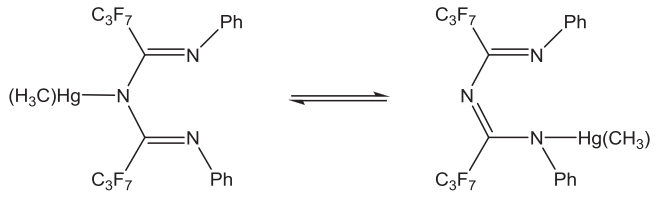


Scheme 19.

Rh(cod), Ir(cod) and $Rh(CO)_2$ to form heteroligand organometallic complexes (Scheme 17) [19,27]. Moreover, the chelates $[M\{C_3F_7–C(=NPh)–N–C(=NPh)–C_3F_7\}_2]$ (M = Mg, Mn, Fe, Co, Ni, Cu, Zn, and Pd) were also prepared [27].

An interesting feature of perfluoroalkyltriazapentadienes, of a high coordination significance (see above), concerns their behavior as weak monoprotic acids with pK_a *ca.* 13–14 [27]. Hence, the corresponding salts of, *e.g.* alkaline or alkali earth metals may be obtained using a variety of their bases. Thus, treatment of $C_3F_7–C(=NPh)–N=C(NHPh)–C_3F_7$ with *n*-BuLi affords $Li[C_3F_7–C(NPh)–N–C(NPh)–C_3F_7]$ which can be used for further synthesis. Its reactions, *e.g.* with MeI, Me_3SiCl, $[(Ph_3P)AuCl]$ or MeHgCl give $[C_3F_7–C(NPh)–N–C(NPhR)–C_3F_7]$ where R = CH_3, $SiMe_3$, $Au(PPh_3)$ or HgMe, respectively. Interestingly, in the last three cases, the ligand exhibits the unusual *tap* monodentate coordination mode [27,28,77]. In the solid state, Hg was proved (by X-rays) to be coordinated by the central N atom, whereas NMR and IR spectroscopies show that in solution the coordination bond shifts to one of the terminal N-atoms, according to the equilibrium between the two binding modes shown in Scheme 18.

One of the most intriguing properties of such ligands with sterically demanding substituents is the ability to create air and thermally stable half-sandwich type complexes leaving the other side of the metal center opened to some extent for further transformations, including catalytic reactions. Thus, it was shown that copper(I) oxide reacts with $C_3F_7–C(=NR_{dipp})–N=C(NHR_{dipp})–C_3F_7$ (where R_{dipp} = 2,6-diisopropylphenyl) in acetonitrile leading to the stable unsymmetrical adduct with acetonitrile $[Cu\{C_3F_7–C(=NR_{dipp})NC(=NR_{dipp})C_3F_7\}(S)]$ (Scheme 19, S = MeCN) [40]. This complex undergoes displacement reactions of the labile acetonitrile ligand to give isocyanide, carbonyl or ethylene



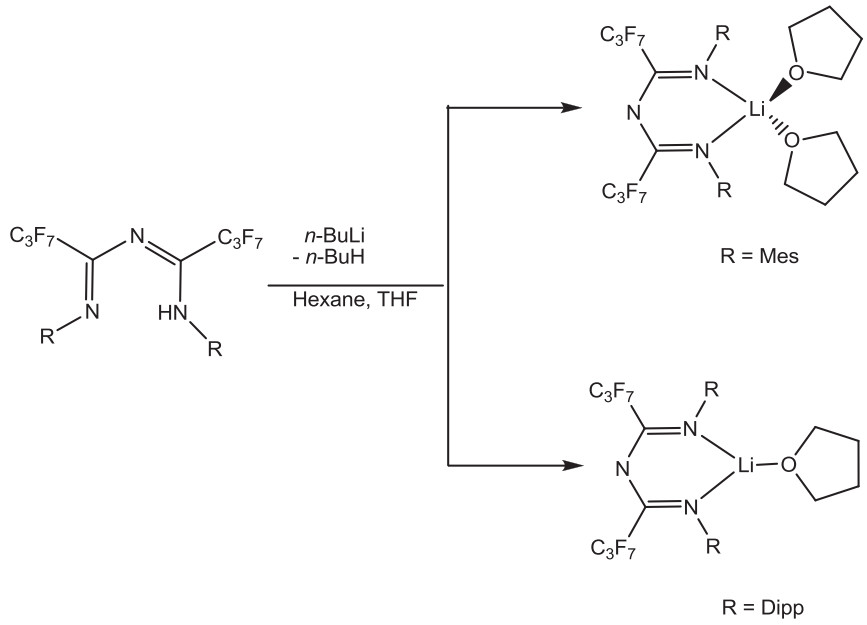
Scheme 18.

complexes (S = *n*-BuNC, CO or C_2H_4, respectively) that are also air and thermally stable [31,40]. Such complexes are similar to metal-dipyrazolylborates and thus potentially can be used for the same purposes and applications (*e.g.* in catalysis).

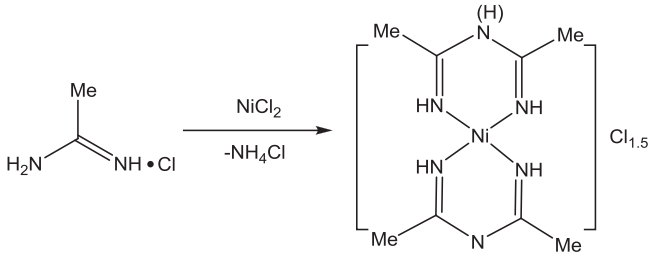
The silver nitrile adduct $[Ag\{C_3F_7–C(=NR_{dipp})–N–C(=NR_{dipp})–C_3F_7\}(NCMe)]$ was synthesized in the same way [29], but the *tap* ligand coordinates through the central nitrogen atom, similarly to the Hg complex depicted in Scheme 18. This Ag complex can be converted to the corresponding chelate by reacting with triphenylphosphine which displaces acetonitrile, and the *tap* NCNCN core switches its coordination mode forming a chelate complex of the type shown in Scheme 19 [29]. Lithium ions can also be *tap* chelated to give four- or three-coordinate adducts (with auxiliary THF ligands) with a corresponding distorted tetrahedral or planar geometry featuring boat- or U-shaped metallacycles (Scheme 20) [30].

The N-substituted sterically hindered ligand **1** shown in Scheme 3, synthesized by the Ley and Muller method (see Section 2.3), was used for the preparation of Co(II), Ni(II), Pd(II), Co(II) and Zn(II) *tap* complexes [6]. In most cases, half-sandwich complexes of the type [MX(*tap*)] (X = counter-ion of the used metal salt) similar to those of Scheme 19 were formed. If copper(II) triflate, instead of chloride, is used for the synthesis, a copper symmetrical octahedral complex with two chelating *tap* and two ligated counterions can also be formed, $[CuX_2(tap)_2]$. In these cases, a proton shift from the terminal nitrogen atom in the free *tap* to the central one in the complexed form was observed, the *tap* remaining in the acid neutral form. In a similar way, Pd(II) complexes containing higher azapolyenes (which also can be considered as *tap* upon coordination) were synthesized and characterized [22].

Another sterically demanding *tap* ligand, *i*-$Pr_2C_6H_3N(C(Me)NC_6H_3$*i*-$Pr_2)_2$, was prepared by Masuda et al. by reacting two equivalents of imidoyl chloride with 2,6-diisopropylaniline in the presence of Et_3N in refluxing toluene. Reactions with AlI_3 or $AlMe_3$ afforded $[AlI_2\{i\text{-}Pr_2C_6H_3N(C(Me)NC_6H_3i\text{-}Pr_2)_2\}][AlI_4]$ and $[Al(Me)_2\{i\text{-}Pr_2C_6H_3N(C(Me)NC_6H_3i\text{-}Pr_2)_2\}][Al(Me)_4]\cdot AlMe_3$, respectively [43]. When aluminium(III) hydride was used as a starting material, Al-*tap*-hydride adducts were obtained.



Scheme 20.



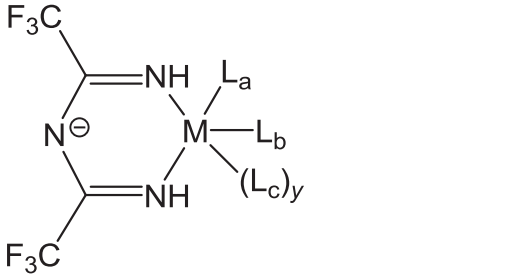
Scheme 21.

3.2. Template condensation of amidines

One of the first studies describing the template condensation of amidines to form a *tap* complex was reported by Norrestam [17] concerning the formation of a 2,4-dimethyl-1,3,5-triazapentadiene Ni(II) complex (which he named as N^1-acetimidoylacetamidine-N^1,N^3)nickel(II) chloride) upon self-condensation of acetamidine under the templating influence of nickel(II) ions (Scheme 21). As in most of other complexes with N-unsubstituted *tap* ligands, nickel(II) is coordinated by two of such ligands forming a symmetrical low-spin square-planar complex. Curiously, one of the ligands is partly deprotonated, giving an overall charge of +1.5 to the complex.

The more activated trifluoroacetamidine, NH=C(CF_3)–NH_2, underwent a condensation reaction in the presence of Ru, Os or Ir hydride species in boiling toluene, to liberate ammonia and form complexes containing the chelating anionic 2,4-di(trifluoromethyl)-1,3,5-triazapentadienate ligand NHC(CF_3)NC(CF_3)NH, as well as ligated carbonyl, triphenylphosphine, hydride or perfluoroacetate, in various combinations, depending on the metal ion and on the synthetic procedure (Scheme 22) [19].

In another study [18], the reactions of trimethylgallium with trifluoroacetamidine H_2NC(CF_3)NH or of trimethylaluminium with benzamidine H_2NC(Ph)NH, giving similar



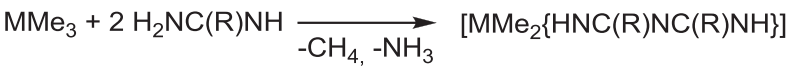
Scheme 22.

[$GaMe_2${HNC(CF_3)NC(CF_3)NH}] and [$AlMe_2${HNC(Ph)NC(Ph)NH}] complexes, were discovered, involving deprotonation with evolution of methane (Scheme 23).

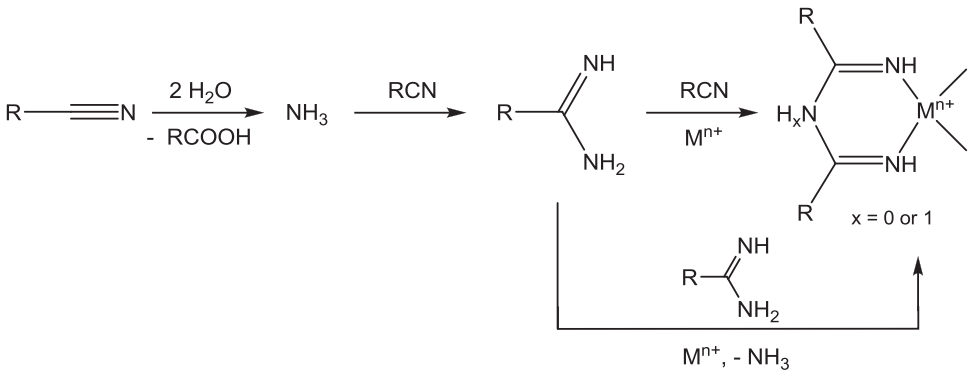
3.3. Direct one-pot template synthesis from nitriles

For a successful application of the direct one-pot synthesis of *tap* from a nitrile, the NCR used must be activated by an electron-withdrawing group and/or by coordination to a metal center. This method is somehow related to the that described above (Section 3.2) because, though the full mechanism is still not established, most probably it involves the complete hydrolysis of nitrile with formation of ammonia and subsequent coupling, conceivably through amidine intermediates (Scheme 24) [33,55,61].

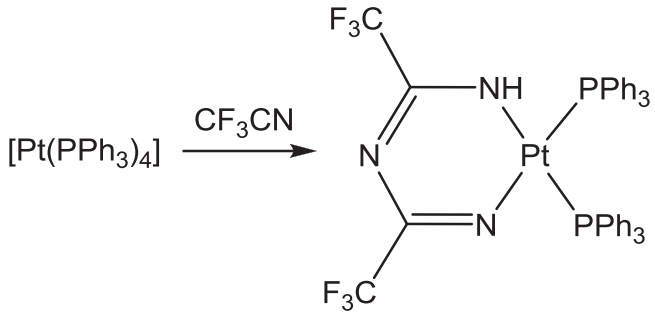
One of the first studies describing such a transformation was reported by Bland et al. [84] who found that trifluoroacetoni-



Scheme 23.



Scheme 24.



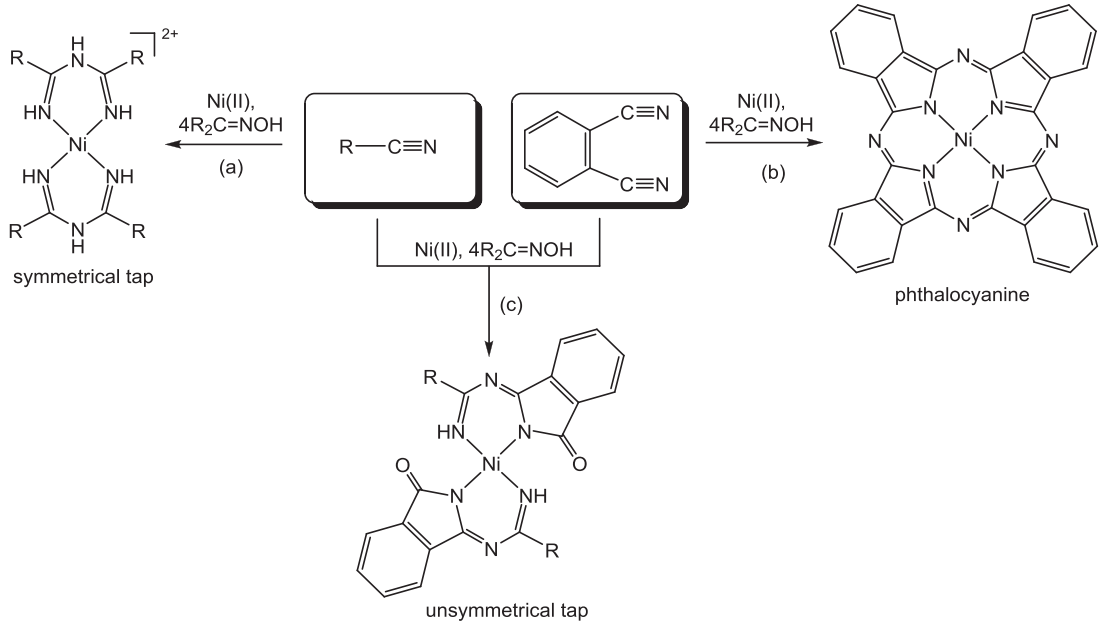
Scheme 25.

trile reacts with tetrakis(triphenylphosphine)platinum(0) forming the platinum(II) complex [Pt{HNC(CF_3)NC(CF_3)N}(PPh_3)$_2$] bearing a doubly deprotonated(2-) *tap* ligand (Scheme 25). The authors proposed that the central N atom of the formed *tap* ligand is presumably derived from hydrolytic degradation of CF_3CN. In agreement with this proposal, addition of water to the initial reaction mixture resulted in an increased yield of the Pt-*tap* complex. From the latter reaction, further complexes containing trifluoroacetonitrile in varying degrees of polymerization were also obtained, but the detailed structural characterization was not achieved.

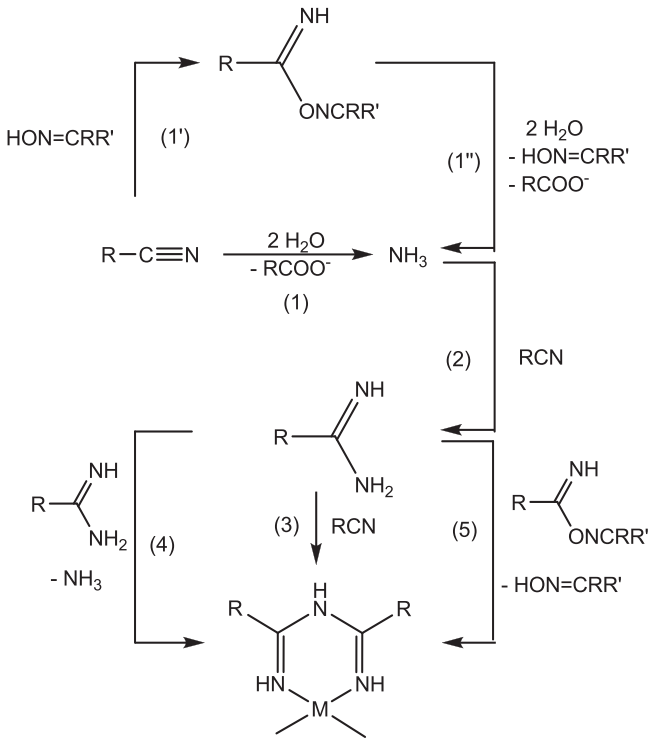
The approach was extended by Bottrill et al. [79] to iridium(I). In this case, the reaction of trifluoroacetonitrile with [Ir(η^3-MeC_3H_4)(CO)(L)$_2$] (L = PPh_3 or $AsPh_3$) yields the *tap* complex [Ir{NH=C(CF_3)N=C(CF_3)NH}(CO)(PPh_3)$_2$] together with [Ir{NHC(CF_3)=C(CH=CH_2)C(CF_3)=NH}(CO)(PPh_3)$_2$]. Robinson et al. [80] expanded it to ruthenium(II), with the synthesis of the complexes [Ru(η^5-C_5H_5){HN=C(CF_3)N=C(CF_3)NH}(L)] [L = PPh_3 or $P(OMe)_3$]. The reaction leading to the formation of the *tap* complexes occurs only in methanol (wet or dry) and these products do not form to any appreciable extent when dry THF is used. This is indicative that not only hydrolysis but also methanolysis (or oxolysis in the case of oximes or hydroxylamines—see below [62,85,86]) can be involved in the nitriles degradation.

After a significant time gap, this research line was continued by a report [55] on the reaction of acetonitrile with the dinuclear compound [Ni_2(μ-OH)$_2$(tpa)$_2$][ClO_4]$_2$ [tpa = tris-(2-pyridylmethyl)amine] forming the square-planar nickel(II) complex [Ni{HN=C(Me)–N=C(Me)–NH}$_2$].

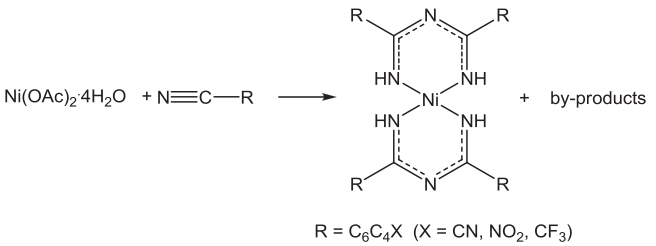
More recently, we achieved a novel route to *tap* complexes based on the combined use of nitriles and oximes R_2C=NOH. This provided the synthesis of a number of Ni(II)-*tap* complexes of the type [Ni{N(H)=C(R)NHC(R)=NH}$_2$]$^{2+}$ in good yields and by an easy and convenient procedure (Scheme 26, route (a)) [33]. Initially this route was used for liquid nitriles in a high excess which acted also



Scheme 26.



Scheme 27.



Scheme 28.

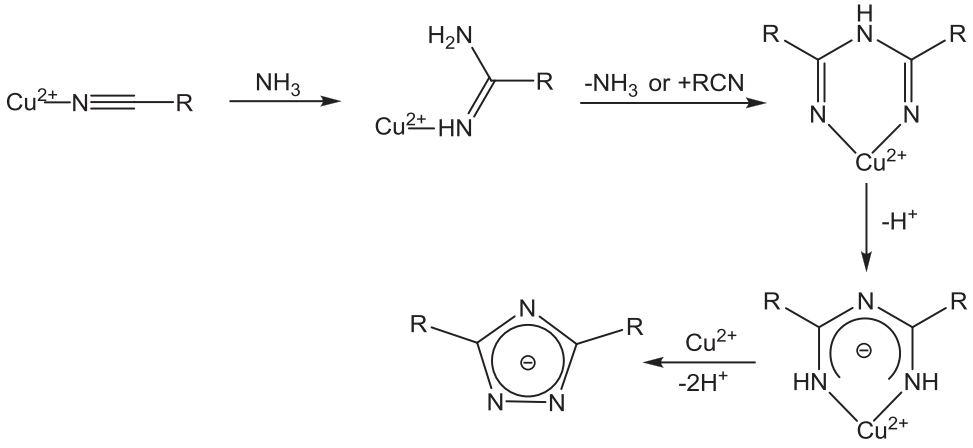
as solvents. However, the procedure was extended to solid nitriles (in this case a liquid oxime was used as the solvent) [58,59], and further to other metal centers (in particular Pd(II)) [62].

Although the full establishment of the mechanism was not achieved, a reasonable mechanistic description has been proposed [33,55]. It was observed [33] that the template reaction does not proceed in the absence of the oxime or the metal(II) salt, which play an essential role. On the other hand, when nickel(II) and palladium(II) oxime complexes were synthesized and used as starting materials, the reactions proceeded with a similar rate and the same M(II)-*tap* products were obtained with comparable yields. Hence, M(II)-oxime complexes can be involved as intermediates in the template conversion. The overall process (Scheme 27) conceivably involves the complete hydrolysis of nitrile to ammonia and carboxylic acid (reaction 1) [which can be assisted by the oxime—(1′) and (1″)], followed by the metal(II)-mediated reaction of the thus formed ammonia with nitrile to yield an amidine (reaction 2) which then couples with the cyano group of a nitrile ligand to achieve the M-*tap* complex (reaction 3). This product can also be obtained via amidine-amidine condensation (reaction 4) or reaction of amidine with the iminoacylated oxime (reaction 5) derived from nucleophilic addition (reaction 1′) of the oxime to the nitrile [87–90]. The reaction promoting role of the oxime is thus accounted for by reactions (1′) and (5).

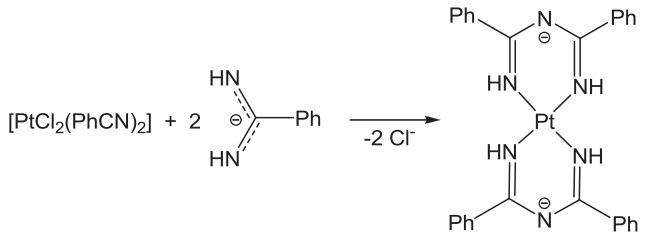
Phthalocyanines can be viewed as macrocyclic analogs of *tap* containing four condensed N=C–N=C–N structural motifs. Hence, one could think that they would be formed by a procedure similar to that we have discussed, although starting from phthalonitriles as the nitrile source. In fact, this approach was successful and allowed one to synthesize a number of phthalocyanines by this novel route (Scheme 26, route (b)); an intermediate involving nucleophilic addition of two oximes per one phthalonitrile was isolated and fully characterized [91]. In comparison to the known procedures of phthalocyanine preparations [92], this method utilizes low-cost reagents with hydrolytic stability and easy accessibility, has a high simplicity and does not require harsh conditions. The use of a mixture of a phthalonitrile with a nitrile in that method allowed the synthesis of unsymmetrical Ni-*tap* complexes (Scheme 26, route (c)), which combine phthalocyanine and classical *tap* motifs [81].

Another way for the direct synthesis of *tap* complexes from nitriles involves a solvothermal procedure. The authors [56] prepared neutral symmetric double-metallacycle nickel(II) bis[2,4-di(aril)-1,3,5-triazopentadienato] complexes $[Ni\{N(H)=C(R)NC(R)=NH\}_2]$ by a "one-pot" solvothermal (autoclave, 110 °C, several days) reaction in methanol of tetrahydrous nickel(II) acetate with six molar equivalents of benzonitrile derivatives $N\equiv C(C_6H_4X)$ bearing a strong electron withdrawing substituent (X) such as –CN, $-NO_2$ or $-CF_3$, located at the *m*- or *p*-position (Scheme 28). Analogous reactions of nitriles lacking such a type of substituent do not occur under similar conditions.

The formation of Cu and Ni *tap* complexes was also observed [61] in the course of triazole synthesis upon reaction of organonitriles, ammonia, and metal(II) salts. These *tap* compounds are



Scheme 29.



Scheme 30.

important intermediates in the solvothermal synthesis of triazoles (Scheme 29) [61,93].

3.4. Nucleophilic addition of amidines or related reagents to coordinated nitriles

Upon coordination, nitriles can be strongly activated toward nucleophilic attack [87–90,94]. Amidines can thus act as nucleophiles toward the triple CN bond in nitrile ligands to give *tap* complexes. One of the first reports of this type of metal-*tap* synthesis was given by Baker et al. [20] who obtained the symmetrical Pt(II)-*tap* complex [Pt{HNC(Ph)NC(Ph)NH}$_2$] by nucleophilic addition of lithiobenzamidine (prepared *in situ* from benzamidine chloride and Li(Bu-*n*) in diethyl ether solution) to the ligated benzonitrile in [PtCl$_2$(NCPh)$_2$] (Scheme 30).

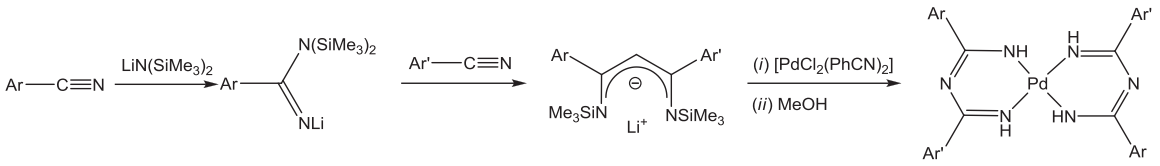
A similar approach allowed Guo et al. [60,63] to synthesize pyridyl-containing *tap* complexes of nickel(II) and palladium(II). The reaction of LiN(SiMe$_3$)$_2$ with cyanopyridine was used to produce in situ lithium amidinate, which further condenses at the metal center (Scheme 31; Ar = pyridyl; Ar′ = pyridyl, Ph).

Although lithiation of benzamidine was believed [20,60,63] to be necessary to enhance the nucleophilicity of this species and to promote its coupling with a nitrile, the amidine PhC(=NH)NHPh is a sufficiently good nucleophile to react without additional activation, even under mild conditions, with Pt(II)-bound nitriles, thus providing an easy access to Pt(II)-*tap* complexes [73,74]. For example, PhC(=NH)NHPh reacts with different nitriles RCN (R = Me, Et, Ph, NEt$_2$) coordinated to Pt(IV) or Pt(II) [74]. In the former case, *trans*-[PtCl$_4${NH=C(R)NC(Ph)=NPh}$_2$] with a "frozen" *tap* ligand, coordinated only by one N atom, is formed. Dehydrochlorination of these Pt(IV) complexes with the help of the carbonyl-stabilized phosphorus ylide Ph$_3$P=CHCO$_2$Me, or the use of [PtCl$_2$(RCN)$_2$] as a starting material, leads to coordination of the formed 1,3,5-triazapentadienes also via the NHPh end to the Pt(II) center with ring closure (Scheme 32) [74].

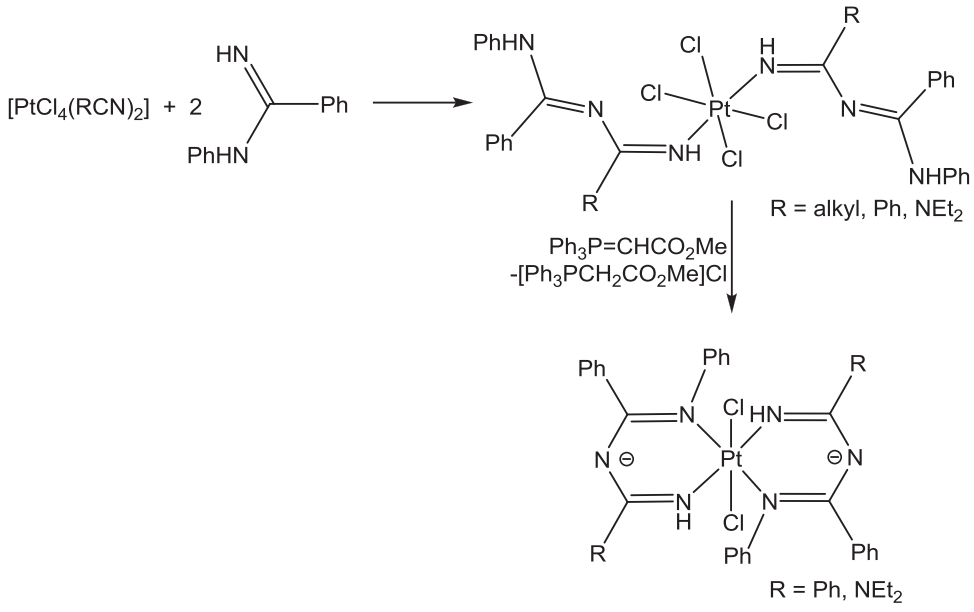
The phenyl containing *tap* Pt^{II} luminescent complexes [Pt{NH=C(R)NC(Ph)=NPh}$_2$] (R = CH$_2$Ph, C$_6$H$_4$Cl-4, Ph) were prepared by nucleophilic addition of the amidine PhC(=NH)NHPh to the nitriles RCN activated by coordination to platinum(II) in *trans*-[PtCl$_2$(RCN)$_2$] (Scheme 33, route (a)) [73]. The addition of the amidine to the coordinated nitriles followed by ring-closure of the newly formed 1,3,5-triazapentadienes is accompanied by dehydrochlorination and HCl is trapped with another amidine molecule to form amidinium chloride.

Alkylation of the internal amide N at [Pt{NH=C(Ph)NC(Ph)=NPh}$_2$] was achieved by MeOSO$_2$CF$_3$ with formation of [Pt{NH=C(Ph)N(Me)C(Ph)=NPh}$_2$](SO$_3$CF$_3$)$_2$ (Scheme 33, route (b)) [73]. As a result of the *tap* alkylation, the planarity of the metallacycles is lost, as well as the luminescent behavior.

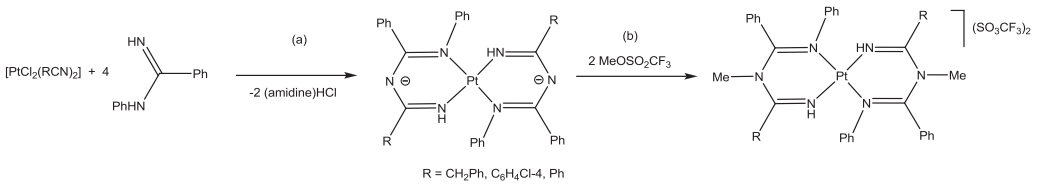
Iminoisoindolinones (Iii) can be considered as a particular case of amidines and thus the synthesis of derived *tap* complexes is discussed in this section. Hence, Iii were readily condensed with various nitriles at Ni(II) or Cu(II) producing the corresponding unsymmetrical M-*tap* complexes [82,83]. This template reaction at a nickel(II) center may be achieved by either single-pot or step-



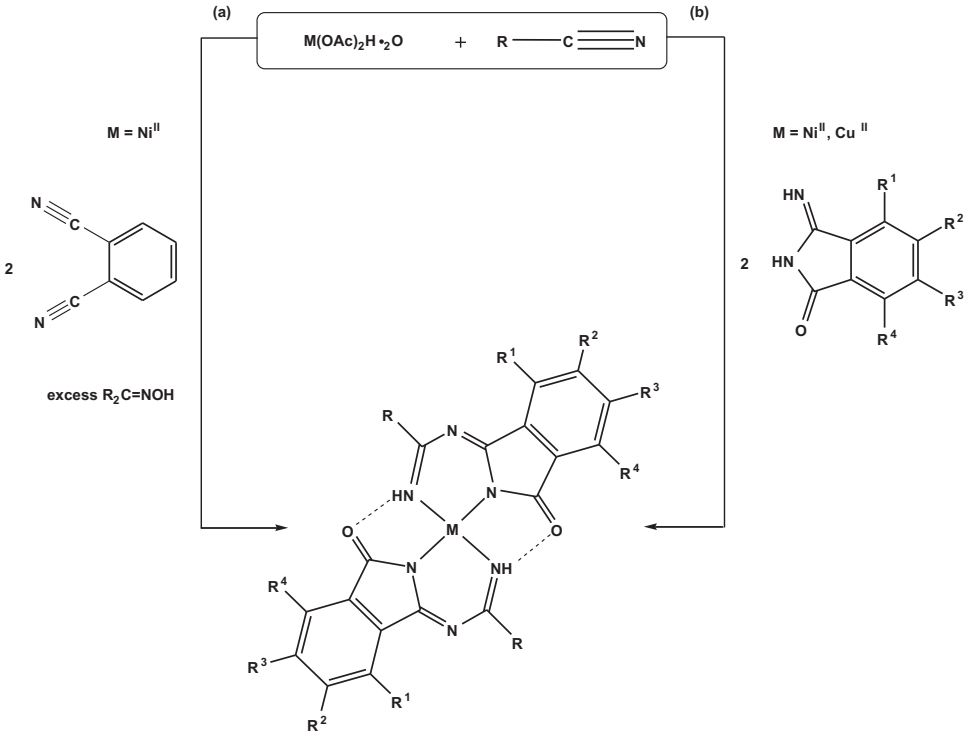
Scheme 31.



Scheme 32.



Scheme 33.



Scheme 34.

wise approaches (Scheme 34, routes (a) or (b), respectively). In the former method, 3-iminoisoindol-1-one is generated *in situ* by an oxime-mediated conversion of phthalonitrile and reacts with a nitrile at a Ni(II) center, furnishing the target *tap*-Ni(II) complexes bearing an incorporated iminoisoindolinone fragment [81]. However, this technique was relatively specific, appearing to proceed exclusively at Ni(II) and being limited to the unsubstituted phthalonitrile reagent. The plausible mechanism for this single-pot method (route a) involves the oxime-promoted generation of an Iii from phthalonitrile followed by the coupling of Iii and a nitrile at the Ni(II) center.

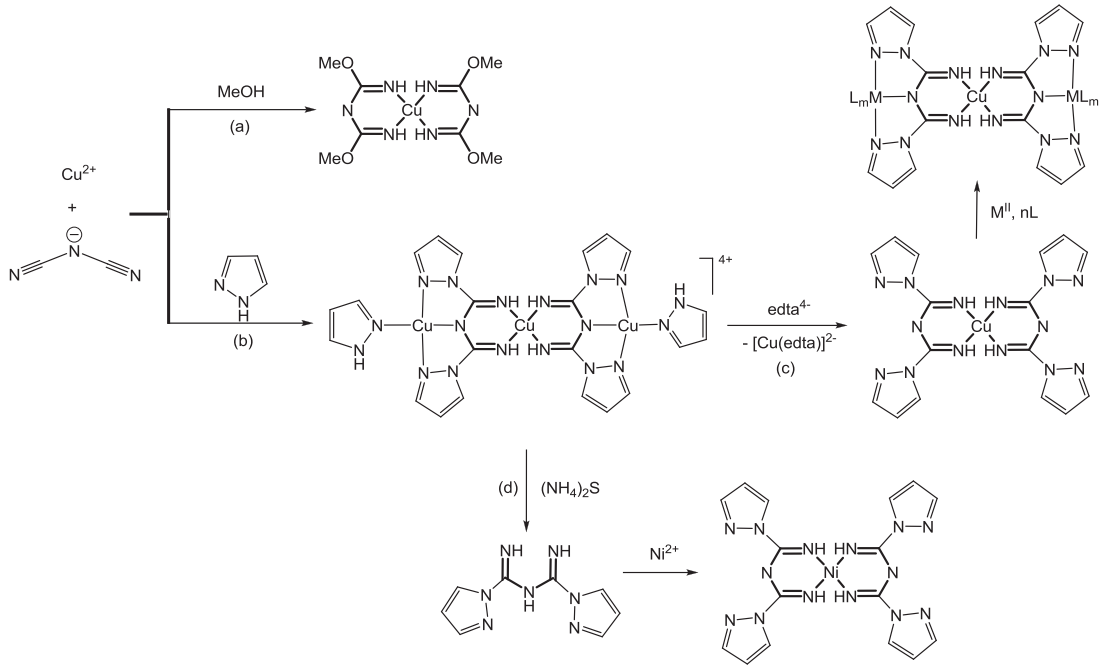
The stepwise method (route b) involves the reaction of nickel or copper acetate with a pre-prepared Iii in neat nitrile RCN (acting as both solvent and reactant) to give the corresponding unsymmetrical *tap* complex. Compared to route (a), a more general character is disclosed by (b) insofar as this method is not limited to only the unsubstituted Iii. Route (b) can be applied to Iii bearing substituents with various donor/acceptor properties and also to a wide range of nitriles with either donor or acceptor groups of different sterical hindrances [82,83].

3.5. Nucleophilic additions to dicyanamidate

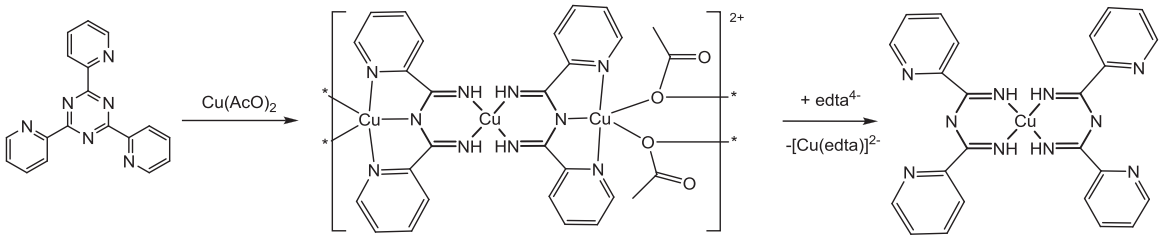
In Section 3.3, phthalonitriles, dicyano containing molecules, participate in the synthesis of *tap* complexes. We now consider another dicyano species, dicyanamidate N≡C–N–C≡N$^-$ (dca), which can also be used as a convenient starting material for *tap* preparation. In fact, both cyano moieties can undergo nucleophilic addition by an alcohol or by pyrazole (Hpz) at Cu(II), to produce complexes with *tap* containing alkoxy (dcaOMe) or pyrazolyl [dcadpz = (pz)C(=NH)–N$^-$–C(=NH)(pz)] substituents, *i.e.* [Cu(dcaOMe)$_2$] or [Cu$_3$(dcadpz)$_2$(Hpz)$_2$]$^{4+}$, correspondingly (Scheme 35, routes (a) and (b), respectively) [65,66,70]. These pyrazole-containing Cu(II) trinuclear complexes possess interesting magnetic properties, and the study was further extended by others [95] to the synthesis of heteronuclear complexes of Cu(II), Co(II), Ni(II) and Mn(II) (Scheme 35, route (c)) whose magnetic properties were studied in detail showing that the complex ligand Cu(dcadpz)$_2$ can be regarded as a ferromagnetic coupler. This approach was further developed [37] with the isolation of dipyrazolyl *tap* species and a salt of the protonated form, that are able to sequester another metal ion, in particular Ni(II) (Scheme 35, route (d)).

3.6. Hydrolytic conversion of triazines

The formation of a *tap* complex upon hydrolysis of a triazine was first achieved by reaction of Cu(ClO$_4$)$_2$·6H$_2$O with 1,3,5-triazine in 95% ethanol, which resulted in the partial hydrolysis of the triazine ring and isolation of the violet bis(1,3,5-triaza-1,4-pentadieno)copper(II) perchlorate [64]. The bis-chelated copper(II) ion displays a planar coordination geometry with Cu–N$_{(ave)}$ bond length of 1.97 Å and the perchlorate ions weakly coordinated (Cu–O distance of 2.84 Å) in the axial positions. Application of



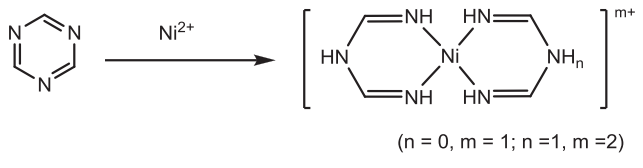
Scheme 35.



Scheme 36.

the approach to 2,4,6-tripyridyltriazolene and copper(II) acetate produces a copper(II) containing *tap* coordination polymer with interesting magnetic properties; isolation of the monomeric Cu(II) unit was achieved upon treatment of the polymeric species with Na_4(edta) (Scheme 36) [71].

Later, the same group used a similar strategy to produce other magnetically active species [54,95]. The new mononuclear complexes $[Ni(Htap)_2][ClO_4]_2$ and [Ni(*tap*)(Htap)][ClO_4] were synthesized by reaction of nickel(II) perchlorate with 1,3,5-triazine which readily decomposes to form Htap (Scheme 37). In the latter complex, the neutral Htap and the monoanionic tap^- coordinate to the nickel(II) ion (square planar, low-spin state) in a bidentate, chelating fashion (Scheme 37, $n = 0$, $m = 1$). Using the central N of tap^- as a donor atom, the multinuclear complexes $[\{Cu(tren)\}_2\{Ni(tap)_2\}][ClO_4]_4$ (tren = tris(2-aminoethyl)amine) and $[Ni(Htap)_2]_2[Ni\{Ni(tap)(Htap)\}_2(NCS)_4][Ni\{Ni(tap)(Htap)\}(NCS)_5]_2$ were synthesized. In both complexes, tap^- binds two metal ions in a $\kappa^1N{:}\kappa^2N$ bridging mode. This type of approach was also applied to synthesize the half-sandwich homodinuclear complex [ClCu(*tap*)$CuCl_2$] with 2-pyrimidyl substituents, the magnetic properties of which were studied [76].

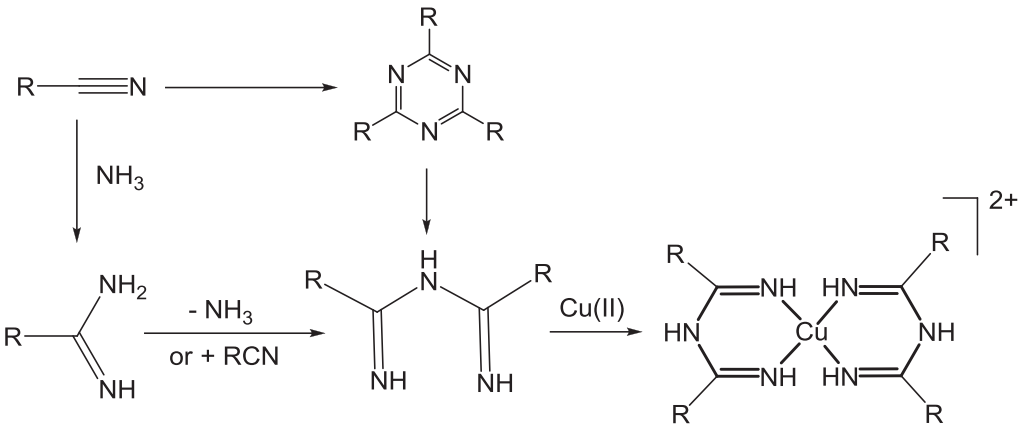


Scheme 37.

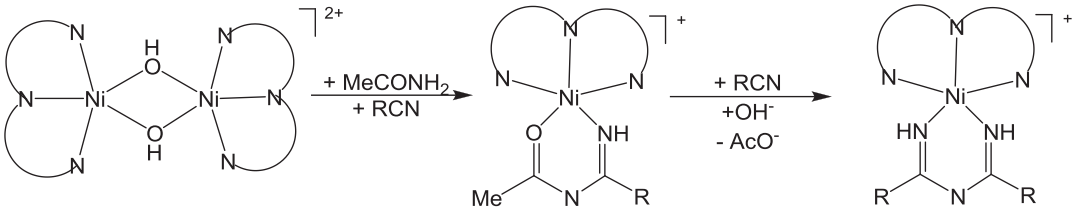
3.7. Other methods

In situ reactions carried out in systems containing a metal ion (*e.g.* Cu(II) or Ni(II)) and a nitrile at elevated temperatures (*i.e.*, under solvothermal conditions) have been recognized as a powerful technique for the construction of *tap* complexes [56,57,61]. In spite of the special conditions used, solvothermal syntheses of *tap* ligands can correspond to the above mentioned methods. Thus, the formation of some Ni(II)-*tap* complexes was proposed to go via condensation of an acetamidine molecule, generated *in situ*, with either the acetonitrile solvent (see Section 3.4) or another acetamidine (Section 3.2) [56]. On the other hand, the formation of Cu(II)-*tap* complexes under solvothermal conditions can proceed [61,93] not only through condensation of ammonia with nitriles, but also by decompositions of the first formed triazines (Section 3.6) (Scheme 38).

A recent publication [96] describes one further route to *tap* by condensation of nitriles with amides or ureas promoted by the coordinatively unsaturated bis(μ-hydroxy)nickel(II) dimeric complex $[Ni_2(\mu\text{-}OH)_2(t\text{BuDPA})_2](ClO_4)_2$ (*t*BuDPA = bis(2-pyridylmethyl)tert-butylamine). In the presence of acetamide and aromatic nitrile, the complex is first converted to a tBuDPA nickel(II) acetyl(imino(phenyl)methyl)amide intermediate (by condensation of the amide with nitrile), which further



Scheme 38.



Scheme 39.

transforms to the final Ni(II)-*tap* complex (Scheme 39). Mass spectrometry studies with ^{15}N-acetamide and unlabeled benzonitrile showed that one nitrogen in each of the intermediate and final complexes originates from acetamide. However, it was proved [96] that coordinated nitriles are also somehow involved in ammonia abstraction from acetamide.

4. Final comments

The numbers of 1,3,5-triazapentadienes (*tap*) and their complexes synthesized to date, as well as their *synthetic methods*, are still rather limited and deserve further exploration. In particular, the application of the Pinner synthesis for *tap* production is still very rare. Further attention should be paid toward the generalization of some modifications of the Lay and Muller synthesis, *e.g.* as described in [43] (Scheme 7) or [9] (Scheme 8). In spite of the high synthetic potential [47–49], the preparation of perfluoro containing *tap* by reaction of perfluoro-5-aza-4-nonene with primary amines concerns only a few examples [27–32,39–41] and a deeper insight in this method can lead to new and interesting compounds. The synthesis of *tap* from 1,2,4-dithioazolium salt [52] is also underinvestigated and deserves particular attention. The coordination chemistry of cyclic *tap*s such as (5-imino-4,5-dihydro-3H-pyrrol-2-yl)amines [53] (Scheme 14) is completely unknown, and should be interesting to explore in view of the constrained structures involved. The direct template synthesis of *tap* complexes is also a very attractive area and new exciting results [85,96] continue to appear in the area.

On the other hand, the search for unusual or particular *properties* of *tap* and their complexes with potential *applications* constitutes a fast growing area of research. Thus, an interesting pH-dependent luminescence was discovered [73] for Pt(II)-*tap* complexes which also exhibit a blue shift of both the absorption and emission with increasing solvent polarity and with decreasing π-electron withdrawing properties of the ligand substituent. *Tap* with, e.g. pyrazolyl or pyridine substituents is a valuable ligand to create a variety of new molecular magnets where Cu(II)-*tap* complexes behave as ferromagnetic couplers [37,70,71,95]. Furthermore, copper(I), silver(I) or gold(I) *tap* complexes can be used [78] as π-activation agents for alkynes, and for catalysis of carbene and nitrene transfer to a variety of substrates [97]. Ni(II)-*tap* complexes with sterically hindered *tap* ligands are effective catalysts for ethylene polymerization [98]. Also recently we have applied copper(II) 2,4-alkoxy-1,3,5-triazapentadienato complexes as catalysts for facile, efficient and selective solvent-free syntheses of ketones from secondary alcohols [99]. On the other hand, related copper(II) complexes were used for anion recognition and crystal engineering [100,101], as DNA binding or cleaving agents [102] or promote a proton induced conformational change [67], and can be applied as molecular switches.

Hence, a continuously growing interest on this class of coordination compounds and further developments of their chemistry are expected, namely as functionalized species with useful properties in a variety of field, including catalysis in which their application is still rather underdeveloped.

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