# More Hydra than Janus - non-classical coordination modes in complexes of oligopyridine ligands

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ABSTRACT

Oligopyridine ligands and the related compound 1,10-phenanthroline have played a critical role in the development of coordination chemistry. This class of ligands probably constitutes the most commonly adopted metal-binding scaffold used in supramolecular and nanoscale chemistry. The adoption of the oligopyridine metal-binding domain in such areas is often predicated upon the assumption that the ligands will adopt chelating polydentate bonding modes. This review highlights the fact that these ligands are a great deal more versatile than this assumption would suggest. In addition to the chelation, cyclometallated and hypodentate bonding modes are also commonly observed.


Keywords: Ligand, 2,2'-bipyridine, 1,10-phenanthroline, 2,2':6',2"-terüyridine, oligopyridine, cyclometallation, hypodentate, reactivity

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**Dedication:** This review is dedicated to our friend and colleague, Pierre Braunstein and celebrates his contributions to organometallic and coordination chemistry as well as to the scientific culture of our region.

Contents

## 1. Introduction

2,2'-Bipyridine (bpy, **1**) is the parent compound of a series of classical chelating polydentate nitrogen donor ligands including 1,10-phenanthroline (phen, **2**) and 2,2':6',2"-terpyridine (tpy, **3**) (Scheme 1). These ligands define a paradigm of classical coordination chemistry and ever since the first description of bpy by Fritz Blau in 1888 [1], the tacit assumption is that they behave as multidentate N-donor species in which all of the available donor atoms coordinate to a metal centre [2,3,4,5,6,7,8,9]. In recent years, exceptions to this behaviour have defined new bonding modalities with important consequences for the structural and reaction chemistry of these compounds. As the title of this article[†] indicates, these ligands have not just one or even two but a multiplicity of coordination modes. This review attempts to present a coherent overview of this multiplicity, including hypodentate coordination and cyclometallated binding in addition to the chelating mode. Excluded from the review are divergent oligopyridines which cannot present a polydentate chelating donor set to a metal centre; these have been partially reviewed elsewhere [10,11]. All searches of the Cambridge Structural Database (CSD) made for this review used the CSD version 5.38 with updates November 2016 and February 2017 [12] and Conquest v. 1.19 [13].

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[†] The Lernaean Hydra was a multi-headed water monster of Greek mythology. In contrast, the Roman God Janus is usually depicted as having (only) two faces. The image in the graphical abstract is taken from the watercolour "Janus" by Tony Grist and made available under the Creative Commons CC0 1.0 Universal Public Domain Dedication (https://commons.wikimedia.org/wiki/File:Janus_.jpg).
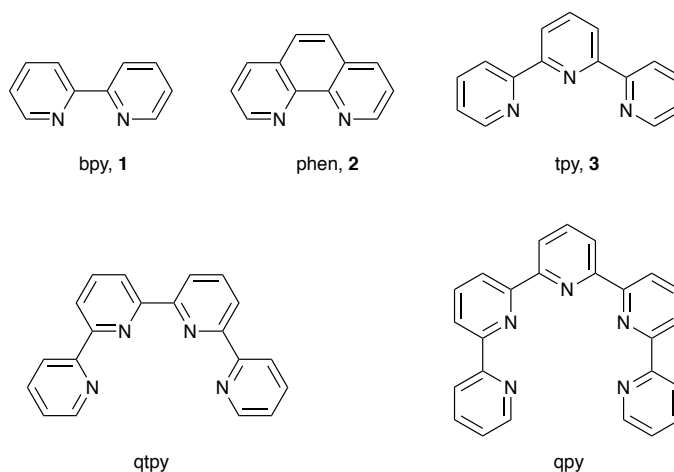
**Scheme 1** The commonest oligopyridine ligands and the abbreviations used throughout this review.. The IUPAC names are given in the table of ligand abbreviations (Table 1).

Table 1. Ligand abbreviations including typical examples to illustrate how substituted ligands are presented in a shortened form in the body of the text.

| | |
|---|---|
| bpy | 2,2'-bipyridine |
| 3,3'-(HO)$_2$bpy | 2,2'-bipyridine-3,3'-diol |
| Hhfacac | 1,1,1,5,5,5-hexafluoropentane-2,4-dione |
| 3,3'-Me$_2$bpy | 3,3'-dimethyl-2,2'-bipyridine |
| N-Mebpy | N-methyl 2,2'-bipyridinium |
| N-Metpy | N-methyl 2,2':6',2"-terpyridinium |
| 6,6'-Ph$_2$tpy | 6,6'-diphenyl-2,2':6',2"-terpyridine |
| phen | 1,10-phenanthroline |
| qpy | 2,2':6',2":6",2''':6''',2""-quinquepyridine |
| qtpy | 2,2':6',2":6",2'''-quaterpyridine |
| septipy | 2,2':6',2":6",2''':6''',2"":6"",2''''':6''''',2''''''-septipyridine |
| spy | 2,2':6',2":6",2''':6''',2"":6"",2'''''-sexipyridine |
| tpy | 2,2':6',2"-terpyridine |

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## 2. Hypodentate coordination

### 2.1 What is hypodentate coordination?

One of us introduced the term hypodentate a number of years ago to describe complexes of tpy in which one of the nitrogen atoms was not coordinated, resulting in a bidentate N,N'-bonding mode [14]. The term is now generic for coordinated ligands in which fewer than the maximum possible number of chelating donors are bound to a metal centre. Hypodentate bonding modes are emerging both as interesting and important isolated species and as postulated intermediates in the formation and dissociation of chelate complexes of these ligands as well as in novel dynamic processes. Although originally formulated for oligopyridines, the hypodentate concept has found broader acceptance, especially in the study of polydentate amines [15,16,17,18,19,2021,22,23,24,25,26,27,28,29,30,31,32,33,34,35]. The description hypodentate has been used to refer both to the ligand and to the complexes incorporating such ligands. This section will consider hypodentate complexes containing oligopyridine and related ligands, especially monodentate bpy and phen ligands, mono- and bidentate tpy ligands, mono-, bi- and tridentate quaterpy ligands, mono-, bi-, tri- and tetradentate qpy ligands, and mono-, bi-, tri-, tetra- and pentadentate qpy ligands. Excluded are compounds in which the full complement of donor atoms is distributed between multiple metal centres in a bridging mode.

### 2.2 Design strategies for complexes containing hypodentate ligands

It is useful to consider design strategies for the synthesis of complexes containing hypodentate ligands. A number of approaches have been identified and implemented with various degrees of success. The first approach is to utilize a kinetically inert metal centre
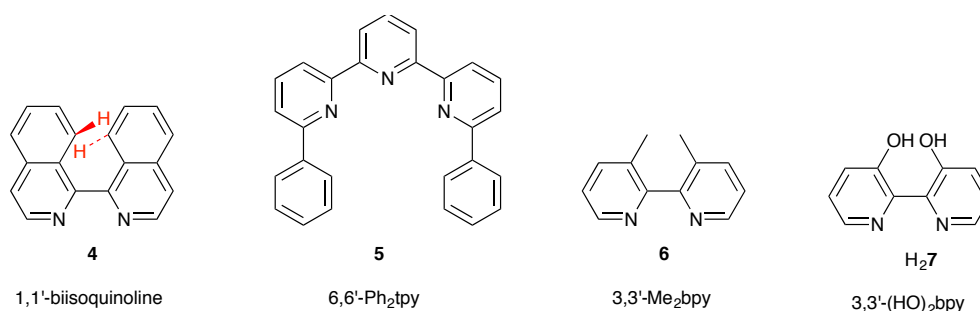
(typically possessing a $d^3$, $d^6$ or $d^8$ electron configuration) in which non-labile ligands occupy sufficient sites that the incoming oligopyridine cannot exhibit its maximum chelating denticity. A typical example of this approach is shown in Scheme 2, where a $d^6$ octahedral metal centre has four of the six coordination sites occupied by bidentate bpy ligands. Upon reaction with tpy, only two binding sites are available, resulting in a complex with a bidentate tpy ligand [14,36].
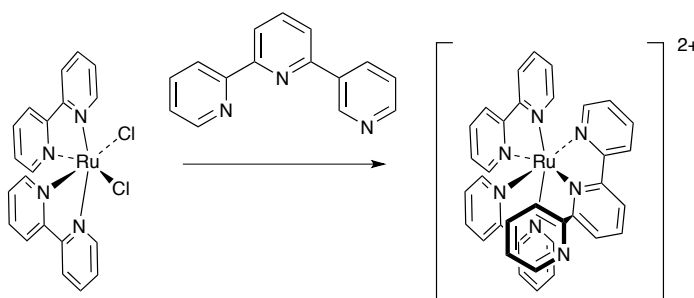


**Scheme 2.** The kinetically inert $d^6$ six-coordinate complex [Ru(bpy)$_2$Cl$_2$] has two chlorido ligands which can be replaced by incoming donors. Upon reaction with tpy, only two of the three nitrogen donors of the tpy ligand can bind, giving the six-coordinate complex [Ru(bpy)$_2$(tpy-*N,N'*]$^{2+}$ containing a hypodentate (bidentate) tpy ligand [36].

A more subtle approach is when sterically demanding substituents in the complex determine that the oligopyridine cannot exert its maximum denticity. A number of types of steric interaction may be considered. Substituents adjacent to the interannular bonds in oligopyridines disfavour the cisoid near-planar mode associated with chelation. An example of such a ligand is 1,1'-biisoquinoline (**4**, Scheme 3) in which the interactions between the 8- and 8'-hydrogen atoms force the ligand out of planarity. This is reflected in its structural chemistry, and the CSD contains more examples of complexes containing bridging or monodentate **4** ligands than with chelating ligands. Similarly, substituents adjacent to the nitrogen donors of the oligopyridine can interact with the other ligands in the complex or the

metal centre itself. A good example is seen in the coordination behaviour of 6,6'-Ph$_2$tpy (**5**, Scheme 2) with iron(II); the complex [Fe(**5**)$_2$]$^{2+}$ is a high-spin four-coordinate species containing two bidentate **5** ligands and in which the four Fe-N bonds (2.09-2.2059 Å) are significantly shorter than the non-bonded Fe-N contacts (2.436-2.456 Å) [37].



|  |  |  |  |
|---|---|---|---|
| **4** | **5** | **6** | H$_2$**7** |
| 1,1'-biisoquinoline | 6,6'-Ph$_2$tpy | 3,3'-Me$_2$bpy | 3,3'-(HO)$_2$bpy |

**Scheme 3.** Some ligands in which steric interactions can lead to hypodentate bonding modes in metal complexes.

With labile metal centres, the balance between the preferred coordination number and intra- or interligand steric effects can determine the denticity of a ligand. Very often these effects are subtle and difficult to predict, as exemplified in the case of methylmercury(II) complexes which typically exhibit linear two-coordinate structures. The complex [MeHg(bpy)][NO$_3$] is three-coordinate with a bidentate bpy ligand [38], whereas in [MeHg(3,3'-Me$_2$bpy)][NO$_3$] (3,3'-Me$_2$bpy, **6**) the interactions between the methyl-substituents destabilize the chelating mode and result in a complex in which the metal is linear two-coordinate with a monodentate 3,3'-Me$_2$bpy ligand [39]. These examples also exemplify the difficulties of defining coordination number in complexes of this type. In reality, the description of [MeHg(bpy)][NO$_3$] is also not so simple, and although the bpy is bidentate, one Hg-N bond is shorter (2.240 Å) than the other (2.426 Å). The strongly-bonded nitrogen exhibits an N-Hg-C angle of 164.39°. In the next sections, we show that

hypodentate oligopyridine ligands often exhibit ambiguous metal-nitrogen distances which are not fully "non-coordinated".

Another factor which can lead to a hypodentate bonding mode is the presence of additional donor groups on the oligopyridine ligand that can coordinate in preference to one or more of the ring nitrogen atoms. A good example is in the complex, $[(2\text{-py-}N\text{=}NPh)_2Ru(\mathbf{7})Ru(2\text{-py-}N\text{=}NPh)_2]^{2+}$, in which the doubly deprotonated 3,3'-$(HO)_2$bpy ($H_2\mathbf{7}$) ligand binds to each of two ruthenium centres as a chelating NO donor [40].

### 2.3    *Quantifying and identifying hypodenticity*

The comments made at the end of the preceding section hint that identifying hypodentate complexes is not always a simple question of "either it is or it isn't coordinated". For a quantitative identification of hypodentate modes, structural data are a prerequisite, although spectroscopic methods provide excellent tools for identifying the presence of hypodentate ligands and investigating dynamic behaviour associated with hypodenticity.

If we consider the simplest structural unit in oligopyridine complexes (Scheme 4), a number of parameters define the coordination mode. We start with the assumption that at least one nitrogen ($N_1$) is coordinated to the metal. Three distances are readily defined: $d_1$ ($M$–$N_1$), $d_2$ ($M...N_2$) which is the distance between the metal and the second nitrogen (which may or may not be coordinated) and $d_3$ ($N_1...N_2$) which is related to the torsion angle within the ligand. The ratio $d_2/d_1$ is useful; in chelate complexes, the ratio $d_1/d_2$ is close to 1 and significant deviations from unity are good indications of hypodenticity. Two angles, the bite- or pseudo-bite angle $\theta$ and the torsion angle $\phi$ are also useful indicators. A word of caution is needed here. Although the bite angle is widely used in discussions of chelating ligands, the concept of a unique ligand bite-angle is a fallacy - the bite angle subtended at the metal depends on $d_1$ and $d_2$ (i.e. on the size of the metal ion) and is not a fundamental property of

the ligand. For comparisons between metal ions of similar sizes, typically transition metal ions in the same $n$d-series, the approximation is useful, but cannot be transferred between ions of different ionic radii, for example, 3d and 4d metal ions. This is seen by comparing $[Fe(bpy)_3][PF_6]_2$ and $[Ru(bpy)_3][PF_6]_2$; the longer M–N distances in the ruthenium(II) complex result in a smaller bite-angle $\theta$ (Table 2). The N...N distance $d_3$ is relatively constant indicating that there is no great distortion from planarity in the coordinated ligands, as also seen in the torsion angles $\phi$.
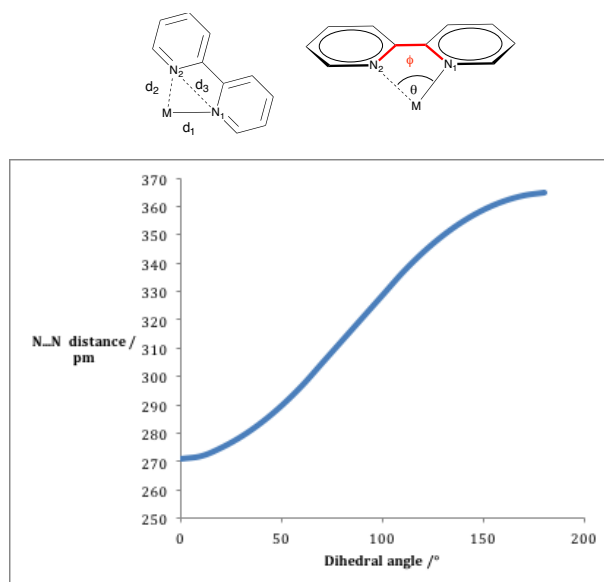


**Scheme 4.** The parameters which are useful in defining metal oligopyridine interactions. The chart shows the variation in the distance $d_3$ with rotation about the interannular C-C bond.

**Table 2**

Comparison of the structural parameters used to define chelating and hypodentate bonding modes. The bite-angle $\theta$ is not a characteristic of the ligand, but rather a function of the distances $d_1$, $d_2$ and $d_3$.

| Complex | $d_1$/Å | $d_2$/Å | $d_3$/Å | $\theta$/° | $\phi$/° | ref. |
|---|---|---|---|---|---|---|
| $[Fe(bpy)_3][PF_6]_2$ | 1.967 | 1.967 | 2.578 | 81.86 | 6.43 | 41 |
| $[Ru(bpy)_3][PF_6]_2$ | 2.056 | 2.056 | 2.607 | 78.67 | 5.82 | 42 |

*2.4    Forcing hypodenticity*

One approach to to ensuring that an oligopyridine adopts a hypodentate bonding mode is to ensure that a nitrogen cannot coordinate to a metal centre because its lone pair is used in another bond. The commonest ways of doing this are by coordination to another metal centre, protonation, quaternization or N-oxidation. In general, pyridine N-oxides have a rich coordination chemistry, which is dominated by the bonding of the oxygen atom to a metal centre and this class of ligands will not be further considered [43,44,45].

Only relatively few simple complexes with quaternized ligands are known and the tendency is to give cyclometallated species in which the metal has formally inserted into the C–H bond of the aromatic ring (**8**) [46,47,48,49,50,51,52,53,54] or the methyl (or α-methylene) of an N-alkyl chain (**9**) [55].

The reaction of 1-methyl-2,2'-bipyridinium salts with $[MCl_4]^{2-}$ salts (M = Co, Cu, Zn, Cd, Hg, Pd, Pt) gives complexes formulated $[(1\text{-Mebpy})MCl_3]$ (**10**) [47,48,53,56,57,58]. In the case of M = Pd or Pt, the chlorido ligands may be replaced by a variety of other anionic ligands; all of the palladium and platinum complexes are readily converted to the cyclometallated analogues containing motif **8**. The only structurally characterized example is $[Pd(\mathbf{11})X_3]$ [59] (Fig. 1d) with an 1-(4-chlorophenacyl) substituent, which is obtained as a X = Cl/Br 1:1 composite from the reaction of [**11**]Br with $PdCl_2$.

The reaction of [1-Mebpy]I with CuI gives the tetranuclear complex $[(1\text{-Mebpy})Cu_4I_6][(1\text{-Mebpy})]$ (Figure 1a) [60]. The more highly functionalized ligand N-carboxymethyl 1,10-phenanthroline (H**12**) forms chelated NO-donor complexes $[M(\mathbf{12})(H_2O)_2Cl_3]$ with lanthanides (M = La, Sm, Eu, Er, Y) in which the free phen nitrogen and the carboxylate are both coordinated to the metal [61].

(a)                                              (b)

(c)                                              (d)
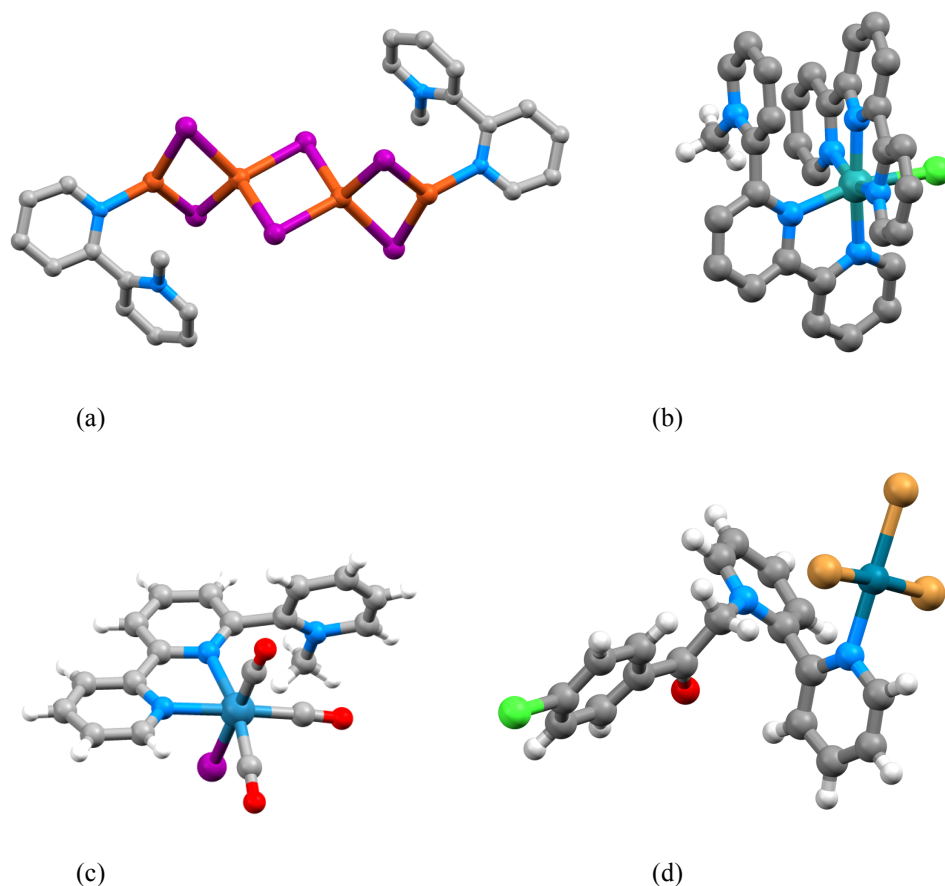
**Fig. 1** The structures of some complexes containing alkylated oligopyridine ligands (a) [(1-Mebpy)Cu$_4$I$_6$(1-Mebpy)] [60] (b) [Ru(tpy)(1-Metpy)Cl][PF$_6$]$_2$ [54] (c) [Re(1-Metpy)(CO)$_3$Cl]$^+$ [62] and (d) [Pd(**11**)Br$_3$][59].

Methylation of tpy occurs on the terminal ring to give the 1-methyl-2,2':6',2"-terpyridinium cation 1-Metpy which forms cyclometallated complexes and compounds containing bidentate 1-Metpy ligands. The complex [Ru(tpy)(1-Metpy)Cl][PF$_6$]$_2$ with the pendent 1-methylpyridinyl ring trans to the chlorido-ligand has been structurally characterized (Fig. 1b) [54]; a second isomer of this complex was also isolated in which the the pendent 1-methylpyridinyl ring is cis to the chlorido-ligand. In an interesting development, the N-Metpy complexes [Re(1-Metpy)(CO)$_3$X]$^{n+}$ ($n$ = 1, X = I; $n$ = 2, X = MeCN) have been prepared directly by methylation of the hypodentate compounds [Re(tpy)(CO)$_3$(MeCN)]$^+$ with MeI and [Me$_3$O][BF$_4$] respectively. The complex [Re(1-Metpy)(CO)$_3$I]$^+$ can also be obtained directly from the reaction of [Re(tpy)(CO)$_3$Cl] with

MeI, whereas reaction with [Me$_3$O][BF$_4$] yields [Re(1-Metpy)(CO)$_3$Cl]$^+$. The solid-state structures of [Re(1-Metpy)(CO)$_3$X][PF$_6$]$_n$ ($n$ = 1, X = I, Cl; $n$ = 2, X = MeCN; Scheme 6) have been reported and the [Re(1-Metpy)(CO)$_3$Cl]$^+$ cation is presented in Fig. 1c [62].



**8**      **9**      **10**      **11**      **H12**
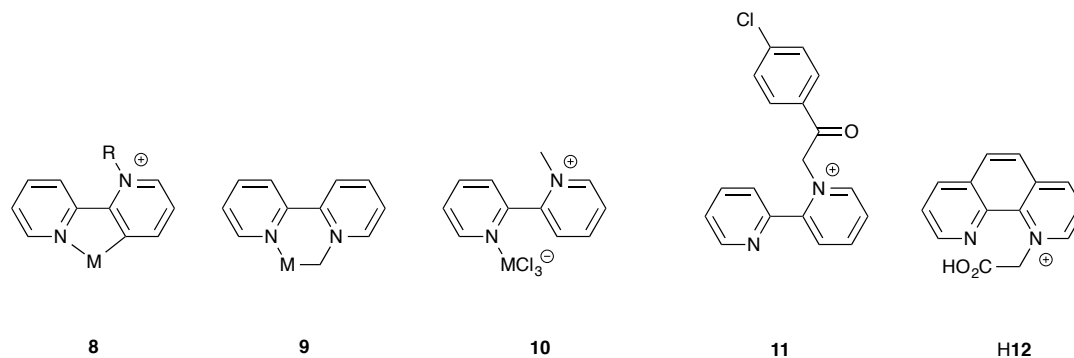
**Scheme 5** Complexes of oligopyridines containing quaternized nitrogen atoms exhibit various structure types. Insertion into the C-H bonds of an aromatic ring (**8**) or an alkyl group (**9**) can give cyclometallated structures. With 1-Mebpy salts, complexes containing monodentate 1-Mebpy ligands may be obtained (**10**).
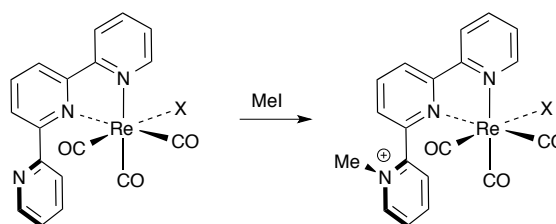


**Scheme 6** An elegant route for the preparation of complexes of quaternized ligands is the alkylation of complexes containing hypodentate ligands [62].

## 2.5    Hypodentate bpy and phen ligands

In this section, the emphasis is upon structurally characterized examples of complexes containing bpy and phen ligands in which bonding to a metal is through a single nitrogen atom of the potentially bidentate ligand. Specifically excluded is a discussion of the erroneous assignment of monodentate structures to complexes subsequently shown to contain cyclometallated ligands and which are discussed in Section 3. It is sometimes surprisingly difficult to unambiguously confirm hypodentate bonding for bpy or phen

ligands, even in those cases where solid state structural data are available as metal-nitrogen distances are often in an "ambiguous" range, in particular with complexes involving four-coordinate metal centres. Structural data were initially identified on the basis of $d_2/d_1$ (or $d_1/d_2$) values greater than 1.2 as discussed in the preceding sections.

### 2.5.1 Hypodentate phen complexes

It is convenient to commence the discussion with complexes containing phen ligands as the N…N distance $d_3$ is relatively constant. The vast majority of phen complexes (19055 $d_2/d_1$ data) exhibit the expected bidentate chelating mode (Scheme 7) with approximately equal $d_2/d_1$ (or $d_1/d_2$) ratios between 1.0 and 1.2. After the exclusion of N-oxide and cyclometallated complexes, some 95 data remain, many of which are multinuclear complexes in which both phen nitrogen atoms are coordinated but to different metal centres. These coordinatively saturated multidentate complexes are not further discussed in this section. A common motif is seen in complexes with ligands bearing multidentate substituents such that only one of the two nitrogen donors of the phen can coordinate. A typical example is seen in the complex [Cu(**13**)][ClO$_4$]$_2$ (Fig 2a) in which the steric bulk of the (EtO)$_2$CH-substituent at C9 of the phen prevents the second nitrogen coordinating to the copper, resulting in a long non-bonded Cu…N distance of 2.983 Å [63]. Asymmetric bond lengths are common for the data with ratios <1.2 and are a consequence of the fixed N...N distance $d_3$. Although the concept of bite angle was criticized earlier, it can still be useful, and the angle subtended at the metal by the two nitrogen donors in phen ligands cannot be optimal for trigonal (120°), T-shaped (180°, 90°), tetrahedral (109.5°) or square-planar (90°) complexes. A commonly observed structural motif is one in which a short M–N distance is exhibited within one of these common coordination geometries and a longer M…N distance which is defined by the fixed ligand geometry. In the context of this analysis, is it interesting

to note that the complex [(2,4,6-$(NO_2)_3C_6H_2$)Au(2,9-Me$_2$phen)] has a near-linear arrangement of the aryl ring and a strongly bonded nitrogen (∠C–Au–N, 168.35°; C–N, 2.136 Å) with the second nitrogen of the phen lying 2.573 Å from the gold and giving and ∠N–Au–N of 71.28° (Fig. 2b) [64]. Increasing the bulk of the 2,9-substituents on the phen accentuates this asymmetry and in the complex [Au(2,9-Ph$_2$phen)Cl$_3$] [65] the non-bonded Au…N distance increases to 2.704 Å. Even the presence of a bulky substituent adjacent to the weakly-bonded nitrogen is enough to significantly influence the asymmetric binding of phen ligands, an extreme example of which is seen with a 9-(1,2-dicarba-*closo*-dodecaborane) substituent in the complex [Cu(**14**)(hfacac)$_2$], in which the distance to the less strongly bonded nitrogen of the phen is 2.681 Å (Fig 2d) [66].

Ligands such as 4,5-diazafluoren-9-one (**15**) and related compounds also contain a constrained motif which results in a structural chemistry closely resembling that of phen, with many examples exhibiting one short and one long M-N contact.

In summary, although many phen complexes show an asymmetry in the M…N vectors, the constraint of the phen ring systems prevents the adoption of unambiguously monodentate structures because the relative positions of the two nitrogen donors is effectively fixed.
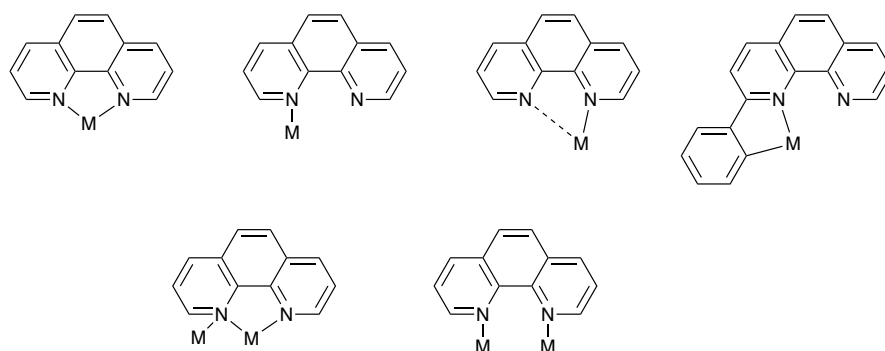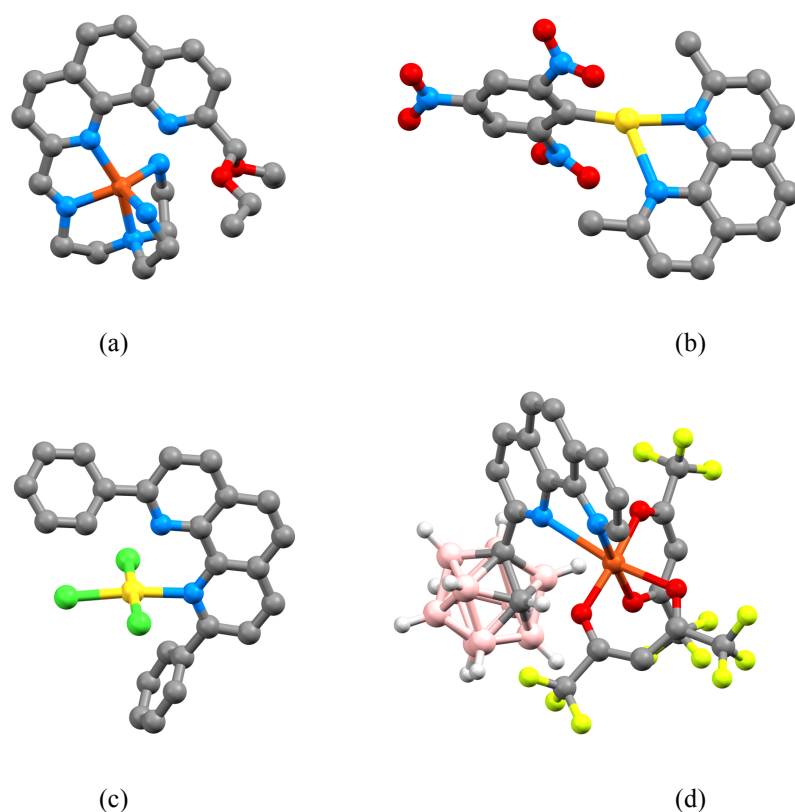


**Scheme 7** Bonding modes for 1,10-phenanthroline ligands identified in structurally characterized complexes.

The dinucleating modes are not further discussed in this review.
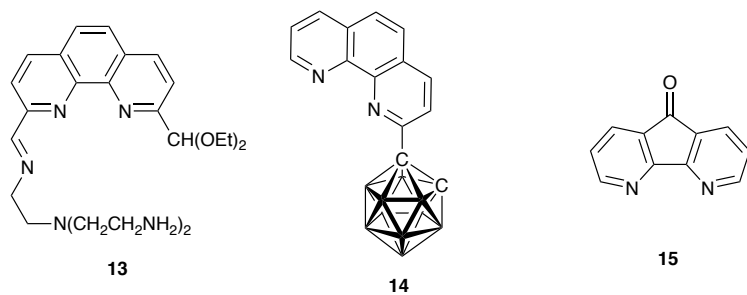
**Scheme 8** Ligand structures for phen ligands which have substituents favouring bonding modes approaching hypodentate.



(a)

(b)

(c)

(d)

**Fig. 2** Complexes in which the phen binding mode approaches monodenate (a) [Cu(**13**)][ClO$_4$]$_2$ [63] (b) [(2,4,6-(NO$_2$)$_3$C$_6$H$_2$)Au(2,9-Me$_2$phen)] [64] (c) [Au(2,9-Ph$_2$phen)Cl$_3$] [65] (d) [Cu(**14**)(hfacac)$_2$] [66]. In all cases, one of the M…N contacts to the phen is significantly longer than the other.

### 2.5.2 Hypodentate bpy complexes

In comparison to phen, rotation about the interannular C–C bond in bpy ligands allows access to monodentate bonding modes. Iridium compounds that were earlier reported as

containing monodentate bpy ligands have been shown unequivocally to contain cyclometallated 2,2'-bipyridines [67,68]. In view of the ubiquitous nature of bpy ligands in coordination and supramolecular chemistry, it is remarkable how few monodentate bpy complexes have been structurally characterized. The general trends are somewhat similar to those observed for phen ligands, but the free rotation about the interannular C–C bond allows access to fully monodentate bonding modes associated with a transoid or near-transoid conformation. Although the vast majority of bpy complexes are chelating bidentate, a number of trends may be observed that lead to hypodentate bonding. Once again, we will not consider structures in which the bpy acts as a bridging bidentate ligand, but will concentrate upon those compounds with unused donor capacity from the bpy domain. The commonest examples are those in which additional donor capacity attached to the bpy core preferentially coordinates to the metal centre at the expense of the second bpy donor. The additional donors are most commonly attached at the 6, 4 or 3-positions of the bpy. A second common class comprise compounds in which a square-planar metal centre has an additional long M…N contact to the second bpy nitrogen, resulting in structural motifs very similar to those observed with phen. In addition to the (very few) compounds which unambiguously contain monodentate bpy ligands, there is a series which provides a bridge in which there is a short M…N contact to the second bpy nitrogen but the conformation is such that the lone pair vector is not oriented towards the metal centre. The introduction of substituents at the 3- and 3'-positions of the bpy also favours the adoption of bridging or monodentate bonding modes.

The best known example of a monodentate bpy ligand is found in the compound [MeHg(3,3'-Me$_2$bpy)](NO$_3$) (Fig. 3a) [39] in which the Hg…N distance is 3.289 Å, the angle between the least squares planes of the pyridine rings is 74.27°, the N…N distance within the bpy is 3.042 Å and the ratio $d_1/d_2$ is 1.56. These metrical parameters provide a good comparison for other monodentate bpy complexes. Although the methyl substituents at the 3-

and 3'-positions provide a steric destabilization to the planar chelating mode, their presence is not sufficient to enforce a hypodentate mode, and complexes typically exhibit bidentate chelating 3,3'-Me$_2$bpy [69,70,71,72,73,74,75,76,77] or 3,3'-Me$_2$biquin [78] ligands in which the M–N distances are a little longer than is usual with bpy, and the ligand has a significant rotation about the interannular C-C bond to give a non-planar structure with angles between the least-squares planes of the pyridine rings in the range 29–41°. An interesting example is seen in the complex [Au(3,3'-Me$_2$biquin)Br$_3$] [79,80] (Fig. 3b) in which the twisting in the biquin ligand (angle between least-squares planes 66.2°) is so great that although the non-coordinated nitrogen lies only 2.976 Å from the gold, little orbital overlap is possible. Similar structures are observed in the complexes [Au(3,3'-Me$_2$biquin)Cl$_3$] [80], in which the twisting about the interannular bond enforces a monodentate bonding mode, even though the non-coordinated nitrogen lies relatively close to the metal centre. In contrast, the gold(I) complex [Au(1,1'-biisoquin)(PPh$_3$)](CF$_3$SO$_3$) [ 81 ] contains a monodentate 1,1'-biisoquinoline ligand with an 80° torsional angle between the two isoquinoline ring systems (Fig 3d).

Additional unambiguous examples of monodentate bpy ligands are found in the complexes [Ir(bpy)(acac)$_3$] [82], which not only contains a monodentate bpy ligand (N-C-C-N torsion angle 58°) but also two O,O'- and one C-bonded acac ligands, [Pd($\eta^3$-allyl)(**16**)Cl] [83]. More generally, there is a tendency to form structures in which the non-coordinated nitrogen lies above a square-planar metal centre and the orientation of the pendant pyridyl ring is such that orbital interaction with the metal is not precluded, although the M…N distance is relatively long. Examples of such interactions include the complexes [Pt(bpy)$_2$(PhP(C$_6$H$_4$SO$_3$)$_2$] [84] (in which one of the two bpy ligands is monodentate (M…N 2.753 Å) but the metal-nitrogen interaction is strong because the hypodentate bpy ligand is near-planar), [Au(4,6-Ph2-2-pyquin)Cl$_3$] [85] (Fig 3e), [Au(6-Me-4-Ph-2-pyquin)Cl$_3$] [85],

[Au(6-MeO-4-Ph-2-pyquin)Cl$_3$] [85], [MePd(6-$^{sec}$Bubpy)$_2$][PF$_6$] [ 86 ] and [MePd(6-(Me(MeO)CH)bpy][PF$_6$] [86] in which one of bpy ligands is monodentate with the non-coordinated nitrogen lying above the square planar palladium centre.



(a)



(b)



(c)



(d)
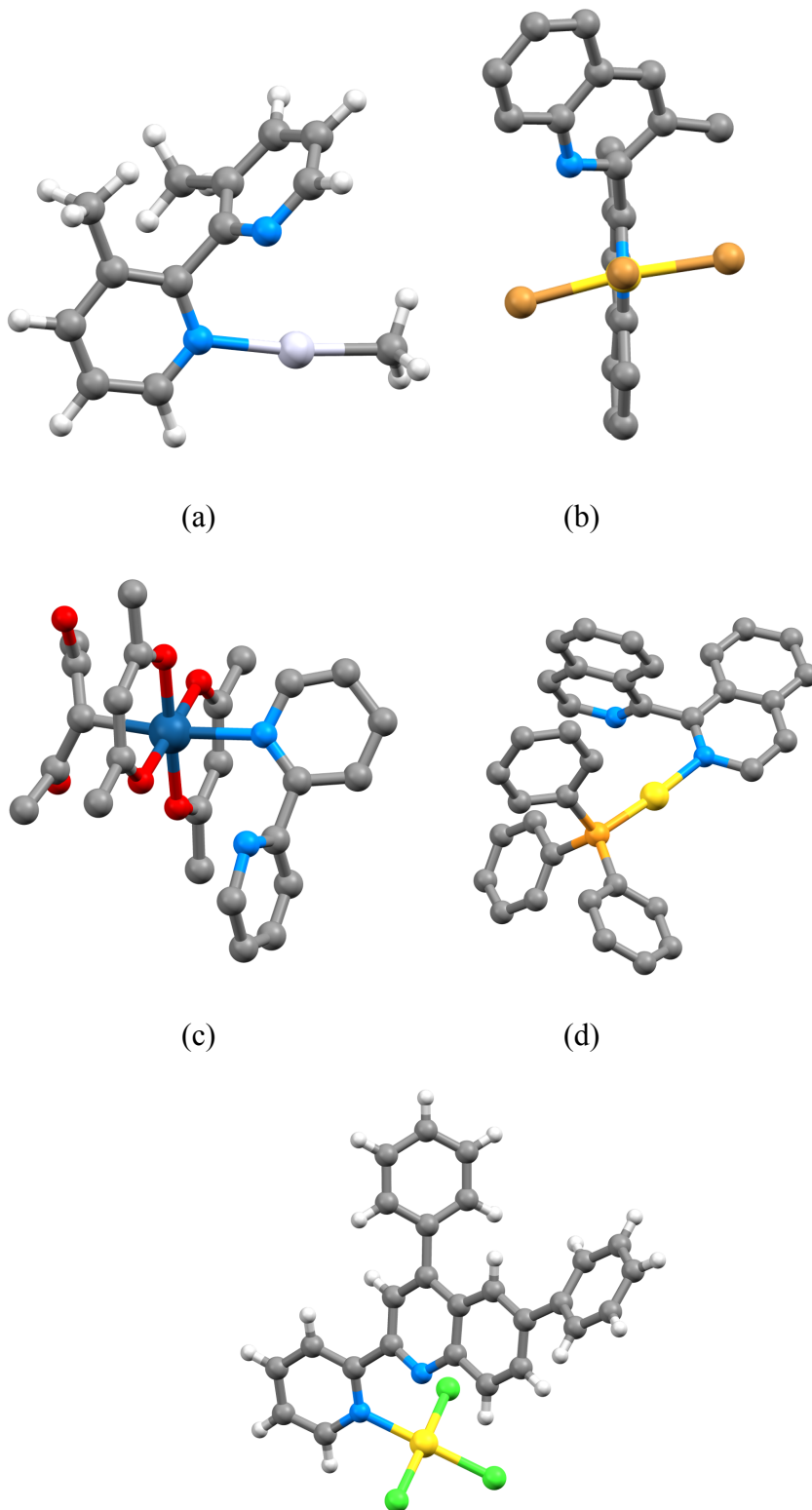
(e)

**Fig. 3** (a) [MeHg(3,3'-Me$_2$bpy)](NO$_3$)[39] (b) [Au(3,3'-Me$_2$biquin)Br$_3$] [79] (c) [Ir(bpy)(acac)$_3$] [82] (d)

[Au(1,1'-biisoquin)(PPh$_3$)](CF$_3$SO$_3$) [81] (e) [Au(4,6-Ph$_2$-2-pyquin)Cl$_3$] [85]



**16**　　　　　　H$_2$**17**　　　　　H$_4$**18**
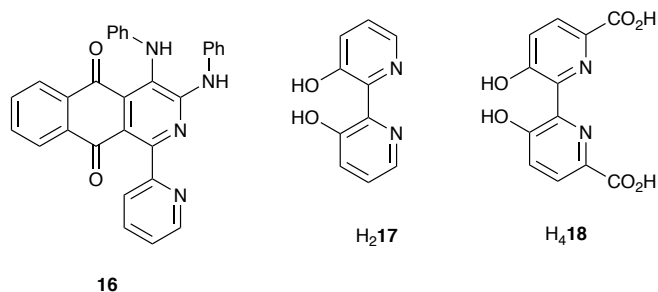
**Scheme 9** Ligand structures for bpy ligands which have substituents favouring monodentate bonding modes.

A new structural complexity emerges if the substituents at the 3 or 3,3'- positions of the bpy contain additional donor atoms. In the case of 3,3'-(HO)$_2$bpy (H$_2$**17**) a common coordination mode is for the ligand to act as a chelating bidentate NO donor, enforcing a transoid conformation of the bpy metal-binding domain. Examples of this are found in the complexes [Os(bpy)$_2$(H**17**)](ClO$_4$)87 (Fig. 4a) and [Os(2-PhN=Npy)$_2$(H**17**)](ClO$_4$) [87]; in these hypodentate complexes, the hydrogen bonding between the remaining 3-hydroxy substituent and non-coordinated nitrogen of the bpy provides an additional stabilization. In general, however, H$_2$**17** forms binuclear complexes with [**17**]$^{2-}$ ligands presenting a chelating NO donor set to each of two metals [40,87,88,89]. In the complex [Cu(H$_2$**18**)(H$_2$O)$_2$] [90] of the related ligand H$_4$**18**, the copper centre is five-coordinate and bonded to the carboxylate oxygen and nitrogen of one ring and the deprotonated 3-hydroxy of the second ring, a bonding mode that constrains the transoid bpy ligand to near-planarity (Fig. 4b). When carboxylic acids are introduced into the 3-position, the coordination chemistry becomes more complex and multimetallic coordination networks containing hypodentate ligands may be obtained [91,92].

<div align="center">(a)                      (b)</div>
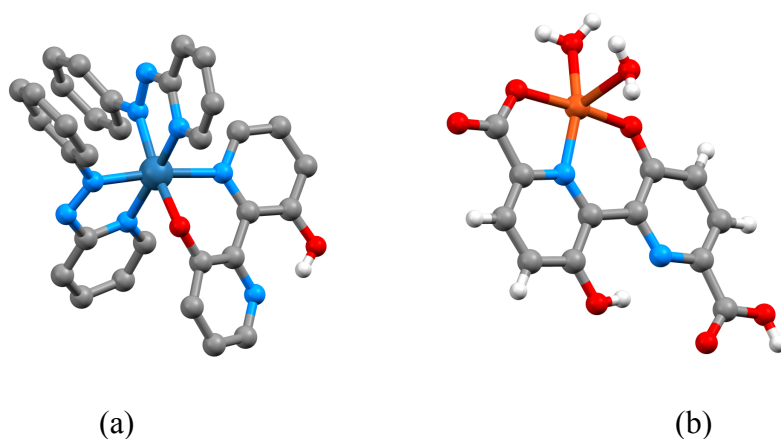
**Fig. 4** Examples of complexes in which a coordinating substituent on a bpy gives rise to a hypodentate bonding mode in which one of the nitrogen atoms is not coordinated to the metal (a) $[Os(bpy)_2(H\mathbf{17})](ClO_4)$ [83] (b) $[Cu(H_2\mathbf{18})(H_2O)_2]$ [87]
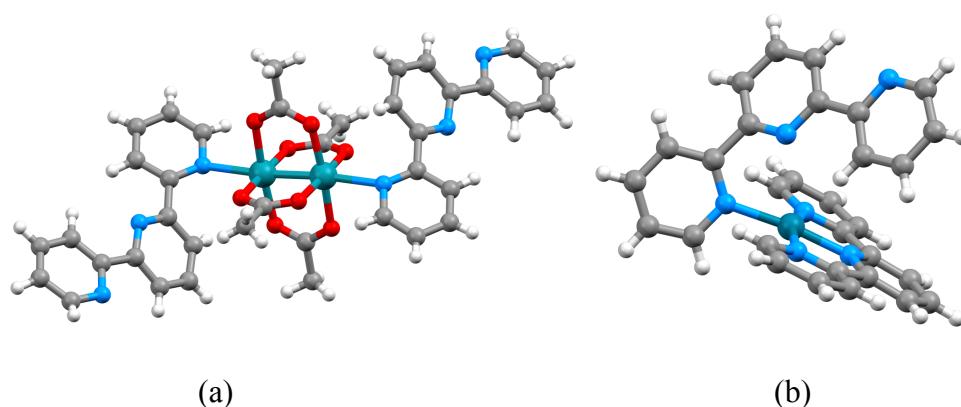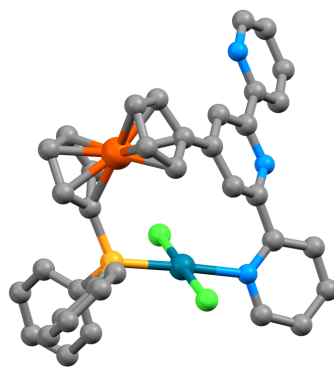
## *2.6 Hypodentate tpy ligands*

As mentioned in the introduction, we defined the term hypodentate to describe the bonding mode of tpy ligands in which one of the potential nitrogen donors was not coordinated to a metal. In this section we review hypodentate complexes containing tpy ligands. The emphasis is on structural data but a section is devoted to dynamic behavior in hypodentate complexes. Excluded from the review are complexes in which all nitrogen atoms of the tpy are coordinated to multiple metal centres. Hypodentate tpy ligands are a surprisingly common motif, in particular with kinetically inert metal centres.

### 2.6.1 Monodentate tpy ligands

Complexes containing monodentate tpy ligands are relatively rare and exotic species, and only a few have been structurally characterized. The logical approach is to select a coordination scaffold in which only one coordination site is available for occupancy or substitution. The dinuclear carboxylate complexes $[Rh_2(O_2CR)_4]$ can accept a single additional two electron donor at each of the metals. Complexes in the family

[Rh$_2$(O$_2$CR)$_4$(tpy)$_2$] contain monodentate tpy ligands coordinated through the terminal ring of which [Rh$_2$(O$_2$CMe)$_4$(tpy)$_2$] [ 93 , 94 ] (Fig 5a), [Rh$_2$(O$_2$C$^t$Bu)$_4$(tpy)$_2$] [ 95 ] and [Rh$_2$(O$_2$CMe)$_4$(4'-Cltpy)$_2$] [93] have been structurally characterized. In these compounds, the tpy adopts a *transoid,transoid* configuration as found in the free ligand, although the deviation from planarity is considerable with torsion angles N–C–C–N varying between 1 and 43°. The simplest example of a monodentate tpy is found in the compound [Pd(tpy)$_2$][BF$_4$]$_2$ [96] (Fig 5b) which contains one tridentate and one bidentate tpy. In this complex, a *cisoid,transoid* configuration is adopted with the *cisoid* arrangement of the bonded and central rings imposed by an interaction between N2 of the central ring and the palladium (Pd…N 2.901 Å). The constrained ferrocene ligand **19** forms the complex [Pd(**19**)Cl$_2$]97 (Fig 5c) in which the *trans* sites are occupied by the PN donor. The monodentate tpy metal-binding domain adopts a *transoid,transoid* configuration in this complex. The complex [Au(C$_6$F$_5$)$_3$(tpy)] is also reported to contain a monodentate tpy ligand [98], whereas the structurally characterized species [Au(CN)$_2$Br(tpy)] is of interest in exhibiting one typical Au–N bond (2.080 Å) and one longer Au…N contact in the axial position (2.839 Å) and an unambiguously non-bonded *transoid* pendant ring [99].



(a)                                        (b)

(c)

**Fig. 5** Examples of structurally characterized complexes containing monodentate tpy ligands include (a) [Rh$_2$(O$_2$CMe)$_4$(tpy)$_2$] [94] (b) [Pd(tpy)$_2$][BF$_4$]$_2$ [96] and (c) [Pd(**19**)Cl$_2$] [97].
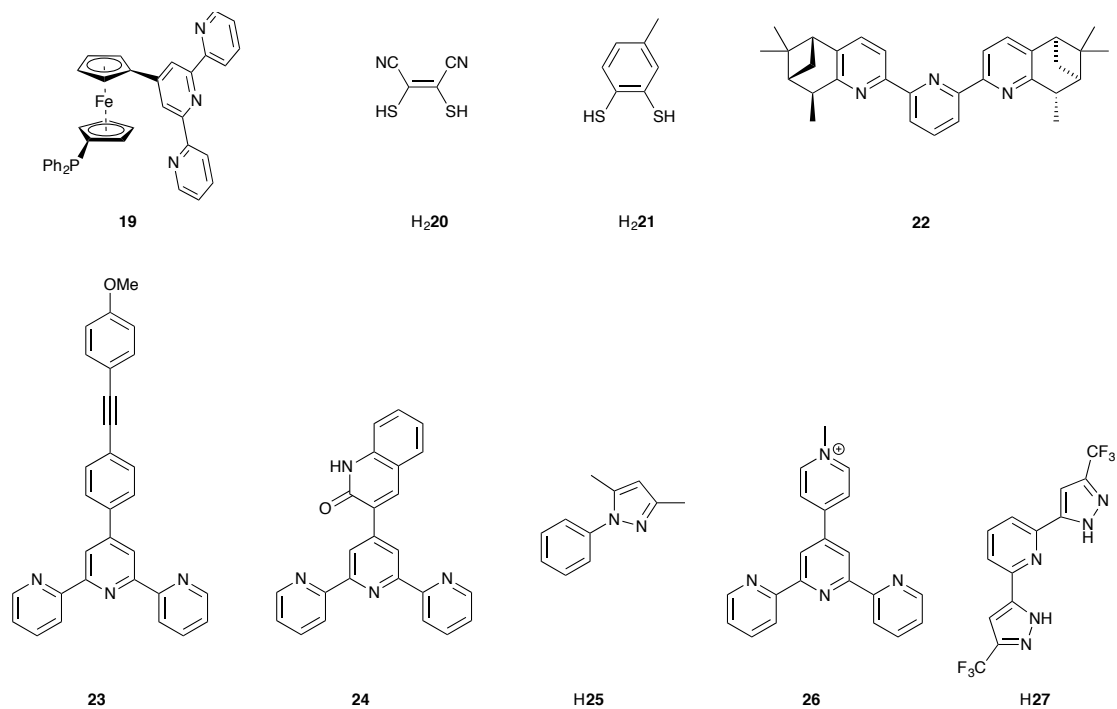


**Scheme 10** Substituted tpy ligands which have been shown to form hypodentate complexes and some ancillary ligands discussed in the text.

## 2.6.2   Bidentate tpy ligands

A number of strategies have been adopted for the designed synthesis of complexes containing bidentate tpy ligands. Probably the commonest is the use of kinetically inert six-

coordinate metal centres (usually d$^6$) in which four of the coordination sites are occupied and the remaining two bind two of the three nitrogen atoms of the tpy.

Structurally characterized ruthenium(II) complexes containing bidentate tpy ligands include [Ru(bpy)$_2$(tpy)][PF$_6$]$_2$ [36] (Fig. 6a), [Ru(bpy)$_2$(6-Brtpy)][PF$_6$]$_2$ [36] two isomers of [Ru(bpy)(CO)(CH$_2$OMe)(tpy)][PF$_6$] [ 100 ], [Ru(bpy)(CO)(CO$_2$H)(tpy)][PF$_6$] [ 101 ], [Ru(bpy)(CO)(CH$_2$OH)(tpy)][PF$_6$]$_2$ [ 102 ], [Ru(bpy)(CO)(CH$_2$OAc)(tpy)][PF$_6$] [ 103 ], [Ru(bpy)(CO)$_2$(tpy)][PF$_6$]$_2$ [102], [Ru(4,4'-Me$_2$bpy)(CO)$_2$(tpy)][PF$_6$]$_2$ [103], [Ru(tpy)(CO)$_2$Br$_2$][ 104 ], [Ru(tpy)(**20**)(CO)$_2$] [ 105 ], [Ru(tpy)(**21**)(CO)$_2$] [105], [Ru(phen)$_2$(4'-Phtpy)][PF$_6$]$_2$ [ 106 ], [Ru(PPh$_3$)(cp)(4'-Phtpy)][PF$_6$]$_2$ [ 107 ] and [Ru(tpy)([9]aneS$_3$)Cl] [108]. A number of general structural comments relevant for all bidentate tpy complexes arise from a consideration of these ruthenium complexes. Firstly, the pendant pyridine ring is significantly out of the least squares plane of the bpy metal-binding domain with typical N–C–C–N torsion angles in the range 40–60$^o$ or 100–135°. The precise torsion angle is often defined by a face-to-face stacking of the pendant ring with another aromatic ring in the complex. The second general observation relates to the two ranges of torsion angles, corresponding two conformations of the pendant ring with the pyridine ring oriented "towards" and "away from" the metal centre (Scheme 11).
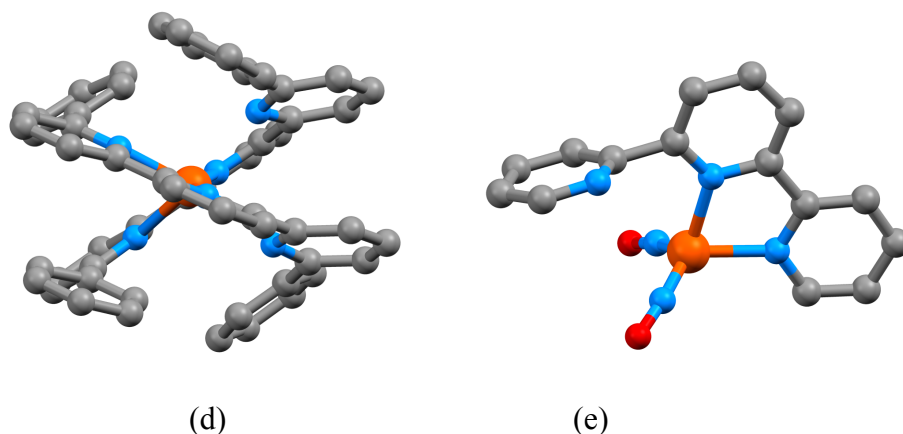
Further examples of bidentate tpy ligands at kinetically inert octahedral centres include [Re(tpy)(CO)$_3$Br] [109,110,111] (Fig 6b), [Re(tpy)(CO)$_3$Cl] [111,112,113] [Re(4'-(2-furanyl)tpy)(CO)$_3$Cl] [ 114 ], [Re(4'-(2-thienyl)tpy)(CO)$_3$Cl] [114], [Re(4'-(2,2'-bi-5-thienyl)tpy)(CO)$_3$Cl] [114], [Re(4'-HOtpy)(CO)$_3$X] (X = Cl, Br) [ 115 ], [Re(4'-(4-XC$_6$H$_4$)tpy)(CO)$_3$Cl] (X = Ph, Me$_2$N, Cl, Br) [116], [Re(4'-Ph$_2$Ntpy)(CO)$_3$Cl] [117] and [Re(tpy)(CO)$_3$(MeCN)][PF$_6$]$_2$ [62]. Various conformations of the pendant pyridine ring in the complex [Re(tpy)(CO)$_3$Br] have been reported. A final example of a rhenium complex is found in the compound [Re(**22**)(CO)$_3$Cl] containing the chiral ligand **22** and which

crystallizes in the non-enantiogenic space group $P2_12_12_1$ [118]. A number of platinum(IV) and manganese(I) complexes containing bidentate tpy ligands have been characterized including $[PtMe_3(L)I]$ (L = tpy,119 4'-(4-NCC$_6$H$_4$)tpy [120], 4'-(4-MeC$_6$H$_4$)tpy [120], 4'-Cltpy [120] and **23** [121]) and $[Mn(CO)_3Br(L)]$ (L = tpy [122], 4,4',4"-$^t$Bu$_3$tpy [122], 4'-(4-MeC$_6$H$_4$)tpy [122]).

Complexes containing $[Ir(ppy)_2(N{\wedge}N)]^+$ cations (N^N = bidentate bpy metal-binding domain or analogue) are of current interest as electroluminescent components in organic light-emitting diodes (OLEDs) or light-emitting electrochemical cells (LECs) and systematic variation of the N^N ligand is a key strategy in colour-tuning. Structurally characterized complexes containing bidentate tpy ligands in this series include $[Ir(ppy)_2L]^+$ (L = tpy [123], 4'-(4-py)tpy [123], 4'-(4-H$_2$NC$_6$H$_4$)tpy [123], 4'-(4-MeSC$_6$H$_4$)tpy [123], 4'-(4-MeOC$_6$H$_4$)tpy [123], 4'-PhStpy, [124], 4'-Me2Ntpy [124], 4'-EtOtpy [124], 4'-Cltpy [124], **24** [125]) together with the complexes $[Ir(\mathbf{25})_2(tpy)][PF_6]$ , $[Ir(\mathbf{25})_2(4'-(4-py)tpy)][PF_6]$ and $[Ir(\mathbf{25})_2(\mathbf{26})tpy][PF_6]_2$ [123].



(a)      (b)      (c)

(d)          (e)
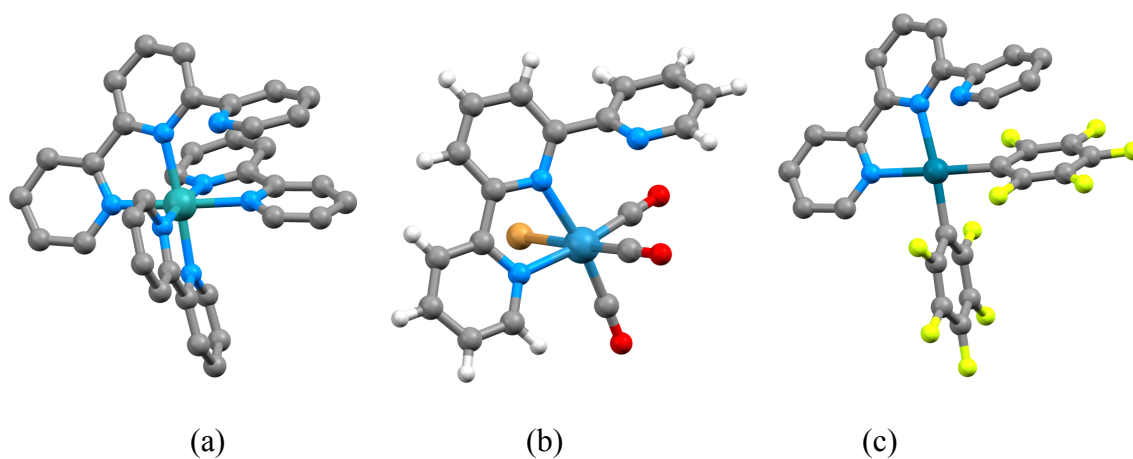
**Fig. 6** Some examples of structurally characterized complexes containing bidentate tpy ligands (a) include [Ru(bpy)$_2$(tpy)][PF$_6$]$_2$ [36], (b) [Re(tpy)(CO)$_3$Br] [109], (c) [Pd(C$_6$F$_5$)$_2$(tpy)] [126], (d) [Fe(6,6"-Ph$_2$tpy)$_2$][PF$_6$]$_2$ [37] and (e) [Fe(tpy)(NO)$_2$] [131].

The design of four-coordinate complexes containing bidentate tpy ligands is dominated by two strategies; the first is the use of a d$^8$ metal centre in which two of the coordination sites are occupied and the second is the use of bulky ligands which prevent the planar tridentate bonding mode of the tpy. The former strategy allows the preparation of the complexes [Pd(C$_6$F$_5$)$_2$(tpy)] [126] (Fig 6c), [Ni(CF$_2$CF$_2$CF$_2$CF$_2$)(tpy)] [127], [Pd(C$_6$F$_5$NN=NNC$_6$F$_5$)(4,4',4"-$^t$Bu$_3$tpy)][128] and [Pd(CH$_2$CHCH$_2$)(tpy)][ClO$_4$][129] . In [Pd(C$_6$F$_5$)$_2$(tpy)] the π-stacking between the pendant pyridine of the tpy defines the torsion angle within the tpy (N-C-C-N, 45.96° and the relatively long Pd…N distance of 3.455 Å) whereas in [Ni((CF$_2$CF$_2$CF$_2$CF$_2$)(tpy)], [Pd(CH$_2$CHCH$_2$)(tpy)][ClO$_4$] and [Pd(C$_6$F$_5$NN=NNC$_6$F$_5$)(4,4',4"-$^t$Bu$_3$tpy)] the pendant ring has a transoid arrangement with the bpy metal-binding domain. Steric constraints are important in iron(II) complexes with 6,6"-Ar$_2$tpy ligands, which often give purple low-spin and orange high-spin forms. In these complexes the aryl substituents have a significant influence and the iron either exhibits two rather long Fe…N contacts as in [Fe(6,6"-(4-MeOC$_6$H$_4$)$_2$tpy)$_2$][PF$_6$]$_2$ (four Fe–N bonds, 2.069–2.228 Å and two Fe…N contacts 2.399, 2.403 Å) [130] and in [Fe(6,6"-Ph$_2$tpy)$_2$][PF$_6$]$_2$ (Fig. 6d) (two Fe…N contacts 2.436, 2.536 Å) [37]. The complex

[Fe(tpy)(NO)$_2$] (Fig 6e) is unambiguously four-coordinate with the Fe…N distance slightly under 4 Å [ 131 ]. Steric control is also observed in the complexes [Cu(2,9-(2,6-Me$_2$C$_6$H$_3$)$_2$phen)(tpy)][PF$_6$], in which the pendant ring is *transoid* and near coplanar with the bpy metal-binding domain [ 132 ], [Cu(PPh$_3$)$_2$(4'-(2-Br-4-py)tpy)][BF$_4$] [ 133 ] and [Cu(POP)(L)][PF$_6$] (L = tpy, 4'-(4-BuOC$_6$H$_4$tpy) [134]. The compound [Cu(POP)(L)][PF$_6$] is remarkable in that it contains two different molecules in the unit cell, both of which have two short Cu–N bonds (2.090–2.231 Å) and two long Cu…N contacts (2.602 Å and 3.146 Å) leading to formal descriptions of both bidentate and tridentate isomers in the same lattice.



(a)                                                                                           (b)
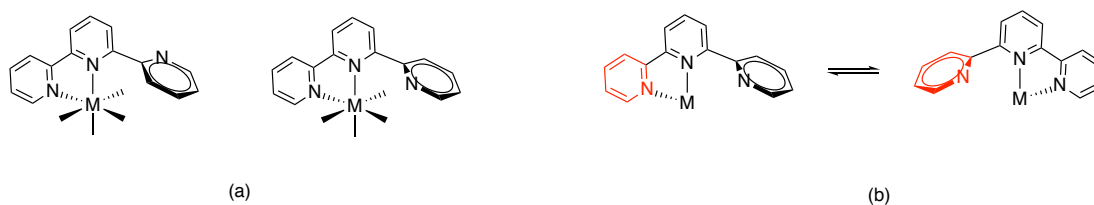
**Scheme 11** (a) The *cisoid* and *transoid* rotamers found for the pendant ring in bidentate tpy complexes and (b) the metallotropic process observed for some bidentate tpy species.

Additional examples of mononuclear complexes containing bidentate tpy ligands include [Os(**27**)(CO)(tpy)] [135], [Rh(cp)Cl(4'-Phtpy)][BF$_4$] [136] and [Co(**22**)Cl$_2$] [137]. Isolated examples of homo- and heteropolynuclear complexes [110,138,139,140,141,142,143] and coordination polymers [144] containing hypodentate tpy ligands exist, the latter often without a great deal of rationale for the coordination mode that is adopted.

Complexes containing bidentate tpy ligands often exhibit interesting dynamic behavior in solution involving metallotropic shifts in which coordinated and non-coordinated rings interconvert [109,119,145,146,147,148]. The NMR spectra indicate a number of different dynamic processes associated with both the interconversion of cisoid and transoid

rotamers (Scheme 11a) and the metallotropic interchange of coordinated and pendant rings in bidentate tpy complexes [ReLX(CO)$_3$] (L = tpy, X = Cl, Br or I; L = 4-Me-4'-(4-ClC$_6$H$_4$)tpy, 4,4"-Me$_2$-4'-(4-ClC$_6$H$_4$)tpy, 4-Me-4'-MeStpy, 4-$^t$Bu-4'-MeStpy, X = Br), [PtLMe$_3$X] (L = tpy, X = Cl, Br or I; L = 4-Me-4'-(4-ClC$_6$H$_4$)tpy, X = I), [M(tpy)(CO)$_4$] (M = Cr, Mo or W), [RuX$_2$(CO)$_2$(tpy)] (X = Cl, Br or I) and [ML(C$_6$F$_5$)$_2$] (M = Pd or Pt; L = 4-Me-4'-(4-ClC$_6$H$_4$)tpy). It is proposed that the exchange mechanism is associative and intermediates of higher coordination number are involved.

## 2.7    Hypodentate qtpy ligands

The ligand qtpy typically acts as a planar quadridentate donor or partitions into two bidentate domains to form dinuclear double helicates. Nevertheless, a few examples of hypodentate qtpy ligands have been described. Attempts to prepare heteroleptic double helicates yielded the complex [Cu(tpy)(6,6'''-Me$_2$qtpy)][PF$_6$]$_2$ (Fig 7a) in which both the tpy and 6,6'''-Me$_2$qtpy are tridentate and coordinated to a six coordinate copper(II) centre [149]. The pendant pyridine ring is *transoid* with an N–C–C–N torsion angle of 140.5°, but the qtpy ligand as a whole is significantly distorted from planarity. The *transoid* arrangement is also found for the pendant ring in the complex [Cu(6,6'''-Me$_2$qtpy)Cl$_2$] (Fig. 7b) which also contains a tridentate 6,6'''-Me$_2$qtpy ligand [150]. The preference of first row transition metal divalent cations to form octahedral complexes is dominant and the complexes [Fe(qtpy)$_2$][ClO$_4$]$_2$ [151], [Ni(qtpy)$_2$][ClO$_4$]$_2$ [152] (Fig 7c) and [Zn(qtpy)$_2$][ClO$_4$]$_2$ [152] all contain two tridentate qtpy ligands. Structurally the complexes differ significantly in the orientation of the pendant rings.
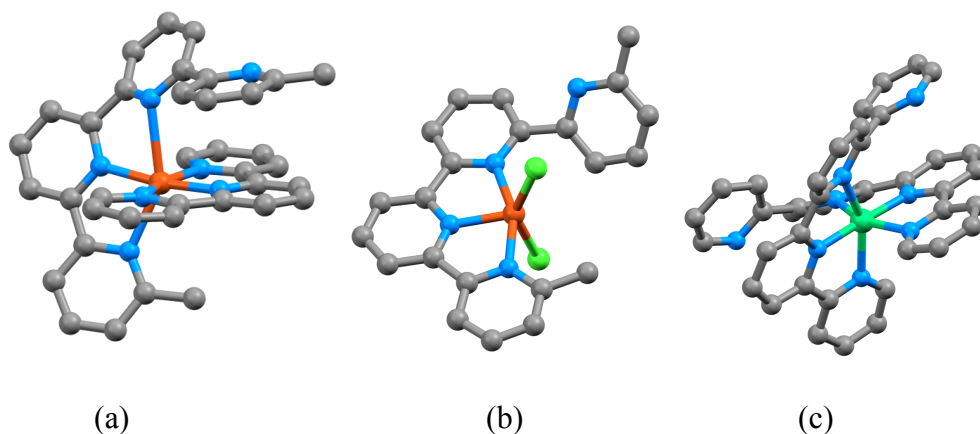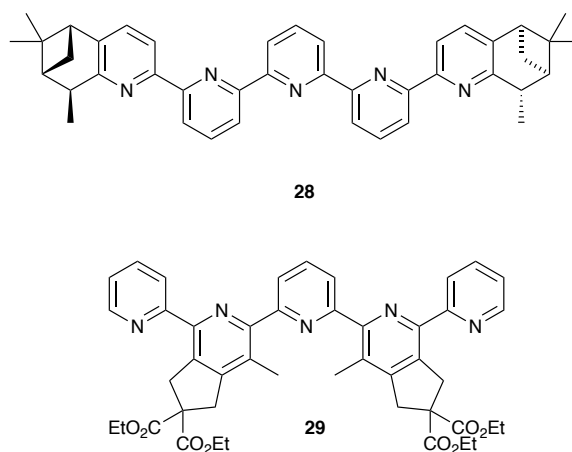
**Fig. 7** Some examples of hypodentate qtpy ligands (a) [Cu(tpy)(6,6'''-Me$_2$qtpy)][PF$_6$]$_2$ contains a tridentate qtpy with a transoid pendant pyridine [149], (b) [Cu(6,6'''-Me$_2$qtpy)Cl$_2$] [150] and (c) [Ni(qtpy)$_2$][ClO$_4$]$_2$ [152].

Detailed NMR spectroscopic studies of the complex [Re(qtpy)(CO)$_3$Br], obtained from the reaction of qtpy with [ReBr(CO)$_5$]; the complex contains a bidentate qtpy ligand coordinated to the nitrogen atoms of rings 1 and although dynamic behavior involving the interconversion of *cisoid* and *transoid* rotamers of the pendant bpy metal-binding domains were observed, there was no metallotropic shift of the type observed in analogous tpy complexes in which coordinated and non-coordinated metal-binding domains interconvert [153].

## 2.8    *Hypodentate qpy ligands*

Ligands based on qpy have a number of typical coordination modes, dominated by helical motifs. Typically, all of the nitrogen donors are coordinated to a single metal centre or {M$_2$L$_2$}$^{n+}$ complexes are formed in which the ten donor atoms of the two qpy ligands are fully engaged in binding to either a six-coordinate and a four coordinate metal, two five-coordinate metals or two six coordinate metals in which the remaining coordination sites are occupied by ancillary ligands. Nevertheless, a small number of hypodentate complexes have been described. Only two hypodentate complexes have been structurally characterized. In the

double-helicate $[Cu_2(\mathbf{28})_2][PF_6]_2$ with the chiragen ligand **28**, each qpy presents two bidentate bpy metal-domains to each copper(I) centre with a pendant ring from each ligand capping the head and tail of the complex (Fig. 8a). In this complex, which is effective in the catalytic asymmetric cyclopropanation of alkenes, the non-coordinated nitrogen donors are relatively far from the copper (Cu…N > 2.8 Å) [154]. In the cobalt(II) complex [Co(bpy)Cl(**29**)]Cl, the qpy ligand **29** is tridentate (Fig 8b) [155].



**28**



**29**

**Scheme 12** Functionalized qtpy ligands which give rise to hypodentate complexes.



(a)             (b)
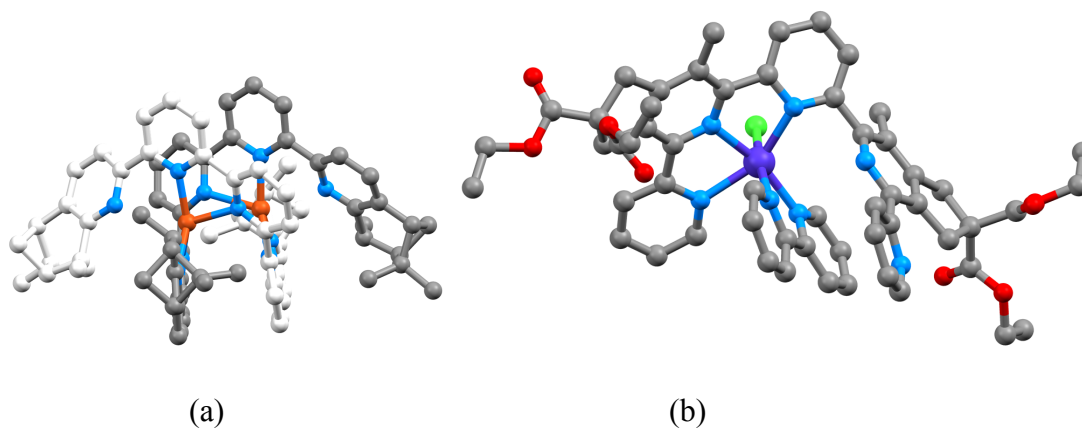
**Fig. 8** Hypodentate qtpy ligands are found in the complexes (a) $[Cu_2(\mathbf{28})_2][PF_6]_2$ [154] and (b) [Co(bpy)Cl(**29**)]Cl [155].

## 2.9 Hypodentate sexipy ligands

To date, no examples of complexes containing hypodentate sexipy ligands have been structurally characterized. The sexipy ligand was designed to form $[M_2L_2]^{n+}$ double helicates

with six-coordinate metal centres and this motif dominates the chemistry. The only relevant species that has been reported to date is $[(AcO)Pd(sexipy)Pd(OAc)]^{2+}$ in which it is assumed that the sexipy ligand is partitioned into two tridentate domains [156].



**30**
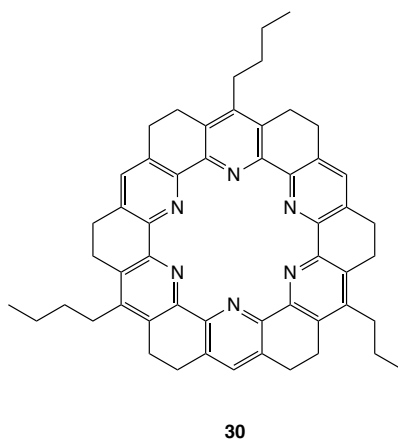
**Scheme 13** A torand is a cyclosexipyridine derivatives that forms hypodentate complexes with group 1 metal ions.

The torands are derivatives of cyclosexipyridine and structural studies of the complexes $[K(\mathbf{30})]^+$ and $[Rb(\mathbf{30})]^+$ reveal similar sets of metal nitrogen distances in each case [157], but the complex $[Li_2(\mathbf{30})_2(H_2O)_2(\mu\text{-}H_2O)]^{2+}$ is very different [158]. The lithium is too small to fit into the centre of the cavity and retain strong Li…N interactions, and is each is displaced to bind strongly to just two nitrogens of a torand ligand (Fig. 9). The overall coordination number of four is attained through one terminal water on each metal and a bridging water molecule.
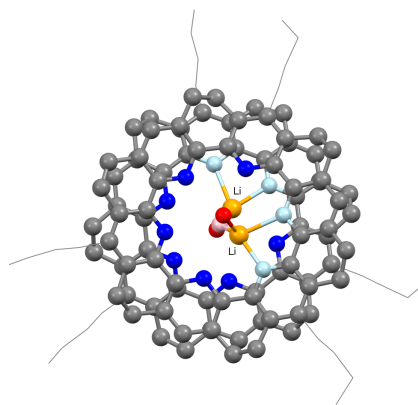
**Fig. 9** In the complex $[Li_2(\mathbf{30})_2(H_2O)_2(\mu\text{-}H_2O)]^{2+}$ each lithium only binds to two of the six nitrogen donors of a torand ligand [158]. Hydrogen atoms have been omitted and substituents rendered in wireframe for clarity, non-coordinated nitrogen atoms deep blue, coordinated nitrogen atoms pale blue, bridging water pink, terminal water red.

### 2.10    Higher oligopyridines

Although reasonable proposals may be made for hypodentate complexes of the higher oligopyridines, there is relatively little structural data available. In the case, of septipy ligands double-helical compounds $[M_2L_2]^{4+}$ (L = septipy, M = Fe; L = 4",4""-($^tBuC_6H_4$)$_2$septipy, M = Zn; L = 4',4""'-(MeS)$_2$-4",4""-($^nPrS$)$_2$septipy, M = Co) have been structurally characterized. The two septipy ligands present a total of 14 nitrogen donors, of which 12 are utilized in binding two six-coordinate metal centres. Interestingly, the three complexes exhibit different patterns for the distribution of the non-coordinated pyridine donors. In      $[Fe_2(septipy)_2]^{4+}$, the two central pyridine rings (N4A and N4B) are not coordinated (Figure 10a) [159]; this result is of some interest as the complex has been shown to be an efficient catalyst for the oxidation of a variety of substrates including arenes, alkanes and tiary amines with Oxone. In contrast, in the complex cation $[Zn_2(4",4""'-($^tBuC_6H_4$)_2septipy)_2]^{4+}$, the two sox-coordinate metal centres are supported in a ligand manifold in which pyridine nitrogens N7A and N7B remained non-coordinated (Fig 10b) [160]. Finally, in the first reported structural determination of a septipy complex,

$[Co_2(4',4''''-(MeS)_2-4'',4''''-(^nPrS)_2septipy)_2]^{4+}$ exhibits an unsymmetrical structure in the solid state in which the two six-coordinate cobalt centres are bonded such that pyridine nitrogens N7A and N4B are non-coordinated (Fig. 10c) [161].



(a)                                         (b)



(c)
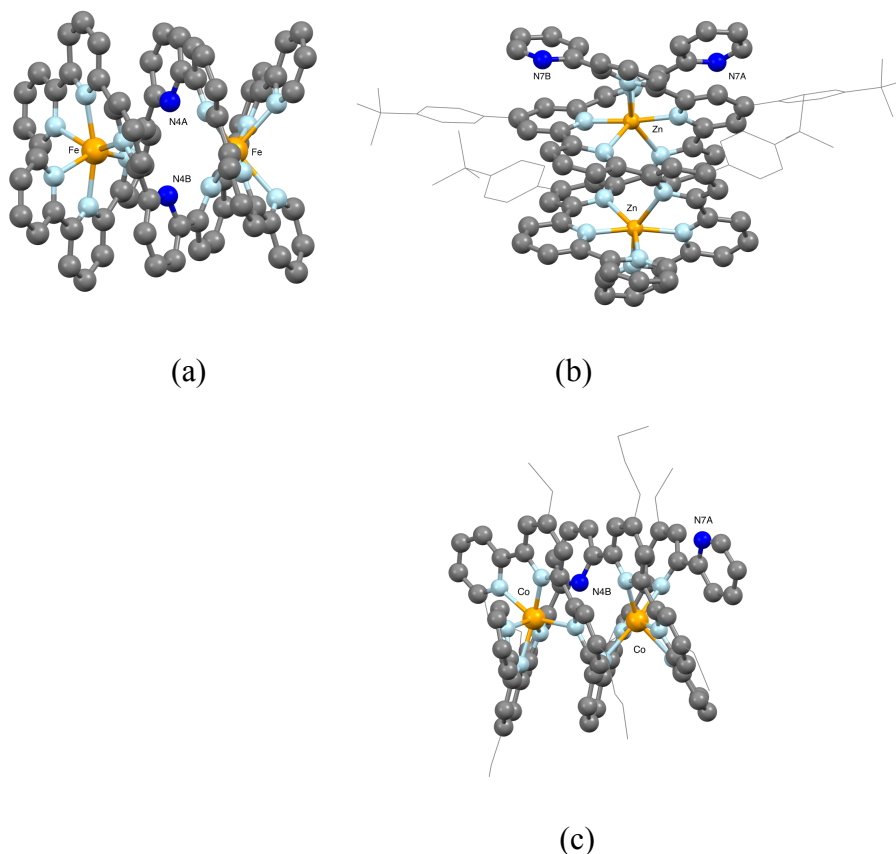
**Fig. 10** (a) The $[Fe_2(septipy)_2]^{4+}$ cation showing the hypodentate structure with N4A and N4B non-coordinated [159], contrasts with (b) the $[Zn_2(4'',4''''-(^tBuC_6H_4)_2septipy)_2]^{4+}$ cation in which N7A and N7B are pendant [160] and (c) with the even less symmetric structure of $[Co_2(4',4''''-(MeS)_2-4'',4''''-(^nPrS)_2septipy)_2]^{4+}$ in which N7A and N4B are free [161]. Hydrogen atoms have been omitted and substituents rendered in wireframe for clarity, non-coordinated nitrogen atoms deep blue, coordinated nitrogen atoms pale blue.

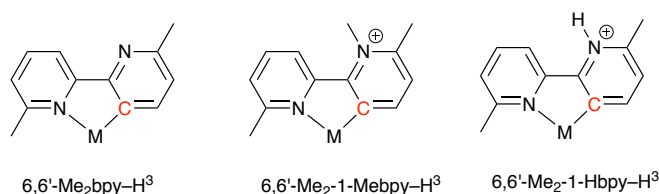## 3. Cyclometallated bonding modes

Oligopyridine complexes can exhibit two different types of complex in which the ligand is cyclometallated. In the first, the site of cyclometallation is an aromatic substituent on the ligand or a benzo ring of a fused oligopyridine derivative, whereas in the second class the site of metalation is on one of the pyridine rings. Ligands which give rise to complexes of the

first type include 6-phenylbpy [162]. We will only consider complexes of the second class in this review as it exemplifies the diversity of bonding modes within the parent oligopyridine scaffold.

In formulae, the site of metalation of the cylometallated ligand will be indicated using the notation bpy–H$^3$, indicating the site of metalation to be C3. Substituents are denoted using the usual scheme adopted in this manuscript for substituted bpy ligands and substituents on the non-coordinated nitrogen precede the ligand core nomenclature: for example 6,6'-Me$_2$bpy–H$^3$, 6,6'-Me$_2$-1-Mepy–H$^3$, 6,6'-Me$_2$-1-Hbpy–H$^3$, refer to the structural motifs in Scheme 14.



6,6'-Me$_2$bpy–H$^3$          6,6'-Me$_2$-1-Mebpy–H$^3$          6,6'-Me$_2$-1-Hbpy–H$^3$

**Scheme 14** The nomenclature adopted in this review to indicate the position of cyclometallation in oligopyridine complexes.

It is perhaps not surprising that the bidentate cyclometallated bonding mode is found relatively commonly. In this section, we only discuss complexes in which the cyclometallation occurs at a pyridine ring and initially consider compounds in which the nitrogen of the cyclometallated ring is not further functionalized or coordinated. The cyclometallated coordination mode is particularly common with square-planar complexes and structurally characterized examples include [Au(6,6'-(MeO)$_2$bpy–H$^3$)(OAc)Cl] [163], [Pt(6-(MeO)bpy–H$^3$)(dmso)Me] [164], [Pt(bpy–H$^3$)(PPh$_3$)Cl] [165], [Pt(4-$^t$Bubpy–H$^3$)(Me$_2$S)Cl] [166], [Pt(bpy–H$^3$)(PPh$_3$)Me] (Fig 11a) [167] as well as the bridged dimers [(6-$^i$Prbpy–H$^3$)Pd(μ-Cl)$_2$Pd(6-iPrbpy–H$^3$)][166]                and                [(6,6'-(MeO)$_2$-bpy-H$^3$)Pd(μ-OAc)$_2$Pd[(6,6'-(MeO)$_2$-bpy-H$^3$)] [168]. The more structurally developed ligands 2-(2'-pyridyl)quinoline (pq) and form the analogous square-planar complexes [Pt(pq–H$^3$)Me(CO)]

(Fig. 11b) and [Pt(pq–H$^3$)Me(PPh$_3$)] [169] and [Pt(L–H$^3$)Cl(PPh$_3$)] (Fig 11c, L = 2-(2'-pyridyl)naphtha[1,2-f]quinoline) [170].



(a)

(b)

(c)
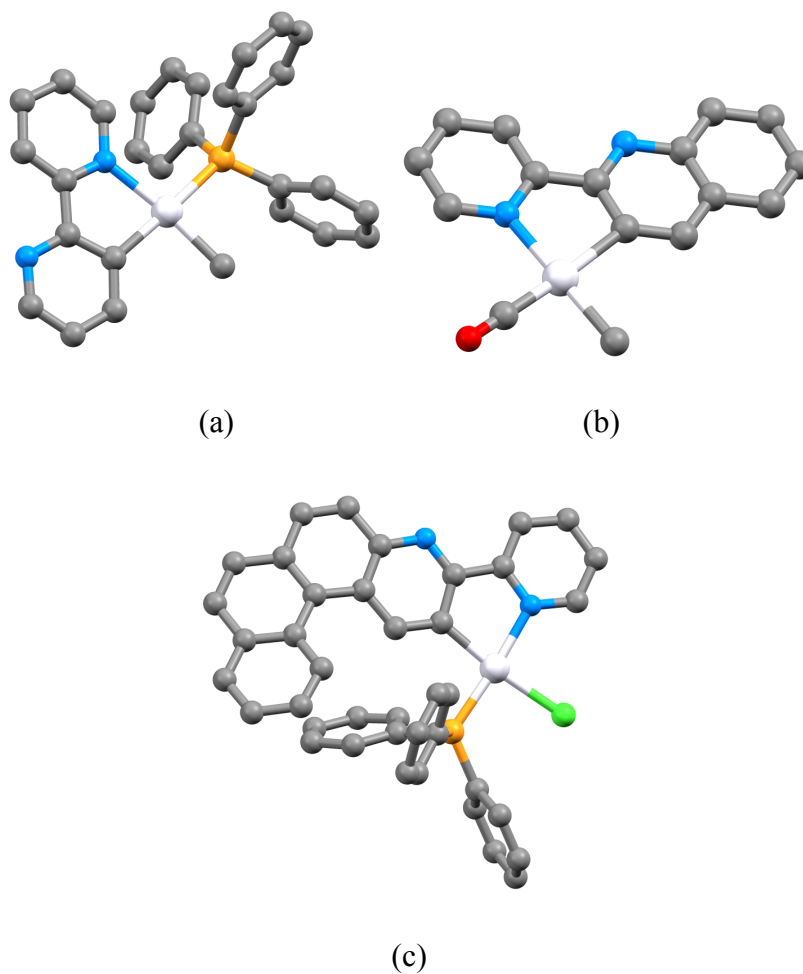
**Fig. 11** Examples of structurally characterized cyclometallated bpy ligands in four-coordinate complexes (a) [Pt(bpy–H$^3$)(PPh$_3$)Me] [167], (b) [Pt(pq–H$^3$)Me(CO)] [169] and (c) [Pt(L–H$^3$)Cl(PPh$_3$)] [170].
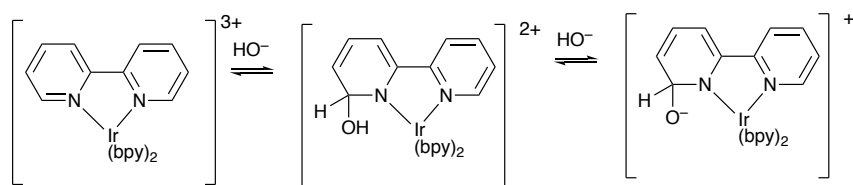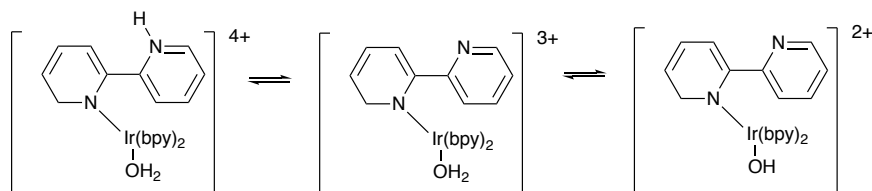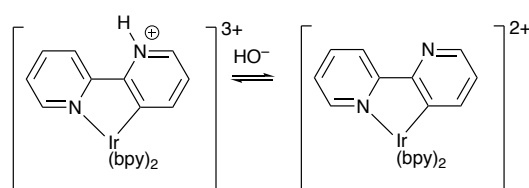
**Scheme 15** Alternative structures proposed for the "anomalous" iridium bpy complexes included (a) covalently hydrated ligands and (b) monodentate bpy ligands. The anomalous pH behavior is explained in the equilibria presented above. (c) In reality these compounds contain cyclometallated bpy ligands which can protonate on the non-coordinated nitrogen.

Complexes related to $[Ir(bpy)_3]^{3+}$ are of interest for their photophysical and photoelectrocatalytic properties and the early literature is very confusing, with complexes of apparently similar composition being reported as exhibiting variable colours and characteristics. In particular, some of the complexes exhibited unusual pH dependent properties associated with a strongly acidic proton and this lead to the proposal that they contained not bpy ligands, but rather the covalently hydrated form (Scheme 15). The inorganic community did not readily accept the presence of the covalent hydrated form of the ligand in these complexes and it was alternatively proposed that they contained monodentate bpy ligands and coordinated water molecules, the latter being responsible for the observed acidity. Ultimately. crystallographic studies combined with detailed NMR spectroscopic

studies revealed that these complexes contained cyclometallated bpy–H$^3$ ligands, with the unusual pH profiles being explained by protonation of the uncoordinated nitrogen (Scheme 15). Structurally characterized complexes include [Ir(bpy)$_2$(1-Hbpy–H$^3$)][ClO$_4$]$_3$ (Fig 12a) [68,171] and [Ir(bpy)$_2$(bpy–H$^3$)][ClO$_4$]$_2$ [172]. The tendency for cyclometallation of bpy ligands at iridium(III) centers seems to be high, and additional complexes exhibiting these motifs include [Ir(4,4'-$^t$Bu$_2$bpy)(4-Phbpy–H$^3$)(CF$_3$SO$_3$)Me] [173], [Ir(4,4'$^t$Bu$_2$bpy)(4-Phbpy–H$^3$)(py)Ph](CF$_3$SO$_3$) [173], [Ir(6-Phbpy–H$^3$)(py)$_2$Cl$_2$] [174], [Ir(4,4'-$^t$Bu$_2$bpy)(4-Phbpy–H$^3$)Cl$_2$] [174], [Ir(4,4'-$^t$Bu$_2$bpy)(4-Phbpy–H$^3$)Cl(Me)] [174] and [Ir(1-Hbpy–H$^3$)(PPh$_3$)$_2$HCl]X (X = CF$_3$CO$_2$ or BF$_4$) [175]. In all cases, the cyclometallated bpy ligands are near-planar in the complexes. Additional octahedral compounds containing cyclometallated bpy ligands include the triply cyclometallated complex [Ir(6-Phbpy–H$^3$)(3-(2'-pyridyl)biphenyl–2H$^{2,2'}$)(CO)] (Fig 12b) [176], [Ir(3,5-(CF$_3$)$_2$-4'-Me-ppy)(acac)(4,4'-Me$_2$bpy–H$^3$)] [177], [Pt(bpy–H$^3$)Me$_2$I(PMe$_3$)] (Fig 12c) [178] and [Pt(6,6-Me$_2$bpy–H$^3$)(dmf)Cl$_3$] [179].



(a)          (b)
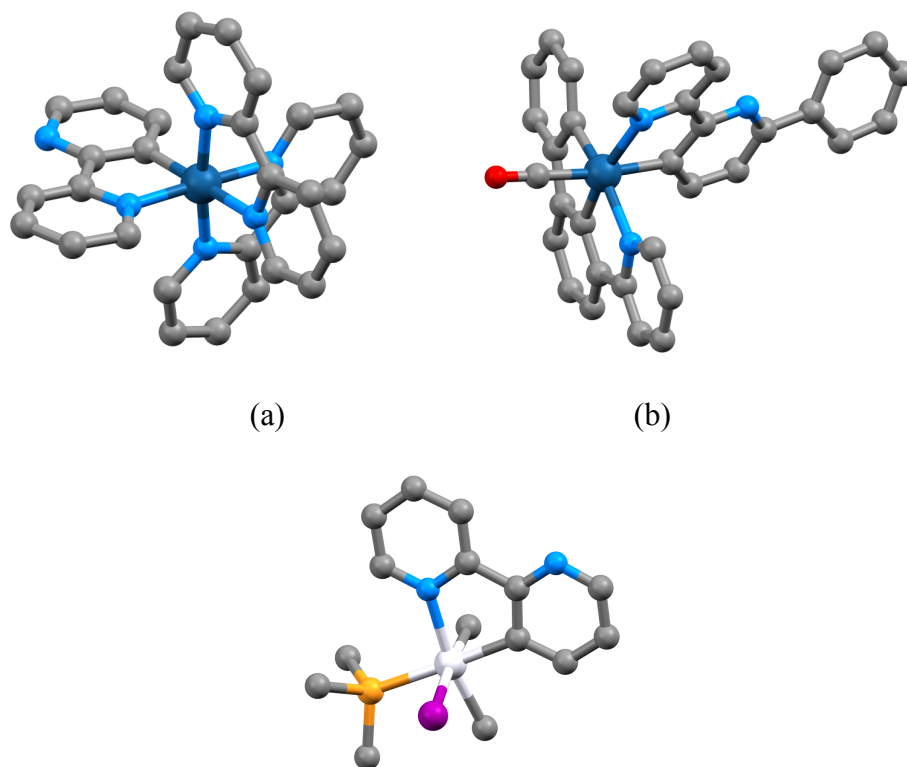
**Fig. 12** Structurally characterized cyclometallated bpy ligands in six-coordinate complexes (a) [Ir(bpy)$_2$(1-Hbpy–H$^3$)][ClO$_4$]$_3$ [171], (b) [Ir(6-Phbpy–H$^3$)(3-(2'-pyridyl)biphenyl–2H$^{2,2'}$)(CO)] [176] and (c) [Pt(bpy–H$^3$)Me$_2$I(PMe$_3$)] [178].

We finish this section on cyclometallated bpy ligands by considering the consequences of the nitrogen on the cyclometallated ring interacting with a second metal. In principle, two types of structure are possible (Scheme 16) in which the bpy is singly or double cyclometallated. To the best of our knowledge, no examples of the bonding mode III in Scheme 16 have been reported to date. Cyclometallated N-oxides are omitted from the discussion that follows. The bis cyclometallated bonding mode is II exemplified in the complexes [(4-$^t$Bupy)PhPt(bpy–2H$^{3,3'}$)PtPh($^t$Bupy)] [ 180 ][((PPh$_3$)ClPt(bpy–2H$^{3,3'}$)Pd(3,5-Me$_2$py)Cl] [181].
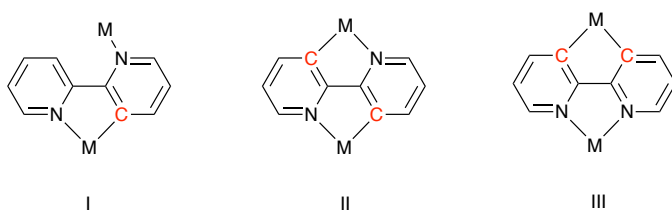


**Scheme 16** Possible dinucleating cyclometallated modes of bpy.
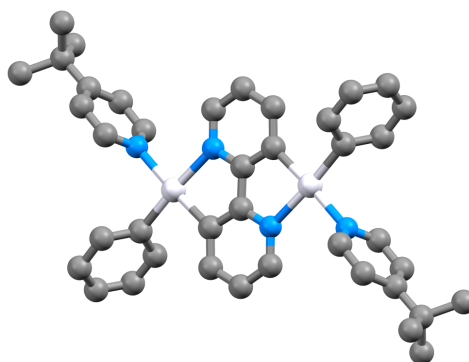


**Fig. 13** The complex [(4-$^t$Bupy)PhPt(bpy–2H$^{3,3'}$)PtPh($^t$Bupy)] [180] is a rare example of the bonding mode II in Scheme 16.

A number of possible bonding modes involving cyclometallated tpy ligands may be envisaged (Scheme 17) although such compounds are relatively rare to date. A single structurally characterized example of a mononuclear compound exhibiting a structure related to mode I has been reported in the compound [Zn{4'-(2,4-(SO$_3$)$_2$C$_6$H$_3$)-1'-Htpy-H$^{3'}$}(H$_2$O)$_2$] (Fig 14a) in which the cyclometallated CN donor mode with a pendant pyridine domain is stabilized by coordination of one of the sulfonate groups and protonation of the pendant nitrogen of the cyclometallated pyridine ring [182]. Bonding mode I is surprisingly rare but is also found in the dinuclear complex **31** (Scheme 18) [183]. The doubly cyclometallated bonding mode IV is found in the structurally characterized compounds [(tpy-2H$^{3',5'}$)(Pt(PPh$_3$)Cl)$_2$] [184] and [(tpy-2H$^{3',5'}$)(Pt(PPh$_3$)Me)$_2$] Fig. 14b [185]. Cyclometallated intermediates of type II are proposed as intermediates in the novel alkylation of tpy ligands at the 3' and 5'-positions observed in the reaction with alkenes in the presence of rhodium catalysts [186]. In this latter work, no products derived from cylometallated intermediates of type II were detected. In fact, the structural motifs II and III are surprisingly rare, but examples include [Ru(4'-C$_6$F$_5$tpy)(4'-C$_6$F$_5$tpy–H$^3$)]$^+$ obtained in low yield from the reaction of 4'-C$_6$F$_5$tpy with [Ru(dmso)$_4$Cl$_2$] [187], [Ru(4',5'-(CO$_2$Me)$_2$-4-Cltpy)(4',5'-(CO$_2$Me)$_2$-4-Cl-1-Htpy–H$^3$)]$^+$ also obtained as by-product [188], and finally the iridium complexes [Ir(**32**–H$^3$)$_2$] and [Ir(**32**–H$^3$)(**32**)] (Scheme 18) [189,190].
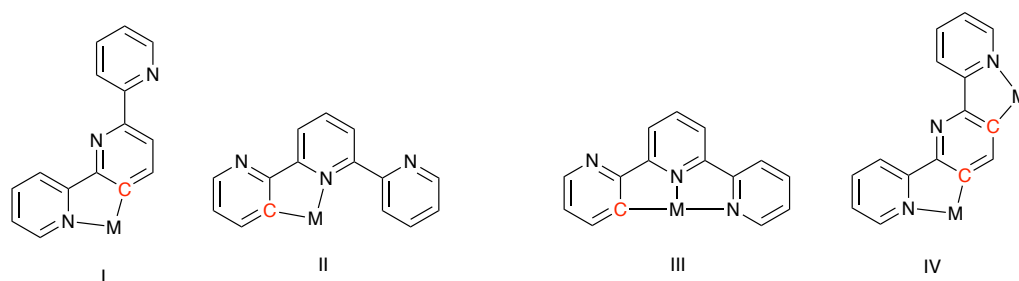


**Scheme 17** Possible cyclometallated bonding modes for tpy ligands.
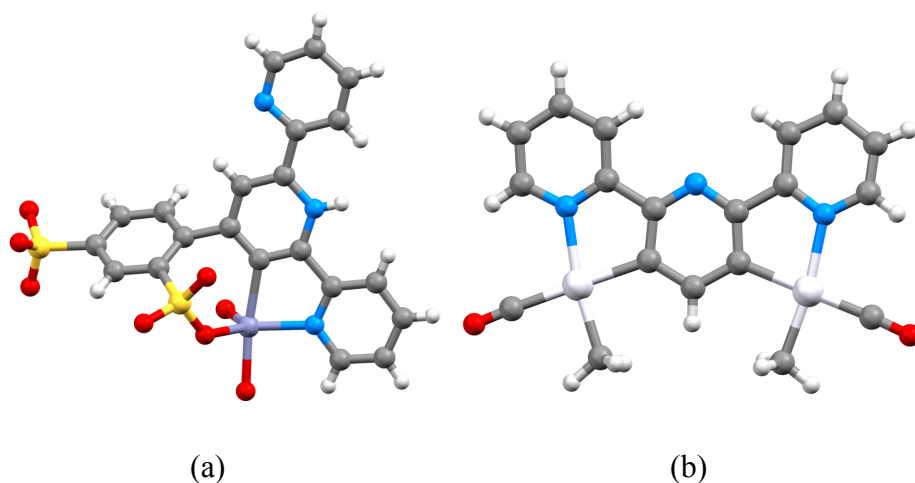
**Fig. 14** Complexes containing cyclometallated hypodentate tpy ligand include (a) [Zn(4'-(2,4-(SO$_3$)$_2$C$_6$H$_3$-1'-Htpy–H3'] [182] and (b) [(tpy-2H$^{3',5'}$)(Pt(PPh$_3$)Me)$_2$] [185].



**31**

**32**
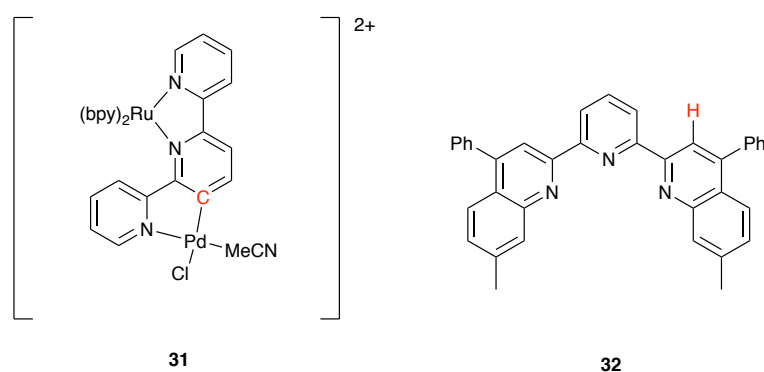
**Scheme 18** The dinuclear complex **31** is an unusual example of a dinuclear cyclometallated tpy complex [183] and ligand **32** forms the complexes [Ir(**32**–H$^3$)$_2$] and [Ir(**32**–H$^3$)(**32**)] containing cyclometallated quinolone rings [189,190].

Only two examples of cyclometallated qtpy ligands have been reported, both involving 6,6'''-Me$_2$qtpy and the hypodentate CNN-donor structural motif shown in Scheme 19. The reaction of platinum(II) chloride with 6,6'''-Me$_2$qtpy gives the platinum(IV) compound [Pt(6,6'''-Me$_2$qtpy-H$^{3''}$)Cl$_3$] (Fig 15a) which has been shown to be an effective and highly selective catalyst precursor for the hydrosilylation of styrene and terminal alkynes [191]. The platinum(II) compound [Pt(6,6'''-Me$_2$qtpy-H$^{3''}$)Cl] (Fig 15b) is obtained from the reaction of PtCl$_2$ with 6,6'''-Me$_2$qtpy in dmso, whereas the complex [Pt(6,6'''-Me$_2$qtpy][Pt(CH$_3$CN)Cl$_3$]$_2$ is obtained in MeCN/CH$_2$Cl$_2$ [192]. In both [Pt(6,6'''-Me$_2$qtpy-

H$^{3''}$)Cl$_3$] and [Pt(6,6'''-Me$_2$qtpy-H$^{3''}$)Cl] the cyclometallated 6,6'''-Me$_2$qtpy ligand is near planar with a transoid conformation of the pendant ring. No structurally characterized examples of cyclometallated qpy ligands or of higher oligopyridines have been reported to date.
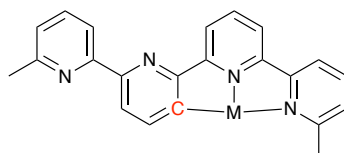


**Scheme 19** The cyclometallated mode observed in 6,6'''-Me$_2$qtpy complexes



(a)                                    (b)
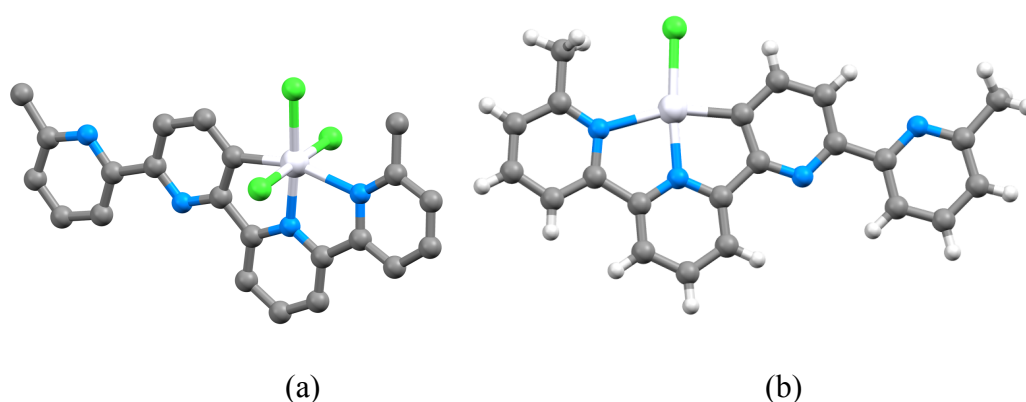
**Fig. 15** Structurally characterized cyclometallated qtpy complexes (a) [Pt(6,6'''-Me$_2$qtpy-H$^{3''}$)Cl$_3$] [191] and (b) [Pt(6,6'''-Me$_2$qtpy-H$^{3''}$)Cl] [192].

We noted earlier that one strategy for the design of hypodentate ligands was the blocking of a nitrogen donor by quaternization. This also has the consequence of activating the quaternized ring to cyclometallation and some of the earliest examples of cyclometallated bpy ligands exhibit this motif. The first example described was [Pt(1-Mebpy–H$^3$)Cl$_2$] (Fig. 16a), obtained by heating [Pt(1-Mebpy)Cl$_3$] with excess [1-Mebpy](NO$_3$) [46,51]. Interestingly, the palladium analogue [Pd(1-Mebpy-H$^3$)Cl$_2$] could not be obtained under similar conditions [46] but was obtained by heating [Pd(1-Mebpy)Cl$_3$] in water for 22 h [47]. In general, in these palladium and platinum compounds, the cyclometallated 1-Mebpy-H$^3$

ligands are near-planar and the coordination geometry about the $d^8$ metal centre is square-planar and the compounds exhibit typical substitution reactions with the derivatives [M(1-Mebpy-H$^3$)(py)$_2$]$^{2+}$ (M = Pd, Pt) [48,50,52], [M(1-Mebpy-H$^3$)(bpy)]$^{2+}$ (M = Pd, Pt) [48,50,52] [Pt(1-Mebpy-H$^3$)(py)Cl]$^+$ [48], [Pd(1-Mebpy-H$^3$)(NO$_3$)$_2$] [49] [Pd(NO$_3$)(H$_2$O)(1-Mebpy-H$^3$)][ClO$_4$] (Fig. 16b) [49,53] and [Pt(1-Mebpy-H$^3$)Cl$_2$] [ 51]. An interesting variation on this latter theme is in the complex [($^t$BuCOCHCO$^t$Bu)Pt(3'-Mes$_2$BCH$_2$bpy-H$^3$) in which the lone pair of the nitrogen of the cyclometallated ring forms a bond with the Lewis acid boron [193].



(a)                    (b)                    (c)
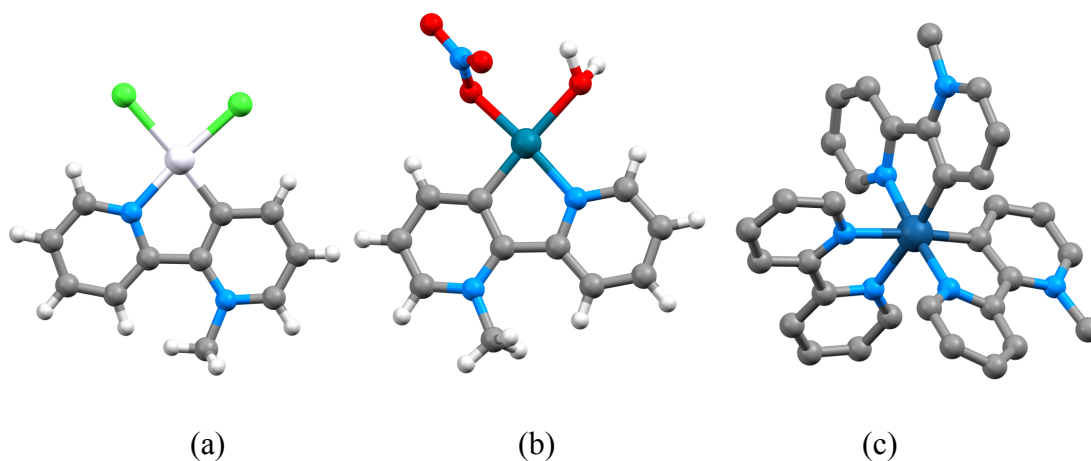
**Fig. 16** Solid state structures of (a) [Pt(1-Mebpy-H$^3$)Cl$_2$] [51] (b) [Pd(NO$_3$)(H$_2$O)(1-Mebpy-H$^3$)][ClO$_4$] [49] and (c) [Ir(bpy)(1-Mebpy-H$^3$)$_2$][PF$_6$]$_3$ [194].

Fewer examples of octahedral complexes containing quaternized bpy ligands are known. The structurally characterized complexes [Ir(4,4'-R$_2$bpy)(1-Mebpy–H$^3$)$_2$][PF$_6$]$_3$ (R = H, CF$_3$ or $^t$Bu) (Fig 16c) are prepared by the reaction of the appropriate 4,4'-R$_2$bpy ligand with the dimer [(1-Mebpy-H$^3$)$_2$Ir($\mu$-Cl)$_2$Ir(1-Mebpy-H$^3$)$_2$][PF$_6$]$_4$ (prepared directly from the reaction of [1-Mebpy-H$^3$](PF$_6$) with iridium trichloride) exhibit an intense green emission arising dominantly from the $^3$LC state of the cyclometallated ligand [194]. The same work

reported the preparation and structural characterization of the compound [Ir(1-Mebpy–H[3])$_2$(MeCN)Cl][PF$_6$]$_3$ (R = H, CF$_3$ or $^t$Bu)

## 4. Deuteration of coordinated ligands

One series of observations for which the mechanistic origin remains unclear is the deuteration of coordinated ligands under basic conditions. This phenomenon was first observed when solutions of [Ru(bpy)$_3$]$^{2+}$ salts in dmso-d$_6$ were treated with NaOCD$_3$ in CD$_3$OD [195]. A relatively rapid and specific exchange occurs at the 3- and 3'-positions to give [Ru(3,3'-$d_2$-bpy)$_3$]$^{2+}$ (Scheme 20) which is characterized by the loss of the signals for the 3-protons in the $^1$H NMR spectrum. Earlier studies by Wernberg had shown that there was no deuterium exchange when [Fe(phen)$_3$]$^{2+}$ was treated with NaOD in D$_2$O [196].
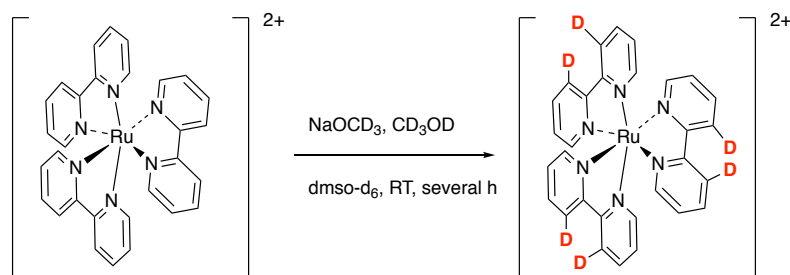


**Scheme 20.** The reaction of [Ru(bpy)$_3$]$^{2+}$ salts in dmso-d$_6$ with NaOCD$_3$ in CD$_3$OD results in site-specific deuteration to give [Ru(3,3'-$d_2$-bpy)$_3$]$^{2+}$[195].

Two mechanistic explanations can be offered for this reaction (Scheme 21). The first is a simply sequential deprotonation at the 3-position and subsequent redeuteration with the deuterated solvent. This has the benefit of simplicity but implies that the 3,3'-protons are the most acidic protons in the cation. The alternative mechanism involves sequential reversible cyclometallation with the reverse step involving deuterated solvent and cosnsequent deuteration of the ligand. This latter mechanism satisfactorily explains the specificity for the

3,3'-positions of the bpy ligand but implies that a cyclometallated intermediate (which has, to date, not been observed) is involved in the reaction.
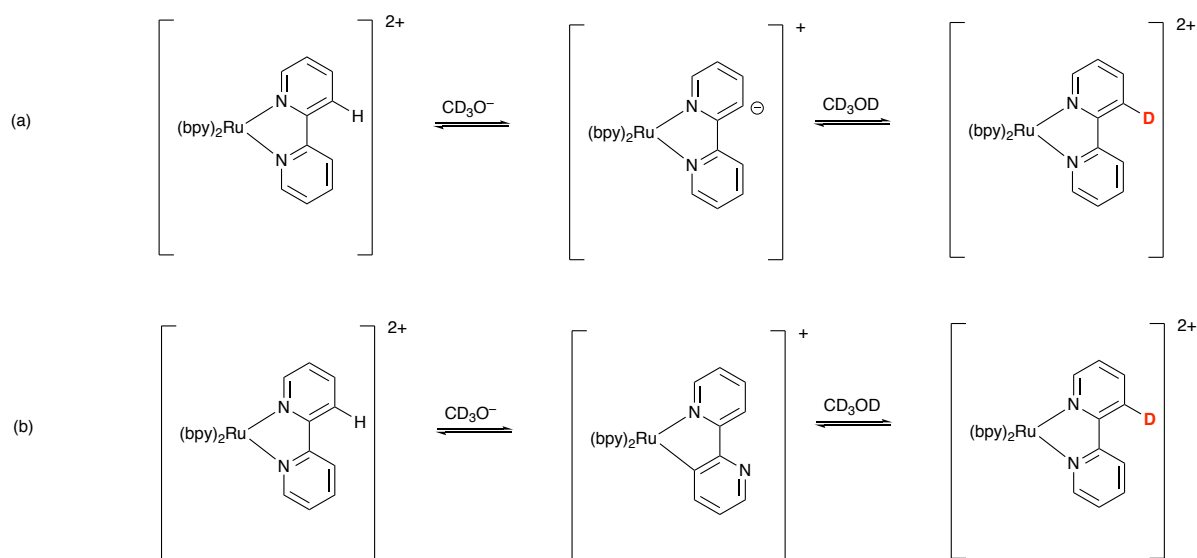


**Scheme 21.** The site-specific deuteration of $[Ru(bpy)_3]^{2+}$ can be explained (a) by a simple sequential deprotonation of the bpy ligand at the 3-position, whose acidity is enhanced by coordination to the 2+ charged ruthenium(II) centre or (b) by sequential reversible cyclometallation which leads specifically to exchange at the 3-position.

The deprotonation model was supported by the observation that the electronic environment of the 3,3'-protons is perturbed as a result of steric repulsions resulting from their proximity in the cis-conformation adopted in the chelating bonding mode. In particular, the ^{1}H NMR chemical shifts and relaxation times were interpreted in terms of van der Waals de-shielding arising from this steric effect [197,198].

Subsequent studies by McClanahan and co-workers confirmed the exchange reactions in $[Ru(bpy)_3]^{2+}$ and demonstrated that slower exchange of the remaining protons occurred [199]. McClanahan also reported and compared the resonance Raman spectra of the ground and excited states of $[Ru(bpy)_3]^{2+}$ and $[Ru(3,3'-d_2-bpy)_3]^{2+}$. Subsequently, resonance Raman studies of $[Ru(bpy)_3]^{2+}$, $[Ru(3,3'-d_2-bpy)_3]^{2+}$ and $[Ru(6,6'-d_2-bpy)_3]^{2+}$ were reported,

with the latter compound being prepared directly from 6,6'-$d_2$-bpy [200]. Comparative studies on the $^3$MLCT states of [Ru(bpy)$_3$]$^{2+}$, [Ru(3,3'-$d_2$-bpy)$_3$]$^{2+}$, [Ru(3,3',5,5'-$d_4$-bpy)$_3$]$^{2+}$ and [Ru(6,6'-$d_2$-bpy)$_3$]$^{2+}$ clearly demonstrated lifetime differences between the various compounds [201]. The complex [Ru(3,3',5,5'-$d_4$-bpy)$_3$]$^{2+}$ was obtained from the deuterium exchange reaction of [Ru(bpy)$_3$]$^{2+}$ over longer periods. Wernberg later showed that the exchange of the 3,3'-protons in [Os(bpy)$_3$]$^{2+}$ also exchanged rapidly (< 15 minutes after treatment of a 0.027 M solution in dmso-d$_6$ with NaOD in D$_2$O) to give [Os(3,3'-$d_2$-bpy)$_3$]$^{2+}$ [202]. It was also shown that the other protons underwent much slower exchange reactions in the sequence 3,3' >> 5,5' > 6,6' > 4,4'. This latter observation argues strongly for a simple deprotonation mechanism (using Occam´s razor[‡]) as cyclometallation cannot account for exchange at positions other than 3 and 3´ *or* different mechanisms for exchange at various sites. We subsequently extended the studies to [Rh(bpy)$_3$]$^{3+}$, arguing that the different influences of σ- and π-bonding components to the overall electron density at the bpy hydrogen atoms might be reflected in their acidity and exchange rates [203]. This prediction was confirmed and it was observed that rapid exchange of the 6,6'-protons occurred to give [Rh(6,6'-$d_2$-bpy)$_3$]$^{3+}$, followed by a slower but still rapid exchange of the 3,3'-protons to give [Rh(3,3',6,6'-$d_4$-bpy)$_3$]$^{3+}$. After prolonged reaction times the compounds [Rh(3,3',5,5',6,6'-$d_6$-bpy)$_3$]$^{3+}$ and [Rh($d_8$-bpy)$_3$]$^{3+}$ could be isolated as pure species.


## 5. Conclusions

As generations of undergraduates have learnt, the majority of complexes of bpy, tpy and phen are chelating with all nitrogen atoms coordinated to a single metal centre. Nevertheless,

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‡ "*Pluralitas non est ponenda sine necessitate*" is a problem-solving principle formulated by William of Ockham (c. 1287–1347) and is best translated as meaning that given competing hypotheses, the one with the fewest assumptions should be chosen.

a significant number of hypodentate complexes of bpy and tpy are known in which one or more nitrogen atoms remain uncoordinated. The higher oligopyridines tend to form complexes with less than the maximum number of donors coordinated to a single metal centre, with a consequence that polynuclear complexes are common. Although not discussed in this review, there is a significant number of polynuclear complexes in which oligopyridines act as bridging ligands.

In addition to the hypodentate complexes, there are increasingly more examples of cyclometallated complexes of oligopyridines described, in which a pyridine rings has "turned around" and the metal has inserted into a C-H bond.

These unexpected bonding modes should be taken into account when utilizing oligopyridines in extreme reaction conditions or unusual electronic or steric environments.

## 6. Acknowledgements

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