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Tris(2-pyridyl) tripod ligands[1]

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Contents

Abstract

This review covers the recent literature involving tris(2-pyridyl) tripod ligands which use nitrogen, phosphorus, arsenic, or carbon as central bridging atoms. In general, tripod ligands

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[1] Dedicated to Daryle H. Busch on the occasion of his 70th birthday.

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are facially coordinating, tridentate chelate ligands which have received considerable attention in both coordination and organometallic chemistry. Over the past 20 years, there have been hundreds of published reports concerning various aspects of metal complexes which contain tripod ligands, with the majority of these reports involving polypyrazolylborate ligands. In light of the extensive and also very recent literature coverage of ligands which contain pyrazole donors, this review is a timely examination of the literature concerning tripod ligands that use pyridine donors. Further, this review contains the first summary of the chemistry of carbon-bridged tris(2-pyridyl) tripod ligands as well as an examination of recent studies involving nitrogen-bridged, phosphorus-bridged and arsenic-bridged analogues to the carbon-bridged ligands. There is a particular focus on tris(2-pyridyl) tripod ligands that coordinate in a facial manner to a single metal center through the pyridyl nitrogens.

Abbreviations

bpy	2,2′-dipyridyl
mIm	methylimidazole
phen	1,10-phenanthroline
tpAs	tris(2-pyridyl)arsine
tpb	tris(pyrazolyl)borate
tpm	tris(2-pyridyl)methane
tpmOH	tris(2-pyridyl)methanol
tpN	tris(2-pyridyl)amine
tpP	tris(2-pyridyl)phosphine
tpP=O	tris(2-pyridyl)phosphine oxide
tpzm	tris(pyrazolyl)methane
trpy	2,2′,2″-terpyridine

1. Introduction

In general, tripod ligands are facially coordinating, tridentate chelate which have received considerable attention in both coordination and organometallic chemistry. Over the past 20 years, there have been hundreds of published reports concerning various aspects of metal complexes which contain tripod ligands, with the majority of these reports involving polypyrazolylborate ligands (for recent reviews see [1,82–85]. In light of the extensive literature coverage of ligands which contain pyrazole donors, this review will focus on tripod ligands that use pyridine donors.

Prior to a review of the literature involving tris(2-pyridyl) tripod ligands, it may prove useful to briefly state some of the significant differences between tris(pyrazolyl) and tris(pyridyl) tripod. First, the majority of tris(pyridyl) tripod ligands are neutral whereas tris(pyrazolyl)borate is monoanionic. Second, the $\mathrm{p}K_\mathrm{a}$ values of the conjugate acids (BH^+) of pyrazole (2.48) and pyridine (5.25) are very different which suggests that pyridine is a better sigma donor than pyrazole. Furthermore, pyridine is reported to be a better π-acidic ligalid than pyrazole [2]. Therefore, transition metal complexes which use tris(pyridyl) tripod can display significant differences in overall charge, solubility, and redox properties from the analogous complexes which contain tris(pyrazolyl) tripod ligands.

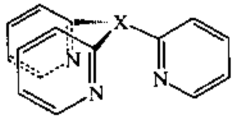
This review covers the recent literature involving tris(2-pyridyl) tripod ligands which use either nitrogen, phosphorus, arsenic, or carbon as the central bridging atom. Previously, there were two reviews in the literature which covered some aspects of tris(2-pyridyl) tripod ligand chemistry. In 1970, the coordination properties of chelating containing non- or weakly conjugated 2-pyridyl groups, including tpN, were reported where it was noted that unlike bpY, phen, or trpy, the N-bridged pyridine ligands are flexible, forming six-membered chelate rings with little distortion from ideal octahedral geometry [3]. In 1993, Newkome reviewed the pyridylphosphine literature, including tpP and tpP=O. The synthesis and the coordination properties of pyridylphosphine as well as the catalytic reactivity of transition metal complexes containing these ligands were discussed [4]. This article contains the first review of carbon-bridged tris(2-pyridyl) tripod ligands as well as a review of recently reported nitrogen-bridged, phosphorus-bridged and arsenic-bridged analogues to the carbon-bridged ligands, with a particular focus on tris(2-pyridyl) tripod ligands (Fig. 1) that coordinate in a facial manner to a single metal center through the pyridylnitrogens.

2. Preparation

2.1. Tripod ligands with nitrogen as the bridgehead atom

Tris(2-pyridyl)amine, tpN, which is a pyridine analog of triphenylamine, was first prepared by Wibaut and La Bastide in 1933 [5]. This tertiary amine was prepared by sequential condensation of 2-halopyridine with 2-aminopyridine. The first condensation generates the secondary amine, di(2-pyridyl)amine and this intermediate is then further reacted with excess 2-halopyridine to give the desired product (Fig. 2). Direct reaction of the halopyridine with dipyridylamine gave 50% yields of tpN.

The syntheses of the mono-substituted tpN ligands were reported later in 1970 by Lancaster and McWhinnie [6]. Modifying Wibaut and La Bastide's synthesis for



X	Ligand
CH	tpm
COH	tpmOH
N	tpN
P	tpP
As	tpAs

Fig. 1. Tris(2-pyridyl) tripod ligands.

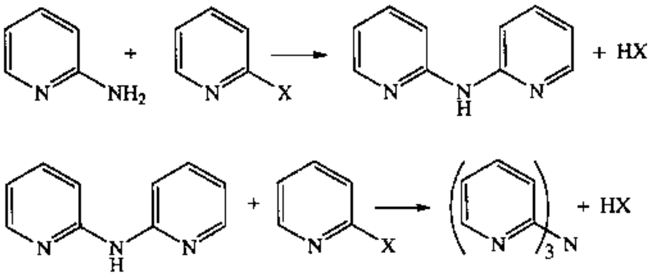


Fig. 2. Preparation of tpN adapted from Wibaut and La Bastide [5].

tpN, either 5-nitro-2-aminopyridine or 4-, 5- or 6-methyl-2-aminopyridine was condensed with 2-halopyridine generating 5-nitro-2-pyridyldi-(2-pyridyl)amine and 4-, 5-, or 6-methyl-2-pyridyldi-(2-pyridyl)amine.

2.2. *Tripod ligands with phosphorus as the bridgehead atom*

Tris(2-pyridyl)phosphine, tpP, was first synthesized in 1944 by Davies and Mann [7] as part of a study on the optical resolution of tertiary phosphines. By reacting the Grignard reagent 2-pyridylmagnesium bromide with PCl_3, a 13% yield of tpP was obtained. In 1948, Mann and Watson [8] formed salts of tpP, tpN and tpAs. Notably, only two pyridyl nitrogens of tpN can be protonated whereas all three pyridyl nitrogens of tpP and tpAs are basic enough to be protonated in hydrochloric acid, this observation is one of the first reported examples of the importance of the nature of the bridging atom in the chemical behavior of the pendant pyridine groups for pyridine based tripod ligands bridged by a heteroatom. The authors proposed that the nitrogen atom of tpN is an effective conduit for the communication of charge (due to protonation) among the three pyridines, while the central phosphorus atom (of tpP) or arsenic atom (of tpAs) minimizes the effect of the protonated pyridyl nitrogen on adjacent pyridines.

In 1957 [9], tpP was synthesized in a manner analogous to the preparation of tpmOH (vide infra). The 2-bromopyridine was first reacted with *n*-butyllithium and then PCl_3 was added to yield tpP in a 35% yield (Fig. 3). This procedure has been modified several times in the literature [10–12] with improved yields up to 60%.

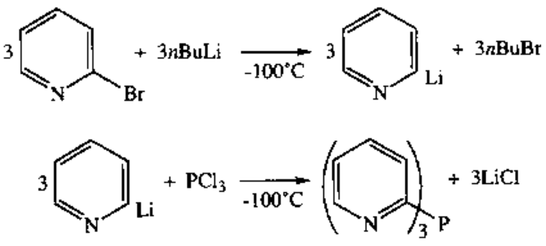


Fig. 3. Preparation of tpP as described by Keene et al. [12].

Oxidation of tpP by H_2O_2 results in the formation of tpP=O [13]. In 1988, Keene et al. [14] reported the crystal structure of the free tpP ligand. The geometry around the phosphorus atom is trigonal pyramidal, with C–P–C angles of 102.7, 101.9 and 101.0°. In the solid state, the ligand deviates from a C_{3v} symmetry, where one pyridyl nitrogen is directed towards the lone pair of electrons on the phosphorus atom.

2.3. Tripod ligands with carbon as the bridgehead atom

The syntheses of the pyridyl-based tripod ligands with carbon bridgeheads are based on a reaction developed by Wibaut et al. [15] where lithiopyridine reacts with dipyridyl ketone. In 1951, in the course of investigating the utility of 2- and 3-lithiopyridine as reagents in organic synthesis, the pyridine-based analog to triphenylcarbinol, tds(2-pyridyl)methanol (tpmOH), was prepared (Fig. 4). It was noted that in strongly acidic solutions tpmOH did not undergo spectroscopic changes similar to triphenylcarbinol. It was proposed that the change in this behavior was due to the high electronegativity of nitrogen (in pyridine), which inductively caused the central carbon bridgehead atom to become partially positive, thereby strengthening the bond between the carbon and the hydroxy group. This enhanced interaction caused the dissociation of the hydroxy group to become less favorable in tpmOH than in triphenylmethanol [16].

In 1956 [17], the synthesis of tris(2-pyridyl)methane (tpm) was reported by Ousch and Levine. These authors were primarily interested in the alkylation of picoline by organolithium reagents, but the authors also studied the reaction of 2-picolyllithium with 2-bromopyridine [Fig. 5(a)]. This reaction resulted in the preparation of bis- and tris-(2-pyridyl)methane in 30 and 25% yields, respectively.

In designing a new series of chelating ligands, White and Faller [18] synthesized several derivatives of tpmOH, including tpm. In their preparation, tpmOH was converted to tris(2-pyridyl)bromomethane which was then reacted with *n*-BuLi. Subsequent reaction with water yielded tpm in a 55% yield [Fig. 5(b)]. White and Faller also reported the synthesis of the following chelates: tris(2-pyridyl)-bromomethane, tris(2-pyridyl)chloromethane, tris(2-pyridyl)ethoxymethane, tris(2-pyridyl)methyl acetate, tris(2-pyridyl)methoxy-$\kappa N,\kappa O$](difluoroborane), and *N*-[tris(2-pyridyl)methyl] aniline. This series of compounds demonstrates the richness of chemistry associated with the tpm core structure. By changing substituents on the bridgehead carbon, properties such as solubility, overall charge of the complexes, and the potential modes of attachment to supports were varied, demonstrating the potential utility of the tpm structure in a variety of applications.

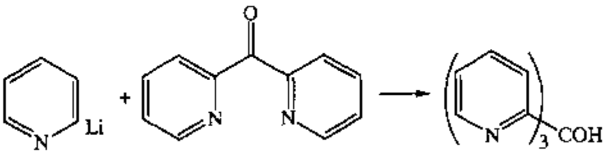


Fig. 4. Synthesis of tpmOH adapted from Wibaut et al. [15].

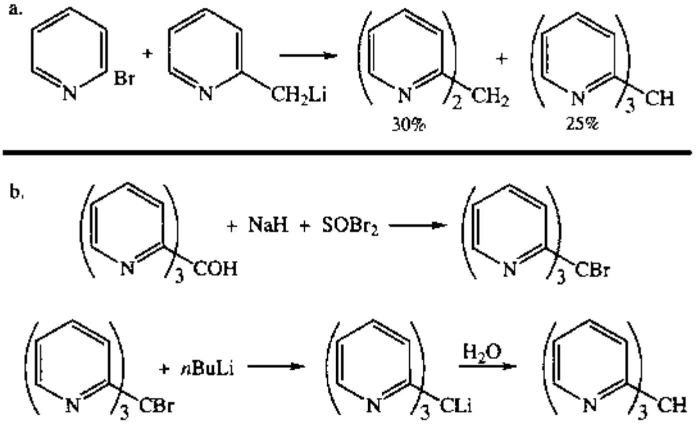


Fig. 5. Synthesis of tpm: (a) as first described by Osuch and Levine [17]; and (b) the modified synthesis as described by White and Faller [18].

The crystal structures of tpmOH and tpm were published in 1988 and 1990, respectively. In tpmOH, two of the nitrogens point away from the hydroxy group while the third nitrogen appears to possess a weak intramolecular attraction to the C–OH group [19]. In tpm, the geometry about the bridgehead carbon is slightly distorted from tetrahedral. One of the pyridyl rings is disordered and in the major conformation (~ 58%) two of the N atoms point in the same direction as the methane hydrogen [20].

In 1992, Adolfsson et al. [21] reported the synthesis of a chiral tris(2-pyridyl) tripod ligand (Fig. 6). This ligand has C_3 symmetry and was prepared from tpmOH by substitution at the 6-position of the pyridine group and subsequent asymmetric modification of the substituents. The authors predicted that this type of ligand would enhance the enantiomeric excess of reactions at the metal center because tridentate coordination would leave the three remaining coordination sites equivalent, which would make the three primary approaches that a substrate can take towards the metal center identical. A rhodium complex was prepared by reaction of this ligand with $RhCl_3$ and ^1H NMR spectroscopy indicated that the resulting complex also had C_3 symmetry. Use of this species as a catalyst for hydrosilylation reactions is currently under investigation.

3. Transition metal complexes

3.1. Chromium, molybdenum and tungsten

The coordination of tpN to transition metals was first reported by McWhinnie et al. in 1966 [22] establishing the ability of tpN to coordinate TpN was bonded to $Mo(CO)_6$ to form $Mo(tpN)(CO)_3$, facially to transition metal centers (Fig. 7).

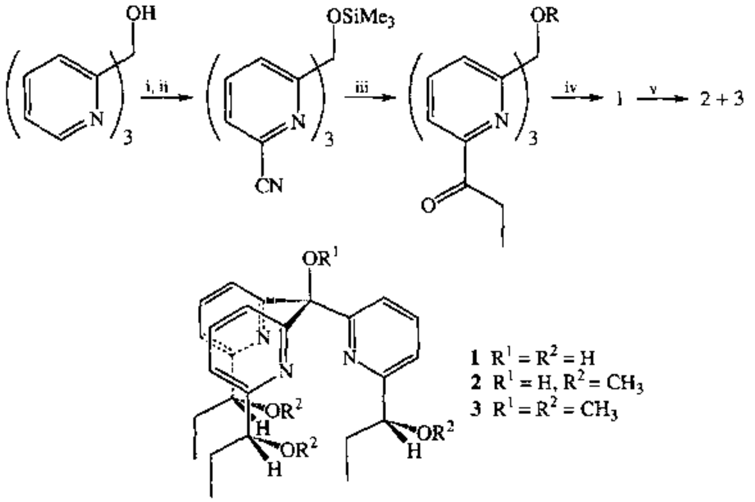


Fig. 6. The synthesis of the first chiral C_3 symmetric tris(2-pyridyl) tripod ligand, adapted from Adolfsson et al. [21] (i = *m*-chloroperbenzoic acid, ii = *N*,*N*-dimethylcarbamoyl chloride, trimethylsilyl cyanide, iii = EtMgBr, iv = (-)-Ipc$_2$BCl, 2,2′-iminodiethanol. and v = NaH, MeI).

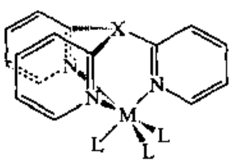


Fig. 7. The basic structure of octahedral transition metal complexes containing a single tris(2-pyridyl) tripod ligand.

Subsequent to this report, a number of transition metal complexes which utilize tpN have been prepared.

Kaizaki and Legg [23] reported the synthesis of [Cr(tpN)Cl$_3$] in their structural characterization of octahedral metal complexes of the type [MX$_3$(py-d_5)$_3$] (M = Cr(III), Mo(III); X = Cl$^-$, Br$^-$, F$^-$, NCS$^-$) by ^{1}H NMR spectroscopy. [Cr(tpN)Cl$_3$] was prepared to help determine the *fac* or *mer* arrangement of the pyridine groups in the metal complexes studied. The UV-vis spectrum of [Cr(py-d_5)$_3$,Cl$_3$] is similar to [Cr(tpN)Cl$_3$], indicating a *fac* arrangement of the pyridine groups; however, [Cr(py-d_5)$_3$Cl$_3$] was shown by X-ray diffraction to have the *mer* configuration like the other tris(pyridyl) complexes reported in this study.

Faller and Ma [24] replaced the negatively charged cyclopentadienyl ligand in [MCp(CO)(NO)$_2$](PF$_6$)(M = Mo or W) with the neutral tpm ligand. The increase in charge on the newly synthesized [M(tpm)(CO)(NO)$_2$](SbF$_6$)$_2$ (M = Mo or W) complexes facilitates the dissociation of CO to generate [M(tpm)(NO)$_2$](SbF$_6$)$_2$. These complexes are strong Lewis acids and were found to form Lewis acid–organic carbonyl base adducts with aldehydes, ketones and esters. Interestingly, the

$[M(tpm)(NO)_2](SbF_6)_2$ complexes catalyze the Diels–Alder reaction between methyl vinyl ketone and 1,3-butadiene as well as the polymerization of butadiene. The catalytic properties of $[M(tpm)(NO)_2](SbF_6)_2$ are further discussed in Section 7.2.

In 1996, Mosny and Crabtree [25] reported the preparation of $[W(tpN)Cl_4]$ through the reaction of tpN with $[WCl_4(PPh_3)_2]$. While tpN was proposed to coordinate in a tridentate fashion, no ^{1}H NMR spectroscopic data could be obtained due to the fact that the complex is paramagnetic and crystals suitable for crystallographic analysis were not obtained.

3.2. *Manganese and rhenium*

The preparation of manganese complexes containing tripod ligands coordinated in a tridentate fashion was first reported in 1975 [10]. The reaction of $Mn(ClO_4)_2$ with tpP, tpP=O and tpAs yielded the octahedral complexes $[Mn(L)_2](ClO_4)_2$ (where L = tpP, tpP=O and tpas) (Fig. 8).

In 1990, Anderson et al. [26] investigated the coordination of tpN, tpP, tpm and trpy to carbonylrhenium(I) centers in designing organometallic-based elecumatalysts for the reduction of CO_2. These π-acceptor tripodal ligands were selected because of their ability to stabilize low transition metal oxidation states and because of their synthetic versatility (i.e. possible variations in the bridgehead atom, the heterocyclic rings, and the substituents on the heterocyclic rings). This versatility could allow for control of the redox potentials of metal complexes. All four ligands coordinated in a bidentate manner when simply reacted with $[Re(CO)_5Cl]$, yielding *fac*-$[Re(L)(CO)_3Cl]$ (where L = tpm, tpN, tpP, or trpy). However, when the reaction is conducted under intense irradiation by visible light, tpN and tpm coordinate in a tridentate fashion yielding $[Re(L)(CO)_2Cl]$ (where L = tpm or tpN). It is proposed that the irradiation labilizes one of the CO ligands, allowing the third pyridine ring to coordinate. While $[Re(L)(CO)_3Cl]$ and $[Re(L)(CO)_2Cl]$ were observed to mediate the electrochemical reduction of CO_2, each of the newly reported complexes has reduction potentials which are shifted to more negative values compared with $[Re(bpy)(CO)_3Cl]$, making them less attractive electrocatalysts for CO_2 reduction.

In 1996, tpN was utilized in the preparation of non-organometallic rhenium coordination complexes. Reaction of tpN with $[ReCl_3(PPh_3)(benzil)]$ yielded $[Re(tpN)Cl_3]$, which was shown to have all three pyridine rings of the tpN ligand coordinated to the metal center. The high oxidation state complexes,

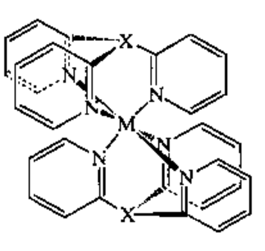


Fig. 8. The basic structure of bis(tris(2-pyridyl) tripod) octahedral transition metal complexes.

$[Re(O)_3(tpN)][ReO_4]$ (prepared by reaction of tpN with Re_2O_7) and $[Re(O)(OCH_2CH_2O)(PPh_3)(tpN)]Cl$, were also prepared, demonstrating the ability of tpN to stabilize transition metal oxo complexes. In these complexes, the tpN ligand displays tridentate and bidentate coordination, respectively [25].

3.3. *Iron and ruthenium*

In 1967, McWhinnie et al. [27] reported the vibrational, electronic and Mössbauer spectroscopic data of iron(II), complexes containing tpN and di-2-pyridylamine ligands. When $Fe(ClO_4)_2$ was reacted with tpN, the spectroscopy and diamagnetism indicated the formation of $[Fe(tpN)_2](ClO_4)_2$, however, when $FeCl_2$ and $FeBr_2$ were used as starting materials, $[Fe(tpN)_2]^{2+}$ was generated, but the counterions were found to be $FeCl_4^{2-}$ and $FeBr_4^{2-}$, respectively. Mössbauer spectroscopy corroborated the high symmetry of $[Fe(tpN)_2]^{2+}$ in that there was no resolvable quadrupole splitting. An X-ray crystal structure analysis was performed on the $[Fe(tpN)_2](ClO_4)_2$ complex and the complex was found to be only slightly distorted from octahedral geometry, with N–Fe–N angles averaging 88.1° and a small range of Fe–N distances (1.970–1.995 Å) [28]. Lancaster and McWhinnie [29] also reported that the reaction of 4- and 5-methyl-2-pyridyldi(2-pyridyl)amine (4- and 5-mpdpN) with $Fe(ClO_4)_2$, yielded the octahedral bis(tripod) complexes, $[Fe(L)_2](Cl_4)_2$ (where L = 4- or 5-mpdpN) similar to the above reaction. However, the reaction of $Fe(ClO_4)_2$ with 5-nitro-2-pyridyldi(2-pyridyl)amine (5-npdpN) yielded $[Fe(5\text{-npdpN})_2(H_2O)_2](ClO_4)_2$, where 5-npdpN is coordinated in a bidentate fashion.

Subsequently, in 1978, Fernandopulle et al. [30] reported the synthesis and characterization of both iron(II) and iron(III) complexes containing tpN, substituted tpN, and di(2-pyridyl)amine. The reaction of tpN and substituted tpN with $FeCl_3$ resulted in the formation of two types of complexes. The first type had the formula $(LH^+)_2[Cl_3Fe\text{-}O\text{-}FeCl_3]$(L = tpN or 5-mpdpN), where the protonated ligand did not coordinate to the metal, but rather acted as the counter cation. The second type had the formula $[FeLCl_3]$(L = tpN or 4-mpdpN), where L coordinated in a tridentate fashion to the metal center. The reaction of tpN with $Fe(NCS)_3$ yielded the complex, $[Fe(tpN)_2(NCS)_2][Fe(tpN)(NCS)_4]$, where the tpN ligand coordinates in a bidentate manner. However, reaction of tpN and 5-mpdpN with $Fe(NCS)_2$ resulted in the formation of $[Fe(L)_2][Fe(NCS)_4]$ where the tripod ligands coordinate in a tridentate fashion. Reaction of $Fe(NCS)_2$ with 4-mpdpN resulted in the formation of the intermediate, $[Fe(4\text{-mpdpN})_2(NCS)_2]$, which upon heating was converted to $[Fe(4\text{-mpdpN})_2][Fe(NCS)_4]$.

In 1987 Keene et al. [31] reported the synthetic, spectral, and structural studies of the first (tris(2-pyridyl)tripod)ruthenium(II) complex. $[Ru(tpmOH)_2]^{2+}$. He later extended these studies to include analogous complexes containing tpm, tpN, tpP and tpP=O as well as the phosphinate complex, $[Ru(py_2P(O)O)(tpP{=}O)](BF_4)$ [12,13]. X-ray crystal structure analyses of all but the $[Ru(tpP{=}O)_2](PF_6)_2$ complex confirmed the facial, tridentate coordination of the tripod ligands. TpN, tpP and tpm coordinated through the three pyridyl nitrogens while tpmOH displayed two modes of coordination, (N,N′,N″) and (N,N′,O) (see Section 5.1). The $[Ru(L)_2]^{2+}$(L = tpN, tpm and tpP) cations showed an increasing distortion from ideal D_{3d} symmetry with an increase in the (α-carbon atom (py)-bridgehead atom length, where the largest distortion was observed in the tpP containing complex. This distortion was also observed in solution as evidenced by the $^1H/^{13}C$ 2D NMR spectra. The possibility of a ligand steric effect as a rationale for the distortion was mentioned.

Moritz et al. [32] reported the reaction of tris(2-pyridyl) tripod with $[Ru(NH_3)_3(OH_2)_3]^{2+}$. Reactions of $[Ru(NH_3)_3(OH_2)_3]^{2+}$ with tpN or tpmOH resulted in products of the general formulation, $[Ru(tripod)(NH_3)_3]^{2+}$. However, the analogous reaction with tpm gave $[Ru(NH_3)_2(OH_2)(tpm)]^{2+}$ and reaction with tpP produced several unidentified species. The N- and CH-bridged ligands are coordinated in a tridentate fashion through the three pyridine nitrogens, whereas tpmOH is coordinated in an (N,N′,O) mode. An X-ray crystal structure of $[Ru(NH_3)_3(tpmOH)]Br2 \cdot H_2O$ confirmed this assignment. The ruthenium(III/II) reduction potentials for the $[Ru(L)(NH_3)_3]^{2+}$(L = tpN and tpmOH) and $[Ru(NH_3)_2(OH_2)(tpm)]^{2+}$ complexes are all less positive than the ruthenium(III/II) reduction potentials for the analogous bis(tripod) complexes, consistent with the difference between the σ-donating properties of the amine and aqua ligands compared with the π-accepting properties of pyridyl rings.

Recently, Mosny et al. [33] utilized tpN in the preparation of a number of organometaffic and coordination complexes of ruthenium. In each of the following coordination complexes, $[Ru(tpN)Cl_3]$,$[Ru(tpN)Cl_2L]$(L = py or PPh_3), and $[Ru(tpN)H_2O)_2(PPh_3)](SbF_6)_2$, tpN was found to coordinate in a tridentate fashion. The preparations of organometallic complexes were also reported. Depending on the number of equivalents of $AgSbF_6$ that were reacted with the $[Ru(p\text{-cymeneCl}]_2$ staffing material, complexes containing a bidentate tpN, $[Ru(p\text{-cymene})(tpN)Cl]^+$, as well as tridentate tpN, $[Ru(p\text{-cymene})(tpN)]^{2+}$ were obtained. Reactivity studies conducted on each of the reported complexes, including the $[Ru(tpN)(H_2O)_2(PPh_3)]^{2+}$ complex which contains labile aqua ligands, showed that they were inactive as catalysts towards alkane dehydrogenation.

Schutte et al. [34] isolated a ruthenium complex containing a single tpP ligand, namely $[RuCl_2(PPh_3)(tpP)]$. Besides $Zn(tpP)(NO_3)_2$, $[RuCl_2(PPh_3)(tPP)]$ is the only other example of a half-sandwich complex containing tpP. An X-ray crystal structure analysis of this complex was reported, proving the facial, tridentate coordination of the tpP ligand. Ligand substitution studies were conducted and it was noted that $[RuCl_2(PPh_3)(tpP)]$ undergoes ligand substitution reactions similar to the $[Ru(Cp)(PPh_3)_2Cl]$(Cp = cyclopentadienyl) complex. For example, in MeOH, one of the chloride ligands of $[RuCl\ _2(PPh_3)(tpP)]$ is replaced by a neutral ligand such as CO, MeCN or PhCN to give a racemic mixture of chiral transition metal complexes. However, in a non-polar solvent such as benzene, the PPh_3 ligand of $[RuCl_2(PPh_3)(tpP)]$ is substituted instead of the chloride. In the presence of O_2 (1 atm in $CDCl_3$) the tpP ligand of $[RuCl_2(PPh_3)(tpP)]$ is oxidized to tpP = O resulting in the formation of $[RuCl_2(PPh_3)(tPP = O)]$.

3.4. Cobalt, rhodium and iridium

Reaction of $Co(ClO_4)_2$ with the tripod ligands tpN, tpP, tpP=O, or tpAs results in the formation of the bis(tripod) complexes, [Co(tripod)21$(ClO_4)_2$, where the tripod ligands are coordinated in a tridentate fashion to the metal center [10,22]. Similarly, reaction of $Co(NO_3)_2$ with tpN results in the formation of $[Co(tpN)_2](NO_3)_2$ [35]. A single crystal X-ray structural analysis of $[Co(tpN)_2](ClO_4)_2$ was performed where, unlike the iron(II) analog which was reported to deviate only trivially from octahedral geometry, the cobalt(II) species was found to show greater deviations. The N–Co–N angles ranged from 84.86(7) to 86.09(8)° and Co–N lengths ranged from 2.100(2) to 2.152(2) Å [36]. Reaction of CoX_2 (where $X = Br^-$, Cl^- or NCS^-) with two equivalents of tpN yieldled the octahedral $[Co(tpN)_2X_2]$ complexes where tpN coordinates in a bidentate fashion. These complexes readily isomerize to form the $[Co(tpN)_2](CoX_4]$ complexes, where the tripod figand binds in a tridentate fashion [35,37].

Szalda and Keene [38] reported the preparation of two cobalt bis(tpmOH) complexes, $[Co(N,N',N''\text{-tpmOH})_2]^{3+}$ and $[Co(N,N'N''\text{-tpmOH})(N,N',O\text{–tpmO}^-)]^{2+}$. These bis(tpmOH) cobalt complexes were initially investigated by Boggess and Boberg [39]. However, the conclusions by Boggess and Boberg about the coordination mode of the tpmOH ligand, which were first questioned by structural data reported by White and Faller [18], were proven incorrect by Szalda and Keene (see Section 5.1 for a discussion on the coordination mode of the tpmOH ligand).

White and Faller reacted tpm with $CoCl_2$ generating $[Co(tpm)_2](PF_6)_2$ which was then chemically oxidized to $[Co(tpm)_2](PF_6)_3$ [18]. Without the hydroxy group, tpm can only coordinate through the pyridyl nitrogens. ^1H NMR spectroscopic studies confirmed the equivalency of the pyridine rings of the tpm on the diamagnetic cobalt(III) complex, with each tpm coordinating in a tridentate fashion through the three pyridyl nitrogens. The same geometry was suggested for the paramagnetic Co(II) complex.

In 1967, Kulasingam and McWhinnie [37] reported the preparation of the first rhodium(III) and iridium(III) complexes containing tris(2-pyridyl) tripod ligands, $[Rh(tpN)X_3]$ and $[Ir(tpN)X_3]$ (where $X = Cl^-$ or Br^-). Each of these complexes was determined to be octahedral with a tridentate coordination of the tpN ligand. In 1996, $[Ir(tpN)Cl_3]$ was prepared via a different route, by reaction of $(NH_4)_2IrCl_6$ with tpN in the presence of KI which facilitates the reduction of iridium(IV). In addition, the first tpN hydride complex, $[Ir(H)_2(PPh_3)_2(tpN)](BF_4)$, was prepared from the reaction of $[Ir(H)_2(PPh_3)_2(acetone)_2](BF_4)$ with tpN. Notably, in $[Ir(H)_2(PPh_3)_2(tpN)](BF_4)$ the tpN ligand is coordinated in a bidentate fashion [25].

Ertan et al. [40] prepared $[Rh(tpmOH)Cl_3]$ and Ertan subsequently reported the X-ray crystal structure of $[Rh(tpmOH)Cl_3]\cdot CH_3OH$. Unlike the case of ruthenium(II), where *N,N',O* bonding is observed, tpmOH coordinates to rhodium(III) in a tridentate fashion through the three pyridyl nitrogens (*N,N',N''* bonding).

3.5. Nickel, palladium and platinum

McWhinnie et al. investigated the reaction of various nickel(II) salts with tpN. Reacting NiX_2 (where $X = Cl^-$, Br^- or NO_3^-) with one equivalent of tpN yields the octahedral complexes $[Ni(tpN)(H_2O)_2X]X$, while the combination of NiX_2 (where $X = ClO_4^-$ or NO_3^-) with two equivalents of tpN results in the formation of $[Ni(tpN)_2]X_2$. These complexes are octahedral and the tpN coordinates in a tridentate fashion in both cases. However, reaction of $Ni(NCS)_2$ results in the formation of two complexes, $[Ni(tpN)_2(NCS)_2]$ and $[Ni(tpN)(NCS)_2]$, both of these complexes are octahedral, but the tpN ligand is believed to coordinate in a bidentate and tridentate fashion, respectively. In the latter complex, one of the thiocyanate groups is believed to act as a bridging ligand in the solid state [22,35,37]. Reaction of two equivalents of substituted tpN with $Ni(ClO_4)_2$ results in both bidentate and tridentate coordination modes of substituted tpN, depending on the basicity and steric bulk of the substituents on the substituted tpN ligand. For example, spectroscopic data suggests that 5-nitro-2-pyridyldi-(2-pyridyl)anmine coordinates in bidentate manner, while 4- and 5-methyl-2-pyridyldi(2-pyridyl)amine coordinates in a tridentate manner, and 6-methyl-2-pyridyldi(2-pyridyl)amine coordinates in both a bi- and tridentate manner [29]. Astley et al. [41] prepared nickel(II) complexes containing tpm and tpP from $Ni(NO_3)_2$, while Boggess and Zatko [10] prepared nickel(II) complexes containing tpP, tpP=O and tpAs from $NI(ClO_4)_2$. All of these complexes are analogous to $[Ni(tpN)_2](ClO_4)_2$ in that they have an octahedral geometry and each of the tripod coordinates in a tridentate fashion.

In 1986, Canty et al. [42] investigated the coordination of tpm, tpzm and tpb to palladium(II). Each of these potentially tridentate ligands coordinated in a bidentate fashion both in the solid state and in solution, yielding complexes of the type $[PdL_2]^{n+}$ ($n = 0$ for L = tpb and $n = 2+$ for L = tpm and tpzm). Variable temperature ^1H NMR spectroscopy indicated the presence of a rapid equilibria between the uncoordinated and the coordinated donor atoms in solution, implying the formation of a 5-coordinate intermediate containing the tripodal ligand, coordinated in a tridentate fashion. Canty et al. [43] also reported the synthesis and X-ray crystal structure analysis of $[pd(tpmH^+)Cl_2][PdCl_4]_{0.5} \cdot 2H_2O$. Again, the potentially tridentate ligand is found to coordinate in a bidentate fashion; the only difference is that the uncoordinated pyridine ring is protonated. The studies by Canty appear to indicate that the binding modes of tripodal ligands can be effectively controlled by the square planar nature of palladium(II). Given the variety of binding modes observed with nickel(II) and tripodal, Canty's studies demonstrate nicely that palladium(II) centers resist octahedral geometry even with tripodal ligands that induce octahedral geometry with nickel(II) centers.

In 1984, Clark et al. [44] reported the synthesis of trimethylplatinum(IV) complexes containing the tripod ligands tpm and tpzm as well as bidentate pyrazolyl and pyridyl ligands. For the complexes containing the tris-chelating , the ^1H and ^{13}C NMR spectral data indicated the formation of octahedral $[PtLMe_3](PF_6)$ (L = tpm or tpzm) complexes where the tripod ligand coordinates in a tridentate fashion. Later, Visalakshi and Jain [45] reported the preparation of

$[Pt(tpm)Me_3](SSP(OCMe_2)_2)$ in his study of trimethylplatinum(IV)dialkyldithiophosphates.

In 1990, Byers et al. [46] synthesized the first organopalladium(IV) compounds incorporating tripodal nitrogen donor containing pyrazolyl, pyridyl, and imidazole groups as well as bidentate nitrogen donor ligands in his study of the inorganic chemistry associated with palladium(IV). Here, the preparation of $[PdMe_3(tpm)]I$ was reported. This complex is analogous to the $[Pt(tpm)Me_3]^+$ complex reported earlier, where the tripod ligand coordinates in a facial tridentate manner. Further studies showed that the $[PdMe_3(tripod)]I$ complexes were more stable than the $[PdMe_3(L)I]$ (where L = bidentate N donor ligand) complexes. It was proposed that the complexes using bidentate ligands are less stable because reductive elimination is facilitated by ionization or partial ionization of the bonded iodo group.

The fact that the tripod tpm and tpmOH act as bidentate ligands towards square-planar platinum(II) and palladium(II) centers while acting as tridentate ligands towards octahedral platinum(IV)_and palladium(IV) centers, was nicely eploited by Canty et al. [47,48] in studies concerning the oxidation by water of organoplatinum(II) and -palladium(II) complexes containing tpmOH. The square planar $[PtR_2(tpmOH)]$ (R = Me or Ph) complexes were oxidized to the octahedral $[Pt(OH)R_2(tpmOH)][OH \cdot H_2O$ complexes, which could be further protonated in dilute nitric acid to generate $[PtR_2(OH_2)(tpmOH)]^{2+}$ (Fig. 9). Similarly, square-planar $[PdMe_2(tpmOH)]$ was oxidized in the presence of water to form the octahedral complex, $[PdMe_3(tpmOH)]^{2+}$. Canty proposed that in both cases the uncoordinated pyridine ring of the tpmOH ligand in the square-planar complexes could provide inumnolecular assistance in the oxidation reactions by increasing the nucleophilic character of the metal center upon coordination.

3.6. Copper and gold

A number of copper(II) complexes incorporating tripod ligands have been reported in the literature. A few of these display octahedral geometries, such as $[CuL_2](ClO_4)_2$ (where L = tpN, 4-mpdpN, 6-mpd:pN, tpP, tpP = 0 and tpas), where the tripod ligand is coordinated in a tridentate fashion. However, a number of the complexes containing the amine bridgehead atom as well as tpP=O can be iso-

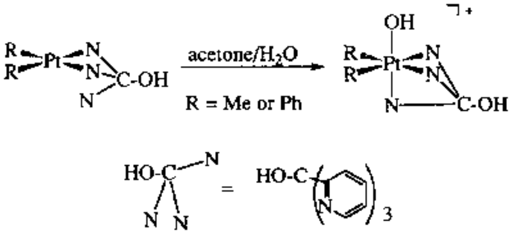


Fig. 9. Oxidation of the square planar $[PtR_2(tpmOH)]$ complex by water to form the octahedral $[PtR_2(tpmOH)(OH)]$+complex (R = Me or Ph), adapted from Canty et al. [48]. The tpmOH ligand is drawn without detail to aid in displaying the geometries of the platinum centers.

merized to complexes containing bidentate tripod ligands. For example, the blue coldred [Cu(tpN)$_2$](ClO$_4$)2 (tridendtate tpN) readily isomerizes to a yellow-green isomer, [Cu(tpN)$_2$(ClO$_4$)$_2$], where the tpN ligand coordinates in a bidentate fashion [10,22,49]. Therefore, even though tpN can coordinate in a tridentate fashion to Cu(H) (only 5-npdpN coordinates strictly in a bidentate fashion), these ligands appear to favor bidentate coordination to copper(II), as can be seen by the reactions of tpN with copper(II) halides, nitrates, and thiocyanates [35,37,50].

While copper(II) complexes had been shown spectroscopically to contain bidentate tpN, it was not until 1982 that the bidentate coordination of tpN with Cu(II) centers was demonstrated using X-ray crystallography. Ibers and Marks et al. prepared the complexes, [Cu(tpN)$_2$(CH$_3$CN)$_2$](SO$_3$CF$_3$)$_2$ and Cu(tpN)2(SO$_3$CF$_3$)$_2$, as models of the active site in certain copper proteins. The crystal structure of [Cu(tpN)$_2$(CH$_3$CN)$_2$](SO$_3$CF$_3$)$_2$ showed a tetragonally distorted octahedron, with tpN coordinated in a bidentate fashion and the CH$_3$CN groups occupying axial positions. Spectroscopic analyses (infrared, optical, and EPR) of Cu(tpN)$_2$(SO$_3$CF$_3$)$_2$ suggest by analogy that tpN binds in a bidentate fashion with axially coordinated triflate ligands [51].

In 1992, Boys et al. [52] confirmed through an X-ray crystal structure analysis the structure predicted by McWhinnie et al. [22] for the complex [Cu(tpN)$_2$(ClO$_4$)$_2$]. The coordination geometry was a tetragonally distorted octahedron, with each tpN coordinating in a bidentate fashion. The tpN were found to coordinate along the equatorial positions while the two perchlorate anions were weakly coordinated along the axial positions.

Astley et al. [53] reported the synthesis and characterization of [Cu(tpm)$_2$](NO$_3$)$_2$. The crystal structure of this complex showed that all six Cu–N bonds were crystallographically equivalent, which is unusual because copper(II) complexes with a coordination number of six usually display a tetragonally distorted octahedral geometry. Despite the crystal structure, the electronic spectrum of the complex in solution was consistent with a tetragonally distorted octahedral geometry. In addition, EXAFS confirmed that the copper(II) center was a tetragonally distorted octahedron. To support the theory that the directions of the long and short bonds interchange in the solid state, EPR was measured at 295 and 150 K. Indeed, at room temperature, the copper complex had an isotropic signal (indicating all bonds are equivalent) and at low temperatures, the copper complex had a signal characteristic of a tetragonally distorted octahedron. Therefore, by cooling the complex, the rate of interchange between long and short bonds was slowed to permit the observation of the anisotropic arrangement.

In a similar study, Astley et al. [54] reported the crystal structure of [Cu(tpP)$_2$]Br$_2 \cdot 8$H$_2$O. This complex has two Cu–N bond distances that are considerably shorter than the other four Cu–N bonds. The remaining four bonds are not equivalent, and the temperature dependence of the EPR spectra suggests that the complex is a tetragonally elongated octahedral structure. The crystal lattice contains the tetragonally elongated octahedron in two different orientations which are in a dynamic-equilibrium, where the direction of the long and intermediate Cu–N bonds interchange.

In 1982, Canty et al. [55] reported the coordination of tpmOH, tpm and tpzm with dimethylgold(III). The potentially tridentate ligands, tpmOH and tpm, coordinate in a bidentate fashion in both the solid state and solution, while only tpzm coordinates as a tridentate ligand, with weak axial Au...N interaction [3.139 (7) Å]. The crystal structure of the $[AuMe_2(tpm)](NO_3)\cdot 2H_2O$ complex showed that the nitrogen atom of the uncoordinated pyridine ring remained above the metal center, instead of directed away from the metal center. The ^1H NMR spectroscopie data indicated that the solution structure was consistent with the solid state structural data.

3.7. *Zinc and mercury*

The first study of a facially coordinated tripod ligand coordinated to zinc(II) was reported in 1975 by Boggess and Zatko. $Zn(ClO_4)_2$ was reacted with tpP, tpP=O or tpAs generating the octahedral complexes $[ZnL_2](ClO_4)_2$ (L=tpP, tpP=O or tpAs) [10]. Previously, McWhinnie reported on the reaction of ZnX_2 with tpN. However, the tetrahedral complexes prepared by McWhinnie, namely $[Zn(tpN)X_2]$ ($X=Cl^-$ or Br^-), contained bidentate tpN [37].

In 1992, Gregorzik et al. [56] reported the synthesis of several Zn(II) complexes with tpP and tpAs, investigating the effect of different Zn starting materials on the identity of the resulting product. Zn halides gave different complexes for tpP and tpAs: $\{[Zn(tpP)X]_2[ZnX_4]\}$ and $Zn(tpAs)X_2$. With $Zn(SCN)_2$, two tpP ligands bind to zinc(II) to give $[Zn(tpP)_2]^{2+}$, while only one tpAs bonded to zinc(II) in the compound $[Zn(tpAs)(SCN)_2]$. Reacting tpP and tpAs with $Zn(NO_3)_2$ resulted in the formation of $[Zn(L)(NO_3)_2]$ (L=tpP or tpas) where L is coordinated in a tridentate manner and one nitrate ligand is monodentate and the other is bidentate. Using non-coordinating anions, ClO_4^- or BF_4^-, the bis(tripod) complexes, $[ZnL_2](ClO_4)_2$ (where L=tpP or tpas) were formed, which was reminiscent to what was observed by Boggess and Zatko [10]. The crystal structure of the $[Zn(tpP)_2]^{2+}$ cation was reported first by Vahrenkamp et al. as the perchlorate salt and later by Ke-Wu et al. [57] as the $[Zn(NCS)_4]^{2-}$ salt. These structures showed the cation to have an octahedral geometry with each tpP coordinating in a tridentate fashion through the three pyridine nitrogens.

In 1995, Zvargulis et al. [58] attempted the synthesis of Zn(II) complexes containing only one tripodal ligand. Although the target molecules were designed to coordinate one tripod ligand, the bis(tripod) $[Zn(L)_2]^{2+}$, (L=tpm or tpzm) complexes were isolated and characterized by X-ray crystallography. The authors hypothesized that both the chelate effect and the lack of strong interligand repulsion caused the bis-tripod products to be thermodynamically preferred.

Astley et al. [54] reported the X-ray crystal structure of the $[Zn(tpP)_2]Br_2\cdot 8H_2O$ complex. As was observed for the analogous copper(II) complex, the zinc(II) species has two Zn–N bond distances that are considerably shorter than the other four Zn–N bond distances, which are crystallographically equivalent. By doping the zinc(II) compound with ≈1% of Cu^{2+}, EPR data similar to the pure zinc compound was obtained, suggesting similar geometries for the guest copper complex.

Canty et al. [59] reported methylmercury(II) complexes with aromatic nitrogen donor tripod ligands including tpmOH. While organomercury(II) species typically have a coordination number of two, complexes with a coordination number of four were observed in both the solid state (X-ray crystallography) and in solution (NMR spectroscopy). The X-ray crystal structure analyses of the [HgMeL](NO_3) (L = tpmOH and py_2(*N*-mIm)COH complexes indicate irregular four-coordination geometries (Fig. 10). Previously, coordination of potentially tridentate ligands such as trpy produced complexes that were four coordinate in the solid state, but only three coordinate in solution. In an earlier study, Canty was unable to assign the coordination mode of tpm in the [HgMe(tpm)](NO_3) complex, however, after further study, it was concluded that tpm also coordinates in a tridentate fashion in solution [60].

4. Complexes containing indium or thallium

Hudman et al. [61] investigated the spectroscopy of thallium(I) complexes with bpy and phen, and thallium(III) complexes with bpy, phen, di(2-pyridyl)amine, and tpN. The tpN in [Tl(tpN)X_3] ($X = Cl^-$, Br^-) was observed to coordinate in a tridentate fashion. However, when [Tl(tPN)X_3] was placed in the potentially coordinating solvent DMF, results from infrared spectroscopy suggested that one of the pyridine rings of tpN dissociated from the metal center in order to accommodate the solvent into the sixth coordination site, resulting in a bidentate tpN ligand and the halides in a facial arrangement. This bidentate behavior was supported by the similarity between the spectra of [Tl(tPN)$(Cl)_3$(DMF)] and that of the (DMF)thallium(III) complexes containing bpy, phen, and di(2-pyridyl)amine.

Canty et al. [62] combined [$InMe_2$]NO_3 with tpmOH to produce monomethylindium(III) complexes containing bimetallic cations. This is the first

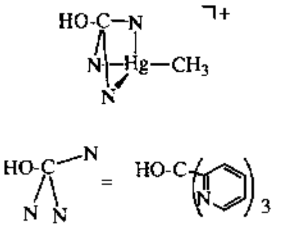


Fig. 10. The irregular four-coordinate geometry of [MeHg(tpmOH)]$^+$, adapted from Canty et al. [59]. The tpmOH ligand is drawn without detail to aid in displaying the geometry of the mercury center.

and only report of tpmO$^-$ acting as a bridging ligand between two metal centers. See Section 5.2 for further details regarding this study.

5. Specific coordination behaviors

5.1. Coordination modes of tpmOH (N,N′,N″ versus N,N′,O)

As mentioned in Section 1, this review focuses on the facial coordination of tds(2-pyridyl) tripod ligands to a single transition metal center. These typically coordinate in a tridentate fashion through the pyridyl nitrogens; however, other modes of coordination, such as bidentate coordination through two pyridyl groups or one pyridyl group plus the bridgehead heteroatom have been observed. Of the ligands considered here (tpN, tpP, tpP=O, tpAs, tpm and tpmOH), only tpmOH has been shown to coordinate in a tridentate manner through two pyridyl groups and the bridgehead group to a single transition metal center. Much work has been done to determine the charge and the binding mode of these ligands, (Fig. 11: *N*,*N*′,*N*″-tpmOH, *N*,*N*′,*O*-tpmOH, or *N*,*N*′,*O*-tpmO$^-$; vide infra).

Boggess and Boberg were the first to report the synthesis and characterization of transition metal complexes containing two tpmOH ligands [39]. In these studies the coordination modes of the ligands were based on spectroscopic data (no structural data was obtained). Later, Boggess et al. reported titration and further spectral studies which helped clarify the coordination mode of each of the tpmOH ligands [63]. The transition metals which were studied include: nickel(II), iron(II), manganese(II), copper(II) and zinc(II). $[Cu(tpmOH)_2](ClO_4)_2$ is paramagnetic ($\mu = 1.91$ B.M.) and its UV-vis spectrum is similar to $[Cu(tpN)_2]^{2+}$ indicating a symmetric (*N*,*N*′,*N*″-tpmOH) coordination mode for both tpmOH ligands. The zinc(II) complex was proposed to have a similar coordination mode based on ^{1}H NMR spectroscopy. Three different iron(II) complexes were isolated and identified as [Fe(*N*,*N*′,*N*″-tpmOH)(*N*,*N*′,*N*″-tpmOH)]$^{2+}$, [Fe(*N*,*N*′,*N*″-tpmOH)(*N*,*N*′,*O*-tpmOH)]$^{2+}$, and [Fe(*N*,*N*′,*N*″-tpmOH)(*N*,*N*′,*O*-tpmO$^-$)]$^+$. The formation of these complexes dependes on the mediod of preparation as well as the pH of thesolution. For example, when the symmetric form is dissolved

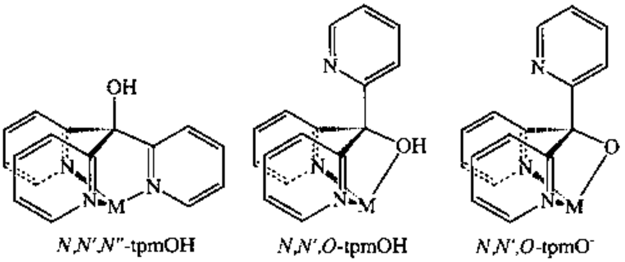

N,*N*′,*N*″-tpmOH *N*,*N*′,*O*-tpmOH *N*,*N*′,*O*-tpmO$^-$

Fig. 11. The observed charges and binding modes of the tris(2-pyridyl)methanol ligand.

in a water–ethanol solution, it remains as the symmetric isomer, however, when the complex is formed in situ by mixing iron(II) chloride and tpmOH in a similar water–ethanol mixture, the complex that is formed is the unsymmetrical form (i.e. (*N*,*N′*,*N″*-tpmOH)/(*N*,*N′*,*O*-tpmOH)), and titrates as a strong acid. The manganese(II) complex also titrates as a strong acid and consumes one equivalent of base per equivalent of complex, which suggests that it has a coordination sphere similar to the above unsymmetrical iron(II) complex. The nickel(II) species consumes one equivalent of hydroxide per mole of complex, however, it differs from the manganese(II) and iron(II) complexes in that it titrates as a weak acid. The same coordination (*N*,*N′*,*N″*-tpmOH)/(*N*,*N′*,*O*-tpmOH) was nevertheless proposed; however, this assignment appears uncertain.

In addition to the above complexes, Boggess and Boberg also reported the preparation of a bis(tpmOH) cobalt complex [39] (see Section 3.4). Crystal structure data was not available, so the assignment of the coordination mode as (*N*,*N′*,*O*-tpmOH)(*N*,*N′*,*O*-tpmO$^-$), was based on spectroscopic (IR and electronic) data. However, in a report on the reactivity of tpm with first row transition metals, White and Faller mentioned in a footnote that they prepared a bis(tpmOH)cobalt(III) complex [18] and that structural data indicated the formation of the unsymmetrical [Co(*N*,*N′*,*N″*-tpmOH)(*N*,*N′*,*O*-tpmO$^-$)]$^{2+}$ complex. Most recently, Szalda and Keene investigated the coordination of tpmOH to cobalt [38]. Depending on the solvent in which the reaction was conducted, two complexes were prepared; the symmetrical [Co(*N*,*N′*,*N″*-tpmOH)$_2$](ClO$_4$)$_3$ complex and the unsymmetrical [Co(*N*,*N′*,*N″*-tpmOH)(*N*,*N′*,*O*-tPMO$^-$)](ClO$_4$)$_2$ complex. A crystal structure of the symmetric complex, Li[Co(*N*,*N′*,*N″*-tpmOH)$_2$](S$_2$O$_6$)$_2$ · 10H$_2$O, was obtained, proving the (*N*,*N′*,*N″*-tpmOH)/(*N*,*N′*,*N″*-tpmOH) coordination mode. Structural data were not available for the unsymmetrical complex, however, the UV-vis spectroscopic data of the unsymmetrical complex matched the spectral data reported by Boggess and Boberg for their bis(tpmOH)cobalt(III) complex. Additionally, the ^{13}C NMR spectroscopic data were consistent with a [Co(*N*,*N′*,*O*-tpmOH)(*N*,*N′*,*O*-tpmO$^-$)]$^{2+}$, or a [Co(*N*,*N′*,*N″*-tpmOH)(*N*,*N′*,*O*-tpmO$^-$)]$^{2+}$ complex. Szalda and Keene proposed that the [Co(*N*,*N′*,*N″*-tpmOH)(*N*,*N′*,*O*-tpmO$^-$)]$^{2+}$ complex was identical to the complex prepared by Boggess and Boberg as well as the complex prepared by White and Faller. Therefore, two distinctly different cobalt(III) species can be prepared with the tpmOH ligand, depending on the solvent of reaction. Interestingly, these complexes undergo a linkage isomerization in the presence of activated charcoal. For example, a mixture of the symmetrical and unsymmetrical isomers will isomerize almost quantitatively to the symmetrical isomer after an aqueous mixture of the isomers is heated to reflux for 18 h in the presence of activated charcoal. The use of charcoal appears to be the best way to prepare the symmetrical species.

Keene et al. also reported the preparation of bis(tpmOH)ruthenium(II) complexes. Similar to the cobalt(III) complexes, the tpmOH ligand was found to coordinate to the ruthenium(II) center via the two different coordination modes (*N*,*N′*,*N″*) and (*N*,*N′*,*O*). The following complexes, [Ru(*N*,*N′*,*N″*-tpmOH)(*N*,*N′*,*O*-tpmOH)]$^{2+}$ and [Ru(*N*,*N′*,*N″*-tpmOH)(*N*,*N′*,*O*-tpmO$^-$)]$^+$, were isolated and structurally characterized, where the only difference between these complexes is that in the later complex. the tpmOH ligand is deprotonated. It was noted that the preference of the metal center for N_5O-coordination as opposed to N_6-coordination was unusual, given the affinity of rudienium(II) for imine-type ligands such as pyridine. Further, referring to structural data of similar ruthenium(II) complexes containing tpm, tpP and tpN ligands, the authors hypothesized that the N_5O-coordination was unlikely to be due to a steric effect. Thus, N_5O-coordination may reflect a kinetic effect in the synthetic process [31].

5.2. Tripodal ligands which bridge two metals

Canty et al. [62] discovered another mode of coordination for tpmOH while attempting to prepare dimethylindium(III) complexes. Reaction of $[InMe_2]NO_3$ with the following ligands: tpmOH, $(mIm)_3COH$, $(py)(mIm)_2COH$, $(py)_2(mIm)COH$ and $(py)_2(Ph)COH$, resulted in the isolation of monomethylindium(III) complexes containing bimetallic cations. The structures of two of these complexes, $[(InMe)_2\{(py)(mIm)_2CO\}_2(NO_3)(H_2O)]NO_3$ and $[(InMe)_2\{(py)_2(Ph)CO\}_2(NO_3)(H_2O)]NO_3$, were determined crystallographically. For both structures the cations have inequivalent InMe groups bridged by two deprotonated tridentate ligands (alkoxide bridges) yielding an In_2O_2 core. For all of the bimetallic complexes mentioned earlier, each tridentate ligand has one py or mIm group bonded to one indium center and a second py or mIm bonded to the other indium center; the remaining py, mIm or Ph group remains uncoordinated. The last coordination site is occupied by either an aqua or a nitrate ligand such that each indium center is 6-coordinate. The $[(InMe)_2\{tpmO\}_2(NO_3)(H_2O)]NO_3$ complex is believed to have a structure as depicted in Fig. 12; this is the first and only report of $tpmO^-$ acting as a bridging ligand between two metal centers. The solution properties of the binuclear monomethylindium(III) complexes were also investigated where, in contrast to the solid-state structures, the solution studies indicated the presence of equivalent indium environments. It was proposed that the aqua and

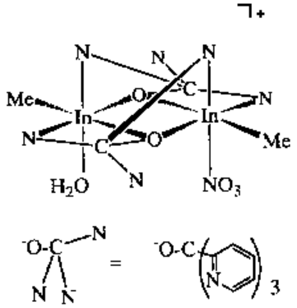


Fig. 12. The structure of $[(InMe)_2\{tpmO\}_2(NO_3)(H_2O)]^+$, the first complex containing a bridging tris(2-pyridyl) tripod ligand, adapted from a general scheme from Canty et al. [62]. The tpmO-ligand is drawn without detail to aid in displaying the geometries of the iridium centers.

nitrate groups, present in the solid state, are replaced by solvent, aqua or rapidly exchanging solvent and aqua groups in solution resulting in the formation of a comple) with a two-fold axis of symmetry. The temperature dependence of the NMR spectra for the tpmO$^-$ complex is believed to,be due to the exchange among the axial, equatorial, and free coordination environments of the N-donor groups.

6. Physical studies

6.1. Electrochemical measurements

As mentioned in Section 3, a number of bis(tpx) transition metal complexes have been reported in the literature, where each tpX ligand is coordinated in a tridentate fashion through the pyridyl nitrogens to the metal center. Other complexes such as $[M(py)_6]^{n+}$, $[M(bpy)_3]^{n+}$, $[M(phen)_3]^{n+}$, and $[M(trpy)_2]^{n+}$ are known to possess a similar six pyridyl nitrogen coordination sphere. A number of the complexes using bpy, phen and trpy ligands contain stable, low formal oxidation states of transition metals. The stabilization of low oxidation states of transition metals has been attributed to the ability of the ligands to accept electron density from the metal center via a $t_{2g} \rightarrow \pi^*$ backbonding mode. Notably, there are no reports that pyridine alone (in complexes such as $[M(py)_6]^{n+}$) stabilizes low oxidation states of transition metals. In light of this observation, Boggess and Zatko [64] proposed that the 2,2′-di-imine moiety accounts for the stabilization of these low oxidation states and that due to a lack of a 2,2′-di-imine moiety, tpX ligands coordinated in a tridentate fashion would more closely resemble py than bpy, phen or trpy in the stabilization of low oxidation states of transition metals.

Initially Boggess and Zatko [65] investigated the electrochemical redox properties of the cobalt(II) complexes: $[Co(tpX)_2](ClO_4)_2$ and $[Co(tpX)(NO_3)_2]$ (where tpX = tpN, tpP, tpP=O and tpas) and found that tpN was the only ligand that did not form a compound containing a stable cobalt(I) center. They concluded that a nitrogen bridging atom is not capable of delocalizing the charge across the pyridine rings in a manner similar to the 2,2′-di-imines while a phosphorus or arsenic bridging atom is capable of delocalizing charge. Similar results were obtained by Boggess et al. in a subsequent study of the redox properties of an analogous series of iron(II) complexes.

In 1986, Szalda and Keene prepared a complex which was determined to be the unsymmetrical complex, $[Co(N,N',N''\text{-tpmOH})(N,N',O\text{-tpmO}^-)]^{2+}$. They also reported the preparation of the symmetrical complex, $[Co(N,N',N''\text{-tpmOH})_2]^{3+}$ [38]. These complexes displayed different electrochemical properties; the unsymmetrical complex displayed only one quasi-reversible cobalt(III/II) couple while the symmetrical complex displayed one reversible cobalt(III/II) couple and one quasi-reversible cobalt(II/I) couple. In 1988, Hafeli and Keene [66] published additional studies on the electrochemistry of cobalt(II) complexes containing bis(tpX) (tpX = tpN, tpP, tpP=O, tpm or tpmOH) ligands. As was observed by Boggess, the $[Co(tpN)_2](ClO_4)_2$ complex displayed irreversible reductive electrochemistry in acetonitrile. However, in propylene carbonate, the cobalt(I) complex was found to be stable. In fact, the cobalt(I) complex, $[Co(tpN)_2](ClO_4)$, was isolated from chemical reduction of the analogous cobalt(II) complex and was stable as a solid as well as in solution for several days under an inert atmosphere. This data clearly shows that the argument made by Boggess et al. regarding the stabilization of tris(2-pyridyl) cobalt(I) complexes via delocalization through the bridging atom was incorrect. To explain the ability of the facial ligand to stabilize cobalt(I), Hafeli and Keene proposed a steric argument. The α-carbon atom-to-bridgehead atom (X) bond lengths become shorter in the sequence $P > CH > N$. With shorter bond lengths, the bite angle of the facial ligand becomes smaller, therefore, when the metal ion increases in size as it becomes reduced, the smaller bite angle is not able to accommodate the larger ion. Therefore, cobalt(I) complexes are predicted to be the least stable with tpN.

Recently, Adam et al. [67] investigated the nature of bonding in the $[CoL_2]^{n+}$, (L = tpm or tpP, $n = 1–3$) complexes using single crystal X-ray diffraction, EXAFS, electrochemistry, and density functional theory ab initio calculations and compared their data with data obtained for the $[Co(bpy)_3]^{n+}$ ($n = 1–3$) complexes in order to understand the stability of the formally cobalt(I) state. The X-ray and EXAFS data showed that Co–N bond lengths for the cobalt(I) and cobalt(II) complexes were similar, but longer than for the cobalt(III) complex. This trend was observed for the bis(tpm), bis(tpP) and the tris(bpy) complexes and suggests a similarity in the local metal environment between the cobalt(I) and cobalt(II) states. In addition, the C–X (X = bridgehead atom) bond distance was dependent on the nature of X, but not on the oxidation state of the metal. Two possible interpretations of these observations were considered: (1) the cobalt(I) complex just has unusually short copper(I)–N distances due to back-donation; or (2) that the cobalt(I) complex actually exists as a cobalt(II)–(ligand radical anion) complex. The electrochemical, spectroscopic and computational studies suggest that the $[CoL_2]^+$ (L = tpm or tpP) species are better described as d^8 cobalt(I)–ligand complexes rather than d^7 cobalt(II)–(ligand radical anion) complexes. This interpretation corroborates Keene's previous assertion that the stabilization of the cobalt(I) state does not occur because of charge delocalization, but rather due to ligand steric considerations. If this proves to be true in general, then a variety of ligands could possibly stabilize the cobalt(I) state.

6.2. Spectroscopic measurements

Edwards and Marshalsea [68] compared the IR spectral features of the complex $[M(CO)_3(tpN)](ClO_4)$ (M = Mn or Re) with spectra of over 20 other facial tricarbonyl manganese(I) and rhenium(I) complexes containing mono-, bi- and tridentate ligands. The tpN complex was synthesized by displacing CH_3CN from $[M(CO)_3(NCCH_3)_3](ClO_4)$ with tpN. Cotton–Kraihanzel CO stretching parameters were successfully calculated for the complex.

In 1967, Kulasingam and McWhinnie synthesized metal complexes using metal halides and investigated the ligand field strength of tpN. Manganese(II) and zinc(II) form tetrahedral complexes where tpN acts as a bidentate ligand and halides occupy the other two coordination sites. Both cobalt(II) and copper(II) form tetrahalometalate(II) salts, where the cation is $[M(tpN)_2]^{2+}$. When tpN coordinates to palladium(II), it forms a square planar complex (bidentate tpN). Nickel(II), rhodium(III) and iridium(III) all formed octahedral structures. Comparing the magnetic properties of $[Fe(tpN)_2]^{2+}$ with the iron(II) complex containing three bidentate ligands [di(2-pyridyl)amine], McWhinnie observed that the tridentate ligand had a greater ligand field strength than the bidentate ligand. TpN was classified as a strong field ligand, proving that a ligand does not need conjugation between the aromatic centers in polypyridyl ligands to be classified as strong field [37].

In 1968, Berrett et al. [69] reported the Mössbauer spectra of $[Fe(tpN)_2](ClO_4)_2$ and $[Fe(tpN)_2][FeCl_4]$ as part of a series of spectra from other iron(II) and iron(III) complexes containing di-imine ligands such as phen and bpy. Unlike the tris-bidentate ligand complexes, the iron(II) complexes with two tpN ligands gave no quadrupole splitting at 300 K, indicating that $[Fe(tpN)_2]^{2+}$ is a highly symmetrical octahedral cation.

Kulasingam et al. [70] investigated the electronic spectra of nickel(II), copper(II), and chromium(III) complexes containing two tpN ligands. By assigning the longest wavelength band to the transition ${}^3A_{2g} \rightarrow {}^3T_{2g}$. (assuming similar octahedral symmetry as iron(II)), tpN was placed between phen and nitro in the spectrochemical series with respect to nickel(II). This observation corroborated McWhinnie's work with iron(II), namely that tpN is a stronger field ligand than di(2-pyridyl)amine. With the smaller chromium(III) ion, the bidentate di(2-pyridyl)aniine field strength was stronger than the tridentate tpN. The difference was attributed to tpN being too rigid to maintain strong a bonding to small metal centers, relative to the more flexible di-2-pyridylamine.

In 1977, Brown et al. [71] introduced infrared studies with isotopically labeled metals as a new characterization technique for iron(II) and copper(II) complexes containing two tpN ligands. By comparing the complexes of the two isotopes, the unambiguous assignments of metal–nitrogen stretching frequencies were made, leading to a better description of the geometries of the complexes. For instance $[Fe(tpN)_2](ClO_4)_2$, which was predicted to possess octahedral symmetry from Mössbauer spectroscopy, was confirmed to have an octahedral symmetry because it contained only one metal sensitive mode. Studies with copper(II) showed these complexes possessing lower symmetry. $[Cu(tpN)_2](PF_6)_2$ complexes contained two significant isotopic shifts in the spectra, suggesting a tetragonally distorted structure. $[Cu(tpN)_2(ClO_4)_2]$ possessed three metal sensitive IR modes, supporting the previous postulate that this complex has a C_{2h} symmetry with trans perchlorato groups.

Astley et al. [41] studied the structural and spectroscopic properties of facial pyridine ligands with nickel(II) and zinc(II). With these characterizations, the angular-overlap model (AOM) established the effect of the bridgehead atom, X (X = CH, N or P). The metal–pyridine bond lengths are significantly shorter than those in complexes containing monodentate pyridine ligands. Comparison of the CH, N and P bridgeheads showed that the larger the size of the bridgehead atom, the more the pyridine rings can lie symmetrically about the M–N bond, creating a larger "bite" angle of the facial ligand. Using AOM, the three different ligands have the same bonding parameters, suggesting that the nature of the bridgehead atom has little effect on the metal–ligand interaction. Therefore, the short M–N bonds found in the crystal structures account for the spectroscopic differences. This interpretation is consistent with the steric argument proposed by Keene et al. in 1988 (vide supra) [12].

7. Applications

7.1. Modeling biological systems

X-ray diffraction studies of carbonic anhydrase suggest that the active site consists of a zinc(II) ion coordinated pseudotetrahedrally to three histidine imidazoles and an ionizable aqua ligand. Brown and Huguet [72], interested in studying synthetic analogs for the active site of this enzyme, utilized tpmOH and other tridentate tripodal ligands to prepare a number of zinc(R) complexes which were investigated as possible models of carbonic anhydrase. A total of nine ligands were studied and the pK_a values as well as the binding abilities ($pK_{M^{2-}}$) towards zinc(II), cobalt(II), nickel(II) and copper(II) were determined. For carbonic anhydrase the order of binding constants is copper(II) > zinc(II) > nickel(II) > cobalt(II); while the tpmOH and substituted analogs displayed their highest binding affinity for copper(II), only one ligand (a tripodal ligand which used a combination of substituted imidazoles) displayed exactly the same trend with all of the metals as carbonic anhydrase. In addition, the zinc(II) complex using this ligand displayed reversible H_2O ionization similar to carbonic anhydrase. Unfortunately, the zinc(II) complex did not catalyze the hydrolysis of *p*-nitrophenol or the hydration of acetaldehyde. Both 1:1 and 2:1 M:L adducts were formed with the less sterically hindered ligands such as tpmOH and these complexes were determined by ^1H NMR spectroscopy to be symmetrically coordinated to the zinc(II) center. The tpmOH complexes were not good structural models for carbonic anhydrase.

Cote was interested in stabilizing molybdenum(III) and tungsten(III) centers due to their possible involvement in biological systems. In 1983, there were few examples of stable molybdenum(III) and tungsten(III) complexes since most were easily oxidized to yield M(IV) species. However, it was found that monomeric molybdenum(III) and to a lesser extent monomeric tungsten(III), were stabilized by the tridentate ligand tpb. Therefore, Cote [73] investigated the ability of tpN to stabilize these metal centers. Using the $[Mo(CO)_6]$ as a starting material, $[Mo(CO)_3(tpN)]$ was prepared. The tpN ligand was found to stabilize the molybdenum(III) oxidation state in the presence of thionyl chloride, a strong oxidant. Interestingly, the tpb ligand could not similarly stabilize the molybdenum(III) center where the analogous reaction between $[Mo(CO)_3(tpb)]$ and $SOCl_2$ produced a Mo(IV) species. In the tungsten case, both the $[W(CO)_3(tpN)]$ and $[W(CO)_3(tpb)]$ complexes were oxidized to tungsten(IV) in the presence of thionyl chloride. Therefore, while tpN stabilized molybdenum(III) more efficiently than tpb, tpN was unable to stabilize stronger reductants such as tungsten(III).

Kodera et al. prepared (6-Mepy)py$_2$CH and a dinucleating version of this ligand to stabilize oxo-bridged di-iron species. While many oxo-bridged di-iron complexes have been synthesized as models for the active sites of non-heme iron proteins, the core structures of these binuclear structures are typically kinetically unstable in polar solvents. In attempts to stabilize the core di-iron structure, some researchers have used dinucleating ligands; this strategy has led to the production of tetranuclear species instead of the desired dinuclear species. Kodera reported the preparation of two iron complexes, one containing the tris(2-pyridyl) tripod ligand (6-Mepy)py$_2$CH (L in Fig. 13) and the second containing the dinucleating tris(2-pyridyl) tripod ligand, (L′ in Fig. 13). Both complexes were proposed to contain the (μ-oxo)bis(μ-acetato)di-iron(III) core [74]. An X-ray crystal structure determination of $[Fe_2(O)(OAc)_2(L')](ClO_4)_2$ confirmed the formation of the first discrete (μ-oxo)bis(μ-acetato)di-iron(III) core with a dinucleating ligand. Notably, Mössbauer data for $[Fe_2(O)(OAc)_2(L')](ClO_4)_2$ are reminiscent to those for the azido-metHr, which suggests that viable hemerythrin models can be prepared using tpm based tripod ligands.

In 1982, Dedert et al. [75] reported the synthesis, characterization, and crystal structure of a copper(II) cluster containing bidentate tpN ligands. Because copper(I) ions are employed as catalysts in a variety of oxidation-based enzymatic and non-enzymatic reactions and because copper(I) ions are readily oxidized aerobically, Marks and Ibers were interested in the copper based products formed as a result of the oxidation of copper(I) to copper(II). They utilized tpN as a ligand for copper(I) in an attempt to simulate the multiimidazole binding environments in copper proteins

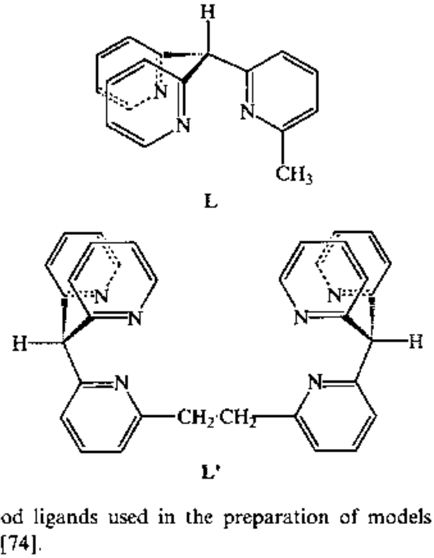


Fig. 13. Tris(2-Pyridyl) tripod ligands used in the preparation of models of non-heme iron proteins, adapted from Kodera et al. [74].

with tridentate ligands composed of imidazole-like heterocyclic bases such as pyridine. Reaction of $[Cu(tpN)(SO_3CF_3)]$ with O_2, resulted in the formation of the copper cluster $[Cu_4(OH)_4(SO_3CF_3)_2(tpN)_4]\,[SO_3CF_3]_2 \cdot C_3H_6O$. The X-ray crystal structure of this cluster showed a cubane-like cluster with four copper atoms at alternating vertices and oxygen from hydroxy groups at the remaining four vertices (i.e. bidentate coordination of tpN). Notably, this study showed that oxidation of mononuclear copper(I) complexes can result in the formation of rather complex copper(II) cubane-type clusters, which are structurally reminiscent of the iron cubane-type clusters which are often associated with biological processes.

7.2. *Catalysis*

In 1979, Davies et al. [76] investigated the products of the oxidation of CuCl by O_2. With pyridine as the solvent, one of the products of the aerobic oxidation of CuCl is a polymeric "CuO" material stabilized by pyridine. This polymeric material can catalyze the oxidative coupling of phenols by molecular oxygen to form polymers. Unfortunately, the complex in pyridine is easily converted to the catalytically inactive copper(II) oxide when the "CuO" core is allowed to polymerize further and precipitate from solution. Therefore, the catalyst had never been isolated to characterize its structure in an attempt to better understand the mechanism of the coupling reaction. Davies investigated the use of other pyridine derivatives, including tpN, to stabilize the "CuO" core in polar, aprotic solvents. Most of the pyridine derivatives were oxidized, but preliminary results suggested that tpN may stabilize the "CuO" core, and the species was isolated by gel permeation chromatography.

As mentioned in Section 3.1, Faller and Ma prepared Lewis acids of the type, $[(tPM)M(CO)(NO)_2](SbF_6)_2$ (M = Mo or W). These complexes readily lose CO, generating $[(tpm)M(NO)_2]^{2+}$ (M = Mo or W), which catalyze Diels–Alder reactions between methyl vinyl ketone and 1,3-butadiene. They are also active butadiene polymerization catalysts when a less basic dienophile such as methyl acrylate is used [24]. Faller and Gundersen [77] further investigated the catalytic properties of these complexes and reported that $[(tpm)W(NO)_2](SbF_6)_2$ catalyzes the addition of silylated *C*-nucleophiles to carbonyl compounds as well as the addition of TMS-CN to carbonyl compounds (Fig. 14). The catalyst can be recovered with ease and used in further reactions with high relative percent yields, and since the work-up does not require aqueous solvents, the *O*-silylated products can be easily isolated.

Hafeli and Keene conducted some preliminary studies on the use of cobalt(I) complexes containing tpm and tpP to reduce water to hydrogen and to reduce carbon dioxide to carbon monoxide and formate ion. Both complexes, $[CoL_2]^+$ (L = tpm or tpP), catalyze the reduction of water to hydrogen but do not show any reactivity towards the reduction of CO_2. Previously, with the bidentate polypyridyl ligand 2,2′-bipyridine (bpy), the presence of excess ligand dramatically reduced the yield of H_2 by $[Co(bpy)_3]^+$. This observation lead to a possible mechanism involving the complete dissociation of one of the bpy ligands, leading to the production of the suspected intermediate, a hydridocobalt species [78]. Using the flexible tripod ligand, the presence of excess ligand does not dramatically affect the yield of H_2. Therefore,

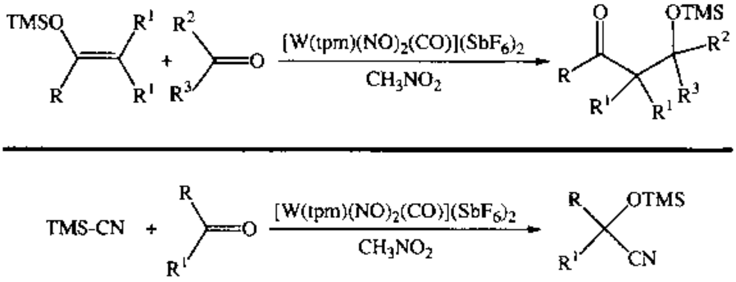


Fig. 14. $[W(tpm)(CO)(NO)_2](SbF_2)_2$ readily loses CO and is an active catalyst in the above reactions, adapted from Faller and Gundersen [77].

it was proposed that the well characterized bidentate and tridentate nature of tpm and tpP could be exploited to form the hydridocobalt species through the dissociation of only one of the pyridyl rings, with no net dissociation of the entire ligand [66].

Interested in extending the catalytic properties of homogeneous transition metal complexes containing tds(2-pyridyl) tripod ligands, Moberg et al. investigated ways of attaching complexes containing tpmOH onto polymeric supports to yield heterogeneous catalysts. TprmOH was reacted with a chloromethylated 1% crosslinked gel-type polystyrene polymer in the presence of potassium hydride and 18-crown-6 to form a polymeric tridentate ligand. A similar macroporous polymer was prepared after a phenolic spacer was added onto the tpmOH ligand. The incorporation of a transition metal into the polymeric support was achieved by first reacting $FeCl_3$ With silver triflate in a 1:3 ratio and then adding the filtered solution to a suspension of the desired polymer. The resulting polymeric material displayed catalytic activity towards the ring opening of epoxides (such as styrene oxide) by methanol. For example, complete conversion of styrene oxide was obtained in 30 min, where the nucleophilic ring opening occurs exclusively at the benzylic position. It was noted that the polymer could be reused, although the reactivity decreased somewhat after each cycle [79].

8. Recent advances

Beswick et al. [80] prepared the first tris(2-pyridyl) tripod ligand containing a p-block metal bridgehead. $[\{n\text{-BuSn(2-py)}_3\}\text{LiBr}]$ is prepared in a one-pot synthesis and when reacted with $CuCl_2$ forms the $[\text{Cu}\{n\text{-BuSn(2-py)}_3\}\text{Br}]$ complex. A single crystal X-ray diffraction analysis was conducted as well as electrochemical measurements (cyclic voltammetric measurements show that the copper(II) species is unstable). It was noted that coordination of the $[n\text{-BuSn(2-py)}_3]$ ligand to copper(I) had an effect on the chemistry of the tin(IV) center; the tin(IV) bridgehead was more resistant to reduction when the ligand was coordinated to copper(I) than when the ligand was coordinated to a lithium cation. This behavior indicates the significant π-acid behavior of this novel ligand.

Beswick et al. [81] also prepared a tris(2-pyridyl) tripod ligand containing lead as the bridgehead atom. This species, [Pb(2-py)$_3$]- is the first functionalized tris(organo)plumbate(II) species. The coordination chemistry of this ligand has not yet been investigated.

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